Nanocrystalline Zeolites: Synthesis, Mechanism, and Applications

DISSERTATION

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By
Michael Andrew Severance
Graduate Program in Chemistry

The Ohio State University
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Dissertation Committee:
Professor Prabir K. Dutta, Advisor
Professor Terry L. Gustafson, Advisor
Professor Susan V. Olesik
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ABSTRACT

Nanocrystalline zeolite particles are becoming an important material in many technical applications (e.g. zeolite membranes). Synthetic methods that minimize the zeolite crystal diameter, while providing a narrow particle size distribution, are of primary importance in these technical applications. However, there are several limitations to currently existing synthetic routes aimed at producing nanozeolites and zeolite membrane devices. For example, zeolite growth in these contexts typically requires days to weeks at high temperature to crystallize. Despite excellent performance of zeolite membranes in several separation applications, the long synthesis times required undermine any practical application of these technologies. This work focuses on chemical manipulation of zeolite nucleation processes in sol gel systems in effort to address such limitations. The primary findings indicate that careful control of the nucleation stage of a clear zeolite synthesis (optically transparent sol gel) allow the formation of zeolite Y nanocrystals less than 50 nm in diameter with a polydispersity index less than 0.2. Furthermore, chemical perturbations made during the nucleation stage of zeolite Y hydrogel synthesis is shown to accelerate crystal growth by a factor of 3-4, depending on the specific sol gel chemistry. These findings are applied to the nanocrystal seeding and rapid hydrothermal growth of zeolite Y membranes on inexpensive polymeric supports. A novel synthetic method is developed to this end. Also, the chemical and physical
properties of monodisperse nanocrystalline zeolite Y synthesized herein are explored by electrochemical impedance spectroscopy. It is found that the particle interface plays an important role in the ionic conductivity of nanocrystalline zeolites in contrast to their larger zeolite counterparts in analogy to other ceramic and metal oxide ion conductors. Finally, the possibility to produce novel organic and inorganic composite systems through zeolite host-guest chemistry is explored. A nanozeolite-silver nanoparticle host-guest system is synthesized and a mechanism describing its evolution is developed. Also, the photochemistry of a colloidal nanozeolite-organic dye host-guest system is explored with ultrafast transient UV-Vis absorption spectroscopy. This allows some of the fastest chemical events to be probed within the host-guest system.
DEDICATION

This document is dedicated to my family.
Acknowledgments

First and foremost I must thank my loving girlfriend Betsy Heck for all her support. I could not have done this without her.

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VITA

June 2002 ........................................Columbus Whetstone High School
2008..................................................B.S. Chemistry, The Ohio State University
2009-2011 ..........................................Metro Fellow, The Ohio State University
2011 to present ....................................Graduate Research Associate, Department of Chemistry and Biochemistry, The Ohio State University

Publications


Fields of Study

Major Field: Chemistry
# TABLE OF CONTENTS

Abstract ......................................................................................................................... ii

Dedication ....................................................................................................................... iv

Acknowledgments .......................................................................................................... v

Vita ................................................................................................................................... vii

Table of Contents .......................................................................................................... viii

List of Tables .................................................................................................................. xv

List of Figures ................................................................................................................. xvi

Chapter 1: Introduction ................................................................................................. 1

1.1 A Brief Introduction to Zeolites ............................................................................. 1

1.2 Zeolite Structure ..................................................................................................... 2

1.3 Zeolite Synthesis in General ................................................................................ 2

1.3.1 Nanozeolites and their Synthesis ..................................................................... 3

1.3.2 Conventional Clear Gel and Hydrogel Synthesis of Zeolite Nanocrystals .. 5

1.3.3 Confined Space Synthetic Approaches ............................................................. 6

1.3.4 Specialized Approaches .................................................................................... 7

1.4 Scope of this Thesis ................................................................................................. 7

1.5 References .............................................................................................................. 9

Chapter 2: Synthesis and Optimization of Nanocrystalline Zeolite Y from a Clear
Solution For Seeding and Secondary Growth of Hybrid Zeolite-Polymer Membranes... 15
# 2.1 Introduction

2.1 Introduction

2.2 Experimental Methods

2.2.1 Materials

2.2.2 Synthesis

2.3 Characterization

2.4 Results

2.4.1 Synthesis of nanozeolite particles for deposition

2.4.2 Deposition of zeolite on polymeric and surface modification polymeric supports

2.4.3 Membrane growth on seeded supports

2.5 Discussion

2.5.1 Synthesis and Optimization of Nanozeolite Suspensions for Seeding Polymeric Supports

2.5.2 Optimizing Nanozeolite Seed Layer Deposition on Porous Polymeric Supports

2.5.3 Membrane Growth on Seeded Polymeric Supports by Secondary Hydrothermal Treatment

2.5.4 X-Ray Diffraction Kinetics of Zeolite Growth on Polymer Supports

2.6 Conclusion

2.7 References

2.8 Figures

Chapter 3: Development of a Simple Synthetic Approach to Accelerating Nucleation and Crystallization in Hydrogel Systems and its Application to FAU Zeolite

3.1 Introduction

3.2 Experimental Methods
Chapter 3: Accelerated Zeolite Growth

3.2.1 Experimental strategy ................................................................. 76
3.2.2 Synthesis Protocols ..................................................................... 76
3.2.3 Control Experiments .................................................................. 78
3.2.4 Conventional Hydrothermal Synthesis ........................................ 78
3.2.5 Characterization ......................................................................... 79

3.3 Results and Discussion .................................................................. 81
3.3.1 Acceleration of Zeolite Growth by Controlling the Gel Composition .... 81
3.3.2 Examination of the Rapid Crystallization of Zeolite in the Context of Controls ................................................................. 86
3.3.3 A Mechanistic Study of the nucleation stage of a Rapidly Grown Faujasitic Gel ................................................................................................................. 90
3.3.4 A Proposed Mechanism for Accelerated Zeolite Growth ............... 98
3.3.5 The Nucleation Phase ................................................................. 99
3.3.6 The Crystallization Phase .......................................................... 99

3.4 Selected Applications of the Rapid Synthesis Approach .................. 100
3.4.1 Extension of the Approach to More Siliceous Zeolites ................. 100
3.4.2 In-situ Incorporation of Ions ....................................................... 105
3.4.3 Rapid Growth of Membranes .................................................... 107

3.5 Conclusions ................................................................................ 112

3.6 References .................................................................................. 113

3.7 Figures & Tables ........................................................................... 119

Chapter 4: The Crystal Size Dependent Nature of Ionic Conduction Through Polycrystalline Zeolite Y Spanning the Nano to Micron Length Scales ........... 154

4.1 Introduction .................................................................................. 154
4.2 Experimental Methods ................................................................. 156
  4.2.1 Synthesis of Zeolites............................................................... 156
    4.2.1.1 Nanozeolite Synthesis.................................................. 156
    4.2.1.2 Submicron Zeolite Synthesis....................................... 157
    4.2.1.3 Micron zeolite synthesis........................................... 157
    4.2.1.4 Zeolite Membrane Synthesis..................................... 157
    4.2.1.5 Zeolite Surface Modification.................................... 158
  4.2.2 Characterization...................................................................... 158
    4.2.2.1 X-Ray Diffraction...................................................... 158
    4.2.2.2 X-Ray Photoelectron Spectroscopy............................. 158
    4.2.2.3 Electron Microscopy................................................ 159
    4.2.2.4 Nuclear Magnetic Resonance Spectroscopy..................... 159
    4.2.2.5 Dynamic Light Scattering.......................................... 159
    4.2.2.6 Infrared Absorption Spectroscopy................................ 159
    4.2.2.7 Electrochemical Impedance Spectroscopy....................... 160
  4.3 Results....................................................................................... 160
    4.3.1 Zeolite Y membrane.......................................................... 160
    4.3.2 Micron-sized zeolite particles....................................... 161
    4.3.3 Sub-micron sized particles............................................ 161
    4.3.4 Nano-sized particles....................................................... 162
    4.3.5 Impedance Spectroscopy................................................. 162
    4.3.6 Surface Modification..................................................... 164
  4.4 Discussion................................................................................... 165
  4.5 Conclusions............................................................................... 168
4.6 References .................................................................................................................. 169

4.7 Figures & Tables ........................................................................................................ 172

Chapter 5: Evolution of Silver Nanoparticles Within Nano-sized Zeolite Y Matrices: A
Mechanistic Study ........................................................................................................... 187

5.1 Introduction ............................................................................................................... 187

5.2 Experimental Methods ........................................................................................... 192

5.2.1 Synthesis .............................................................................................................. 192

5.2.2 Characterization ................................................................................................... 194

5.3 Results ....................................................................................................................... 196

5.3.1 Preparation of colloidally a stable silver zeolite precursor .................................. 196

5.3.2 Synthesis of Intra-Zeolitic Silver Nanoparticles ................................................. 196

5.3.3 Dynamics of Intra-Zeolitic Silver Nanoparticle Growth ...................................... 199

5.3.4 Intra-Zeolitic pH Measurements .......................................................................... 206

5.4 Discussion ................................................................................................................ 207

5.4.1 Synthesis of a Colloidally Stable Silver-Zeolite Composite ............................... 207

5.4.2 Evolution of Silver Within Nano-Zeolite Micropores: Mechanism ................. 210

5.4.2.1 Silver Growth Model ....................................................................................... 210

5.4.2.2 Specific Mechanism for Intra-Zeolitic Silver Growth ..................................... 212

5.4.3 Application of Silver Loaded Zeolite as a SERS Substrate ............................... 220

5.5 Conclusions .............................................................................................................. 221

5.6 References ............................................................................................................... 222

5.7 Figures & Tables ....................................................................................................... 229

Chapter 6: Intra-Zeolitic Ultrafast Dynamics of a Bipyridinium Dication Within
Colloidal Nanometer-Sized Zeolite Y: A Spectroscopic Study ..................................... 254
Chapter 2 References ................................................................. 316
Chapter 3 References .................................................................. 320
Chapter 4 References .................................................................. 325
Chapter 5 References .................................................................. 328
Chapter 6 References .................................................................. 333
Appendix A References ............................................................... 337
Appendix B References ............................................................... 337
LIST OF TABLES

Table 1: Chemical conditions and chemical and physical properties of the as-synthesized zeolites. ............................................................................................................................................... 69
Table 2: Gas permeation properties (permeance and selectivity) of nanozeolite seed layers (a), and nanozeolite seed layers grown by secondary hydrothermal treatment (b). ... 69
Table 3.1: Comparison of physical and chemical properties of hydrothermal and rapid synthesized products. .......................................................................................................... 153
Table 3.2: NOx conversion as a function of temperature for the copper containing zeolite. ........................................................................................................................................ 153
Table 4.1: Chemical and physical properties of the zeolite samples prepared herein. ... 184
Table 4.2: Activation Energies (kJ/mol, error ±2-3 kJ/mol) from Impedance Spectroscopy (all Na⁺ form). .............................................................................................................. 185
Table 4.3: The fitting parameters for the equivalent circuit model in Figure 4.12........ 186
Table 5.1: Colloidal properties of nanozeolites determined by DLS ................................. 253
Table 5.2: Gas adsorption properties as a function of reaction time. .............................. 253
Table 6.1 Physical and chemical properties of nanozeolite dispersions .................... 308
Table 6.2: TCSPC fitting parameters .............................................................................. 308
Table 6.3: Transient absorption fitting parameters ...................................................... 308
LIST OF FIGURES

Figure 1.1: Model structures of several of the most industrially relevant zeolites. Oxygen atoms are omitted in these models for clarity. Each line intersection represents a T atom where T=Si or Al. Figure 1.1a is zeolite A (LTL), figure 1.1b is zeolite Y (FAU), figure 1.1c is silicalite-1 (MFI), and figure 1.1d is zeolite L (LTL). ............ 12

Figure 1.2: Wire model depictions of the secondary building units that comprise the zeolite Y (FAU) structure. Figure 1.2a is a model of the sodalite building unit and figure 1.2b is a model of the hexagonal prism, or double six-membered ring (d6r), building unit. In these models red represents oxygen atoms and blue represents Si or Al atoms. ........................................................................................................... 13

Figure 1.3: Models of the primary repeating unit of the zeolite Y (FAU) structure viewed from several perspectives. The crystal plane [h,k,l] perpendicular to the viewing direction is displayed in each of these cases. The crystallographic locations of the extra-framework cations are occupied by red spheres in each case labeled with their corresponding site designation: SI, SI', etc. ....................................................................................... 14

Figure 2.1: XRD of sub-micron zeolites synthesized from a clear solution. The average particle diameter of the zeolite particles as determined by DLS is 214 nm. ............ 47

Figure 2.2: XRD pattern of powdered products isolated from nanozeolite reaction 1. Bragg reflections characteristic of zeolite Y are observed above the large, broad contribution from the amorphous background................................................. 48

Figure 2.3: XRD of the powdered products isolated from nanozeolite synthesis 2 using aluminum hydroxide as the aluminum source. The pattern is representative of zeolite Y with a minor contribution from zeolite A (<5 %). Size analysis of these crystals by XRD indicate an average crystallite diameter of 74 nm. ........................................ 49
Figure 2.4: XRD pattern of powdered products isolated from nanozeolite reaction 3 which uses a 1 hr pre-hydrolysis step to dissolve the aluminum source. This reaction forms boehmite when subject to reaction conditions identical to reaction 1 as indicated by the characteristic diffraction pattern.  

Figure 2.5: XRD pattern of powdered products isolated from nanozeolite reaction 4 where a 20 min pre-hydrolysis step is used to dissolve the aluminum source. All peaks observed are characteristic of zeolite Y. Size analysis by XRD and DLS yield an average particle diameter of 40 and 48 nm, respectively.  

Figure 2.6: XRD Pattern of the powdered products isolated from nanozeolite reaction 5 where a small amount of NaOH was added prior to growth. The diffraction pattern observed is characteristic of zeolite A. Size analysis by XRD and DLS indicate an average particle diameter of 48 and 180 nm respectively.  

Figure 2.7: XRD pattern of powdered products isolated from nanozeolite reaction 6 where LUDOX SM-30 was utilized as the silica source. Both zeolite Y and zeolite A phases are observed in this reaction. Some intense zeolite A peaks are marked with an asterisk.  

Figure 2.8: Intensity-intensity autocorrelation function for the sub-micron zeolite dispersion (red dotted line) and the intensity weighted particle size distribution obtained from a NNLS fit of the autocorrelation data (blue). The average diameter is 235 nm.  

Figure 2.9: Intensity-intensity autocorrelation function measured for the nanozeolite reaction 4 dispersion (red dotted line). The intensity averaged particle size distribution obtained by NNLS fit of the correlation function (blue). The average size is 56 nm.  

Figure 2.10: Intensity weighted particle size distribution determined from a NNLS fit of the intensity-intensity autocorrelation function. The average size is 192 nm.  

Figure 2.11: SEM images of a 1000 kDa cutoff polymer filter used to separate zeolite Y/A mixtures derived from nanozeolite reaction 6 after 0 filter cycles (a), 5 filter cycles (b), 10 filter cycles (c), and 15 filter cycles (d).
Figure 2.12: Nitrogen adsorption isotherm (red, open circles) and nitrogen desorption isotherm (blue, crosses) of sub-micron zeolites indicating the microporous nature of the sample and a BET surface area of 635 m$^2$/g.

Figure 2.13: Nitrogen adsorption isotherm (red, open circles) and nitrogen desorption isotherm (blue, crosses) of nanozeolites isolated from reaction 4 indicating the microporous nature of the sample and a BET surface area of 475 m$^2$/g. There is some hysteresis above 0.4 P/P$_0$ due to particle packing.

Figure 2.14: Optical micrographs of a bare PES support (a), and a PES support spin coated at 450 rpm with a suspension of 0.5 wt% sub-micron zeolite in water (b). A coating pattern can be observed in image b.

Figure 2.15: ATR-FTIR spectra of an unmodified PES support (a), a PES support modified with a 5 wt% aqueous potassium persulfate solution at 60 °C for 24 hrs (b), a PES support modified as in b but for 36 hrs (c), and a PES support modified as in b but for 48 hrs (d). The development of a carbonyl stretching band is observed with treatment.

Figure 2.16: Optical micrographs of a PES support modified for 24hrs and spin coated with a 0.5 wt% aqueous dispersion of sub-micron zeolite (a and b), and a PES support modified for 48 hrs and coated identically to image a (c and d). A more dense pattern of zeolite can be observed on the support surface.

Figure 2.17: Photograph images of supports coated as in figure 2.16 but ion exchanged with rhodamine 6G dye viewed under ambient lighting (a, c, and e), and their respective photograph images viewed under 254 nm UV excitation (b, d, and f). The inset in figure f illustrates the boundary between the coated and un-coated region of the support by the difference in fluorescence intensity. Arrows indicate coated regions.

Figure 2.18: Optical micrograph of a PES support vacuum dip coated with sub-micron zeolite seed crystals. The iridescent coloration indicates a thin, uniform coating.

Figure 2.19: SEM of seed layers deposited on PES supports by vacuum dip coating. Figure 2.19 a-c show the top view of the bare 1000 kDa PES support (a), the top view...
of the support after coating with an aqueous 0.1 wt% dispersion of sub-micron seeds (b), and the cross-sectional view of b (c). Figure 2.19 d-f show the top view of a bare 300 kDa PES support (d), the support coated with an aqueous 0.1 wt% dispersion of nanozeolites from reaction 4 (e), and a cross-sectional view of e (f). 

Figure 2.20: XRD patterns of membranes grown on 1000 kDa PES supports (a), and 300 kDa PES supports (b). Support peaks are marked with an asterisk.

Figure 2.21: SEM images of the top view of a nanozeolite seed layer on 300 kDa PES support after 8 hrs secondary growth (a), a close up of a grown region (b), and the cross-sectional view of this layer (c).

Figure 2.22: XRD patterns of membranes grown from nanozeolite seeded 300 kDa PES supports as a function of time. The seed layer is the starting material in (a), followed by 2 hrs (b), 4 hrs (c), 6 hrs. (d), and 8 hrs. hydrothermal growth (e).

Figure 3.1: A general crystallization curve illustrating the chemical evolution of zeolite crystals in a typical reaction.

Figure 3.2: A schematic of the apparatus used for the rapid synthesis of zeolite Y (a) and the water concentration vs. time schematic illustrating water dynamics of the rapid synthesis process (b).

Figure 3.3: Crystallization curves comparing the reaction progress for a hydrothermal synthesis of zeolite Y (red circles), and a rapid synthesis of zeolite Y (blue squares).

Figure 3.4: Comparison of the raw X-ray diffraction patterns as a function of time for the hydrothermal synthesis of zeolite Y (a), and the rapid synthesis of zeolite Y (b).

Figure 3.5: Crystallization kinetics of a rapidly synthesized zeolite as measured by the evolution of the BET surface area for each of the times listed in the table inset.

Figure 3.6: A nitrogen adsorption isotherm comparison of the crystals isolated from a hydrothermal synthesis after 8 hrs (a) with the crystals isolated from a rapid synthesis after 120 min (c). A magnified view of the mesopore region of the hydrothermal and rapid synthesis products are shown in (b) and (d) respectively.
Figure 3.7: $^{29}$Si and $^{27}$Al MAS NMR of the products isolated form a rapid synthesis of zeolite Y after 120 min. reaction time (a and b respectively), and the same for the products isolated from a traditional hydrothermal synthesis of zeolite Y after 8 hrs reaction time (c and d respectively). The Si/Al ratio calculated from teh silicon NMR is included as an inset in each case. The assignments of each resonance are colored coded and denoted with a black dotted line in the silicon NMR. Only one band is observed in the aluminum NMR. All other bands are spinning side bands. 

Figure 3.8: SEM comparison of the particle morphology of crystalline products isolated from a conventional hydrothermal reaction of zeolite Y after 8 hrs. reaction time (a), and a rapid synthesis of zeolite Y after 2 hrs reaction time (b).

Figure 3.9: A color coded schematic of the water concentration vs time for each of the control experiments performed. The XRD patterns of products isolated from each reaction was analyzed after 2 hrs, denoted with a verticle dotted red line in the schematic.

Figure 3.10: XRD of each control experiment (I-VI) in figure 3.9 after 2 hrs reaction time. Pattern (a) corresponds to reaction I, (b) to reaction II, (c) to reaction III, (d) to reaction IV, (e) to reaction V, and (f) to reaction VI.

Figure 3.11: SEM images of the amorphous products isolated from a rapid synthesis of zeolite Y after 0 min (a), and 60 min reaction time (b). The insets contain the surface areas of the products as determined by BET analysis of the nitrogen adsorption isotherms.

Figure 3.12: TEM images of the amorphous gel isolated from a rapid synthesis of zeolite Y after 60 min reaction time at low magnification (a), and high magnification (b) illustrating the porous structure of the gel.

Figure 3.13: Nitrogen gas sorption analysis of products isolated form the rapid synthesis of zeolite Y after 0 min (a) and 60 min reaction time (b). Pore size analysis of the 0 and 60 min products are contained in (c) and (d) respectively. The NLDFT fits the 0 and 60 min material are contained in (e) and (f) respectively.
Figure 3.14: FTIR of rapid synthesis products isolated after a) 0, b) 60, c) 70, d) 80, e) 90, f) 100, g) 110, & h) 120 min. The zeolite crystal bands are marked with black dotted lines with their respective frequencies.

Figure 3.15: Raman spectra of products isolated from a rapid synthesis of zeolite Y after 0 min (a), and 60 min reaction time (b). The curve deconvolutions are graphed as black curves below (a). The major features are marked with black dotted lines with their respective frequency.

Figure 3.16: De Boer's t plot analysis of products isolated from a rapid synthesis of zeolite Y at 0 min (a), 60 min (b), 100 min (c), and 120 min (d). The t-plot fit is extrapolated to the y-axis for clarity as denoted by the black dotted lines.

Figure 3.17: Simultaneous bright field (BF) TEM imaging (a) and dark field (DF) TEM imaging of the same region of a isolated after 70 min of rapid synthesis (b). Small crystalline surface regions can be seen in both images as they are marked with an arrow in a and a circle in b.

Figure 3.18: A high Resolution TEM image of a zeolite Y product isolated after 70 min of rapid synthesis where the crystalline nature of the interface is highlighted. The magnified inset of the boxed region clearly shows the barrier between the amorphous precursor gel and the propagating surface crystal (as denoted with the red solid line).

Figure 3.19: $^{23}$Na MAS NMR of powders isolated from a rapid synthesis of zeolite Y after 0 min (a), 60 min (b), 120 min reaction time (c). The dotted lines indicate the signature of amorphous aluminosilicates at -8.7 ppm, the aluminosilicate intermediates at -16.5 ppm, and the zeolite crystal at -1.8 ppm.

Figure 3.20: Crystallization kinetics of the rapid synthesis procedure as followed with Raman spectroscopy of the structure sensitive bending region after 0 min (a), 60 min (b), 80 min (c), 90 min (d), 100 min (e), and 120 min (f). The dotted line marks the T-O-T bending mode of the zeolite Y crystal at 505 cm$^{-1}$.
Figure 3.21: SEM analysis of crystallization kinetics. These images show the morphological evolution of the gel during the rapid synthesis process after 60 min (a), 70 min (b), 80 min (c), 90 min (d), 100 min (e), 110 min (f), and 120 min (g)......

Figure 3.22: SEM of crystalline products after 100 min of rapid growth. The three magnifications illustrate an increasing level of complexity of the scale becomes smaller. Part a illustrates the density of the crystalline regions. Part b illustrates the aggregation of discrete crystals. Part c illustrates the complex surface structure of the aggregated surface where many individual crystals, thought to derive from discrete nuclei, can be seen. .................................................................

Figure 3.23: Mechanistic scheme starting with the acquisition of equilibrium by gel dissolution in panel 1, followed by microstructure formation and supersaturation in panel 2, then interfacial crystallization of nuclei in panel 3, and finally propagation of the crystalline regions to yield the crystalline product in panel 4. The TEM inset in panel 2 shows the structural development of the gel surface. The branched species in the circular inset of the panel 2 TEM illustrates the beginning of order. The TEM inset in panel 3 signifies the appearance of crystalline regions. The circular inset in the panel 3 TEM illustrates the crystal structure of zeolite Y. ........................................

Figure 3.24: XRD of SAR X gels. Composition SAR 1.4 grown hydrothermally for 3 hrs (a), and grown by rapid synthesis for 3 hrs (b). Composition SAR 2.1 grown hydrothermally for 4 hrs (c), and grown by rapid synthesis for 4 hrs (d). Composition SAR 2.5 grown hydrothermally for 48 hrs (e), and grown by rapid synthesis for 48 hrs (f).................................................................

Figure 3.25: Crystallization Curve for the composition SAR 2.1 showing the crystallization time scale for hydrothermally grown zeolite Y represented by the small red circles, the crystallization of co-phase zeolite P represented by the blue squares. The large red circles represent the time scale for the crystallization of SAR 2.1 under rapid synthesis conditions. .................................................................

Figure 3.26: SEM of SAR 1.4 crystals. Crystalline products isolated after 6 hrs of hydrothermal growth imaged at three magnifications (a, c, and e). Crystalline
products isolated after 3 hrs of rapid synthesis imaged at the same three magnifications for comparison of the resultant crystal morphology (b, d, and f). ... 144

Figure 3.27: SEM of SAR 2.1 crystals. Crystalline products isolated after 12 hrs of hydrothermal growth imaged at three magnifications increasing from a, to c, and finally to e. Crystalline products isolated after 4 hrs of rapid synthesis imaged at the same three magnifications for comparison of the resultant crystal morphology (b, d, and f). ................................................................. 145

Figure 3.28: SEM comparison of SAR X gels. Crystalline products isolated from composition SAR 1.4 after 6 hrs hydrothermal growth (a) and after 3 hrs of rapid synthesis (b). Crystalline products isolated from composition SAR 1.5 after 8 hrs hydrothermal growth (c) and after 2 hrs of rapid synthesis (d). Crystalline products isolated from composition SAR 2.1 after 12 hrs hydrothermal growth (a) and after 4 hrs of rapid synthesis (f). ................................................................. 146

Figure 3.29: Raman of TMA\textsuperscript{+} incorporation into the sodalite cages of a TMA\textsuperscript{+} templated zeolite reaction replicated from the literature\textsuperscript{76} (a), and a rapidly synthesized zeolite powder after 20 min of reaction while rehydrating with an aqueous TMAOH solution (b). ........................................................................................................ 147

Figure 3.30: XRD of copper containing zeolite products isolated after 110 min of rapid synthesis while rehydrating with an aqueous solution of [Cu(NH\textsubscript{3})\textsubscript{4}]\textsuperscript{2+}. .......... 148

Figure 3.31: SEM images of the as-synthesized membrane. SEM Image of the top view of a 300 kDa cutoff PES support (a), SEM image of the top view of rapidly synthesized nanozeolite seed layer deposited on a PES support (b), cross-sectional SEM image of the rapidly synthesized membrane after 1 hr of growth (c), and a close up cross-sectional SEM view of the membrane-support intergrowth layer accompanied with a color coded schematic (d). ................................................................. 149

Figure 3.32: Membrane and seed layer XRD where the support peaks are marked with asterisks. The XRD pattern of a rapidly grown membrane after 1 hr (a), and the XRD pattern of the seeded support that was used as a starting material (b). Close up views
of the FAU [111] peak are seen for the membrane in part (c), and for the seed layer in part (d).......................................................................................................................................................... 150

Figure 3.33: Membrane nitrogen gas adsorption analysis (a) and pore size distributions (b) for the as prepared materials. Nitrogen adsorption measurements of the bare support (purple), the seeded support (blue), and the rapidly grown membrane (red) are presented in part a. Pore size distributions derived from these measurements for the support (purple), the seed layer (blue), and the membrane (red) are contained in part b....................................................................................................................................................... 151

Figure 3.34: A close up view of the pore size distributions derived for the support (purple), the seeded support (blue), and the grown membrane (red) are contained in part a. Part b illustrates the difficulty of fitting the experimental isotherm of the membrane (blue circles) using the NLDFT method by comparing it with the model fit (red line). ........................................................................................................................................ 152

Figure 4.1: X-Ray diffraction powder patterns of a) Zeolite membrane (the strong peaks above 25° 2θ are from the alumina support), b) Micron-sized commercial powder c) synthetic micronsized powder d) Sub-micron powder and e) nano-sized powder ... 172

Figure 4.2: Electron micrographs of a) Cross-section view of the zeolite membrane b) Syntheticmicron-sized commercial powder c) Commercial micron-sized Synthetic micron-sized powder d) Sub-micron powder and e) Nano-sized powder (a TEM image). ........................................................................................................................................ 173

Figure 4.3: Comparison of the Si/Al ratio obtained by 29Si MAS NMR and XPS for synthetic and commercial micron-sized (zeolite X), sub-micron sized and nano-sized zeolites. ........................................................................................................................................ 174

Figure 4.4: 29Si – magic angle spinning (MAS) NMR of commercial micron-sized zeolite, along with the curve deconvoluted bands from the differently coordinated silicon........................................................................................................................................ 175

Figure 4.5: Impedance (Nyquist/Argand) plots of commercial micron-sized zeolite at different temperatures as designated in the legend (Ω = Ohms)......................... 176
Figure 4.6: Impedance (Nyquist/Argand) plots for zeolite membrane (a), submicron-sized (b), nano-sized (c), and synthetic micron-sized (d) zeolites. .................. 177

Figure 4.7: Modulus ($M''$) plot against frequency for commercial micron-sized zeolite at various temperatures, along with the relaxation times calculated from the peak frequency (included in the legend). .......................................................... 178

Figure 4.8: Modulus ($M''$) plots for zeolite membrane (a), submicron-sized (b), nano-sized (c), and synthetic micron-sized (d) zeolites. Again, the relaxation times are included for each sample at each temperature (contained in the legend). ............... 179

Figure 4.9: Comparison of the normalized curves for $Z''$ and $M''$ for micron-sized commercial zeolite. .......................................................... 180

Figure 4.10: Plots of activation energy trends for Li$^+$, Na$^+$ and K$^+$ exchanged zeolite membrane (black square), commercial micron-sized (red dot), submicron-sized (blue triangle), and nano-sized zeolites (purple inverted triangle). On average, an error of $\pm 1$ kJ/mol was observed based on replicate measurements on the Na$^+$ samples. No replicate measurements were made on the Li$^+$ and K$^+$ samples. ...................... 181

Figure 4.11: Surface derivatization scheme illustrating the surface modification reaction between zeolite and TMDS.......................................................... 182

Figure 4.12: a) Equivalent circuit model b) the Nyquist/Argand plot for nano-sized zeolite at 525 °C along with fit using the parameters listed in Table 4.3. .............. 183

Figure 5.1: Particle size distribution of the nanozeolite dispersion obtained from DLS. The average particle size, as indicated with the red dotted line, is 48 nm. .......... 229

Figure 5.2: Average particle diameter (red dots) and zeta potential (black squares) as a function of pH. .......................................................... 230

Figure 5.3: XRD patterns of a standard zeolite Y as simulated from the FAU structure (a), the as-synthesized nanozeolite Y (b), and silver exchanged zeolite Y after 24 hr of reduction with 0.1 M resorcinol (c). Peaks marked with a dot in (c) indicate intensity variations due to silver inclusion. Peaks marked with an asterisk in (c) indicate FCC silver. The inset shows the chemical structure of resorcinol. ...................... 231

xxv
Figure 5.4 XRD patterns of silver exchanged zeolite Y (a), silver exchanged zeolite Y reduced with 0.1 M hydroquinone (b), and silver exchanged zeolite Y reduced with 0.1 M catechol (c). The asterisks in (b) and (c) denote FCC silver. The chemical structures of catechol (top), and hydroquinone (bottom) are included next to their respective pattern. 232

Figure 5.5: Photographs of an aqueous 0.1 wt% silver exchanged nanozeolite dispersion reduced with 0.1 M catechol (left), and 0.1 M resorcinol (right) after 12 hrs. The chemical structures of catechol (bottom left), and resorcinol (bottom right) are included for reference. 233

Figure 5.6: Extinction spectra of an aqueous 0.1 wt % silver exchanged nanozeolite dispersion reduced with 0.1 M resorcinol after 2 hrs. (a), 6 hrs. (b), 12 hrs. (c), and 24 hrs. (d). No observable features were detected in the sample prior to 2 hrs. Also, no change in the extinction spectrum was observed after 24 hrs. The major features in each extinction spectrum are labeled with a dotted black line. 234

Figure 5.7: The diffuse reflectance UV-Vis absorption spectrum (Kubelka-Munk transformed) of the zeolite powder isolated from the resorcinol reduction after 1 hr. 235

Figure 5.8: Photographs of the resorcinol reduced silver zeolite after 0 hrs. (left), 1 hr. (middle), and 2 hrs. (right). 236

Figure 5.9: Kinetics of the 445 nm surface plasmon absorption band of silver during the reduction of an aqueous AgNO₃ solution with 0.1 M resorcinol as measured by UV-Vis spectroscopy. 237

Figure 5.10: Extinction spectra of the aqueous silver colloid formed after reduction for 2 hrs with resorcinol (red line), and 24 hrs with resorcinol (blue line). 238

Figure 5.11: A collection of HAADF-STEM images showing the progress of the silver reduction after 1 hr. (a), 2 hrs. (b), 3 hrs. (c), 6 hrs. (d), 12 hrs. (e), and 24 hrs. (f). The bright spots in these images are due to silver particles. 239

Figure 5.12: Particle size distributions calculated from the HAADF-STEM images in figure 5.14 after 1 hr. (a), 2 hrs. (b), 3 hrs. (c), and 6 hrs. reduction with resorcinol
(d). After 6 hrs., the system becomes too heterogeneous to obtain accurate size
distribution with electron microscopy. ............................................................... 240

Figure 5.13: Nitrogen adsorption isotherms (red open dots) and desorption isotherms
(blue crosses) for sodium exchanged nanozeolite (a), for silver exchanged nanozeolite
(b), silver nanozeolite after 1 hr. (c), after 2 hrs. (d), and after 6 hrs. reduction time
with resorcinol (e). ................................................................................................ 241

Figure 5.14: The evolution of the BET surface area (blue line, black diamonds) and the
relative microporosity (red line, black dots) of the nanozeolite materials as a function
of reduction time. .................................................................................................. 242

Figure 5.15: Photographs of powdered silver exchanged zeolite samples viewed under
ambient light (a) and 254 nm UV light (b) after several designated reduction times. A
close up the photo of the 0 hr (c), a 1 hr (d), and a 2 hr reduced sample (e) viewed
under UV excitation............................................................................................. 243

Figure 5.16: UV-Vis spectra of the aqueous Dsm⁺ dye as a function of pH. .............. 244

Figure 5.17: Emission spectra of the aqueous Dsm⁺ dye as a function of pH excited at
450 nm. .............................................................................................................. 245

Figure 5.18: In-situ emission spectra of the Dsm⁺-Ag⁺-Y mixed cation system excited at
450 nm as a function of reduction time: (a) is before the addition of resorcinol and (b)
is 2 hrs after the addition of resorcinol. ............................................................ 246

Figure 5.19: HAADF-STEM images following migration of silver species through the
zeolite matrix toward large surface particles in samples reduced for 12 hrs. Panel (a)
gives a unified view of a large region while panels (b-d) are magnified views of the
boxes drawn in (a). ............................................................................................ 247

Figure 5.20: HAADF-STEM of silver nanoparticles migrating through the zeolite matrix
toward large surface silver particles observed in the sample after 24 hrs. of reduction.
Panel (a) give a wide field of view while (b-d) magnify each of the boxed regions in
(a). .................................................................................................................... 248

Figure 5.21 HR TEM of silver loaded zeolite after 24 hrs reaction time. Spherical silver
particles of various dimensions are observed in (a). The inset shows clear lattice
planes characteristic of FCC silver and measures the dimensions of one of these particles. In panels (b) and (d) magnified views of the occluded silver particles are examined. Panels (c) and (e) are the FFT images of (b) and (d) respectively. Figure 5.22: Schematic illustration the preparation of the colloidal nanozeolite SERS substrate. Figure 5.23: Surface enhanced Raman spectra as a function of time. The inset plots the change in the intensity of the 999 cm⁻¹ band as a function of time. The enhancement factor calculated for the 2 hr reduced sample is listed in the inset (10⁴). Figure 5.24: Surface enhanced Raman spectra of the colloidal substrate as a function of cuvette depth. The depth increases toward the bottom of the cuvette as the magnitude of the data set increases from 0 to 6 on the data set axis. Figure 6.1: Intensity-intensity autocorrelation function (a) and intensity weighted particle size distribution (b) of the as-synthesized nanozeolite dispersion. Figure 6.2: Intensity weighted (a), volume weighted (b), and number weighted (c) particle size distributions calculated for the as-synthesized nanozeolite dispersion. Figure 6.3: XRD pattern of the as-synthesized nanozeolite powder. Figure 6.4: A TEM image of the nanozeolite particles synthesized herein. Figure 6.5: The nitrogen adsorption (red circles) and desorption (blue crosses) isotherms representative of the nanozeolite synthesized herein. Figure 6.6: Comparison of the UV-Vis absorption spectrum of the BPE²⁺-Na⁺-ZY system (a) and its fluorescence spectrum (b) with the UV-Vis absorption spectrum of the aqueous BPE²⁺ dye (c) and its corresponding fluorescence spectrum (d). Figure 6.7 Experimental TCSPC decay curves (blue circles), instrument response functions (thin red lines), model decay curves (thick red lines) and residuals (black lines) for the aqueous dye system (a) and the BPE²⁺-Na⁺-ZY system fit with a double exponential model function (b) and a triple exponential model function (c). Figure 6.8 Femtosecond transient UV-Vis absorption spectra of the aqueous dye system observed from 0-3 ns (a), 0-5 ps (b), 5-200 ps (c) and 200 ps-3 ns (d).
Figure 6.9: Femtosecond transient UV-Vis absorption spectra of the BPE$_{2}^{2+}$-Na$^{+}$-ZY system observed from 0-3 ns (a), 0-5 ps (b), 5-90 ps (c), and 90 ps-3 ns (d).

Figure 6.10: Femtosecond transient UV-Vis absorption spectra of the BPE$_{2}^{2+}$-TMA$^{+}$-ZY system observed from 0-3 ns (a), 0-10 ps (b), 10-100 ps (c), and 150 ps-3 ns (d).

Figure 6.11: Decay traces derived from the transient UV-Vis absorption measurements of the aqueous dye system (a), and the BPE$_{2}^{2+}$-TMA$^{+}$-ZY system (b) at 465 nm.

Figure 6.12: Decay traces derived from the transient UV-Vis absorption measurements of the aqueous dye system (a), and the BPE$_{2}^{2+}$-TMA$^{+}$-ZY system (b) at 375 nm.

Figure 6.13: Decay traces derived from the transient UV-Vis absorption measurements of the aqueous dye system at 435 nm.

Figure 6.14: Decay traces derived from the transient UV-Vis absorption measurements of the aqueous dye system (a), and the BPE$_{2}^{2+}$-TMA$^{+}$-ZY system (b) at 510 nm.

Figure 6.15: UV-Vis extinction spectrum of the BPE$_{2}^{2+}$-Na$^{+}$-ZY system before UV laser experiments (a) and after UV laser experiments (b). The spectra are offset vertically for clarity.

Figure 6.16: UV-Vis spectra before (red line) and after (blue line) UV laser experiments for the BPE$_{2}^{2+}$-Cs$^{+}$-ZY system (a), for the BPE$_{2}^{2+}$-Tl$^{+}$-ZY system (b), and for the BPE$_{2}^{2+}$-TMA$^{+}$-ZY system (c).

Figure 6.17: Experimental TCSPC decay curves (blue circles), instrument response functions (thin red lines), model decay curves (thick red lines) and residuals (black lines) for the BPE$_{2}^{2+}$-TMA$^{+}$-ZY system (a), the BPE$_{2}^{2+}$-Cs$^{+}$-ZY (b) and the BPE$_{2}^{2+}$-Tl$^{+}$-ZY system fit with a double exponential model function (c).

Figure 6.18: Femtosecond transient UV-Vis absorption spectra of the BPE$_{2}^{2+}$-Cs$^{+}$-ZY system observed from 0-3 ns (a), 0-20 ps (b), 20-350 ps (c), and 350 ps-3 ns (d).

Figure 6.19: Femtosecond transient UV-Vis absorption spectra of the BPE$_{2}^{2+}$-TMA$^{+}$-ZY system observed from 0-3 ns (a), 0-20 ps (b), 10-80 ps (c), and 500 ps-3 ns (d).

Figure 6.20: Decay traces derived from the transient UV-Vis absorption measurements of the BPE$_{2}^{2+}$-Cs$^{+}$-ZY system (a), and the BPE$_{2}^{2+}$-Tl$^{+}$-ZY system (b) at 375 nm.
Figure 6.21: Decay traces derived from the transient UV-Vis absorption measurements of the BPE$^{2+}$-Cs$^+$-ZY system (a), and the BPE$^{2+}$-Tl$^+$-ZY system (b) at 510 nm. .......... 305

Figure 6.22: Decay traces derived from the transient UV-Vis absorption measurements of the BPE$^{2+}$-Cs$^+$-ZY system (a), and the BPE$^{2+}$-Tl$^+$-ZY system (b) at 465 nm. .......... 306

Figure 6.23: A schematic model representing the photophysical dynamics of the aqueous dye system (a) and the BPE$^{2+}$-M$^+$-ZY system (b) where M$^+$ represents Na$^+$, TMA$^+$, Cs$^+$ and Tl$^+$. ........................................................................................................................................................................ 307
CHAPTER 1: INTRODUCTION

1.1 A Brief Introduction to Zeolites

Mineral zeolites were first discovered by the Swedish mineralogist Cronstedt in 1756\textsuperscript{[1]}. He named the materials with the Greek term "zeolites" which means "to boil a stone" after observing the liberation of water upon heating them.\textsuperscript{1} Since their discovery in the mineral form, many new structures have been synthesized in the laboratory. Some common zeolite structures are presented in Figure 1.1. This figure illustrates the crystalline and porous nature of these materials.

A detailed introduction to zeolites can be found elsewhere.\textsuperscript{2} In brief, zeolites are crystalline, microporous aluminosilicates with the following chemical formula: \((\text{SiO}_2)_x(\text{AlO}_2)_y\text{zMO}_a\text{H}_2\text{O}\). The complex, three dimensional structure of a few common zeolite frameworks are shown in Figure 1.2. The open, porous crystal structure has pores of molecular dimensions. The chemical composition requires a net negative charge on the crystal which allows it to uptake cations (denoted by M in the above chemical formula) by ion exchange. These frameworks are thermally and chemically stable. As a result, zeolites find widespread use in chemical industry. Zeolites are a valuable chemical catalyst used commercially to refine gasoline.\textsuperscript{3} Their ion exchange capacity makes them an important additive in detergents.\textsuperscript{4} Several reports use zeolites for chemical gas sensing.\textsuperscript{5} Though it is a useful material, the synthetic mechanism of formation is complex and largely unknown making the rational design of zeolite difficult. In fact, the synthesis of nanozeolites has only recently been realized, and therefore, the chemical and physical behavior of nano-sized zeolite materials has not been fully explored.
There is no true systematic nomenclature developed for zeolite materials. The nomenclature used herein to denote the zeolites structures will be a mix of their Latin alphabet designation (zeolite Y) and their corresponding mineral topology (FAU). For clarity, the zeolites encountered herein and their corresponding designations are zeolite Y (FAU), zeolite X (FAU), zeolite A (LTA), and zeolite P (GIS).

1.2 Zeolite Structure

Zeolite Y is the focus of this work (mineral form Faujasite). It is one of the largest pore aluminosilicate zeolites. It is constructed of sodalite cages connected through 6-MR in a crystallographically cubic structure (space group Fd3m). The primary building units of zeolite Y are illustrated in Figure 1.2. Figure 1.2a illustrates the structure of the sodalite building unit and Figure 1.2b illustrates the structure of the hexagonal prism building unit (also called a double six-membered ring D6R). The tetrahedral arrays of sodalite cages result in a large (7.4 Å), open 12-MR pore network capable of accommodating most organic and inorganic molecules. The structure of zeolite Y is modeled in Figure 1.3.

1.3 Zeolite Synthesis in General

The first synthetic zeolite (zeolite A) was made from Na, Si, and Al at Linde's laboratories in Tonawanda, NY. Shortly after, Linde synthesized zeolite X and Y, the structural analogues of the natural zeolite Faujasite. Zeolite X and Y are iso-structural and differ only in their composition: zeolite X (Si/Al=1-1.5) and zeolite Y (Si/Al=1.5-5). Typically, the laboratory synthesis of zeolites is performed by hydrothermal means. In this approach, a silica source, an aluminum source, and an alkali source are combined with water in a closed system and heated (between 50-200 °C) under autogenous pressure. The hydrothermal reaction is characterized by the gradual transformation of the amorphous aluminosilicate hydrogel to the final crystalline aluminosilicate zeolite. This process takes anywhere from hours to days.
Zeolite synthesis is empirical. The interested reader can find fundamental details of zeolite synthesis and its historical development in several monographs and publications or the references therein.\textsuperscript{2,7} It is widely acknowledged that the mechanism of zeolite nucleation and growth is different, and more complicated, than that of simple condensed inorganic salts. One unit cell of zeolite can contain hundreds of atoms. Also, zeolites are seldom the thermodynamically favored phase. Instead, zeolites are metastable phases and their formation is governed by kinetic control. The systematic study of zeolite synthesis is an active area of research targeting rational design of the crystalline structure. In addition to synthesizing new structures, a few of the primary research frontiers in zeolite science aim at chemical control over the composition, crystal morphology, and the crystallite size. Some approaches to tuning the crystal size to the nanometer scale are discussed below.

1.3.1 Nanozeolites and their Synthesis

As the physical dimensions of condensed matter shrink to length scales approaching nanometers (10\textsuperscript{-9} meters), their physical and chemical properties begin to change, often drastically, forming a new frontier in physical science: nanotechnology. Today, this diverse field addresses some of the most important problems cutting across all disciplines of science ranging from nanoelectronics on the physical end of the spectrum to nanomedicine on the biological end.\textsuperscript{8} Numerous advances in modern technology utilize discoveries from nanotechnology. For example, fluorescent semiconductor crystals ~5 nm in diameter with unique optical properties are candidates to replace chemical dyes for cellular imaging.\textsuperscript{9} In such cases making materials small has important chemical consequences. The work contained in this document investigates the chemical consequences and advantages of nanozeolites: one of the primary frontiers of zeolite science.

The unique chemical bonding and reactivity of surface atoms relative to their bulk counterparts has spurred intense research in nanoparticle synthesis.\textsuperscript{9} Owing to their increasing surface to volume ratio, nanoparticles maximize the number of exposed
surface atoms, and in turn, maximize the distinct chemical properties derived thereof. While the nano-scale behavior of many materials has been explored in the last decade, zeolites are only just getting their start.\textsuperscript{10} Nanozeolites can be broadly defined as zeolites with a crystal diameter less than 1000 nm.\textsuperscript{11} Stable zeolite colloids less than 200 nm in diameter are at the more interesting, yet most synthetically challenging, end of this spectrum. Nanozeolite between 5-20 nm are the current state of the art.\textsuperscript{12} Depending on the zeolite structure these crystals can range from 5-50 unit cells.

Colloidal systems are interesting from a fundamental point of view as they can be monitored during the entire growth process with a number of analytical techniques. Also, due to the relative homogeneity of nanozeolite clear sols, they are often used as the model system for mechanistic investigations of the entire zeolite growth, in general. Furthermore, colloidal systems are interesting from a practical point of view. Driven by their use in zeolite membranes, thin films and hierarchical structures it is widely acknowledged they provide a realistic opportunity to be used as or assembled into devices.\textsuperscript{12-16} Novel nano-structured functional materials can also be constructed by encapsulating optically active guests in the zeolite micropores.\textsuperscript{17} But also, the fundamental properties of the zeolite are expected to change in this size regime (vide supra). This is likely to impact the performance of the materials in traditional applications like catalysis and separation.\textsuperscript{18} Surface activity might be tuned by the size effect. Molecules and adsorbates would be expected to have reduced diffusion paths. In spite of this discussion, nanozeolites have found no key practical application and remain only as laboratory investigations. However, this is likely a result of their low yields and expensive, industrially unfriendly methods by which they are synthesized.

Stable colloidal zeolites were only realized over the last couple decades.\textsuperscript{11} The first report of colloidal synthesis of zeolite appeared in the early 1990s.\textsuperscript{19} Of the 206 currently existing structures, only a few have been prepared as nanozeolites with an acceptably narrow size distribution (MFI, MEL, LTA, FAU, GIS, SOD, LEL, BEA). This reflects the fact that rational control of zeolite synthesis is not yet fully realized. As expressed above, an exact mechanism is unknown despite intense scrutiny by nearly
every analytical technique imaginable. Nevertheless, several approaches have been developed aimed to target the production of nanozeolites. These techniques are outlined below.

1.3.2 Conventional Clear Gel and Hydrogel Synthesis of Zeolite Nanocrystals

The primary method to synthesize nanozeolite Y is the clear gel method that utilizes colloidal precursors and liberal amounts of organic structure directing agents (SDAs). The first SDA-containing clear sol gel methods were first reported in 1993 by Schoeman and co-workers.19 The first synthesis of nanozeolite Y was reported in 1997 and the paradigm for synthesizing nanozeolites remains largely the same today.20,21 Nanozeolite synthesis is governed by the overall chemical composition of the reactant mixture and the thermodynamic conditions employed. The formation process is sensitive to the identity of the reactants, the chemical and physical synthesis conditions, and even the post synthesis treatment conditions. Care is required in all steps of the synthesis process to ensure a quality product.

Based on considerations from homogeneous nucleation theory, and a wealth of empirical results from zeolite science and other nanometer particulate systems, several strategies targeting nanozeolite production have emerged.12,22,23 A key concept in nanozeolite growth is that the increase in the number of viable nuclei must reduce the final crystal diameter. With this in mind, nanozeolite synthesis from clear solutions of homogeneous sub-colloidal amorphous reactants aims to create conditions that favor nucleation over crystallization. It follows that a homogeneous distribution of nuclei is required for uniform distributions of crystals. Therefore, the starting materials must be uniform. This is usually achieved through the utilization of finely dispersed colloidal silica as a precursor.11 The simultaneity of the chemical processes is also important. The events leading to the equilibration of the starting materials into the precursor gel should proceed in unison to ensure temporal uniformity of the nuclei. Once formed, nuclei should evolve similarly in time to ensure the formation of a narrow distribution of crystal sizes. This strategy has long been utilized for the production of simple salts and metals.23
In the case of nanozeolites, this is achieved by diluting the mixture and adding organic solvents or organic structure directing molecules. The rational is to introduce steric constraints on aggregation and decrease the driving force for multisite nucleation.\textsuperscript{12} Due the high activation energy for crystallization relative to nucleation, low temperatures are often employed to limit crystallization speeds and further Ostwald ripening.\textsuperscript{22} As one might expect, this leads to longer reaction times. Viewed through the lens of this paradigm, homogeneity is key from the beginning of the reaction to the end.

There are many examples emerging of nanocrystal synthesis by the hydrogel route. This route is different in that the starting materials are not a uniform colloid. Rather, they are a heterogeneous gel system (precipitated in some cases) with a wide distribution of particle sizes. This approach can use SDAs but most do not. Rather, the paradigm of this approach is to increase the nucleation rate of traditional alkali metal hydrogels by affecting the supersaturation level during synthesis. These routes are successful in terms of decreasing the crystallite size but are seldom successful at producing narrow size distributions; or even at forming discrete crystals. Typically, large agglomerates of nanostructured crystal formations are often produced. These approaches rely on increasing the driving force for nucleation while abandoning any homogeneity of the starting materials or reaction rates. As a result, these experiments are faster, but destabilization of the colloid is usually unavoidable. From a colloidal point of view, these materials are quite useless as their average aggregate size and distribution are too large to form stable dispersions. In general, these materials are made with heterogeneous catalytic applications in mind where colloidal stability is precluded.

\textit{1.3.3 Confined Space Synthetic Approaches}

Physically limiting the size of zeolite crystals is another approach. Confined space synthesis within an inert matrix provides steric hindrance to crystal growth and ripening, thus limiting the crystal size. The prototypical demonstration of this approach was illustrated by Madsen et al. using mesoporous carbon black to prepare ZSM-5 nanocrystals.\textsuperscript{24} Since its inception many frameworks have been synthesized with this
technique including zeolite Y. The zeolite gel must be restricted to crystallizing within the pore system of the matrix. The zeolite gel and related growth species must not diffuse from matrix during synthesis. The success of this method relies on the inertness of the matrix and its pore size distribution. Also, depending on the matrix, high temperature calcination of the matrix is required in order to recover the nanozeolites. Essentially, high temperature treatments undermine the production of nanoparticles as irreversible aggregation of the particles into larger structures results. Calcination free approaches have been developed by Yan et al. utilizing thermoreversible polymers to confine zeolite X growth. Sub 100 nm particles with a relatively narrow size distribution were achieved by this method.

1.3.4 Specialized Approaches

A top-down approach to creating nanozeolite is used in some cases. Physically breaking large zeolite crystals into smaller crystals is re-emerging with the development of sophisticated milling equipment. This approach has been illustrated for zeolite A and ZSM-5. Ryoo et al. have used specialized templates to grow low dimensional zeolite nanostructures. Microfluidic reactors have been used to produce zeolites recently. The focus of this work is the use of clear sol hydrothermal synthesis of nanozeolite and so further discussion of these techniques is omitted. This method was found to produce the smallest and most uniform zeolite nanocrystals while also being convenient. The interested reader should consult recent reviews for detailed discussion of various approaches to nanozeolite synthesis.

1.4 Scope of this Thesis

Despite the fact that the synthesis and application of nanozeolite is in its nascent stages, several potential applications have motivated the research efforts described in this thesis. The central theme is coupling small crystal diameters with the unique porous structure and relative chemical inertness of the zeolite framework to meet the demands of several applications. In addition to the hydrothermal synthesis and optimization of zeolite
nano-crystals from a clear solution for seeded approaches to fabricating zeolite membranes, three basic applications of this research will be explored. Each area utilizes different properties of the zeolite yet all require the zeolite to be small. The three areas are: 1) the size dependent ionic conductivity of zeolite Y, 2) using nanozeolite as a template to support and control metal nanoparticle formation, and 3) the photophysical consequences of organic dye encapsulation within zeolite micropores.

In chapter 2, the hydrothermal synthesis of nanozeolites from a clear solution and its optimization is discussed. Zeolite Y nanocrystals formed through the optimized process are deposited as seed layers on porous polymeric supports. The secondary growth of these layers, by traditional approaches, into dense membranes and their ability to separate CO₂ from N₂ gas mixtures is explored.

Chapter 3 builds on the work from chapter 2 as it follows the development of a novel alternative approach to growing nanozeolite seed layers into zeolite membranes on polymeric supports. The bulk of the chapter outlines the development of an original synthetic approach aimed at accelerating zeolite growth for these membrane applications. The mechanism of zeolite growth acceleration is proposed.

Chapter 4 marks the transition in this thesis from the synthesis of nanozeolites to the applications of nanozeolites and the exploration of some of their unique chemical and physical properties. Chapter 4 examines the fundamental consequences of making zeolite crystals smaller as reflected by their ionic conductivity. Using the emerging field of nanoelectrics to draw analogies, a range of zeolite particle sizes are examined by electrochemical impedance spectroscopy and a model is proposed to describe the experimental results.

The remaining chapters focus on nanozeolite host-guest interactions and their consequences manifested in the chemistry of two separate model systems: one inorganic and the other organic in nature. Chapter 5 outlines the intra-zeolitic chemical evolution of a silver system. This study follows the reductive growth of silver ions into silver clusters and finally to nanoparticle and bulk silver species. The aim of the study is to elucidate the role the nanozeolite plays in this reaction. A mechanism is proposed to this end. Chapter
details the photochemical and photophysical consequences of occlusion of an organic bipyridinium dye within the zeolite pore system. The novelty of the colloidally stable nanozeolite suspension developed in earlier chapters allows access to photophysical time scales not easily studied in other zeolite systems. This allows the analysis of some of the fastest chemical events ever observed in aqueous zeolite systems. A model is proposed to describe the zeolite's role in altering ultrafast photophysical dynamics.

1.5 References

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*Akad Handl Stockholm* 18, 120–130


1.6 Figures

Figure 1.1: Model structures of several of the most industrially relevant zeolites. Oxygen atoms are omitted in these models for clarity. Each line intersection represents a T atom where T=Si or Al. Figure 1.1a is zeolite A (LTL), figure 1.1b is zeolite Y (FAU), figure 1.1c is silicalite-1 (MFI), and figure 1.1d is zeolite L (LTL).
Figure 1.2: Wire model depictions of the secondary building units that comprise the zeolite Y (FAU) structure. Figure 1.2a is a model of the sodalite building unit and figure 1.2b is a model of the hexagonal prism, or double six-membered ring (d6r), building unit. In these models red represents oxygen atoms and blue represents Si or Al atoms.
Figure 1.3: Models of the primary repeating unit of the zeolite Y (FAU) structure viewed from several perspectives. The crystal plane [h,k,l] perpendicular to the viewing direction is displayed in each of these cases. The crystallographic locations of the extra-framework cations are occupied by red spheres in each case labeled with their corresponding site designation: SI, SI', etc.
CHAPTER 2 : SYNTHESIS AND OPTIMIZATION OF NANOCRYSTALLINE
ZEOLITE Y FROM A CLEAR SOLUTION FOR SEEDING AND SECONDARY
GROWTH OF HYBRID ZEOLITE-POLYMER MEMBRANES

2.1 Introduction

Zeolite membranes and membrane devices are emerging as promising
technologies to address a wide range of problems in applications including chemical
separation, catalytic membrane reactors, chemical sensors/electrodes, photofunctional
materials organization, and low-k films.1,2 Zeolite membranes are becoming popular in
chemical separations. Recently, MFI membranes have demonstrated the ability to
separate xylene isomers.3 Progress in membrane research has resulted in the first
commercial product designed to dehydrate alcohols.4,5 Growth in this field, however, has
been slowed by inherent limitations to membrane fabrication, hence, commercialization
of zeolite membrane products is not wide spread.6 Nevertheless, as pointed out by Caro
et al. novel applications of zeolite membranes are emerging all the time.7

Recently, experimentally and theoretical evidence suggests FAU membranes are
capable of highly efficient carbon capture from CO$_2$/N$_2$ mixtures meant to simulate flue
gas from coal burning power plants.8–10 This finding comes at a prime time as the burning
of fossil fuels provides a significant amount of the worlds electrical energy and coal
consumption is projected to increase by more than 50 % by 2035.11 As the global
economy grows, and developing countries continue to industrialize, energy demands are
expected to increase significantly. Importantly, fossil fuel burning power plants are
considered the largest point source of anthropogenic greenhouse gases, most notably
carbon dioxide. 56.6 % of the total greenhouse gas emissions in 2004 was attributed to
CO₂ from use of fossil fuels.¹² The annual emissions of CO₂ have grown by 80 % between 1970 and 2004 and this is implicated in warmer average global temperatures: 11 of the past 12 years have been the warmest in instrumental record.¹² As a result, much research effort is focused on technical approaches to limiting CO₂ emissions from power plants. Zeolite membranes, particularly zeolite Y, constitute one of the budding strategies aimed at addressing this problem.

Producing high quality zeolite membranes is a technically challenging task. Reproducibility of membrane synthesis is one factor contributing to the challenge.⁶ Ideally, membranes should be continuous, densely grown, and defect free layers. In practice, continuous and dense membranes can be obtained by manipulating the chemistry of the growing system but defects are hard to avoid. Despite tremendous effort, the low reproducibility of membrane syntheses protocols is still a major factor limiting the wide spread use of zeolite membranes.

Conventional growth of zeolite membranes relies mainly on primary and secondary hydrothermal growth techniques. Both these techniques aim to grow a zeolite membrane on a suitable solid support material submerged in a zeolite growth gel or clear solution.¹ In the primary hydrothermal approach a suitable support material is submerged in a zeolite growth solution and the system is subject to hydrothermal conditions for an extended period of time. This technique has experienced some success but secondary growth is more common owing to the higher reproducibly of the results. The secondary hydrothermal approach utilizes preformed zeolite crystals (seeds) deposited on the support surface to enhance the membrane growth.²,¹³,¹⁴ Densification of the uniformly deposited seed layer during secondary growth often results in a uniform membrane with low defect density. Seeding the membrane is a common approach to obtaining high quality membranes.¹⁵,¹⁶ Provided a defect-free synthetic route exists, defect introduction often arises from post-synthetic factors. For example, the mismatch in thermal expansion coefficients between the membrane and support can result in crack formation upon heating and cooling. Also, unit cell expansion and contraction can introduce defects during dehydration-rehydration cycles in gas separation modules.¹⁷
Cost is another limiting factor blocking commercial membrane development. Some cost is derived from the time and energy required for the secondary growth process.\textsuperscript{6} For example, secondary growth can require up to one week in some cases. During this week, the support must be sustained at high temperature (e.g. 100 °C or more). There exist faster protocols to produce aluminum rich zeolite membranes.\textsuperscript{18-20} However, most of the cost is derived from producing the membrane support material. Zeolite membranes are conventionally produced on inorganic ceramic supports. Processing ceramic supports also requires long times and temperatures in excess of 1000 °C are common.\textsuperscript{21} While there is successful sustaining efforts to design more reproducible synthesis protocols, it is widely acknowledged that the cost of production must be addressed if zeolite membranes are to be commercially realized.\textsuperscript{6}

Our approach to this problem is the replacement of expensive inorganic supports with inexpensive polymeric supports seeded with nanozeolite crystals. This addresses the cost and reproducibility issues raised above. Polymers can be produced quickly at a low cost using modern casting and phase inversion techniques.\textsuperscript{22} Interestingly, polymers are becoming a mature technology in the field of carbon capture.\textsuperscript{23,24} Combining the zeolites with such polymeric supports that actively separate CO\textsubscript{2} from N\textsubscript{2} not only confronts the cost issues but will produce interesting performance results. This concept has been explored in the context of mixed matrix membranes, but to the best of my knowledge, never with a multi-layer structure device as proposed here.\textsuperscript{25} Furthermore, nanozeolites will be used to address the reproducibility issues. Nanozeolites can pack uniformly during seed deposition while reducing the size of intercrystalline voids. This minimizes the void space zeolite crystals have to span during secondary growth. Maximizing the uniformity of the seed layer with closely packed nanozeolite is expected to yield a more uniform membrane. Also, nanozeolites are ideal for the production of thin membranes. Nanozeolites in principle should dissolve faster owing to their higher surface energy, thus, higher solubility. Designing thinner zeolite layers is desirable as this limits transport resistance; an important issue in systems where a large flux of gas is expected (i.e. flue gas).
To date, there are few reports of zeolite growth on polymeric supports. Most research is aimed at producing zeolite-polymer composites, mixed matrix membranes, which are physical mixtures of the two materials.\textsuperscript{25,26} In these approaches no continuous zeolite layer is grown. Due to repulsive intermolecular forces, synthesizing highly hydrophilic zeolite membranes on hydrophobic supports presents unique challenges to membrane growth. In this chapter, we explore the synthesis of aluminum-rich zeolite Y membranes on inexpensive, porous polyethersulfone (PES) supports designed to separate CO\textsubscript{2}/N\textsubscript{2} gas mixtures.

\section*{2.2 Experimental Methods}

\subsection*{2.2.1 Materials}

All materials for zeolite synthesis were purchased from Sigma-Aldrich and used as received unless otherwise noted. The following chemicals were used: aluminum isopropoxide, aluminum hydroxide, LUDOX HS-30 and SM-30, tetramethylammonium bromide (TMABr), tetramethylammonium hydroxide (TMAOH) (25 \% aqueous), and sodium hydroxide. Deionized water was used in all cases. Polyethersulfone (PES) polymer supports, provided to us by Dr. W. S. Winston Ho's group, were obtained from Millipore.

\subsection*{2.2.2 Synthesis}

Zeolite Y membranes were synthesized on seeded porous PES supports following a procedure adapted from the literature.\textsuperscript{10} In brief, seeded supports were submerged in a zeolite Y synthesis gel with the composition of 17Na\textsubscript{2}O:1Al\textsubscript{2}O\textsubscript{3}:12.80SiO\textsubscript{2}:975H\textsubscript{2}O using a custom built Teflon support holder. The mixture was enclosed in a Teflon lined stainless steel autoclave and placed in an oven at 100 °C for eight hours. Where noted in the text this process was repeated as necessary. After the reaction the supports were rinsed liberally with DI H\textsubscript{2}O and dried in a hydrated atmosphere maintained with a
saturated ammonium sulfate solution to minimize stresses on the membrane that accompany rapid drying at ambient humidity.

Several synthetic routes were employed in this study. They are labeled as follows: Sub-micron synthesis, and nanozeolite reactions 1-6. These reactions all differ in their chemical composition as discussed below.

Sub-micron zeolite Y particles were synthesized from the composition 0.037Na₂O:3.13(TMA)₂O.4.29SiO₂.1.0Al₂O₃.497H₂O using a method reported in the literature²⁷. According to the literature these particles are ~200 nm in diameter. The clear sol was mixed in a polypropylene bottle aged for 4 hrs and subsequently heated in an oven for 5 days at 98 °C. The product was collected by centrifugation at 2500 rpm and washed liberally with DI H₂O. This process was repeated until the supernatant was neutral.

Six nanozeolite experiments were conducted. Nanozeolite reaction 1 was synthesized using a modified procedure similar to that found in the literature.²⁸ The following gel composition was used:

0.048Na₂O:2.40(TMA)₂O(2OH):1.2(TMA)₂O(2Br):4.35SiO₂.1.0Al₂O₃.249H₂O. The resulting clear sol was aged with stirring for 3 days followed by heating at 100 °C in an oil bath for 4 days. The product was isolated by ultracentrifugation (50,000 rpm at 200,000 relative centrifugal force) and washed with DI H₂O until neutral. Colloidal dispersions of zeolite Y were ion exchanged first with 0.2 M NaNO₃ for 24 hours twice to remove TMA⁺ template from the zeolite super cages. The sodium nitrate exchanged product was again washed liberally with water to remove excess ions. All ion exchanges were performed at an estimated loading of 1g zeolite per 10 mL solution.

Nanozeolite reaction 2 was synthesized using the same chemical composition as reaction 1 except aluminum hydroxide, Al(OH)₃, was used in place of aluminum isopropoxide, Al(C₃H₇O)₃.

Nanozeolite reaction 3 was synthesized using the same chemical composition as reaction 1 except the aluminum isopropoxide was pre-hydrolyzed separately from the silica source. This was done by dissolving the appropriate amount of aluminum
isopropoxide in aqueous tetramethylammonium hydroxide in a polypropylene bottle submerged in a water bath at 60 °C for 1hr with stirring. The aluminum isopropoxide solution was combined with the silica source after which it was treated as reaction 1.

Nanozeolite reaction 4 was synthesized as reaction 3 except the pre-hydrolysis step was 20 min instead of 1 hr.

Nanozeolite reaction 5 was synthesized as reaction 1 except the Na₂O/Al₂O₃ ratio was adjusted to 0.15 prior to ageing by addition of extra NaOH. When sodium hydroxide was added to the mixture the composition was

0.15Na₂O.:2.40(TMA)₂O(2OH):1.2(TMA)₂O(2Br):4.35SiO₂:1.0Al₂O₃:2.49H₂O.

Nanozeolite reaction 6 was synthesized as reaction except LUDOX SM-30 colloidal silica was used in place of LUDOX HS-30. When SM-30 was used the zeolite composition was

0.056Na₂O.:2.40(TMA)₂O(2OH):1.2(TMA)₂O(2Br):4.35SiO₂:1.0Al₂O₃:2.49H₂O.

LUDOX SM-30 has a smaller primary particle size compared to LUDOX HS-30 (7 nm vs. 12 nm) and a slightly higher sodium content (Na₂O/Al₂O₃ = 125 vs. 90)

Fluorescent nanoparticles were prepared by adsorption of rhodamine 6G (R6G) dye to the zeolite surface. A dispersion of 1g nanozeolite was mixed with 10 mL of a 0.1 mM aqueous R6G solution with stirring for 12 hrs. The dispersion was washed by centrifugation until the supernatant fluorescence was minimized while leaving the pellet fluorescence intense (~10 wash cycles).

Spin coating was performed with a Laurell Industries WS-400 spin coater in a class III clean room. Zeolite dispersions made with 0.5 wt% zeolite in water were found to be optimal. Vacuum dip coating was performed with a home built apparatus described elsewhere.²⁹

2.3 Characterization

Diffraction patterns monitor the kinetics of crystal growth. Diffraction patterns were collected using a Bruker D8 Advance with Ni filtered Cu Kα radiation using a 1 s dwell time and 0.02° step size. When indicated, pattern profiles were fit using a Pearson
VII line shape. The fitted line profiles were used to calculate crystallinity curves using the integrated areas of the first five FAU Bragg reflections. Due to a complex background below 10° 2θ, a linear background subtraction was performed prior to fitting. Crystallite sizes were calculated from the fitted peaks using Scherrer's equation in conjunction with the appropriate internal size standard (NIST SRM 640c). In most cases the NIST SRM 640c sample was used as an external standard to maintain sample integrity. The [111] reflection of the standard was used for comparison at 28.44° 2θ.

Electron microscopy was used to investigate morphological features. Scanning electron micrographs were obtained using a Quanta 200 equipped with a tungsten filament for low magnification images (>2 μm). High resolution images of the seeds, seed layers, and of the zeolite membrane cross sections, were collected using a Phillips XL-30F ESEM or a Sirion FEG SEM both are equipped with high resolution field emission guns. Measurements were made on washed, gold coated samples. Transmission electron micrographs were collected using a Tecnai F20 field emission 200 kV S/TEM system.

Fourier transform infrared absorption spectra were collected in attenuated total reflection mode with a Renishaw inVia Raman microscope equipped with an IlluminatIR II™ Infrared microprobe FT-IR microspectrometer module. A ContactIR™ II type IIIa diamond attenuated total reflection (ATR) objective (36x Mag, 0.88 NA) was used to collect spectra. Spectra were the average of ~4000 scans at 4 cm⁻¹ resolution. All spectra were ATR corrected for path length variations.

Nuclear magnetic resonance was used to obtain chemical and structural information related to the growing crystals. A Bruker DSX 300 MHz superconducting magnet equipped with a dual channel (H-X) MAS probe was used to collect high resolution ²⁹Si (59.6 MHz) and ²⁷Al (78.2 MHz) spectra. Approximately 100 mg of sample was packed into a 4 mm zirconium rotor with a Kel-F cap. The ²⁹Si{¹H} NMR spectra were acquired using a standard CPMAS pulse program, the acquisition parameters were as follows: spinning rate of 5 kHz, CP contact time of 5 ms, 10 s recycle delay, 6k-16k scans per sample, and line broadening of 20 Hz. The ²⁷Al NMR spectra
were collected using Bloch decay with acquisition parameters as follows: a 4 µs 90° pulse, spinning rate of 5 kHz, 0.5 s recycle delay, 128-1024 scans per samples, and line broadening of 20 Hz. A Bruker DPX 400MHz spectrometer was used to collect solution state ¹H NMR spectra. Silicon to aluminum ratios were calculated using a formalism put forward by Engelhardt et.al.³⁰

Nitrogen adsorption measurements were made using a Quantachrome NOVA 2200e surface area and pore analyzer to determine the surface areas of the reactants and products during the reaction. Adsorption isotherms were analyzed using Brunauer, Emmett, and Teller (BET) theory to determine surface areas.³¹ The external surface area, the presence of micropores, and the micropore volume was estimated using the t-plot method using De Boer's thickness equation for an oxidic surface.³²

Optical micrographs were collected with an Olympus optical microscope. Photographs were taken with a Cannon digital camera. Fluorescence images were collected with this camera by illumination with a compact 4 Watt short wave (254 nm) UV Lamp (UVP LLC. UVGL-25). Fluorescent nanoparticles were prepared as described above.

Transport measurements were made on zeolite-polymer devices using a homebuilt system detailed elsewhere.²³ A gas feed consisting of 25 % CO₂ and 75 % N₂ was used at 57 °C 1atm feed pressure. The compositions of the retentate and permeate gases were analyzed using an Agilent 6890N gas chromatograph with two thermal conductivity detectors (Agilent Technologies, Palo Alto, CA.). Ar was used as the sweep gas to facilitate gas chromatography analysis.

2.4 Results

2.4.1 Synthesis of nanozeolite particles for deposition

X-ray diffraction patterns for the as-synthesized sub-micron zeolite crystals (vide supra), determined to have a diameter of ~200 nm on average, are displayed in Figure 2.1. The diffraction pattern is characteristic of zeolite Y. The size of these sub-micron
zeolite particles is estimated to be 187 nm based on DLS and greater than 100 nm according to Scherrer's equation. The zeolite isolated from this reaction is pure and crystalline. Only a small amount of zeolite A (less than 5%) is detected in the XRD pattern at 7.2° 2θ.

X-ray diffraction patterns for the nanozeolite reaction 1 product (average diameter reported as 32 nm) synthesized as reported (vide supra) is displayed in Figure 2.2. The Bragg reflections observed are characteristic of zeolite Y. These peaks are weak indicating only partial crystallinity. The broad background centered around 25° 2θ is characteristic of amorphous material. This is attributed to aluminosilicate gel precursor that has not crystallized. Basically, this reaction is incomplete. No size analysis was performed on this product.

X-ray diffraction patterns for the nanozeolite reaction 2 products made using aluminum hydroxide as an aluminum source is displayed in Figure 2.3. The pattern observed is characteristic of zeolite Y. The featureless background suggests complete crystallization of the reactants: no amorphous precursor is present. The size of these particles as estimated by Scherrer's equation is 74 nm. This is larger than expected given literature reports using similar chemical compositions.

X-ray diffraction patterns for the nanozeolite reaction 3 products synthesized with aluminum isopropoxide pre-hydrolyzed for 1 hr is displayed in Figure 2.4. This pattern is not characteristic of zeolite Y. This pattern is characteristic of boehmite (AlOOH). Of course, this is an undesirable product and it was not analyzed any further.

X-ray diffraction patterns for the nanozeolite reaction 4 products synthesized with aluminum isopropoxide pre-hydrolyzed for 20 min until a clear aluminum precursor is obtained is displayed in Figure 2.5. In contrast to samples synthesized with longer hydrolysis times, this pattern is characteristic of zeolite Y. No amorphous background is observed in this pattern indicating quality crystal formation. The size of this crystalline product was determined to be 40 nm by Scherrer's equation.

X-ray diffraction patterns for the nanozeolite reaction 5 synthesis protocol synthesized as above except with added sodium hydroxide are displayed in Figure 2.6.
Zeolite A (LTA) is observed in this case instead of zeolite Y. The zeolite A is highly crystalline. The size as determined by Scherrer's equation is 48 nm. Zeolite A is undesirable in our case because its small pore aperture limits diffusive gas transport through the crystal making it a less effective material for our gas separation applications.

X-ray diffraction patterns for the nanozeolite reaction 6 synthesis protocol utilizing an alternative silicon source, LUDOX SM-30, is displayed in Figure 2.7. Two phases are observed in the powdered product: zeolite Y and zeolite A. Some of the primary peaks corresponding to zeolite A are marked with an asterisk. The sizes of each zeolite phase as determined by Scherrer's equation is 36 nm and 161 nm for zeolite Y and A respectively.

Dynamic light scattering experiments were conducted to determine the average particle size and particle size distribution of the as-synthesized crystals. Figure 2.8 shows the correlation function and NNLS size distribution for the sub-micron zeolite crystals. The average particle diameter and peak width are 235 nm and 71 nm, respectively according to NNLS fit. Cumulants analysis yields 214 nm and 0.1, respectively.

Correlation functions and NNLS size distributions of nanozeolites prepared by nanozeolite reaction 4 are seen in Figure 2.9. The average particle diameter and peak width are 56 nm and 25 nm respectively according to NNLS fit. Cumulants analysis yields an average particle diameter of 48 nm and a polydispersity index of 0.16.

Correlation functions and NNLS size distributions of the reaction performed with added sodium hydroxide is seen in Figure 2.10. Based on XRD, this reaction forms no zeolite Y and only alternate zeolite phases form. The average particle diameter and peak width are 192 nm and 50 nm respectively according to NNLS fit. Cumulants analysis yields an average size of 180 nm and polydispersity index of 0.04 respectively. This indicates a much larger size for the zeolite A formed with this composition relative to the zeolite Y formed at lower Na⁺ concentrations.

Based on the difference in particle diameters for the zeolite Y phase and zeolite A phase measured by DLS, simple filtration methods to separate the particle mixtures by size were explored. This approach was explored in effort to maximize the yield of
nanozeolite Y at the cost of purity by increasing the sodium content followed by filtering the undesired phase. This was one of the approaches devised to obtain high yield nanozeolites. The SEM image contained in Figure 2.11 shows the surface of the filter paper used in this experiment. One pass through the filter provides little separation as seen in figure 2.11a. However, as the filtration process is repeated a greater separation is achieved as seen in figure 2.11b-d. As the colloidal mixtures are passed through the polymer filter paper, zeolite A can be seen adsorbed at the filter surface. No zeolite Y is observed. This indicates zeolite Y passes through the filter while some zeolite A becomes trapped. No improvement in separation was observed after 15 cycles of filtering the particle mixture. Therefore, a smaller pore size filter must be used to address this problem.

A Nitrogen adsorption isotherm of sub-micron particles is presented in Figure 2.12. The isotherm resembles a type I isotherm. There is rapid uptake of nitrogen in the monolayer adsorption regime resulting in a plateau extending through the onset of multilayer adsorption (~0.4) relative pressure after which a hysteresis loop is observed. This rapid uptake is indicative of micropore adsorption. The hysteresis loop resembles type H4 hysteresis loops. Analysis of the isotherm by BET theory provides a surface area of ~635 m²/g. This is typical for a microporous zeolite material. De Boer's t-plot method yields a micropore volume of 0.295 cm³/g. This is in agreement with the theoretical pore volume for an FAU framework: 0.3 cm³/g.³³

A nitrogen adsorption isotherm representative of the nano-crystalline product is presented in Figure 2.13. Again, the isotherm resembles a type I isotherm. There is rapid uptake of nitrogen in the monolayer adsorption regime resulting in a plateau extending through the onset of multilayer adsorption (~0.4) relative pressure after which a hysteresis loop is observed. This rapid uptake is indicative of micropore adsorption. The hysteresis loop resembles type H4 hysteresis loops. Analysis of the isotherm by BET theory provides a surface area of ~475 m²/g. Typically, zeolite Y surface areas are greater than 500 m²/g. Nonetheless, the BET C constant is ~3000 indicating an acceptable fit to the data. Nanozeolite Y is reported to have a lower surface area than bulk zeolite. De
Boer's t-plot method yields a micropore volume of 0.156 cm$^3$/g. This is nearly half the theoretical pore volume for an FAU framework: 0.3 cm$^3$/g. Based on these values the relative microporosity of the sample is 52%. In light of this finding the most plausible explanation for the low surface area is poor crystallinity despite the characteristically crystalline diffraction pattern observed for this material.

Table 3.1 summarizes the chemical conditions and the chemical and physical properties of the as-synthesized zeolites. Nanozeolite reaction 4 was determined to have the optimal size, purity, and yield. The products from nanozeolite reaction 4 are used in the remainder of this chapter for deposition and growth on 300 kDa PES supports. The sub-micron zeolites were utilized on 1000 kDa PES supports.

2.4.2 Deposition of zeolite on polymeric and surface modification polymeric supports

Optical Microscope images of bare and spin coated Millipore 1000 kDa cutoff polyethersulfone (PES) supports are seen in Figure 2.14. Figure 2.14a presents an image of a bare PES support prior to spin coating. A smooth featureless surface is observed. Any features (scratches etc.) that exist are defects and tool marks derived from the method from which they are manufactured. Figure 2.14b shows a microscope image of the best coating obtained by spin coating derived from a 0.5wt% dispersion of sub-micron seeds in water at 500 rpm for 30 s. There is little observable difference between the coated support and the bare support despite many efforts to optimize the weight loading, spinning speed, time, and solvent properties. Due to the volume of experiments necessary to optimize the spin coating process, sub-micron seeds were used as they are produced in greater yield. Preliminary experiments utilizing nanozeolites yielded similar results, so they were discontinued and the sub-micron particles were used as a model system to optimize the process.

Chemical surface modification was used in effort to improve seed adhesion to the supports. Supports were treated with aqueous potassium persulfate. The surface of chemically modified polymer supports was analyzed by ATR-FTIR. Figure 2.15 examines chemical bonding as a function of chemical treatment with K$_2$S$_2$O$_8$. Figure
2.15 a. is a bare, unmodified support washed well with ethanol and water. Figure 2.15 b is a support treated with 5 % K₂S₂O₈ for 24hrs at 60 °C with gentle stirring. The spectrum closely resembles that of the unmodified support at wavenumbers below 1600 cm⁻¹. There are slight shifts in the C-O stretching region, but do not follow any clear trend and are small in magnitude (within error of the measurement). The appearance of a new band in the carbonyl stretching region around 1650 cm⁻¹ is observed in the treated sample with significant intensity. This band is assigned to carbonyl functional groups introduced by oxidation of the support surface. Figure 2.15c and d show similar effects after extended treatment with K₂S₂O₈ under similar conditions for 36 and 48 hrs. respectively. The inset in figure 2.15 is a close up of the carbonyl stretching region.

Figure 2.16a-d show microscope images of surface modified supports as a function of time. Optical microscope images of the 24 hr surface modified supports after spin coating with zeolite is seen in Figure 2.16 a-and b. The surfaces are significantly different from those of the bare or unmodified supports shown in Figure 2.14. Dense islands of material can be seen spread over the support surface in Figure 2.16a. These islands are aggregates of zeolite particles. The density and uniformity of this layer was optimized at 0.5 wt% zeolite in water coated at 400 rpm for 30 s. A close up view of this region is presented in Figure 2.16 b where the islands are clearly seen as dark features against the white support. The optimized coating after 48 hrs surface modification is presented in Figure 2.16 c. Overall it resembles the 24 hr modified sample in agreement. A close up image of the surface is contained in figure 2.16 d. To better visualize the coating fluorescent dye was adsorbed on the particles prior to coating. This allows a fast, qualitative method to image the zeolite coating and facilitate optimization of the process. Figure 2.17d-f presents the fluorescent images of the supports photographed in Figure 2.17a-c. The fluorescent images highlight the irregularity of the coating as large, bright islands are observed (marked with an arrow) over relatively bare regions. Although it is difficult to see in the photographs, by eye this provides a fast, clear method to visualize the coating uniformity. The inset in figure 2.17 f shows the boundary between the coated region on the inside of the support and the bare region on the outer region of the support.
An optical microscope image of an unmodified support vacuum dip coated with zeolite seeds are seen in Figure 2.18. Seeding by the vacuum dip coating method was highly effective at forming uniform layers of nanozeolite seed crystals. No surface modification was necessary using this deposition method. The image in Figure 2.18 has a characteristic iridescent coloration that can be seen with the naked eye. This iridescent coloration indicates a thin and relatively uniform coating on the nanometer to micron scale. Again, indentation and scratches are seen in the image and are derived from the support manufacturing process. This image represents an optimized coating hand dipped in a dispersion of 0.1 wt% nanozeolite in water for several seconds. This image is of a seed layer made with sub-micron seed crystals on a millipore 1000 kDa PES support, but is representative of results obtained with 48nm nanozeolite seeds (reaction 4) on a millipore 300 kDa PES support under identical conditions (except nanozeolite dispersions in place of sub-micron zeolites). Matching the support pore size with the zeolite particle size is an important aspect of uniform layer formation. A detailed study of dense uniform zeolite layer formation of various PES supports is described elsewhere.

SEM images of supports that were vacuum dip coated with nanozeolite are presented in Figure 2.19a-f. Figure 2.19a shows a top view of the bare Millipore 1000 kDa cutoff support. Figure 2.19b and c show a top view and cross-section of the sub-micron zeolite layer deposited on a Millipore 1000 kDa PES support respectively. Figure 2.19b indicates uniform surface coverage of densely spaced zeolite particles. The cross-sectional view in Figure 2.19c indicates the layer is roughly 1 μm in thickness. Figure 2.19d shows the top view of a bare Millipore 300 kDa PES support. Significantly smaller pores are observed for this support as expected. Figure 2.19e shows a top view of the same support after vacuum coating a nanozeolite (from reaction 4) layer. Again, the layer appears to be densely packed and uniform. Figure 2.19f presents a cross-section of this seed layer. The thickness as estimated from this SEM image is 500 nm.
2.4.3 Membrane growth on seeded supports

XRD patterns of seeded Millipore 1000 kDa supports subjected to secondary growth are seen in Figure 2.20a. The characteristic FAU diffraction pattern is obvious. Additional peaks, marked with an asterisk, are derived from crystalline regions of the PES support. Similar observations are made on seeded Millipore 300 kDa supports presented in Figure 2.20b. Due to the inherent advantages using smaller crystals as seeds (vide supra), the nanozeolite system deposited on Millipore 300 kDa supports are the focus of the remainder of this report. All nanozeolite depositions are performed with the products of nanozeolite reaction 4.

Figure 2.22 illustrates the development of the zeolite seed layer as a function of reaction time. Figure 2.22a is a pattern characteristic of the nanozeolite seed layer before secondary growth. The FAU pattern is clear in the seed layer. Figure 2.22b–e represent a section of the same sample after hydrothermal reaction in 2 hr increments. After 2 hr reaction, seen in Figure 2.22b, a significant decrease in the intensity of the FAU [111] is observed. The intensity remains low at 4hrs in Figure 2.22c. After 6 hrs, contained in Figure 2.22d, there is a slight increase in peak intensity. After 8 hr reaction the intensity of the FAU [111] is higher than the initial seed layer as seen in Figure 2.22e. No other phases are formed during the reaction.

Gas transport data for the nanozeolite seeded 300 kDa PES support before and after secondary growth are summarized in table 2. There is a significant decrease in the CO\textsubscript{2} permeance after secondary hydrothermal treatment from 4216 to 250 GPU. Also, an increase in the CO\textsubscript{2}/N\textsubscript{2} selectivity of the grown seed layer is observed from 4.4 to 11.

SEM images of the seed layers after secondary growth are presented in Figure 2.21a–c. Figure 2.21a shows the top view of a portion of the grown layer. Large crystals are observed on the support surface. These crystals are zeolite Y as evidenced by XRD. The morphology of these crystals is characteristic of zeolite Y. The crystals are too sparse to be called a membrane, though there are regions of noticeable intergrowth of the crystals as seen in Figure 2.21b. Beneath these particles the seed layer is intact. Note, however, there are regions of the support that were badly damaged and no coverage was
observed. There is a degree of irreproducibility to this growth experiment. Images and transport data were collected for the best samples obtained. Figure 2.21c shows the cross-sectional SEM of the grown structure. The thickness of the layer is estimated at 1.2 μm based on this image. There is clear difference between the surface crystal growth layer and the seed layer in this image.

2.5 Discussion

2.5.1 Synthesis and Optimization of Nanozeolite Suspensions for Seeding Polymeric Supports

Nanozeolites are formed under special conditions. The size, yield, purity, and time of the reaction are all important factors. For a static chemical composition the two factors affecting the production of quality nanozeolite are the aluminum source and the silica source. These essentially influence the size, yield, and to some extent the reaction time. Sodium has an effect on the purity and yield. These effects are illustrated in the diffraction patterns of reactions 1-6 in Figure 2.1-7 as different sizes, yields, and phases are obtained as a function of these variables.

It seems aluminum isopropoxide provides the best crystals with the smallest size as indicated in table 2.1. The products isolated from reaction 4 possess the optimal mix of physical properties. Perhaps the hydrolysis of aluminum isopropoxide precursors provides some kinetic control to the growth process. The original composition reported by Yan et al. (reaction 1 here) calls for aluminum isopropoxide as the aluminum source. However, directly mixing aluminum isopropoxide with the silica source slows the reaction. After four days of hydrothermal reaction, with three days of room temperature pre-aging, there are only weak Bragg reflections characteristic of zeolite Y seen in figure 2.2. Even extended reaction times yield incomplete crystals. Zeolite Y Bragg reflections are seen above an amorphous background. For this reason, reaction 1 was abandoned. The ineffectiveness is likely due to the competition of zeolite Y with condensed phases like boehmite (vide infra). The problems associated with reaction 1 were avoided by pre-
hydrolyzing the aluminum isopropoxide in a basic solution of tetramethylammonium hydroxide prior to aging.

Pre-hydrolysis of aluminum isopropoxide proceeds by the following reaction:

\[
\text{Al(C}_3\text{H}_7\text{)}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{C}_3\text{H}_7\text{OH}
\]

Completion of this reaction results in a clear solution. Aluminum hydroxide is quite hydrophobic as purchased. Upon addition with water the aluminum precursor phase separates: it floats on top of the water. Dissolving this precursor in water requires intense agitation. Based on my observations, at room temperature this reaction requires in excess of twelve hours even with intense stirring. Even under these conditions, the precursor never fully dissolves. This is suspected to limit the formation of zeolite during the reaction. To accelerate the hydrolysis of the aluminum source, a pre-hydrolysis step was performed with intense stirring in a water bath at 60 °C as a function of time: reaction 3 was performed for 1hr and reaction 4 was performed for 20min. These conditions in reaction 4 were found to be the optimal. When the reaction is performed in this way, substantial hydrolysis of the aluminum isopropoxide precursor can be achieved within twenty minutes. However, this reaction is sensitive to the temperature and time under these conditions. If too low (below 50 °C) or too high (above 70 °C) a temperature is used, the solution will not become clear and instead remains cloudy. At 60°C the solution will become clear after 20 min but will become cloudy again within 45-60 min as seen in reaction 3. Based on X-ray diffraction analysis of powder isolated from reaction 3 presented in figure 2.4 we conclude boehmite is formed under extended pre-hydrolysis conditions. Formation of boehmite particles explains the ineffectiveness of the zeolite synthesis reaction 1 when aluminum isopropoxide is used directly without pre-hydrolysis as seen in Figure 2.2 as it is likely a competitive reaction. However, when pre-hydrolysis is performed for only 20 min prior to addition of the silica source (reaction 4) quality nanozeolite can be obtained in four days as seen in Figure 2.5. All Bragg reflections present in figure 2.5 are assigned to FAU. No amorphous background is observed. Furthermore, the crystals are small (48 nm by DLS and 40 nm by XRD) and relatively monodisperse (PDI = 0.16) resulting in a stable colloid as summarized in table 2.1. It is
hypothesized that 20 min pre-hydrolysis time allows enough aluminum isopropoxide to dissolve without reacting with itself to form boehmite. Furthermore, the dissolved aluminum reacts with the silicon source upon mixing to form aluminosilicate species, thus, limiting the further formation of boehmite. Once the aluminosilicates are formed the system is biased toward zeolite formation rather than boehmite formation.

Alternatively, hydrolysis limitations can be avoided by using a more soluble aluminum source. This is supported by observation made on the same composition using aluminum hydroxide in place of the isopropoxide precursor in reaction 2. Aluminum hydroxide is a more water soluble reactant and no pre-hydrolysis step is needed to form a clear solution. Replacing aluminum isopropoxide with aluminum hydroxide has a noticeable effect on the reaction as seen by comparison reaction 1 and 2 in figure 2.2 and figure 2.3. In contrast to the direct aluminum isopropoxide route used in reaction 1 in figure 2.2, crystalline zeolite Y is formed in four days using the aluminum hydroxide as the aluminum source as seen in figure 2.3. Also, no boehmite is formed. By comparison of the peak widths of the FAU [111] peak from reaction 2 in Figure 2.3 and reaction 4 in Figure 2.5 one can see the size of the aluminum hydroxide derived crystals are larger than that of the pre-hydrolyzed isopropoxide derived crystals. In fact, they are nearly twice as large in diameter as tabulated in table 2.1. Either route can be used to produce nanocrystalline zeolite Y, however, the isopropoxide yields the smaller product at a comparable yield.

The yield and purity of reaction 4 also depends on the sodium concentration. Increasing the sodium concentration will increase the yield of zeolite Y; but it also introduces new phases. If sodium is increased too much, the yield of zeolite Y will decrease as new phases are formed instead. This agrees with experimental observation made in the literature. This is seen in Figure 2.6 and Figure 2.7 for reaction 5 with Na₂O/Al₂O₃ = 0.15 and reaction 6 with Na₂O/Al₂O₃ = 0.056. Additional sodium hydroxide results in the formation of zeolite A (LTA). In fact, all the Bragg reflections are due to zeolite A in Figure 2.6. Zeolite A is known to compete with zeolite Y at certain sodium concentrations. At the sodium concentration used in reaction 5 no zeolite Y is
formed. Zeolite P is also reported to contaminate zeolite Y at high alkalinites, but it is avoided in this case.\textsuperscript{34} Basically, if less OH\textsuperscript{-} is used, zeolite P can be avoided. If less Na\textsuperscript{+} is used, then zeolite A can be avoided. Based on these results, reaction 4 was determined to be limited by sodium and not hydroxide. For the composition used in reaction 4, a wide range of OH\textsuperscript{-} can be tolerated as demonstrated by reaction 5, but small changes in Na\textsuperscript{+} have a significant effect on the outcome of the reaction as demonstrated by reaction 6. This is illustrated in Figure 2.7 for reaction 6 where the Na\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3} = 0.056 and small amounts of zeolite A is observed despite the nearly optimized sodium content (vide supra).

The particle size of reaction 4 can be decreased by using a colloidal silicon source with a smaller particle size. Switching from LUDOX HS-30 to LUDOX SM-30 results in a decrease in the silica particle size from 12nm to 7nm but increases the Na\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3} from 0.048 to 0.09. This decreases the size of the zeolite Y from 40 nm to 35 nm as shown in table 2.1. The yield is increased as evident from the density of particles observed in the post synthesis suspension. Although, it is difficult to determine quantitatively as the formation of large zeolite A crystals contributes to the particle density. X-Ray diffraction analysis of this reaction indicates the formation of zeolite A in figure 2.7. Based on the relative intensities of the FAU [111] and LTA [110], zeolite A is present at about 10 %. There is a noticeable difference in the peak width between the FAU [111] and the LTA [110]. The narrow peaks observed in the LTA pattern indicate larger crystallite sizes. Based on Scherrer's equation the crystallite sizes of the FAU and LTA phases are estimated at 36 nm and >100 nm respectively. This indicates the particle size can be decreased by decreasing the size of the colloidal precursors. However, this must be done without changing the sodium concentration else mixtures of zeolite A and Y will form. Based on the size difference of the zeolite A and Y formed in these mixtures, they might be effectively separated based on their size.

Efforts to separate the FAU and LTA phases based on size had only marginal success. SEM images in Figure 2.11 suggest that even repeated filtration of the zeolite mixture cannot fully purify the zeolite Y. It is interesting to note that only zeolite A is
observed in the SEM images of filter after use. Also, the amount of zeolite A collected with the filter increases with repeating the filtration process while zeolite Y does not. This indicates this approach can be effective with further optimization. Experiments utilizing polymeric filters with smaller pore sizes aimed at separating these phases are currently being performed.

In summary, nanozeolites with an average diameter of 40-74 nm can be synthesized through Al(OH)$_3$ and Al(C$_3$H$_7$O)$_3$ pre-hydrolysis routes. The purity of this reaction is best for 0.048Na$_2$/Al$_2$O$_3$. However, the yield and size are optimal for higher sodium concentrations. At a sodium concentration of Na$_2$O/Al$_2$O$_3$ = 0.09 LTA co-precipitates. Preliminary efforts to separation of the LTA and FAU phases were unsuccessful. The 0.048Na$_2$/Al$_2$O$_3$ synthesis will be used throughout this chapter as it provides a good compromise between size, purity, and yield.

### 2.5.2 Optimizing Nanozeolite Seed Layer Deposition on Porous Polymeric Supports

Creating a dense zeolite seed layer on polymer supports present several challenges. First, particle-support repulsion is thought to play a significant role. This is recognized for a wide range of support materials.$^{1,36}$ Chemical approaches to address this problem rely on pH control of the zeta potential or adding intergrowth supporting substances.$^{37,38}$ The inherent incompatibility of a hydrophilic zeolite seed crystal with a hydrophobic support is expected to create a deposition problem for most common coating techniques. Indeed, this was the case for spin coating nanozeolite on the polymer support as seen in Figure 2.14 b. Poor coverage of the support was commonly observed under any spin coating conditions adopted in this experiment. Even when spin coated at low speeds (~50-200 rpm) no continuous layer was observed. Only discrete islands of zeolite material were observed in most cases. The support could only be sparsely covered. Spin coating zeolite layers has experienced some success as indicated in the literature.$^{39}$ Though, in these cases there is a higher degree of intermolecular attraction between the support and seeds. We reason that a continuous seed layer cannot be achieved by spin coating the hydrophilic, aluminum rich zeolite Y on the highly hydrophobic
polyethersulfone support. Support-seed repulsion, in this case, is too great to overcome with spin coating techniques even at low coating speeds.

Chemical modification of the support surface was performed to address the support-seed repulsion. A tremendous amount of literature exists detailing the modification of sulfonated polymers. Simple methods exist to oxidize the support surface. The aim of these methods is to introduce hydrophilic functional groups by oxidizing the polymer backbone. Potassium persulfate is a popular oxidizing agent to this end. ATR-FTIR spectra of supports treated with potassium persulfate show the development of carbonyl functional groups at 1750 cm\(^{-1}\) as a function of treatment time in figure 2.15 a-d indicative of surface oxidation. This is used as a metric to judge the progress of the surface modification. Essentially, 12 hrs or less of surface treatment results is unsatisfactory zeolite coatings, but 24 hrs or more results in more uniform coatings. This is corroborated by the development of the carbonyl stretching band in figure 2.15 b-d.

Improvement in the nanozeolite coverage on 24 hr and 48 hr surface modified supports can be seen in optical micrographs in Figure 2.16. There is a dramatic change in the density of zeolite on the surface when compared to unmodified supports in figure 2.14. The coatings seem more uniform. The coated zeolite still exists as islands, albeit smaller islands, seen as patterned lines optical micrographs. The islands are agglomerates of zeolite nanoparticles likely form during drying. The formation of island couldn't be curtailed even with controlled drying in an atmospheric chamber. Changing the solvent composition, thus, drying rate with ethanol showed no improvement either. The formation of these islands might reflect the residual repulsion between the support and seeds which cause a clustering of the hydrophilic material. These islands can be visualized in Figure 2.17 under UV light excitation (254 nm) after adsorption of Rhodamine 6G dye on the zeolite surface. These images illustrate a definite improvement in coating with surface modification. However, they also reveal a much greater improvement is necessary to obtain uniform surface coverage. Due to the complications
involved informing a continuous seed layer using spin coating, a new approach was adopted.

Dip coating is a commonly employed method to form uniform seed layers on inorganic supports.\textsuperscript{10} Typically, the porous and hydrophilic nature of the support material plays an important role in the success of this method. This presents a problem for polymeric supports that are obviously hydrophobic. Nevertheless, dense seed layers of nanozeolite were formed on polysulfone and polyethersulfone polymer supports by vacuum dip coating. The vacuum method has been used in the literature to prepare zeolite seed layers.\textsuperscript{42,43} A vacuum is necessary to physically pull the coating solution through the polymer support. In the process, zeolite seeds are physically packed onto the polymer surface creating a well formed layer. The details related to the development of this technique for zeolite on porous polyethersulfone supports is outlined elsewhere.\textsuperscript{29} Polymer supports were chosen so that their mean pore diameter was smaller (or comparable) in diameter to that of the zeolite seed crystal. This helps prevent zeolite seed infiltration into the support during vacuum suction ensuring layer formation at the surface. Basically, if large pore supports are used, then the application of vacuum suction will cause seed transport through the entire support resulting in seed loss, thus, no seed layer. Results obtained with larger pore supports are similar to those obtained in the filtration experiment designed to physically separate zeolite A and Y. Scanning electron micrographs of the seed layers formed on Millipore 1000 kDa and 300 kDa polyethersulfone supports with sub-micron and nanozeolites respectively are seen in Figure 2.19a-f. The sub-micron seed layer on a 1000 kDa PES support has a thickness of about 1.2\textmu m according to the cross-sectional view in figure 2.19 c. The nanozeolite seed layer on the 300 kDa PES support has a thickness of about 500 nm according the cross-sectional view in figure 2.19 f.
2.5.3 Membrane Growth on Seeded Polymeric Supports by Secondary Hydrothermal Treatment

Membrane growth is thought to proceed by interconnection of discrete zeolite seed particles present in the seed layer according to experimental observations. In this way, a densely packed zeolite seed layer simply intergrow, while molecular building units or amorphous colloidal gel particles adsorb on the crystal surface and subsequently crystallize. In some instances, the seed layer dissolves as the crystal-growth solution interface equilibrates. This might create a local degree of supersaturation higher than that of the surrounding growth medium. This in turn helps drive the inter-connection of zeolite seeds. An alternative model for membrane growth is the evolutionary growth selection model which models membrane growth from the top of the seed layer.

Seed layers were grown through a secondary hydrothermal treatment. X-ray diffraction evidence of secondary growth of seed layers is presented in Figure 2.20a and b for sub-micron and nanozeolites respectively. In both cases the noticeable increase in intensity of the FAU [111] peak is interpreted as growth. Zeolite growth was successful on both large pore supports seeded with sub-micron particles and small pore supports seeded with nano particles. The nanozeolite system was studied in further detail because of its inherent advantages.

The results from transport experiments on nanozeolite seeded supports before and after secondary growth are contained in Table 3.2. The high permeance measured for the nanozeolite seed layer deposited on 300 kDa PES indicates gas transport occurs through large intercrystalline spaces. These spaces result from packing of the nanozeolite layer. Such high permeance is expected for a seed layer dominated by mesopores and macropores. The CO₂/N₂ selectivity measured for the seed layer approaches that expected for the polydimethylsiloxane (PDMS) cover layer. This indicates the zeolite seeds play no role in separating CO₂ from the gas mixture. Gas flows unchanged through the large intercrystalline spaces of the zeolite seed layer. Instead, all the separation occurs during transport through the PDMS cover layer.
Secondary growth of the zeolite seed layer causes a significant change in the permeance and selectivity measured from the device. The permeance drops drastically from 4216 to 250 GPU. This suggests densification of the intercrystalline spaces thereby decreasing the gas flux through the layer. The CO$_2$/N$_2$ selectivity increases to a value above that expected for the PDMS cover layer: from 4.4 to 11. This indicates the zeolite is beginning to play a role in the separation of CO$_2$ from the gas mixture. This is expected from zeolite membrane formation as mesopores and macropores become dandified through zeolite intergrowth. The selectivities measured for the grown layer are much lower than those reported in the literature.\textsuperscript{2,19,20,49} This could be explained by a higher density of defects formed in our case. It is widely acknowledged that the defect concentration scales with the aluminum content.\textsuperscript{36} This is found to be a general phenomenon. This explanation is in agreement with the high permeance measured in our case in comparison to zeolite Y layers in the literature. An alternative explanation of the transport properties could be that membrane growth is incomplete. Microscopic examination of the grown layer can distinguish between these two possibilities.

HR-SEM images of the surface of the grown support indicate discontinuities in growth. There are several regions of the device where only support is visible and zeolitic material is absent. Obviously seeds are removed during growth. Some seed removal is expected during growth. However, in this case expansive regions are left bare while others are left intact. Images of the intact regions are seen in Figure 2.21. Irregular surface coverage is observed in the grown regions. Large zeolite crystals are observed on a surface similar to that observed for the seed layer structure in Figure 2.21a. These large surface crystals resemble, for the most part, single crystals similar in morphology to those observed to precipitate as a powder. Close inspection of the layer indicates regions where intergrowth has occurred as in Figure 2.21b. These regions are characterized by single crystals that have fused into a dense intergrowth. It appears the seed layer is still intact below this surface layer. SEM cross section of the membrane device confirms this suspicion as seen in Figure 2.21c. Two conclusions can be drawn from these observations. First, secondary growth of the top layer is incomplete. Based on HR-SEM
we cannot conclude if the seed layer underneath is completely dense but transport measurements suggest it is not. To address this problem extended crystallization time were used but this resulted in removal of material from the support surface rather that addition of material. Second, great damage is done to the seed layer during secondary growth. This is likely due to dissolution of seeds in conjunction with de-lamination or seed dispersion into the growth solution. Given the irregularity of the support surface after growth it seems de-lamination of large regions is more likely.

2.5.4 X-Ray Diffraction Kinetics of Zeolite Growth on Polymer Supports

To develop a dynamic picture of the evolution of the zeolite layer during secondary growth XRD patterns were collected and analyzed as a function of reaction time. This system allows us to gain some understand of the growth or dissolution processes that occur during the reaction. The growth process is followed by the FAU [111] peak vs. time Figure 2.22. Based on this experiment we can seed dissolution plays a role in the membrane development. This is obvious from significant decrease in the FAU [111] peak at 6.2 °2θ after 2hrs reaction time in figure 2.22b. A portion of this decrease in intensity could be due to de-lamination or re-dispersion into solution. It is unclear from these measurements just how large a contribution each of these effects contributes. However, when paired with previous electron microscopy measurements in Figure 2.21, it seems delamination plays a larger role. Any attempt to analyze the solution phases for the presence of nanozeolite was unsuccessful. This is not surprising given the small amount of nanozeolite contained in the seed layer. Whatever the processes responsible for the decrease of the FAU [111] intensity, they happen fast compared to the reaction time. This could also explain the nearly bare supports obtained after extended crystallization times. These measurements allow us to estimate that ~2 hr is necessary for seed dissolution/dispersion. To compete with this phenomenon, a zeolite growth process that occurs faster than seed dissolution/dispersion would be optimal for these synthesis conditions.
In summary, the poor coverage of the grown polymeric support cannot be explained by seed dissolution alone. Especially given the fact that some regions contain a sizeable amount of seeds after growth. It seems unlikely that seed dissolution should leave large regions of the support bare of seeds while leaving other regions almost untouched. Based on these finding we conclude that dispersion of the seeds from the support surface as a result of poor adhesion is an important process limiting the growth of membranes on polymeric supports.

These observations might explain the lack of literature reports of zeolite deposition and growth on hydrophobic polymeric supports. Researchers preparing zeolite-polymer layer structures adopt specialized approaches that are necessary for membrane formations. For example, Yan et al. have grown zeolite A membranes on hollow crystal fiber polyethersulfone by first dispersing zeolite A seeds within the polymer during preparation. Essentially, this approach uses a mixed matrix membrane as a support. The zeolite A seeds are physically trapped within the polymer support. Therefore, during membrane growth seed dispersion due to poor adhesion is not a problem. This allows Yan and co-workers to form zeolite A membranes capable of effectively separating water/ethanol mixtures. I think this specialized approach developed out of findings similar to the ones outlined in this report. To the best of my knowledge, no reports of a true secondary growth of seeded polymeric supports exist. Other specialized approaches to forming zeolite-polymer composite systems exist however.

Seed retention, thus, membrane growth might be improved by adding an intermediary chemical. Something similar to intergrowth supporting substances (ISS) used in the literature. A cationic polymer might serve this role. Cationic functional groups at a given density on a hydrophobic polymer backbone could improve adhesion of the negatively charges zeolite seeds the polymer surface. However, whatever the structure of the ISS it must not interfere with gas transport. Changing the support surface in a common approach used in the literature (and used in this study for spin coating). This can be controlled to some extent by pH in inorganic systems by would have be based on some more drastic chemistry for polymeric supports. This could allow some
electrostatic attraction. Chemical modification of the seed surface with hydrophobic functional groups is a common approach to making zeolite-polymer mixed matrix membranes\textsuperscript{53}. However, for our application any modification of the zeolite pore opening is counterproductive as we aim to maximize accessibility of the zeolites internal pore space. Dry gel conversion is an alternative approach to grow zeolite membranes\textsuperscript{54}. No solvent contacts the seed layer in this approach. This could eliminate the dissolution/delamination problem.

In conclusion, the secondary hydrothermal growth of zeolite on seeded polymeric supports prepared in this report provide a relatively simple, fast, and inexpensive way to synthesize devices with high gas flux despite never forming a true membrane. This device has a $\text{CO}_2/\text{N}_2$ selectivity that is above that expected for PDMS or Knudsen transport through mesopores suggesting the zeolite islands formed play a role in separating $\text{CO}_2$ from gas mixtures studied here. Furthermore, a hypothesis for generating continuous membranes on seeded polymeric supports is proposed: zeolite growth must occur faster than seed dispersion from the hydrophobic support.

2.6 Conclusion

For membrane growth from using a seeded method, a uniform seed layer is necessary. Nanozeolites provide a uniform seed layer and minimize the intercrystalline spaces due to their packing. Moderate yields of pure, crystalline nanozeolite with an average diameter of ~48 nm by DLS can be obtained by optimizing the chemical composition. Smaller crystals can be obtained at the cost of purity. $\text{Na}^+$ and $\text{OH}^-$ play the largest role in purity while the size of the colloidal silicon precursor determines the size of the crystalline product. A compromise must be struck unless post synthesis separation of the crystal phases is used. Seeding hydrophobic supports with hydrophilic zeolite seeds requires modification of existing coating techniques. Seeding is best achieved by filtration or vacuum dip-coating. Zeolite membranes can be synthesized on polymer supports if the rate of growth is faster than the rate of seed dissolution/dispersion.
2.7 References


42


2.8 Figures

Figure 2.1: XRD of sub-micron zeolites synthesized from a clear solution. The average particle diameter of the zeolite particles as determined by DLS is 214 nm.
Figure 2.2: XRD pattern of powdered products isolated from nanozeolite reaction 1. Bragg reflections characteristic of zeolite Y are observed above the large, broad contribution from the amorphous background.
Figure 2.3: XRD of the powdered products isolated from nanozeolite synthesis 2 using aluminum hydroxide as the aluminum source. The pattern is representative of zeolite Y with a minor contribution from zeolite A (<5 %). Size analysis of these crystals by XRD indicate an average crystallite diameter of 74 nm.
Figure 2.4: XRD pattern of powdered products isolated from nanozeolite reaction 3 which uses a 1 hr pre-hydrolysis step to dissolve the aluminum source. This reaction forms boehmite when subject to reaction conditions identical to reaction 1 as indicated by the characteristic diffraction pattern.
Figure 2.5: XRD pattern of powdered products isolated from nanozeolite reaction 4 where a 20 min pre-hydrolysis step is used to dissolve the aluminum source. All peaks observed are characteristic of zeolite Y. Size analysis by XRD and DLS yield an average particle diameter of 40 and 48 nm, respectively.
Figure 2.6: XRD Pattern of the powdered products isolated from nanozeolite reaction 5 where a small amount of NaOH was added prior to growth. The diffraction pattern observed is characteristic of zeolite A. Size analysis by XRD and DLS indicate an average particle diameter of 48 and 180 nm respectively.
Figure 2.7: XRD pattern of powdered products isolated from nanozeolite reaction 6 where LUDOX SM-30 was utilized as the silica source. Both zeolite Y and zeolite A phases are observed in this reaction. Some intense zeolite A peaks are marked with an asterisk.
Figure 2.8: Intensity-intensity autocorrelation function for the sub-micron zeolite dispersion (red dotted line) and the intensity weighted particle size distribution obtained from a NNLS fit of the autocorrelation data (blue). The average diameter is 235 nm.
Figure 2.9: Intensity-intensity autocorrelation function measured for the nanozeolite reaction 4 dispersion (red dotted line). The intensity averaged particle size distribution obtained by NNLS fit of the correlation function (blue). The average size is 56 nm.
Figure 2.10: Intensity weighted particle size distribution determined from a NNLS fit of the intensity-intensity autocorrelation function. The average size is 192 nm.
Figure 2.11: SEM images of a 1000 kDa cutoff polymer filter used to separate zeolite Y/A mixtures derived from nanozeolite reaction 6 after 0 filter cycles (a), 5 filter cycles (b), 10 filter cycles (c), and 15 filter cycles (d).
Figure 2.12: Nitrogen adsorption isotherm (red, open circles) and nitrogen desorption isotherm (blue, crosses) of sub-micron zeolites indicating the microporous nature of the sample and a BET surface area of 635 m$^2$/g.
Figure 2.13: Nitrogen adsorption isotherm (red, open circles) and nitrogen desorption isotherm (blue, crosses) of nanozeolites isolated from reaction 4 indicating the microporous nature of the sample and a BET surface area of 475 m$^2$/g. There is some hysteresis above 0.4 P/P$_0$ due to particle packing.
Figure 2.14: Optical micrographs of a bare PES support (a), and a PES support spin coated at 450 rpm with a suspension of 0.5 wt% sub-micron zeolite in water (b). A coating pattern can be observed in image b.
Figure 2.15: ATR-FTIR spectra of an unmodified PES support (a), a PES support modified with a 5 wt% aqueous potassium persulfate solution at 60 °C for 24 hrs (b), a PES support modified as in b but for 36 hrs (c), and a PES support modified as in b but for 48 hrs (d). The development of a carbonyl stretching band is observed with treatment.
Figure 2.16: Optical micrographs of a PES support modified for 24hrs and spin coated with a 0.5 wt% aqueous dispersion of sub-micron zeolite (a and b), and a PES support modified for 48 hrs and coated identically to image a (c and d). A more dense pattern of zeolite can be observed on the support surface.
Figure 2.17: Photograph images of supports coated as in figure 2.16 but ion exchanged with rhodamine 6G dye viewed under ambient lighting (a, c, and e), and their respective photograph images viewed under 254 nm UV excitation (b, d, and f). The inset in figure f illustrates the boundary between the coated and un-coated region of the support by the difference in fluorescence intensity. Arrows indicate coated regions.
Figure 2.18: Optical micrograph of a PES support vacuum dip coated with sub-micron zeolite seed crystals. The iridescent coloration indicates a thin, uniform coating.
Figure 2.19: SEM of seed layers deposited on PES supports by vacuum dip coating. Figure 2.19 a-c show the top view of the bare 1000 kDa PES support (a), the top view of the support after coating with an aqueous 0.1 wt% dispersion of sub-micron seeds (b), and the cross-sectional view of b (c). Figure 2.19 d-f show the top view of a bare 300 kDa PES support (d), the support coated with an aqueous 0.1 wt% dispersion of nanozeolites from reaction 4 (e), and a cross-sectional view of e (f).
Figure 2.20: XRD patterns of membranes grown on 1000 kDa PES supports (a), and 300 kDa PES supports (b). Support peaks are marked with an asterisk.
Figure 2.21: SEM images of the top view of a nanozeolite seed layer on 300 kDa PES support after 8 hrs secondary growth (a), a close up of a grown region (b), and the cross-sectional view of this layer (c).
Figure 2.22: XRD patterns of membranes grown from nanozeolite seeded 300 kDa PES supports as a function of time. The seed layer is the starting material in (a), followed by 2 hrs (b), 4 hrs (c), 6 hrs. (d), and 8 hrs. hydrothermal growth (e).
Table 1: Chemical conditions and chemical and physical properties of the as-synthesized zeolites.

<table>
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<th>Sample Designation</th>
<th>Si source</th>
<th>Al source</th>
<th>Na₂O/Al₂O₃</th>
<th>Phase(\text{a})</th>
<th>Diameter (\text{nm})</th>
<th>Diameter (\text{nm})**</th>
<th>(S_{\text{BET}}) (\text{m}^2/\text{g})**</th>
<th>(V_{\text{micro}}) (\text{cm}^3/\text{g})**</th>
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<tr>
<td>Sub-micron</td>
<td>LUDOX SM-30</td>
<td>Al(OH)₃</td>
<td>0.037</td>
<td>FAU</td>
<td>214</td>
<td>&gt;100</td>
<td>625</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>Nanozeolite 4</td>
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<td>LTA</td>
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<td>Nanozeolite 6</td>
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<td>Al(C₂H₄O)₃</td>
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<td>FAU/LTA</td>
<td>36(&gt;100)(^*)</td>
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* Achieved by added NaOH

\# Phases determined by XRD: zeolite Y (FAU), amorphous materials (AM), zeolite A (LTA)

@ Average diameter determined by DLS (Cumulants analysis)

** Average diameter determined by XRD (Scherrer’s equation)

**# Surface area determined by BET method

@ Micropore volume determined by De Boer’s t-plot method

*** Value in parentheses represents the zeolite A fraction

Table 2: Gas permeation properties (permeance and selectivity) of nanozeolite seed layers (a), and nanozeolite seed layers grown by secondary hydrothermal treatment (b).

<table>
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<th>Membrane</th>
<th>(\text{CO}_2) Permeance (GPU)</th>
<th>(\text{CO}_2/\text{N}_2) Selectivity</th>
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<td>a) 40 nm Zeolite Y seed layer on millipore 300 kDa (with water filling of pores before PDMS coating)</td>
<td>4216</td>
<td>4.4</td>
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<tr>
<td>b) Grown Zeolite Y membrane on the above seed layer</td>
<td>250</td>
<td>11</td>
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CHAPTER 3: DEVELOPMENT OF A SIMPLE SYNTHETIC APPROACH TO ACCELERATING NUCLEATION AND CRYSTALLIZATION IN HYDROGEL SYSTEMS AND ITS APPLICATION TO FAU ZEOLITE.

3.1 Introduction

Zeolites and related porous materials are one of the most important classes of functional materials. They are integral components in a wide range of fine chemical, petrochemical, catalytic and adsorbent-based technologies. Of the over 200 zeolite structures discovered to date a mere 18 have been fully commercialized; most notably BEA, FAU, FER, LTL, MFI, and MOR\(^1\). Zeolite Y (FAU framework type) is the most industrially utilized zeolite of all. The global synthetic zeolite market was estimated at 1.8 billion in 2004 and 27% of this value was dedicated to catalysis.\(^1\) Fluid catalytic cracking (FCC) catalysts are the most intensively used catalysts by volume in refineries geared toward producing transportation fuels. It is estimated that 95% of all synthetic zeolites used for catalysis is used in fluid catalytic cracking (FCC) applications and zeolite Y performs the bulk of these duties.\(^1\) Thus, zeolite Y is produced at the largest volumes (along with A, X and ZSM-5) to meet the demand for these applications.

It is a remarkable testament to the versatility of zeolite materials that so many structures exist yet such few are commercially employed. This versatility stems from the vast array of post synthetic treatments capable of fine tuning the chemical and physical properties of the zeolite crystal to meet various applications.\(^2\) In spite of this, far fewer synthetic methods have been developed to alter the chemistry during synthesis. For example, zeolite Y with virtually any Si/Al ratio can be designed using post synthetic dealumination techniques (1.5-\(\infty\)) yet only a comparably narrow range of Si/Al ratios can be
obtained synthetically(1.5-5); most of which require expensive organic reagents.\textsuperscript{2–5} This is but one example illustrating that while zeolites have experienced wide spread success due to sustaining innovations, there exist inherent limitations to the application of zeolites in many contexts. Synthetic advances could have a large impact in a wide range of applications especially given the extensive use of zeolite Y.

Designing the chemistry of zeolites in-situ is difficult. Zeolites are metastable structures, thus, most methods that drive the reaction kinetics unfortunately drive the formation of more thermodynamically stable, condensed phases in accord with Ostwald's step rule.\textsuperscript{5–7} Interestingly, isolation of many zeolite structures with open frameworks (zeolite Y included) relies on kinetic control of the reaction.\textsuperscript{8} So, the problem becomes isolating a fully formed kinetic product in a shorter time without driving the reaction to thermodynamic equilibrium. Furthermore, a true molecular level mechanism detailing zeolite growth is lacking.\textsuperscript{5} Of course, this undermines the ability to predict rational routes to synthesize new structures or to modify existing ones. The molecular details are shrouded in a large, complex set of interrelated chemical equilibria that often exist across several phases of matter (i.e. liquid, amorphous gel, and solid).\textsuperscript{5,8,9} Like finding a “needle in a haystack” resolving the molecular species that are fundamental to zeolite growth from spectator species is a difficult task. Nonetheless, a large body of work detailing the effects of various physical and chemical parameters provides empirical rules to guide the synthetic chemist.

Because of the lack of understanding, an important limitation of zeolites is the long synthesis times required for their production. Zeolites are typically synthesized from a mixture of silicon and metal precursors dissolved or dispersed in alkaline media. The mixture is subject to hydrothermal conditions under autogenous pressure for a time period typically on the order of days to weeks; though several frameworks exist requiring only hours.\textsuperscript{5,10} For a material produced on as large a scale as zeolite Y it is easy to see the benefits of a shorter synthesis time.

Several potential applications can be envisioned that require zeolites to be produced at demanding rates. One of the best illustrations is the use of zeolite membranes
to capture carbon dioxide from the flue stream of coal burning power plants. In fact, zeolite Y based materials have proved capable of approaching the challenging 2020 performance criteria set by the US Department of Energy for such a technology. However, when viewed in context of carbon capture material performance matters little unless it can be implemented in a cost efficient manner. The eventual application of a zeolite based technology on a large scale (for this application) is limited in part by the time, and hence cost, of synthesizing zeolite membranes at high temperatures. The ease and rapidity of polymer support production technologies set the benchmark for zeolite synthesis. The kinetics of zeolite growth must be competitive with those of polymer synthesis technologies to have maximal impact. So, synthetic advances in zeolite chemistry are necessary to design zeolite growth rates compatible with existing technology built to fabricate devices in a rapid, economical fashion.

Zeolite growth is recognized as a nucleation and growth phenomenon. These processes can be conceptualized as sequential events leading to the formation of zeolite crystals. The understanding of zeolite crystallization has benefited immensely from the development of atomic force microscopy (AFM) and high resolution transmission electron microscopy (HRTEM) and their application to clear zeolite solutions. While clear solution synthesis differs from hydrogel systems it is generally found they share many features of crystal growth (e.g. a linear growth rate). This observation has been used to propose a surface addition mechanism where the primary mode of growth is addition of monomers from solution directly on the nuclei surface. However, detailed investigations of the hydrogel synthesis of FAU zeolite with HRTEM suggest an alternative growth mechanism in which crystallization occurs by nuclei propagation at the gel-crystal interface. Nevertheless, there exists a set of generally accepted mechanisms explaining zeolite crystal growth. As a result, a variety of factors have been used to control the crystallization of zeolite for custom applications. However, it is also recognized that crystallization is often not the rate limiting step in zeolite growth. This can be visualized in the crystallization curve for a typical zeolite Y reaction in Figure 3.1. Once the zeolite crystallization begins it proceeds rapidly and continuously until
completion. Rather, it is the induction period before crystallization that requires the most time. This induction period is broadly characterized by the nucleation of molecular species to form viable nuclei and is widely regarded as the rate limiting step. As a result, most attempts to influence the kinetics of zeolite growth target the induction period.

General approaches to accelerating zeolite growth include microwave heating, seeding, physical conditions (agitation), high temperature synthesis, addition of structure directing agents, and increased alkalinity. Microwave techniques have been shown to accelerate zeolite growth.18–20 The mechanism by which microwaves influence zeolite growth is considered mysterious but likely results from uniform heating, superheating, and specific microwave chemical effects or a combination thereof.21–25 These effects are thought to impact the kinetics of nuclei formation during growth. In general, there are mixed reviews on the effectiveness of microwaves in zeolite growth. Seeding aluminosilicate gels with fully formed zeolite crystals is an effective approach to growth acceleration.5,20 The mechanism of seeding is similar to secondary nucleation.26,27 This approach essentially minimizes the time and activation energy necessary to form viable nuclei from molecular precursors because the seed crystal surface acts as a nucleation site. Therefore, this approach generally decreases the induction time substantially.

Hydrogel systems are usually highly heterogeneous, and so, physical conditions (e.g. stirring) can play a role in the kinetics by enhancing homogeneity and nutrient transport.5 These parameters usually play small roles in the growth kinetics but cannot be ignored.

Synthesis at elevated temperatures accelerate zeolite growth.5,28 This is explained largely by the higher solubility of molecular precursors at higher temperatures. An unfortunate side effect is the rapid approach to thermodynamic equilibrium accompanying high temperatures which favors nucleation of more condensed zeolite phases. Phase purity can be compromised at high temperature. Another important paradigm in zeolite synthesis is the utilization of structure directing agents (SDAs).29,30 Quaternary ammonium cations, often used as SDAs, are thought to influence the kinetics by stabilizing transient species essential for nucleation and crystal growth. Organic structure directing agents are expensive. Templated approaches using SDAs are not cost efficient for frameworks like
FAU which is the focus of this work. Instead, entirely inorganic approaches are favored. Lastly, the alkalinity of the synthesis medium can have an impact on the induction time.\textsuperscript{31,32} Hydroxide ions are thought to catalyze many chemical reactions essential to the nucleation step. This approach is discussed in more detail below.

Manipulating the chemical composition is one of the oldest, most effective methods to alter zeolite growth kinetics. Adjusting the Na\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3} ratio is a simple way to impact the growth kinetics as OH\textsuperscript{-} is found to have a catalytic effect on zeolite growth. Part of the catalytic effect of higher alkalinity is attributed to the higher solubility of aluminosilicate species at higher pH.\textsuperscript{5,33} Adopting a classical nucleation theory (CNT) model this effect is understood in terms of increasing supersaturation, and thus, the nucleation rate.\textsuperscript{9} It follows that solubilizing the reactants allows the achievement of a larger population of viable nuclei prepared to crystallize in a shorter time.\textsuperscript{b} Unfortunately, alkaline conditions that favor rapid nucleation rates are generally poor conditions for crystallization.\textsuperscript{35} As a result, more alkaline conditions tend to produce lower yields and less crystalline products. Generally, this is explained by the increased solubility of the crystal itself at high pH values. In light of this two stage paradigm of zeolite growth, a compromise must be struck between the optimal conditions for nucleation and crystallization. Since nucleation is the rate limiting step it seems reasonable to optimize conditions that favor rapid nucleation. However, most applications also require highly crystalline materials. Conventional optimization of zeolite growth chooses the conditions that maximize the nucleation rate while still producing high quality crystals. The problem is, however, this inevitably results in long induction periods.

Our approach to this problem is to use conditions optimal for both stages using a multi step procedure in which the chemical composition is changed in sequential order: a two step approach for a two step process. A two step procedure was developed to accelerate both stages of growth by controlling the gel chemistry in-situ while the reaction proceeds. This two step procedure allows the cycling of the gel chemistry between concentrated and dilute conditions that favor nucleation and crystallization respectively. Essentially, a zeolite hydrogel is allowed to nucleate under increasingly
basic conditions by evaporating water in the first step followed by crystallization of the nuclei upon rehydration of the gel to its original pH in the second step. The hypothesis is that by briefly dehydrating an optimized hydrogel the induction time can be minimized by rapidly forming large populations of viable nuclei. Then, subsequently re-hydrating the gel to its original composition allows these nuclei to crystallize into fully formed crystals without sacrificing yield or crystallinity. Therefore, using this approach, one can optimize the chemical conditions for both the nucleation and the crystallization steps simultaneously in one system to accelerate the chemistry beyond what can be achieved using any single stoichiometry in a closed system. A schematic representing the change in water vs. time is presented in Figure 3.2.

Herein, the development this new (two-stage) technique to accelerate zeolite growth is described and its application to a zeolite Y hydrogel is discussed. This process is termed the "rapid growth process" throughout this document. The rate of zeolite growth under rapid growth conditions is compared to a series of control reactions designed to understand the effects of gel chemistry on growth kinetics. A mechanism is provided for the acceleration of zeolite growth under these conditions. Finally, some interesting applications of this finding are outlined in context of their implications in zeolite technology.

\[a\] Zeolite membranes fabricated on inorganic ceramic oxide supports are utilized on the commercial scale in other contexts.\[b\] It is debated whether the formation of complex materials like zeolites adhere to the rules of CNT. However, in this case CNT provides a useful conceptual framework that predicts some effects of zeolite growth even though it may not be strictly correct. More detailed models of zeolite growth exist including effects of simultaneous primary and secondary nucleation.
3.2 Experimental Methods

3.2.1 Experimental strategy

To assess the impact of the rapid growth approach developed herein several experiments were performed in parallel. In general, three experimental methods were employed for each gel stoichiometry: hydrothermal growth (traditional method), reflux hydrothermal growth, and the developed rapid growth. A set of control reactions was designed to further understand the experimental results.

3.2.2 Synthesis Protocols

Hydrothermal growth of zeolites was performed by adding zeolite growth gels to Teflon lined stainless steel Parr digestion vessels (bombs) and heating them in an oven at the desired conditions. A single batch of growth gel was split between several bombs and placed under identical reaction conditions. Heating conditions were 100 °C unless otherwise noted (as in the case of the 170 °C synthesis). To minimize the effects of the heating rate on the bomb reactions, bombs were pre-heated in an oven at 100 °C until ready to use. The smallest bombs possible were used to minimize thermal perturbations to neighboring reactions upon removal from the oven. Reactions were performed under static conditions as dynamic conditions (rolling) made little difference.

Reflux hydrothermal growth of zeolites was performed by adding zeolite growth gels to a round bottom flask attached to an open condenser heated to reflux with a heating mantle while stirring at 450 rpm. Purging the system with inert gas and stirring rate had no significant impact on the reaction. Glass or Teflon round bottom flasks were used in this reaction. Glass was found to have negligible impact on the reaction during the time scales examined here. Teflon was used to confirm this finding. Similar results were obtained when comparing reactions using glass to those using Teflon.

Rapid growth of zeolites was performed by adding zeolite growth gels to a round bottom flask attached to a pressure equalizing addition funnel equipped with an open
condenser (Figure 3.1). The reaction was heated to reflux with a heating mantle while stirring at 450 rpm. The reaction was allowed to proceed under reflux for 1hr during which time steam from the gel is collected in the addition funnel, essentially dehydrating the gel. Subsequently, the condensate was re-combined with the gel in a drop wise manner over ~1 hr. Upon complete rehydration the reaction is left under reflux. If the addition of reactants is necessary (vide infra) these chemicals were added to the condensate before rehydration. An equal volume of water was replaced with the appropriate chemical in such cases. A detailed example follows.

Zeolite Y with a Si/Al ratio (SAR) of 1.5 was synthesized from an opaque gel with the following composition: 17Na$_2$O:1Al$_2$O$_3$:12.80SiO$_2$:975 H$_2$O. The gel was prepared by combining a basic clear solution of NaOH, Al(OH)$_3$ and H$_2$O with colloidal silica Ludox SM-30 while stirring in a polypropylene bottle. The resulting opaque gel was aged while stirring for 4hrs at room temperature. The aged gel was transferred to the reactor where it was heated to reflux. The reactor was assembled from a round bottom flask (PTFE, glass) connected to a graduated pressure equalizing addition funnel with a PTFE stopcock topped with a condenser (vide supra). While under reflux for 1 hr, 40 mL (411 moles) of H$_2$O from the original composition was condensed within the addition funnel. The resulting gel had the following composition:17Na$_2$O:1Al$_2$O$_3$:12.80SiO$_2$:564 H$_2$O. The collected water was then re-added drop wise to the concentrated gel returning it to its initial composition. Re-addition of the water took 1 hour after which the gel was allowed to react under reflux without any change in composition. Once removed from reaction, samples were immediately freeze dried. The lyophilized pellets were stored under vacuum (50mTorr) until analyzed. Before analysis, the lyophilized samples were pulverized, washed with ~1.5 liters of water by filtration, and vacuum dried in at 60 °C unless otherwise noted. Often, to minimize disruption of the gel surface chemistry, unwashed samples were analyzed.
3.2.3 Control Experiments

Reaction I was performed as a hydrothermal reaction (*vide supra*). Reaction II was performed as a reflux reaction (*vide supra*). Reaction III was performed as a reflux reaction. Reaction IV was performed as a rapid synthesis. Reaction V was performed as a reflux for the first hour followed by rehydration for the second hour (reaction IV). Reaction VI was performed as reaction IV for the first hour followed by reflux for the second hour (reaction III).

3.2.4 Conventional Hydrothermal Synthesis

Zeolite X with a SAR of 1.4 was synthesized form an opaque gel with the following composition: 18.8Na₂O:1Al₂O₃:10.7SiO₂:850 H₂O. The gel was prepared by combining a basic, clear solution of NaOH, NaAlO₂ and H₂O with colloidal sodium silicate solution (27 % SiO₂, 7 %Na₂O) while stirring in a polypropylene bottle. The resulting opaque gel was aged while stirring for 12 hrs at room temperature.

Zeolite Y with a Si/Al ratio (SAR) of 1.5 was synthesized from an opaque gel with the following composition: 17Na₂O:1Al₂O₃:12.80SiO₂:975 H₂O. The gel was prepared by combining a basic, clear solution of NaOH, Al(OH)₃ and H₂O with colloidal silica Ludox SM-30 while stirring in a polypropylene bottle. The resulting opaque gel was aged while stirring for 4hrs at room temperature.

Zeolite Y with a SAR of 2.1 was synthesized from an opaque gel with the following composition: 14Na₂O:1Al₂O₃:10SiO₂:840 H₂O. The gel was prepared by combining a basic, clear solution of NaOH, NaAlO₂ and H₂O with colloidal sodium silicate solution (27 % SiO₂, 7 %Na₂O) while stirring in a polypropylene bottle. The resulting opaque gel was aged while stirring for 12hrs at room temperature.

Zeolite Y with a SAR of 2.5 was synthesized form an opaque gel with the following composition: 8Na₂O:1Al₂O₃:20SiO₂:320 H₂O. The gel was prepared by combining a basic, clear solution of NaOH, NaAlO₂ and H₂O with colloidal silica Ludox
HS-30 while stirring in a polypropylene bottle. The resulting opaque gel was aged while stirring for 24 hrs at room temperature.

N,N,N,N',N',N'-Hexamethylethylene-1,2-diammonium iodide was synthesized according to procedures outlined in the literature. In brief, ethylene diamine was reacted with excess methyl iodide under reflux in methanol for 6 hrs. The solvent was evaporated and the yellowish residue was treated with acetone and collected by filtration. Recrystallization of the residue from methanol yielded the product as a pure while solid 

$^1$H NMR 400MHz (D$_2$O) $\delta$ 4.06 (s, 4H) $\delta$ 3.33 (s, 18H). N,N,N,N',N',N'-Hexamethylethylene-1,2-diammonium hydroxide was prepared by ion exchange of the bromide salt using standard procedures with Dowex anion exchange resin. In brief, $^1$H NMR 400MHz (D$_2$O) $\delta$ 3.169 (s, 18H), $\delta$ 3.916 (s, 4H).

3.2.5 Characterization

Diffraction patterns monitor the kinetics of crystal growth. Diffraction patterns were collected using a Bruker D8 Advance with Ni filtered Cu Kα radiation using a 1s dwell time and 0.02° step size. When indicated, pattern profiles were fit using a Pearson VII line shape. The fitted line profiles were used to calculate crystallinity curves using the integrated areas of the first five FAU Bragg reflections. Due to a complex background below 10°2θ a linear background subtraction was performed prior to fitting. Crystallite sizes were calculated from the fitted peaks using the Debye-Scherrer equation in conjunction with the appropriate internal size standard (NIST SRM 640c). In most cases the NIST SRM 640c sample was used as an external standard to maintain sample integrity. The [111] reflection of the standard were used at 28.44°2θ. The average particle size of the standard is 1.4 μm.

Electron microscopy is used to investigate the morphological development. Scanning electron micrographs were obtained using a Quanta 200 equipped with a tungsten filament for low magnification images (>2 μm). High resolution images of the early phases of the reaction, and of the zeolite membranes, were collected using a Phillips XL-30F ESEM or a Sirion FEG SEM both are equipped with high resolution field
emission guns. Measurements were made on washed, gold coated samples. Transmission electron micrographs were collected using a Tecnai F20 field emission 200 kV S/TEM system.

Raman and infrared absorption spectra provide structurally specific information about the zeolite growth process. Raman spectra of powders were collected from a Renishaw in via Raman microspectrometer equipped with a CCD. A He-Ne laser was used for 633 nm excitation. A solid state diode laser was used for excitation at 785 nm. Spectra were collected with optical configurations yielding ~4 cm\(^{-1}\) resolution. Laser powers at the sample were 1 and 10mW for the 633 and 785 nm excitations respectively. All spectra were collected on spinning samples to avoid damage or heating. FTIR spectra of powders were collected with a Perkin-Elmer Spec400 equipped with a liquid nitrogen cooled MCT detector. Spectra were collected at a resolution of ~4 cm\(^{-1}\). Measurements were made on pellets consisting of ~3 wt% zeolite/powder in KBR. Transmission measurements were made on 0.5 wt% zeolite/powder-KBr pellets pressed until transparent.

Nuclear magnetic resonance is used to obtain chemical and structural information related to the growing crystals. A Bruker DSX 300 MHz superconducting magnet equipped with a dual channel (H-X) MAS probe was used to collect high resolution \(^{29}\)Si (59.6 MHz) and \(^{27}\)Al (78.2 MHz) spectra. Approximately 100 mg of sample was packed into a 4 mm zirconium rotor with a Kel-F cap. The \(^{29}\)Si\{\(^{1}\)H\} NMR spectra were acquired using a standard CPMAS pulse program, the acquisition parameters were as follows: spinning rate of 5 kHz, CP contact time of 5 ms, 10 s recycle delay, 6k-16k scans per sample, and line broadening of 20 Hz. The \(^{27}\)Al NMR spectra were collected using Bloch decay with acquisition parameters as follows: a 4 \(\mu\)s 90° pulse, spinning rate of 5 kHz, 0.5 s recycle delay, 128-1024 scans per samples, and line broadening of 20 Hz. A Bruker DPX 400 MHz spectrometer was used to collect solution state \(^{1}\)H NMR spectra. Silicon to aluminum ratios were calculated using a formalism put forward by Engelhardt et.al.\(^{37}\)

Nitrogen adsorption measurements were made using a Quantachrome NOVA 2200e surface area and pore analyzer to determine the surface areas of the reactants and
products during the reaction. Adsorption isotherms were analyzed using Brunauer, Emmett, and Teller (BET) theory to determine surface areas.\textsuperscript{38} The external surface area, the presence of micropores, and the micropore volume was estimated using the t-plot method using De Boer's thickness equation for an oxidic surface.\textsuperscript{39} Pore size distributions were estimated using the Barrett-Joyner-Halenda (BJH) method using the desorption branch of a given isotherm.\textsuperscript{40} In cases where a wide range of pore sizes were expected, pore size distributions were estimated by applying the non-local density functional theory (NLDFT) method to the adsorption branch of the isotherm.\textsuperscript{39,41} The adsorbate was treated as nitrogen at 77 K; the adsorbent was treated as silica and cylindrical pore geometry was assumed. Calculated isotherms were compared with experimental isotherms to confirm the validity in each case.

3.3 Results and Discussion

3.3.1 Acceleration of Zeolite Growth by Controlling the Gel Composition

To test the posed hypothesis, a zeolite hydrogel's growth behavior is studied and compared under a series of reaction environments. Traditional hydrothermal synthesis of the zeolite Y hydrogel is used as a benchmark to which the central results of the rapid growth procedure are compared. In this way, the direct effects of cycling the gel chemistry between two stoichiometries in the rapid growth process can be compared to the identical, but static, stoichiometry grown hydrothermally. The hydroxide concentration of a gel with the following composition: 17Na\textsubscript{2}O:1Al\textsubscript{2}O\textsubscript{3}:12.80SiO\textsubscript{2}:975H\textsubscript{2}O is controlled by evaporating, condensing, and re-adding a portion of the hydrogel's original water (Figure 3.2). This process is performed in-situ.

The effect of water cycling on the reaction kinetics can be illustrated in terms of the crystallinity curve in Figure 3.3 which arbitrarily separates the reaction into two time frames: the nucleation stage, and the crystallization stage. According to these results the dehydration-rehydration process performed in the rapid synthesis approach dramatically decreases the nucleation and crystallization times for an aluminosilicate gel. Figure 3.4
compares the XRD patterns of the rapid synthesis process and the hydrothermal reaction as a function of time. The control reaction, denoted as hydrothermal reaction, begins to crystallize after 4hrs at which point the first signs of the Bragg reflections characteristic of the zeolite FAU phase appear in the diffraction pattern as seen in Figure 3.4 d. As the reaction proceeds, these reflections grow nearly linearly in intensity until crystallization is complete at 8 hrs. Inspection of crystallinity curve reveals that nearly half the reaction is spent nucleating. No crystals are formed during this time, rather, it is thought a complicated series of chemical and physical transformations occur between the aluminosilicate gel / solution interface (and within the gel and solution respectively) to reach a pseudo equilibrium state capable of crystallizing. In contrast, the rapid growth reacts much faster. Figure 3.4 b shows the first appearance of FAU Bragg reflections at 80 min. This pattern intensifies reaching full crystallinity after 120 min. As seen in Figure 3.3 fully crystalline FAU zeolite is obtained in 2 hrs time with nucleation and crystallization times each being defined by a 60 min period as determined from the crystallinity curve.

A closer look at the crystallization kinetics, at 10 min intervals, is also displayed in Figure 3.4 b. There is no evidence of zeolite at times before 80 min and only a few peaks assigned to soluble salts are present on top of a characteristic amorphous background. After 80 min, the FAU Bragg reflections evolve rapidly into the final crystalline product at 120 min. Nitrogen adsorption measurements corroborate the XRD. The BET surface areas calculated from the adsorption isotherms are shown in Figure 3.5 as a function of reaction time. The surface area increases as the porous zeolite develops and levels off at 650 m²/g comparable to the highly crystalline hydrothermal product. Figure 3.6 a-d compares the adsorption isotherms of the final crystals. Type I isotherms (characteristic of microporous materials) are observed for both the hydrothermal products in Figure 3.6a and the rapid synthesis products in Figure 3.6c. Figure 3.6 b and d are magnified views of the isotherm highlighting the mesoporous region of the isotherms for the hydrothermal and rapid synthesis products respectively. Any mesoporosity is small and likely circumstantial. Micropore volumes of 0.32 and 0.33 cm³/g were measured for
the hydrothermal and rapid synthesis respectively. These values agree with the theoretical pore volume of 0.30 cm\(^3\)/g for FAU and confirms the well formed microporous nature of the rapidly synthesized product after only 120 min.

Chemical perturbations that occur during the rapid growth process seem to accelerate the growth while having no negative impacts on the reaction. For example, based on diffraction data in Figure 3.4 no alternate crystal phases are produced and only FAU patterns are observed. There are several zeolite co-phases that form under conditions similar to those of FAU: LTA, SOD, GIS. While there are many examples of these phases forming alongside FAU under concentrated conditions it seems they are suppressed in this case\(^{35,44}\). Although several reflections at high angles can be observed throughout the reaction they appear at angles too high to be zeolites. The material responsible for these reflections can be removed by washing. Therefore, we attribute these to peaks to trivial starting materials. It is likely these are a result of various water soluble salts or other condensed phases that precipitate during drying. Based on the above results, cycling the water between 975 moles and 564 moles accelerates the formation of highly crystalline zeolite Y without the formation of undesirable co-phases.

Final crystals collected from the rapid synthesis are chemically similar to those isolated from hydrothermal methods. This fact is illustrated in the \(^{29}\)Si-{\(^{1}\)H} CP-MAS-NMR and \(^{27}\)Al MAS-NMR spectra in Figure 3.7. The aluminum NMR spectra in Figure 3.7 b and d indicate a uniform aluminum environment showing a single resonance at 60ppm characteristic of tetrahedrally bound aluminum: \(\text{AlO}_4\)\(^{(45)}\). No extra-framework aluminum is observed. All other features are spinning side bands at multiples of the spinning frequency. The silicon NMR spectra show qualitatively similar splitting patterns for the five possible silicon resonances of the FAU structure in both cases. Each resonance represents one of the different bonding environments of silicon in the crystal.\(^{45,46}\) The similarities in the spectra confirm that no major chemical changes to the crystal occur during the rapid synthetic method. Nevertheless, there is a minor difference in the relative intensities of the \(\text{Si(AlO)}_4\) to \(\text{Si(SiO)}_3(\text{AlO})_3\) resonances at about -84 ppm and -88 ppm respectively. The band at -84 ppm is lower in the rapidly grown product.
This could be interpreted as a decrease in the concentration of Si(AlO)$_4$ relative to Si(AlO)$_3$ in the rapidly grown crystals. This is however unlikely given the more alkaline conditions characteristic of the rapid growth and that hydroxide concentration correlates with crystal aluminum composition.$^{35}$ Basic conditions like those encountered while the gel is dehydrated during the rapid synthesis favor structures with more aluminum like zeolite X (a lower Si/Al). Therefore, a quantitative analysis of the peak intensities using a formalism developed by Englehardt et al. was used to calculate the Si/Al ratio.$^{37}$ Calculations reveal a difference in the Si/Al ratio for the two crystals as displayed in Figure 3.7. The difference is small in magnitude and within error of the measurement. Furthermore, this difference defies conventional thinking as literature reports tend to observe that SAR correlates inversely with hydroxide concentration (vide supra). Based on this discussion, the observed change in crystal chemistry is due only to random error and there exists no detectable difference between the chemical connectivities of products isolated from either reaction. The highly basic conditions encountered by the gel during dehydration are too short lived to manifest themselves in the chemical bonding detected in the $^{29}$Si NMR. The products are considered chemically equivalent.

Although the products are chemically similar, there is a striking difference in the crystal morphology. Scanning electron micrographs in Figure 3.8 show the final crystal morphology of products isolated from each of the reactions. A typical pseudo-octahedron crystal shape is observed for products isolated from the control reaction. Additionally, there exists a small population of crystals that appear to be twinned. In contrast, the rapidly grown crystals have an irregular, multifaceted morphology that appears to be extensively inter-grown. This is the dominant morphology in this sample. The irregular crystal shape may result from a higher driving force for crystallization due to high super saturation levels acquired during dehydration. Similar effects of supersaturation on crystal morphology have been observed in the literature.$^{47}$ As explained by the Gibbs-Thompson equation increasing the degree of supersaturation forces a crystallizing system to form many small crystallites in effort to balance the changing chemical potential with surface energy.$^{48}$ The crystal morphology of the rapidly grown crystal seems to be a
collection of many smaller zeolite crystals that have fused together. This may be a reflection of the [OH\(^-\)] during formation. High concentrations of NaOH was found to result in an undifferentiated crystal morphology while decreasing the Bragg reflection intensity and broadening the Bragg peaks.\(^{35}\) Close inspection of the rapidly synthesized nitrogen adsorption isotherm in Figure 3.6d reveals some unique features. Increase in adsorbed gas with pressure, and the slight hysteresis between adsorption and desorption branches, is likely due to filling of intercrystalline spaces produced by packing the heterogeneous mix of irregular morphologies This observation is in agreement with literature reports of heterogeneous crystal sizes and morphologies obtained from highly basic synthesis media.\(^{35}\)

In summary, making a cyclic change in the water concentration in the early stages of thermal treatment accelerate nucleation and crystallization times. Crystalline zeolite Y can be obtained in 120 min by the rapid process vs. 480 min by hydrothermal means. The product formed via this rapid method (variable composition) has a crystallinity and phase purity identical to that of the control reaction (static composition) on the time scale studied here. The chemical connectivity of the rapidly grown product is identical to that formed in the control reaction. A markedly different crystal morphology is obtained through the rapid synthetic process compared to the control reaction. This unique crystal morphology is an indicator of the chemical processes by which it is formed which are envisioned as the intense incorporation of amorphous material into crystalline zeolite. These observations are explained in terms of the high degree of supersaturation achieved during the dehydration of the gel which results in rapid nucleation. A further, detailed mechanistic study is required to resolve the chemical events responsible for the increased reaction kinetics and distinct crystal morphology. This investigation will elaborate on the posed hypothesis that rapid, interconnected crystal growth is driven by increased levels of supersaturation achieved during gel dehydration.
3.3.2 Examination of the Rapid Crystallization of Zeolite in the Context of Controls

There appears to be a synergistic effect between the sequential dehydration-rehydration steps of the rapid synthesis method and zeolite growth rate. Based on the observations above, and claims made in the literature, we hypothesize the results obtained through the cyclic manipulation of the water content of the growing gel cannot be replicated by performing either of these processes separately. For example, simply dehydrating the gel cannot impact the growth rate in the same way the rapid growth procedure does. Dehydration and rehydration must be done in sequence to exhibit synergy. Six experiments were designed to test this hypothesis. All six experiments have identical starting compositions and differ only in the amount of water present during reaction. Figure 3.9 presents a schematic meant to represent the concentration of water vs. time profile for each of the control reactions. Each of the control experiments is color coded on this diagram that illustrates their water concentration vs. time. Figure 3.10 contains X-ray diffraction patterns obtained from each of these control experiments after 2hrs reaction time. For example, the water vs. time profile labeled with the Roman numeral II in Figure 3.9 yields a product after 2hrs characterized by the XRD pattern in Figure 3.10 II. Consider these patterns "snap shots" of the crystallization process taken at a time when the rapid crystallization process is complete. Therefore, Figure 3.10 defines the crystallinity of each control reaction in relation to the fully crystallized product obtained from the rapid process. Each control experiment is labeled with a Roman numeral (I-VI) and will be discussed in the following paragraphs.

Reaction I was carried out in a Teflon lined auto clave at 100 °C under static conditions. At 2 hrs the diffraction pattern shows no signs of zeolite in Figure 3.10 I. In contrast to the rapid growth product, the product is amorphous. Weak peaks faintly visible at high angles are assigned to starting materials. Under dynamic conditions (i.e. agitation), similar results are obtained. Therefore, any differences in physical conditions between the two reactions are considered unimportant. Essentially, reaction I typifies zeolite synthesis. Comparing it with the rapid process (reaction IV) emphasizes the kinetic effect of cycling the water. Nevertheless, a second control experiment, reaction II,
was devised to rigorously test the effects of physical reaction conditions: stirring, refluxing, and pressure.

Reaction II was identical to reaction I except it was performed in a round bottom flask under reflux conditions while stirring. In both reaction I and II, the water concentration is thought to be constant: 975 moles H$_2$O as illustrated by the purple dashed line in Figure 3.9 denoting reaction I and II. Both reactions I and II were conducted at 100 °C; although, temperature measurements of the well mixed reaction II indicate the temperature can be as high as 102.5 °C. Assuming this is a negligible difference in temperature, all conditions are the same between reactions I and II, except for the physical agitation inherent to the reflux process. Indeed, it is apparent from Figure 3.10 there is little difference in the diffraction pattern of reaction I and II. Only amorphous materials are observed after 2 hrs. It is interesting to note that while there is no change in the diffraction pattern after 2 hrs there is a marked change at later times. The reflux process alone contributes to the kinetic, albeit on longer time scales. These two control experiments preclude the role of physical conditions during the 2 hr time scale relevant here. As a result, the remaining control experiments will focus on water's role in the kinetics.

Reaction III was designed to examine the role of dehydration on the gel chemistry. Reaction III was started as in reaction II except during the first hour 40 mL water (nearly half the total water) was removed by evaporation during reflux. After this hour long dehydration, the remaining concentrated gel containing 564 moles of H$_2$O was allowed to proceed under reflux. It is presumed the water remains constant after the initial dehydration. It is clear from Figure 3.10 III that zeolite Y has formed 2 hrs. However, poor signal to noise and the presence of substantial amounts of amorphous material (obvious from the broad hump at 30° 2θ) suggest poor crystallinity. The FAU peaks are weak and broad implying small crystallite sizes. It is likely that reaction at the highly alkaline conditions characteristic of reaction III promote greater degrees of supersaturation. This is confirmed by reports in the literature observing greater solubility of aluminosilicate species at high alkalinitities. It is also observed that high levels of
supersaturation promote nucleation as is consistent with nucleation theory. We therefore interpret this result in a similar manner and propose that the dehydration step in reaction III and IV are similar in that they promote nucleation of the amorphous precursor gel. Interestingly, reaction III does not fully crystallize on the time scale of reaction I. Even after extended reaction periods (24 hrs.) there is negligible increase in crystallinity. This observation suggests the dehydration process imparts change in the chemical equilibrium between the solution-gel-crystal interfaces that does not recover upon extended reaction at concentrated conditions.

Reaction IV in Figure 3.9 and Figure 3.10 is the rapid synthesis method: it is identical to reaction III except the initially dehydrated water is returned to the reaction in a drop wise manner over a one hour time period (vide supra) using the reaction vessel in Figure 3.2.

Reaction V in Figure 3.9 and Figure 3.10 was performed to test the effects of hydroxide concentration on the crystallization kinetics. Reaction V was performed under reflux using the following gel composition: 17Na2O:1Al2O3:21.80SiO2:564 H2O. This gel composition is representative of reaction IV after one hour: it is essentially the dehydrated gel's composition. The water concentration reaction V is constant throughout the reaction at 564 moles. Again, the diffraction pattern reveals a largely amorphous product with broad, weak peaks corresponding to FAU phase zeolite indicating small crystallites have formed. A discussion of this gel parallels that of reaction III. Reaction V will not crystallize, even after extended crystallization times (~24 hrs.). This is consistent with general observations that concentrated hydrogels produce small crystallites of intermediate crystallinity. Given these results, it is reasonable to conclude the higher concentrations promote nucleation. If fact, it is likely the nucleation under concentrated conditions is sufficiently extensive that most precursor materials are exhausted making further crystallization difficult. To test this hypothesis control reaction VI was devised.

Reaction VI in Figure 3.9 and Figure 3.10 has a starting composition identical to reaction V (564 mol H2O) except after 1hr under reflux water was added drop wise to the reaction. Drop wise rehydration took one hour giving a final composition containing
975 mol H$_2$O. It is clear from the increased intensity and sharpening of the peaks in Figure 3.10 VI that rehydration promoted crystal formation. This leads to the conclusion that rehydration (dilute conditions) promote crystallization of the gel-nuclei system. While the crystallinity of reaction VI is improved relative to reaction V, it does not fully crystallize over a 24 hr period.

The following conclusions can be made from this series of experiments: 1) physical reaction conditions have only minor effects on the reaction at early times 2) concentrated conditions promote nucleation 3) rehydration (dilute conditions) promotes crystallization and 4) dehydration and rehydration performed together have the most profound impact on the growth rate: the processes are coupled. The accelerated kinetic of reaction IV are a result of this unique chemistry authentic to the rapid process.

In light of the above observations it appears the sequential dehydration-rehydration steps authentic to reaction IV are coupled. The separation of these processes results in a product of poor or intermediate crystallinity on the time scales studied here. These poorly crystalline materials require crystallization times in excess of those necessary under traditional hydrothermal conditions (reaction I) at the same chemical composition. Of course, this is undesirable. It is clear the chemical history of the gel is important to the crystallization kinetics. Evidently, chemical events during the dehydration stage are key to accelerating the growth. Disruption of these events by addition of chemicals during rehydration leads to poorly crystalline products. Regardless of the perturbation to the dehydrated gel (HCl, KCl, or H$_2$O) FAU Bragg reflection are observed in diffraction patterns. This is evidence that FAU nuclei have formed during the nucleation phase and that these nuclei are sufficiently reactive to form zeolite nano-crystals. This is also evidence that the further proliferation of FAU nuclei is extremely sensitive to the chemical environment. To further elucidate the effects of rapid process on the nascent present a detailed study of the gel evolution in the following section.
3.3.3 A Mechanistic Study of the nucleation stage of a Rapidly Grown Faujasitic Gel

All products isolated from the reaction prior to 80 min are X-ray amorphous (Figure 3.4). Long range atomic order has not yet been established. This time scale, arbitrarily defined here as the nucleation phase of growth (*vide supra*), is host to a variety of events occurring on the molecular level. Therefore, insight on the mechanistic details of the gel's chemical evolution during this time scale will rely on a host of analytical techniques at different molecular length scales.

The evolution of the nucleating gel's surface is illustrated in Figure 3.11a and b, which compares the morphology of the initial aged gel (at 0 min in Figure 3.11a) to the dehydrated gel (after 60 min in Figure 3.11b). There are clear microstructural differences between the two materials. Images of the 60 min gel highlight the development of a fine porous network. The SEM images resemble collections of 20-50 nm cylindrical/spherical particulate-like surface features that appear to be connected through a complex network structure. HR-TEM images of the gel at two magnifications in Figure 3.12a and b agree with this observation and show clearly the interconnected-network nature of the gel. The nitrogen adsorption/desorption isotherm provides additional clues as to the nature of the gel. Figure 3.13a-d displays the adsorption/desorption isotherms characteristic of these gels. Figure 3.13a and b are the adsorption desorption isotherms for the 0 and 60 min gel respectively. Figure 3.13c and d are the pore size distribution for the 0 and 60 min gel respectively. A clear hysteresis is observed at high relative pressures in Figure 3.13a and b. An empirical classification of the hysteresis loop observed in Figure 3.13b can be made by comparison to IUPAC classifications which correlate to textural properties of the adsorbent. A clear hysteresis is observed at high relative pressures in Figure 3.13a and b. An empirical classification of the hysteresis loop observed in Figure 3.13b can be made by comparison to IUPAC classifications which correlate to textural properties of the adsorbent. According to this empirical guide, the experimental isotherms can be assigned as Type III and H2 or H3 type hysteresis loops. Type III isotherms are typical of nonporous or macroporous materials. The sample is macroporous in this case as determined from SEM. H2 hysteresis loops are indicative of complex network textures with various pore/channel sizes. H3 is characteristic of aggregates with a wide range of slit pore sizes. The data is best represented by something in between H2 and H3. As indicated in the inset of Figure 3.11b the BET surface area of the 60 min gel

90
is ~45 m$^2$/g ($C_{\text{BET}}=558$). Figure 3.13 d displays the BJH pore size distributions which reveals a wide population of pores with most between 14-50 nm. This distribution tails off as it approaches lower pore sizes, but never truly vanishes as some population of pores are present down to 2 nm. Essentially, the nitrogen adsorption measurements indicate pores spanning the entire measurable range are present. Pore sizes measured by nitrogen adsorption agree qualitatively with those observed in the electron micrographs. 

The external surface area of this material as determined by the t-plot method is 40.5 m$^2$/g while the micropore surface area is 7.8 m$^2$/g suggesting the formation of some micropores despite its amorphous nature. 

The 0 min gel seems less porous according to SEM in Figure 3.11 a. Indeed, the BET surface are calculated for this material is ~4 m$^2$/g ($C_{\text{BET}}=264$) as contained in the inset in Figure 3.11 a. The 0min BJH pore size distribution in Figure 3.13 c gel shows a broad population of large pores (similar but narrower than the 60 min) paired with a large population of pores peaking at ~10-20 nm in diameter. In contrast to the 60 min this peak approaches zero quickly as it approaches small pore sizes. The external surface area is determined to be 5 m$^2$/g and no microporosity is detected. NLDFT analysis of the isotherms yields a similar picture of the pore size development. Based on the above data, the porous network at 60 min forms as a result of the regional dissolution of the initial gel which leads to an order of magnitude increase in the surface area. Dissolution of the gel leads to a wider distribution of pore sizes shifted to higher diameters. However, an appreciable amount of small pores are formed in the process. Dissolution is aided by the increasing alkalinity during the 60 min dehydration phase to satisfy new equilibrium conditions between the gel-solution interface$^{49}$. Alkalinity has been shown to increase the dissolution of amorphous aluminosilicates$^{33}$. Therefore, the morphological changes evident during the first 60 min indirectly suggest chemical changes are occurring, and occurring over the entirety of the material and not just in localized environments. In view of the kinetics of this process, the dissolution of gel and changing microstructure is likely an important step in the progression of equilibrium toward formation of viable nuclei. Indeed, the microstructure of the gel has been shown to be an important factor for zeolite
nucleation.\footnote{Figure 3.13 e and f indicate acceptable agreement between the measured isotherm and that calculated in the NLDFT method for the 0 and 60 min gel respectively.} FTIR spectra of the powders isolated during the first 60 min show minimal changes in the structure sensitive bands between 400-800 cm\textsuperscript{-1}. FTIR spectra are displayed in Figure 3.14. Bands at 685 and 765 cm\textsuperscript{-1} due to T-O-T bending and symmetric stretching are clearly resolved in the crystalline product isolated after 120 min. A shoulder at 570 cm\textsuperscript{-1} is also observed. The first sign of recognizable peaks in region occurs at 90 min. Earlier times are characterized by a broad band centered around 680 cm\textsuperscript{-1}.

In contrast, there is an obvious difference between the Raman spectra of the 0 and 60 min samples (Figure 3.15). The Raman spectra of the 0 min gel in the structure sensitive bending region (300-700 cm\textsuperscript{-1}) contains two prominent bands and is typical of the amorphous gel precursor in FAU type zeolites\footnote{The broad band centered ~500 cm\textsuperscript{-1} is assigned to amorphous polymeric silicate out of plane bending modes (Si-O-Si)\textsuperscript{52,53}. The second band centered at 600 cm\textsuperscript{-1} resembles Al-O symmetric stretching bands observed at 620 cm\textsuperscript{-1} for Al(OH)\textsubscript{4}\textsuperscript{-} and is assigned to amorphous polymeric aluminosilicate stretching modes (Al-O-Si).\textsuperscript{52-54} The broadness of these bands indicates a large degree of bonding disorder in the amorphous gel.\textsuperscript{53} The Raman spectrum of the 60 min gel does not contain these bands. Rather, two new bands are observed at 465 cm\textsuperscript{-1} and 568 cm\textsuperscript{-1}. These two bands are broad, but appear narrower than those observed at 0min (FWHM ~ 50 cm\textsuperscript{-1}) indicating structuring of the gel to a more organized state. The band at 568 cm\textsuperscript{-1} is assigned to highly branched aluminosilicate four membered ring structures. Similar assignments have been made in nucleating zeolite X systems.\textsuperscript{55} In fact, there is an inverse correlation between the intensity of this band and that of crystalline zeolite at 505-515 cm\textsuperscript{-1} suggests its incorporation into the final crystal is essential\textsuperscript{55}. There are several possibilities for the band at 465 cm\textsuperscript{-1}. This band exists in a region coinciding with four membered ring (4MR) out of plane bending characteristic of crystalline zeolite Y.\textsuperscript{51,52} However, the energy of this band doesn't match exactly the 4MR bending in the final crystal which is observed at 505 cm\textsuperscript{-1}. This is because the band
at 505 cm⁻¹ in the final crystal is thought to be a convolution of T-O-T out of plane bending originating from 4MR and 6MR.⁵¹ Since the material is not yet crystalline this is somewhat expected. Another possible assignment is six membered rings (6MR). Li et al. assign bands below 470 cm⁻¹ to 6MR.⁵³ It is worth noting there is some disagreement between the spectral range corresponding to 4MR and 6MR bending modes. It is well recognized that there is a general inverse proportionality between the energy of a mode and the number of T atoms. Assignments of 4MR and 6MR vary⁵¹. The observed band at 465 cm⁻¹ is in an ambiguous location with respect to its identity as a 4MR or 6MR. Lastly, given the nature of the sample it could be a trivial aluminosilicate salt. It is unlikely any monomeric silicate species would contribute at this energy as the stretching modes of these species are commonly observed above 700 cm⁻¹.⁵²,⁵⁴ Symmetric stretching due to [SiO₂(OH)₂]²⁻ has been observed in the 440-450 cm⁻¹ region⁵⁴. Some polymeric silicate species have been assigned to a band observed 480 cm⁻¹ in hydrogel systems⁵³. We therefore assign this band to four membered rings present in an environment intermediate between the crystal (with well defined bond angles) and the amorphous gel (with poorly defined bond angles). This assignment can be justified by the presence of a band at 370 cm⁻¹ which appears at ~90 min and becomes well defined by 120 min. This band is assigned to a double six membered ring structure (d6r): a cage-like structural element of the final crystal⁵². The delayed growth of this band can be interpreted as an under abundance of 6MR. This band is coincident with a 760 cm⁻¹ band in the FTIR with similar assignments⁵¹. However, the band signifying crystalline zeolite at 505 cm⁻¹ grows in much faster. Even though this band is a convolution of effects from 4MR and 6MR it is considerably broadened upon formation and narrows with time. The broadness of the band is attributed to bonding disorder of the 4MR and a variety of silicon and aluminum connectivities as expected given our stoichiometry. The time scale of narrowing coincides with the appearance of the 370 cm⁻¹ d6r band. This can be interpreted as the formation and immediate fusing of 6MR to preformed 4MR resulting in bands resembling the final zeolite Y crystal. A gel composed predominantly of 4MR
structures is concluded and is in general agreement with recent observations in the literature\textsuperscript{55,56}.

Due to the X-ray amorphous nature of the gel during the Raman measurements we hypothesize these four membered rings as the molecular structures necessary for nuclei formation. The change in microstructure evident from SEM paralleled by the appearance of new bands in the Raman spectra lead us to conclude that dehydration plays a key role in nuclei formation. In effect, the high degrees of local supersaturation achieved resulting from gel dissolution during the dehydration can be thought to promote nuclei formation by way of 4MR structures. Using the SEM and Raman as an indicator, it is reasonable to conclude this nuclei formation is promoted extensively throughout the bulk of the gel and not just in localized regions. A closer examination of the gel is in order to confirm this finding.

TEM of the 60 min gel show the finer details of the gel surface structure. The gel is uniformly porous in agreement with the SEM. Close examination of the surface reveals a largely amorphous structure with a distinct surface roughness. Though the gel is X-ray amorphous, electron diffraction spots are observed in several locations in the gel. They are, however, short lived and a high resolution (HR) image is extremely difficult to obtain. In HR mode, any structural information is lost as the labile crystals/nuclei/species melt under the influence of the electron beam. Unfortunately, no clear image of the small, crystalline species can be obtained using the current configuration. The beam sensitivity of zeolites is well known and any organized species formed at this early stage of the reaction can be expected to be highly metastable and beam sensitive. We therefore rely on a combined analysis of the gel by non-destructive analytical methods (e.g. nitrogen adsorption).

The micropore volume of the 60 min gel according to the t-plot method is 0.004 cm\textsuperscript{3}/g. This value is close to zero but is reproducible and reproducibly higher than that of the 0minn gel which consistently yields 0.000 cm\textsuperscript{3}/g as expected. This can be emphasized when the t-plots of each material are viewed together in Figure 3.16 a-d. Figure 3.16 follows the development of the microporosity vs. reaction time starting from
0 min (a) to 60 min (b), to 110 min (c), and finally to 120 min (d). The y-intercept in the t-plot is used as an indicator for porosity. There is a clear difference in their intercepts indicating the formation of micropores with reaction time. Therefore, albeit small, significance is assigned to this micropore volume as it represents the initial formation of zeolite-like order in the gel. It is suspected that this micropore volume originates from the labile species observed in the simultaneous bright field (BF) and annular dark field (DF) TEM images of the 70 min gel in Figure 3.17 a and b respectively. Sharp, dense edges with dimensions of ~ 10 nm x 5 nm are observed as dark features (indicated by arrows) due to thickness contrast in the BF TEM images. The same regions are clearly defined in the DF-TEM images as sharp, bright edges as they satisfy the Bragg condition. At this point in the reaction, the gel is X-ray amorphous (Figure 3.4). Nevertheless, comparison of the simultaneous images therefore confirms the crystalline nature of these fragments observed against a uniform and largely featureless background attributed to amorphous gel. Similar finding have be reported by Valchev et al. while examining an FAU gel\textsuperscript{17}. HR-TEM of similar crystallizing regions are seen in Figure 3.18. Crystalline planes with a 1.4 Å spacing characteristic of the FAU [111] plane are obvious. These planes appear to originate from the gel periphery consistent with previous observations\textsuperscript{16}. There is a clear boundary between the crystalline regions and the surrounding amorphous gel (Figure 3.18 inset a).

\textsuperscript{23}Na MAS NMR is used to follow the evolution of the local environment of extra framework sodium during the reaction. The NMR spectra in Figure 3.19 each contain one broad band representing sodium in the aluminosilicate environment with the second sharp peak at 7 ppm being assigned to residual NaOH. The NaOH can be removed upon washing. Though the bands are broad due to quadrupolar effects (I = 3/2), there is a noticeable shift in the peak position with reaction time. The broad peak around -9 ppm at time zero is observed before the onset of crystallization (Figure 3.19a). After 60 min reaction and dehydration, while the material is still X-ray amorphous, a broad band is observed at about -16 ppm (Figure 3.19b). Crystalline zeolite isolated after 120 min reaction is characterized by a sharper band at -1 ppm (Figure 3.19c). \textsuperscript{23}Na Multiple
quantum magic angle spinning (MQMAS) NMR experiments decreases the peak broadening resulting from 1st and 2nd order quadrupolar effects and have been used to resolve crystallographic positions of sodium with NaX and NaY. Valchev et al. monitored the extent of reaction during a FAU synthesis at 90 °C using MQMAS noting two primary peaks at -1 and -9 ppm corresponding to crystalline and amorphous environments respectively. A broad band at -9 ppm was attributed to sodium in the amorphous gel environment. This band sharpened with reaction time but its intensity decreased proportionally with the growing intensity of a band at -1 ppm assigned to sodium within the crystalline zeolite environment. Similar assignments are made to explain our data as we also observe a band at -9 ppm give way to a band at -1 ppm upon crystallization. However, no intermediate state was observed in studies by Valchev et al. yet we observe an intermediate state with a band position of -16 ppm. MQMAS experiments of dehydrated NaX and NaY have resolved a peak at -20 ppm which was assigned to hydrated sodium. Sodium ions presiding in the SI' position in dehydrated NaX crystals have been assigned to a peak between -13 to -21 ppm. Site SI' in the FAU framework is within the beta cage (a highly symmetric structure) but is off center close to a 4MR. Sodiums at site SIII' of NaX have been assigned to a band around -21 to -24 ppm. Site SIII' like site SI' is close to a 4MR in dehydrated NaX. The appearance of the band at -16 ppm coincides with the appearance of a pair of transient peaks at 465 and 570 cm⁻¹ in the Raman spectrum. These Raman bands are assigned to 4MR aluminosilicate species and their branched counterparts. Therefore, the intermediate peak at -16 ppm is tentatively assigned to sodium ions coordinated to 4MR aluminosilicate environments.

Crystallization proceeds until completion at 120 min. Data collected between 70-120 min largely reflect crystallization as evident in Figure 3.4. Raman spectra as a function of time in Figure 3.20 a-f corroborate the XRD results as the main feature is the growth of a band at 505 cm⁻¹ characteristic of the zeolite T-O-T out of plane bending mode of the zeolite Y crystal. The 505 cm⁻¹ band is the dominant feature after 80 min of reaction as seen in Figure 3.20 c. Signals attributed to monomeric silicate are observed.
~700 cm\(^{-1}\) in Figure 3.20 c-f but become minor compared to the crystal bending mode. Evolution of the BET surface area is presented in Figure 3.5 which exhibits behavior that parallels the XRD and Raman.

SEM of the crystallization kinetics are presented in Figure 3.21. In agreement with XRD, small crystalline regions are observed as sharp edges at the surface of the gel network at 80 min (Figure 3.21a). The gel structure at this point resembles the porous network structure of the 60 min gel. The crystalline regions are observed throughout the sample but appear relatively localized and remain so up to 90 min (Figure 3.21b). At 100 min, the gel makes a transition from a relatively sparse collection of small crystalline inclusions to an extensive collection of large crystalline regions (Figure 3.21c). Crystals can be seen protruding from the gel surface in many locations. Close inspection of the large crystalline portions of the gel reveal a complex surface structure. The surface seems to be composed of several small (~200-500 nm) zeolite Y single crystals that have grown into each other as seen in Figure 3.21d. Each of these single crystals likely originated from a single nuclei. Their proximity in Figure 3.21d suggests they are formed in sufficient density to allow intergrowth. These crystallites continue to grow in size at the expense of the amorphous gel until 120 min after which crystallization is complete (Figure 3.21e). Based on these findings, we assert that the growth of this crystalline region is not just the consumption of the amorphous gel phase. Rather, it is the coalescence of small single crystals derived from discreet nuclei forming large irregularly shaped crystalline domains. Figure 3.22 a-c shows detailed SEM of the 100 min product at three separate magnifications. Figure 3.22 a illustrates the density of the crystalline region. They are observed throughout. Figure 3.22 b captures the intergrowth of what are hypothesized as discrete nuclei marked with an arrow. Figure 3.22 c examines the surface of one of these individual crystalline regions where many single zeolite crystals are seen intergrowing.

In summary, the above results permit a logical connection to be drawn between the dehydration and rehydration stages of the rapid growth method that explain their synergistic effects on the zeolite growth rate. High [OH\(^{-}\)] during the dehydration step
promote dissolution of aluminosilicate precursors that allow extensive microstructural, and hence, chemical changes to occur at the gel-solution interface. A high level of local supersaturation is achieved and 4MR structures are formed. Aluminosilicate 4MR species are present at high concentrations eventually leading to rapid formation of viable nuclei that are too labile to image with electrons. However, the first steps of crystal growth (70 min) are observed in electron micrographs as nano-crystalline fragments existing at the solution-gel interface. Rehydration of the gel initiates growth of the pre-formed nuclei and small crystal fragments. The nuclei grow by consumption of the amorphous gel phase. Discreet crystals of zeolite Y are observed connecting to one another as their surfaces propagate through the amorphous phase. The heterogeneous final crystal morphology reflects the intense interconnection of single crystals.

### 3.3.4 A Proposed Mechanism for Accelerated Zeolite Growth

We propose the following two-part mechanism to explain the results. Part one, the nucleation phase, takes place while dehydrating the system: between 0 and 60 min. This definition is based on the fact that no crystals are observed during this time. Several complex chemical events likely exist during this period and so we will broadly define this as nucleation in line with other reports. Nucleation is thought to be important during the 4hr RT ageing step, but since ageing is constant in all experiments we omit a detailed discussion of its effect. The effects of ageing and ageing time have been reviewed elsewhere\textsuperscript{10,35}. Part two, the crystallization phase, takes place while rehydrating the system: between 60 and 120 min. This definition is based on the fact that there is continuous crystal growth during this time. Although we arbitrarily separate the mechanism into nucleation and crystallization phases, it is for conceptual reasons only and in a strict sense they are likely partially overlapping. Reaction times exceeding 120 min are characterized by somewhat general trends in zeolite growth (i.e. phase transformation to condensed phases), and so details of this period are omitted.\textsuperscript{6} The mechanism herein focuses only on the unique chemistry of our open system during 0 to
120 min. Figure 3.23 shows a cartoon diagram illustrating this process. A detailed discussion of the two part mechanism follows.

3.3.5 The Nucleation Phase

The amorphous precursor gel experiences substantial chemical and morphological changes during the nucleation phase (0-60 min). Changes are driven by the high alkalinity resulting from dehydration. Alkalinity aids the dissolution of the gel yielding a higher surface area precursor\textsuperscript{33,53}. Increased rates of dissolution accelerate equilibration of the system at the gel-solution interface\textsuperscript{49}. Additionally, the porous network morphology of the gel plays the role of promoting high degrees of local supersaturation within the cavities and channels\textsuperscript{50}. Therefore, these semi-isolated microenvironments reach local concentrations that push the equilibrium toward nuclei formation. The combined effect is the extensive chemical equilibration of the high surface area gel precursor with a concentrated solution. The result is the rapid attainment of an extensively nucleated metastable state prepared to crystallize. The metastable state formed in this step is sensitive to the reaction conditions. The hydration environment is critical for proper crystallization of the nuclei. Without rehydrating the gel, crystallization requires over 24 hrs (if it fully crystallizes at all). The rate of rehydration plays a role. Adding water back too fast slows the crystallization process by dissolving nuclei. Adding water back too slowly starves the crystallization process by consuming all nutrients for nuclei formation. The slow drop-wise (0.5 drop/s) addition of water was found to work best as defined by the crystal quality and kinetics.

3.3.6 The Crystallization Phase

Nuclei formed the preceding stage crystallize upon rehydration of the gel. Water added during this stage promotes the growth of individual nuclei at the expense of the surrounding amorphous precursor. Changes in the solution-gel interfacial equilibrium drive the crystallization of nuclei as water causes the net movement of molecular nutrients into the reactive gel phase where they combine with nuclei. This process can be
viewed as hydration of the gel. Greater hydration of the gel increases the transport of reactive species. The model here is that zeolite Y growth is an interfacial phenomenon in agreement with other findings. Therefore, there is the possibility that nutrients can add directly to the crystal face during growth. If fact, the addition of species to the crystal probably happens albeit at a slower rate than contributions from the amorphous gel phase. This mechanism assumes the solution-crystal equilibrium is negligible and instead focuses on the gel-crystal equilibrium as the dominant crystallization mechanism. This assumption is justified somewhat by crystallization kinetics observed with SEM. Continuous addition of water allows transport of essential species to densely spaced nuclei intergrowing throughout the gel until the final multi-faceted polycrystalline product is formed. At this point growth might continue by ripening processes as previously observed, though no new chemistry is expected exist during these times.

3.4 Selected Applications of the Rapid Synthesis Approach

Three applications of the rapid synthesis of FAU are discussed in this section: extension to other zeolite compositions, rapid incorporation of ions for mechanistic studies and for catalysis, and fabricating membranes rapidly on polymer supports.

3.4.1 Extension of the Approach to More Siliceous Zeolites

The question remains as to whether the rapid synthetic process is simply a consequence of the unique chemistry of the gel used in our studies. One explanation of the results discussed above could focus on the gel as being robust and resistant to formation of alternate zeolite phases. This "robustness" could come as a result of fortuitously choosing a gel located within a stable region of the phase diagram. In any case, the generality of the process is called into question.

A general process provides a method to produce and isolate, from one perspective, a new material: an extensively nucleated and reactive gel of a given composition. To establish the generality of the rapid synthesis method several gels were
chosen each with a different starting composition and final crystal silicon to aluminum ratio (SAR) as listed below:

- SAR 1.4: 18.8Na₂O: Al₂O₃: 10.7SiO₂: 850H₂O
- SAR 2.1: 14Na₂O: Al₂O₃: 10SiO₂: 840H₂O
- SAR 2.5: 8Na₂O: Al₂O₃: 20SiO₂: 320H₂O

In addition, each gel listed above requires its own starting materials (*vide supra*). Starting materials are believed to have an important effect on the initial equilibrium which influences subsequent crystal formation. It follows that any general approach must not depend on starting materials. This justifies the choice of compositions.

Figure 3.24 compares the powder patterns of the SAR X (X = 1.4, 2.1, 2.5) gels under traditional hydrothermal and rapid growth conditions at the indicated reaction times. The SAR 1.4 gel crystallizes in 6hrs hydrothermally. Rapid synthesis of the SAR 1.4 gel results in the formation of zeolite Y and zeolite P mixtures at 2 hrs. This indicates a strong driving force that pushes zeolite Y to the more condensed zeolite P phase (GIS framework). Zeolite Y can be stabilized with the addition of 10mM TMAOH yielding highly crystalline, pure zeolite Y after 2hrs. Similar results are observed for the SAR 2.1 gel. The SAR 2.1 gel crystallizes in 12hrs. hydrothermally. Rapid synthesis of SAR 2.1 results again in zeolite Y/P mixtures. The addition of TMAOH stabilizes the zeolite Y phase which forms in 4 hrs. The SAR 2.5 gel forms hydrothermally in 72 hrs. Rapid synthesis of the SAR 2.5 gel results in complex zeolite mixtures: A, P, and SOD. In fact, the formation of multiple phases in this case complicates the experiment greatly. Addition of TMA was not effective at stabilizing FAU. The inability to isolate zeolite Y from this reaction is likely a result of accelerating formation of many different nuclei simultaneously. The remainder of this section focuses on the SAR 1.4 and SAR 2.1 gels.

Figure 3.25 compares the crystallization kinetics of the SAR 2.1 gel under traditional hydrothermal and rapid growth conditions. The SAR 2.1 gel is accelerated by a factor of 3. Experiments to determine if the SAR 2.5 can be accelerated by this method are under way. Experiments are currently under way to define acceleration rate of the SAR 1.4 gel.
Figure 3.26 and Figure 3.27 compare the crystal morphology of the products isolated from traditional hydrothermal and rapidly grown reactions for each composition. Figure 3.26 a and b illustrate the differences in the particle ensemble. Crystals isolated from the rapid growth process appear smaller on average than those grown hydrothermally. There are a wide range of sizes and particle morphologies observed in the rapid growth. This heterogeneity is illustrated in Figure 3.26c and d where the complex surface features of the rapidly grown crystals becomes evident. Evidence of twinning is observed even in the traditional hydrothermal sample. However, this effect is exaggerated in the rapidly grown crystals and a complex surface morphology results. A magnified view of the particle surface in Figure 3.26e and f highlights these similarities and differences in morphology. Both samples have a complex textured surface that appears to be made up of many crystals. Note, however, that these features are smaller and more numerous in the rapid growth case. Hydrothermally grown crystals appear to be composed of one or more primary single crystals of about ~1 μm diameter and a well defined octahedral shape at the core from which many smaller crystals (<500 nm) are protruding. These small crystalline protrusions appear as surface features on a larger FAU crystal. In contrast, the rapidly grown crystals appear as a collection of smaller crystallites (<500 nm) with indistinct morphologies. These crystallites appear smaller on average: many being 100-200 nm. These crystallites are not just surface features on a large core crystal, rather, they are the crystal. A few crystallites have a distinct octahedral shapes characteristic of FAU but most particles have a more complex shape. Several are intergrown and twinned. These intergrown crystals are arranged in a random fashion resulting in a heterogeneous crystal diameter and particle morphology.

Similar trends can be seen in Figure 3.27 which compares the hydrothermal and rapidly grown crystals from a SAR 2.1 composition. Again, the hydrothermally grown crystals are relatively homogeneous in particle size and shape (Figure 3.27a). Characteristic octahedral particle shapes are observed throughout. There is evidence of particle twinning but most imperfections exist as mere surface features on the central crystal. The bulk of the sample is represented by well formed central crystal with its
distinct morphology (Figure 3.27c). The surfaces of these particles contain some smaller outgrowths. This is observed in Figure 3.27e as well. The rapidly grown crystals again have a drastically different morphology. The particle size is much smaller and there is a high degree of heterogeneity in both particle size and shape (Figure 3.27b). Particles exhibit complex surface features. It becomes difficult to define a true crystal diameter as the morphology is convoluted by the high degree of agglomeration of small particles. In general these small primary particles have a distinct shape, though some appear so small that a distinct shape has not yet developed.

Figure 3.28 compares the two growth procedures for all three crystal chemistries studied here. The trend illustrates that moving to rapid growth conditions has a drastic effect on the average crystal size and morphology. In each case the particles reduce in average size and develop a complex surface structure. Similar trends observed in the morphology of all three reactions studied here imply the mechanism is general, because even though the equilibria may be different in each case, crystals appear to follow a common growth pattern. Therefore, a mechanism similar to that of the SAR 1.5 gel discussed above is proposed. Crystal assembly from pre-formed nuclei occurs during the crystallization stage (rehydration). This suggests that we are concentrating essential species for nucleation and growth during dehydration in each case. This provides method to drive equilibrium to a mature state and arrive at the optimal nuclei concentration. Note however that this process is still delicate. As the XRD data suggests pushing the equilibrium too much forms competitive phases. We have shown that a combination of rapid growth processing and SDA addition can curtail this effect, making a favorable equilibrium possible.

In view of the two step mechanism, and the hypothesis for accelerated growth put forth above, we can understand these observations as follows. Concentration via dehydration of the primordial gel accelerates the approach of equilibrium to nuclei formation. Molecular species characteristic of this equilibrium condense to form viable nuclei. This is a metastable state that is sensitive to the environment. Driving the reaction too far by promoting yet higher degrees of supersaturation nucleates more condensed
phases. The complex chemistry of this nucleation step is the source of all uncertainty in the rapid growth process. It essentially determines the course of the crystallization. Finding the right conditions is an empirical matter. This makes the determination of the generality of this rapid process difficult. Nevertheless, if one can produce the correct chemical conditions, via supersaturation, for a given gel then it can be successfully crystallized to the desired product. One can see from XRD in Figure 3.24 that the nucleation equilibrium is not quite perfect for any of the gels studied here. In fact, the equilibrium is overshot as indicated by the formation of GIS phase zeolite: a more condensed phase. This is less of a problem for the SAR 1.4 and SAR 2.1 gels which can be re-equilibrated by addition of millimolar amounts of the SDA tetramethylammonium hydroxide. This observation further suggests the nucleation stage as the source of generality. However, for the SAR 2.5 gel the equilibrium is driven past the "point of no return" and preliminary attempts to re-equilibrate the gel by SDA addition have been unsuccessful. So a balance is struck between number of nuclei and nuclei type. The number of nuclei formed by supersaturation reaches a limit in which it starts to nucleate other phases.

Rehydration of the nucleated gel signals crystallization of the nuclei. Based on the data above, this step is general and the crystal shape is a result of the gel equilibrated state. This means the final crystal morphology reflects the state of equilibrium of the nucleated gel. This is best illustrated by comparison of traditional and rapidly grown crystal morphologies (Figure 3.28). There is a clear difference in every case. According to our model these morphologies reflect the gel equilibrium and number of nuclei which is most easily traced back to the degree of supersaturation. Similar morphologies obtained in each of the gels studied here indicate that we were successful in obtaining a similar nucleation equilibrium despite the chemical differences in the starting composition.

The rapid process appears to be general based on data collected above as it depends primarily of the acquisition of the correct nucleation equilibrium. In principle this equilibrium can be obtained for any arbitrary composition producing FAU zeolite.
Acquisition of this equilibrium is empirical and difficult to obtain in some cases (i.e. SAR 2.5), once reached, crystallization proceeds by a mechanism determined by the nuclei nature and number. Thus, a common morphology is obtained from particles grown rapidly.

In conclusion, it appears the rapid synthetic approach is applicable to other FAU producing aluminosilicate systems. However, each system has its challenges. Optimization is required for each new chemical composition. Zeolite Y is harder to stabilize as the silicon content is increased and the more condensed zeolite P appears to be favored along with A and SOD. Addition of small amounts tetramethylammonium cations stabilizes zeolite Y and suppresses the formation of zeolite P by producing a more conducive environment to viable zeolite Y formation. The crystal morphology is one of the best indicators of this equilibrium. The rapid synthetic approach does not depend on the starting materials but evidence suggests it depends on chemical composition. Efforts to optimize the rapid synthesis of high silicon zeolite Y and extend this rapid method to other frameworks are currently under way.

3.4.2 In-situ Incorporation of Ions

Chemicals were added to the rapid synthesis process during rehydration in effort to affect the kinetics. No significant effects could be measured using several chemicals. TMA$^+$ ions added during the crystallization phase promotes the growth process slightly and stabilizes the zeolite Y phase (vide supra). However, no clear acceleration of the growth was observed upon addition of TMA$^+$ in the hydroxide or bromide form. Several quaternary ammonium salts are reported to influence zeolite growth. The diquat N,N,N,N',N',N'-Hexamethylethylene-1,2-diammonium iodide (TMA$^+$)$_2$ has been reported to favor zeolite crystal growth.$^{61,62}$ Addition of (TMA$^+$)$_2$ in its iodide and hydroxide form show minimal impact on the crystallization kinetics however. Similar observations were made upon the addition of the cationic polymer PDDA: a cationic polymer used to capture zeolite nuclei and promote growth.$^{63}$ It seems these chemicals have no effect on the kinetics of the process.
An interesting observation was made during these experiments. Raman of the final material show the encapsulation of the TMA\(^+\) ion within the sodalite cages of the zeolite Y structure in Figure 3.29 b. The symmetric C-N stretching mode of the TMA\(^+\) ion is blue shifted in the rapid growth case (775 cm\(^{-1}\)) relative to free TMA\(^+\) (750 cm\(^{-1}\)) as seen in Figure 3.29 a. It is thought the TMA\(^+\) ion stabilizes some transient, yet essential, species during the crystallization process. This leads to its incorporation within the structure. Though it is encapsulated, there is no change in the final SAR of the crystalline product. Indicating Na\(^+\) likely play a dominant role in framework charge compensation.

This rapid synthesis method can be extended to producing catalysts simply and quickly. In many applications, zeolite is a desirable catalyst itself when exchanged with various metal ions. One example is copper and iron exchanged ZSM-5 for the selective catalytic reduction of NO\(_x\) byproducts from combustion reactions (e.g. automotive engine exhaust). Silver and copper exchanged FAU has been explored as a NO\(_x\) reduction catalyst. The true mechanism of the catalyst is complex and beyond the scope of this communication. It has been studied extensively elsewhere.

Zones et al. have reported incorporating metals within the framework of several zeolite structures through addition of amine stabilized metal cations during hydrothermal growth.\(^{64}\) Amine ligands can stabilize metal cations against the tendency to precipitate as metal hydroxides or metal oxides in highly basic conditions. Therefore, amines allow the metal cations to exist in a form necessary to associate with the negative zeolite framework during its formation leading to its eventual encapsulation. This is an attractive route to produce catalytic zeolite materials as discussed by Zones et al. However, amines will not stabilize the metal cation indefinitely at the most basic conditions necessary for the synthesis of FAU. For this reason zeolite structures that are formed under mild alkaline condition have been the focus. Though this approach has been used effectively to prepare metal loaded zeolite structures derived from highly basic conditions (e.g. LTA), a limited range of metal precursors are stable for extended periods of time at these pH values. Forming zeolites on a time scale competitive with the precipitation of metal precursors is one paradigm for extending the range of metal loaded zeolite structures like
those made by Zones and company. This approach is discussed in the following paragraphs.

Copper loaded FAU can be prepared quickly with the rapid method discussed above. Rehydration of the concentrated gel with a basic aqueous solution of 0.7 M [Cu(NH$_3$)$_4$]$^{2+}$ in place of water was examined. This procedure resulted in a light blue colored solid product. The blue solid was isolated, washed, and packed within a quartz flow tube where it was used to decompose NO$_x$. The as-synthesized material converted more than 99% of the 84 ppm NOx stream balanced in a 90/10 % mixture of nitrogen and oxygen (Table 3.2: NOx conversion). These results are comparable to earlier reports of copper loaded zeolites. X ray diffraction analysis of the product indicates only FAU reflections. No crystalline copper species are present. There is a small hump in the diffraction pattern between 20-30° 2θ indicating amorphous material is present. The origins of this signal are unknown. Amorphous copper hydroxides, copper oxides, or aluminosilicate species are a few of the possibilities. Further work aimed at identifying the structure and active site of these materials is necessary to address these questions.

3.4.3 Rapid Growth of Membranes

Growing crystalline inorganic nanostructures is an active area of research. Zeolite membranes are used in various separation processes. However, one barrier to the practical application of zeolite membrane devices is the cost associated with long synthesis times: it often takes days to weeks. A rapidly crystallizing zeolite can form a continuous membrane structure under the appropriate conditions. For example, this is demonstrated with zeolite A and X membranes that are grown in a matter of hours on a variety of support materials. Continuing to accelerate the kinetics of zeolite growth beyond the current limits can uncover new approaches and directions in membrane development. To illustrate this we performed a series of membrane growth experiments on highly hydrophobic polyethersulfone supports. We find the key to membrane
formation on such hydrophobic supports is rapid membrane growth kinetics that out compete seed crystal dissolution/re-dispersion.

Polymeric materials have been used as supports for zeolite membrane growth as discussed in the previous chapter.\textsuperscript{67} Most work focuses on hydrophilic polymer supports to maximize intermolecular interaction between the support and the highly charged, hydrated zeolite precursors. Little work has concentrated on hydrophobic polymer supports. Those studies that have, developed unique and specialized methods to accomplish membrane growth under their specified conditions.\textsuperscript{67} Zeolite growth on hydrophobic polymeric supports has proven to be a challenging task. This stems largely from limited stability of various polymers under hydrothermal conditions necessary for zeolite growth and the mismatch between the intermolecular forces of the polymer surface and zeolite suspension or zeolite seed crystals. Despite these differences, zeolite seed layers can be deposited on polyethersulfone supports by vacuum dip coating.\textsuperscript{72} The goal is to grow the seeds into a dense membrane before they succumb to the electrostatic repulsion and re-disperse into the aqueous growth solution, or re-dissolve completely. Rapid zeolite growth kinetics are required to compete with the electrostatic repulsion as re-dispersion of the seed layer is estimated to occur in 180 min. Therefore, our approach to this problem is to grow the zeolite membrane faster than the seeds can disperse using the rapid growth methodology developed above.

Millipore 300 kDa cutoff polyethersulfone supports were seeded with 40 nm zeolite nanocrystals by vacuum dip coating. These seed layers were coated with an amorphous, concentrated gel isolated from a rapid growth reaction after 60 min. This coating is a viscous, densely nucleated gel that has been shown to crystallize rapidly (vide supra). The seed-gel coated support was then placed within a reflux reactor containing the 60 min mother gel (same as coating) and allowed to react for one hour. Rehydration of the gel-support system was performed during this period. The support was removed and rinsed liberally with DI water. The support was stored in a hydration chamber (humidity maintained with a saturated solution of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} until analyzed. XRD of the seed layer and the hydrothermally grown layer are presented in Figure 3.30.
Gold coated samples were analyzed by SEM in Figure 3.31 a-d. Membrane samples were cut to size and analyzed intact by nitrogen adsorption as illustrated in Figure 3.32 and Figure 3.33. Results of these measurements are discussed below.

The morphology of the grown layer was examined by SEM. Figure 3.31b shows the surface view of the as-synthesized membrane. A highly covered surface is observed. Pseudo-octahedron FAU crystals are clearly visible across large regions of the support. These crystals appear to intergrow into a dense membrane layer ~1 μm thick as seen from the cross section in Figure 3.31c. This thickness includes the dense zeolite layer and the apparent interpenetrated layer below the polymer support surface as seen in Figure 3.31d. The difference between the grown membrane structure in Figure 3.31b and the bare support in Figure 3.31a is marked. Support interpenetration by the zeolite membrane during growth provides stability by anchoring the membrane to the support despite their electrostatic differences. XRD measurements in Figure 3.32a indicate crystalline zeolite Y formed on the support. This is clear when the diffraction pattern is compared to the seed layer diffraction pattern in Figure 3.32b. A magnified look at the FAU [111] reflection at ~6° 2θ is contained in Figure 3.32c and d illustrating the significant increase in intensity. There is a slight shift in the peak position due to sample height variation and misalignment originating from the finite membrane thickness. This membrane was grown in 1hr. These results confirm the formation of a thin, continuous zeolite membrane with good surface coverage in a short amount of time.

Electron microscopy combined with nitrogen physisorption were used to examine the membrane structure in more detail. Nitrogen adsorption isotherms for the polyethersulfone support, zeolite Y seeded support, and fully grown membrane are presented in Figure 3.33a. The isotherms resemble type II isotherms characteristic of nonporous or macroporous materials. This is especially evident in the bare support and the seeded support. Isotherms for the grown membrane have a slightly different shape. A sharp increase in the volume of gas adsorbed is seen at low pressures indicative of micropore filling. This change in shape is interpreted as the development of a microporous zeolite film on the support (as supported by SEM and XRD). The isotherms
essentially follows the transformation of a type II material (dominated by the support properties) to a type II-type I hybrid material (characteristic of the membrane and support). The total volume of gas adsorbed corroborates this finding as it increases from bare support to seed coated support, and again upon membrane growth. This increase is attributed to the high surface area of the microporous zeolite seeds, and zeolite membrane, present on the polymer support in each respective case. Based on the estimated dimensions of the membrane obtained from SEM about 20 μg of zeolite is present on the grown membrane analyzed herein. Most of the mass is derived from the polymer support. This explains why even in the membrane sample, the isotherm still has a strong resemblance to the support.

Pore size distributions calculated using the NLDFT method are shown in Figure 3.33b. Each sample is characterized by several features in the pore size distribution. The bare support and seeded support closely resemble each other. They are each characterized by a peak around 5 nm and a broad, weak peak around 34 nm. The strong peak at 5 nm is assigned to noise. This noise is a result the rapid uptake of nitrogen at low pressures (0.001-0.1 P/P₀) which causes an almost discontinuous change in the isotherm (seen in Figure 3.34 b). This feature is difficult to accurately fit to a linear superposition of adsorption isotherms and leads to a misrepresentation of the pore size distribution. In essence, the NLDFT algorithm interprets this vertical rise in adsorption as a pore when in fact it is only an artifact of the detection limits of the instrument. The difficulties in fitting this low pressure range are illustrated clearly in Figure 3.34 b which presents the raw adsorption isotherms and their respective NLDFT fit. This artifact is observed in all the NLDFT pore size distribution calculated here. The pore size distribution for each sample is repeated in Figure 3.34a for convenience. The broad, weak peak at 34 nm is assigned to a mixture of support pores and inter-crystalline spaces between seed crystals. Of course, in the case of the bare support only the support pores play a role. The average pore size of the support estimated from SEM is 62 nm. There is slight disagreement between the average pore size obtained from these two methods. This is likely due to presence of large macropores that are accounted for in the SEM average but cannot be
filled by gas adsorption. The gas adsorption measurements reflect only those pores small enough to be filled with nitrogen (<100 nm).

The features of the pore size distribution of the seeded support remain broad but shift slightly to smaller sizes (32 nm). This likely represents the presence and detection of intercrystalline spaces between seed crystals. Based on geometric packing of spheres the inter-crystalline spaces are expected to be 16 nm in diameter assuming 40 nm diameter seeds. The larger measured size might result from imperfect packing of the seed layer. This feature is weak, thus, making it difficult to judge its true origins. Obviously the support continues to be the dominant contribution to the signal.

Pore size distributions measured for the zeolite membranes exhibit a broad peak centered around 28 nm. This feature is displaced to lower pore sizes relative to the bare and seeded supports. This peak is assigned to inter-crystalline spaces and related defects (e.g. pinholes). Zeolite growth within inter-crystalline seed pores causes densification of the layer, thus, a decrease in pore diameter is observed. It is unclear whether these smaller pores develop as defects during secondary growth or result from incomplete densification of the seed layer. Given the similarities in the peak maximum between the membrane and the seed layer, it is reasonable to assign features to inter-crystalline pores that have not completely grown. The increase in volume of pores in this size range is attributed to the growth of new zeolite particles and networks contributing forming own inter-crystalline space. This random formation of new particles and their interconnection leads to the wide distribution of pore sizes observed.

It is worth noting that formation of new pores formed during growth does not necessarily qualify them as defects. These pores might not be pinholes, rather, their presence should be understood to indicate some roughness and porosity of the membrane layer. They might not provide a path for gas to permeate across the membrane. Gas permperimetry is a more appropriate method to qualify these pores as defects or just inter-crystalline void space. Such measurements are currently being pursued.

Large scale defects were analyzed by electron microscopy. Cracks are observed in the as-synthesized membrane and are thought to be of mechanical origin. These cracks
are hundreds of microns long and several microns wide. These features are invisible to nitrogen adsorption measurements. The origins of these defects, and smaller defects detected proposed from adsorption experiments, are the focus of ongoing research aimed at their elimination.

In conclusion, the rapid growth method can form continuous membrane structures quickly. Zeolite can densify into a reasonably well formed membrane faster than hydrophilic precursors and seed crystals can be repelled from the hydrophobic PES support. Preliminary nitrogen adsorption results indicate the presence of mesopores in the membrane structure. Mesopores are attributed to a mixture of nano-scale defects and intercrystalline void space. Electron microscopy indicates the presence of large scale cracks that are thought to result from mechanical effects (e.g. bending). Aside from the defects formed, the membrane is relatively robust as indicated by the tape test. It adheres well to the polymer substrate once formed. This is likely due to physical anchoring of the membrane by support interpenetration. A detailed study of the membrane structure, formation mechanism, and gas permeation properties is forthcoming. These experiments highlight new and practical approach to forming hybrid membrane structures for gas separation.

3.5 Conclusions

A new approach to rapidly synthesize zeolites has been developed. This approach uses in-situ cycling of the gel composition to shift between optimal nucleating and crystallizing conditions. A mechanism for the acceleration of zeolite growth under these conditions is proposed. This mechanism emphasizes the role of [OH\(^-\)] in promoting morphological and chemical transformations leading to dense populations of viable nuclei that crystallize rapidly upon addition of water. This mechanism is sufficiently general and provides the opportunities to be extended to other framework structures. The application of the process to other zeolite structures must be performed to truly establish the generality of the process. This method can be extended to other zeolite X/Y compositions after optimization. Higher silicon concentrations pose a greater challenge in
the absence of SDAs as many zeolite phases may result. The development of membranes and catalytic materials using the rapid synthesis is ongoing. However, thin continuous membranes (~1 μm) have been synthesized on polyethersulfone supports. These membranes are robust to the tape test and show unusually firm adhesion to the polymer support. It is speculated this structure is the result of support interpenetration by the zeolite growth media leading to firm membrane anchoring. To the best of my knowledge, this is the first report of zeolite membranes on flexible polyethersulfone supports. The success of an application such as this illustrates the impact rapid zeolite growth could have on emerging technologies.

3.6 References


3.7 Figures & Tables

Figure 3.1: A general crystallization curve illustrating the chemical evolution of zeolite crystals in a typical reaction.
Figure 3.2: A schematic of the apparatus used for the rapid synthesis of zeolite Y (a) and the water concentration vs. time schematic illustrating water dynamics of the rapid synthesis process (b).
Figure 3.3: Crystallization curves comparing the reaction progress for a hydrothermal synthesis of zeolite Y (red circles), and a rapid synthesis of zeolite Y (blue squares).
Figure 3.4: Comparison of the raw X-ray diffraction patterns as a function of time for the hydrothermal synthesis of zeolite Y (a), and the rapid synthesis of zeolite Y (b).
Figure 3.5: Crystallization kinetics of a rapidly synthesized zeolite as measured by the evolution of the BET surface area for each of the times listed in the table inset.
Figure 3.6: A nitrogen adsorption isotherm comparison of the crystals isolated from a hydrothermal synthesis after 8 hrs (a) with the crystals isolated from a rapid synthesis after 120 min (c). A magnified view of the mesopore region of the hydrothermal and rapid synthesis products are shown in (b) and (d) respectively.
Figure 3.7: $^{29}\text{Si}$ and $^{27}\text{Al}$ MAS NMR of the products isolated from a rapid synthesis of zeolite Y after 120 min. reaction time (a and b respectively), and the same for the products isolated from a traditional hydrothermal synthesis of zeolite Y after 8 hrs reaction time (c and d respectively). The Si/Al ratio calculated from the silicon NMR is included as an inset in each case. The assignments of each resonance are color-coded and denoted with a black dotted line in the silicon NMR. Only one band is observed in the aluminum NMR. All other bands are spinning side bands.
Figure 3.8: SEM comparison of the particle morphology of crystalline products isolated from a conventional hydrothermal reaction of zeolite Y after 8 hrs. reaction time (a), and a rapid synthesis of zeolite Y after 2 hrs reaction time (b).
Figure 3.9: A color coded schematic of the water concentration vs time for each of the control experiments performed. The XRD patterns of products isolated from each reaction was analyzed after 2 hrs, denoted with a vertical dotted red line in the schematic.
Figure 3.10: XRD of each control experiment (I-VI) in figure 3.9 after 2 hrs reaction time. Pattern (a) corresponds to reaction I, (b) to reaction II, (c) to reaction III, (d) to reaction IV, (e) to reaction V, and (f) to reaction VI.
Figure 3.11: SEM images of the amorphous products isolated from a rapid synthesis of zeolite Y after 0 min (a), and 60 min reaction time (b). The insets contain the surface areas of the products as determined by BET analysis of the nitrogen adsorption isotherms.
Figure 3.12: TEM images of the amorphous gel isolated from a rapid synthesis of zeolite Y after 60 min reaction time at low magnification (a), and high magnification (b) illustrating the porous structure of the gel.
Figure 3.13: Nitrogen gas sorption analysis of products isolated form the rapid synthesis of zeolite Y after 0 min (a) and 60 min reaction time (b). Pore size analysis of the 0 and 60 min products are contained in (c) and (d) respectively. The NLDFT fits the 0 and 60 min material are contained in (e) and (f) respectively.
Figure 3.14: FTIR of rapid synthesis products isolated after a) 0, b) 60, c) 70, d) 80, e) 90, f) 100, g) 110, & h) 120 min. The zeolite crystal bands are marked with black dotted lines with their respective frequencies.
Figure 3.15: Raman spectra of products isolated from a rapid synthesis of zeolite Y after 0 min (a), and 60 min reaction time (b). The curve deconvolutions are graphed as black curves below (a). The major features are marked with black dotted lines with their respective frequency.
Figure 3.16: De Boer’s t-plot analysis of products isolated from a rapid synthesis of zeolite Y at 0 min (a), 60 min (b), 100 min (c), and 120 min (d). The t-plot fit is extrapolated to the y-axis for clarity as denoted by the black dotted lines.
Figure 3.17: Simultaneous bright field (BF) TEM imaging (a) and dark field (DF) TEM imaging of the same region of a isolated after 70 min of rapid synthesis (b). Small crystalline surface regions can be seen in both images as they are marked with an arrow in a and a circle in b.
Figure 3.18: A high Resolution TEM image of a zeolite Y product isolated after 70 min of rapid synthesis where the crystalline nature of the interface is highlighted. The magnified inset of the boxed region clearly shows the barrier between the amorphous precursor gel and the propagating surface crystal (as denoted with the red solid line).
Figure 3.19: $^{23}$Na MAS NMR of powders isolated from a rapid synthesis of zeolite Y after 0 min (a), 60 min (b), 120 min reaction time (c). The dotted lines indicate the signature of amorphous aluminosilicates at -8.7 ppm, the aluminosilicate intermediates at -16.5 ppm, and the zeolite crystal at -1.8 ppm.
Figure 3.20: Crystallization kinetics of the rapid synthesis procedure as followed with Raman spectroscopy of the structure sensitive bending region after 0 min (a), 60 min (b), 80 min (c), 90 min (d), 100 min (e), and 120 min (f). The dotted line marks the T-O-T bending mode of the zeolite Y crystal at 505 cm$^{-1}$. 
Figure 3.21: SEM analysis of crystallization kinetics. These images show the morphological evolution of the gel during the rapid synthesis process after 60 min (a), 70 min (b), 80 min (c), 90 min (d), 100 min (e), 110 min (f), and 120 min (g).
Figure 3.22: SEM of crystalline products after 100 min of rapid growth. The three magnifications illustrate an increasing level of complexity of the scale becomes smaller. Part a illustrates the density of the crystalline regions. Part b illustrates the aggregation of discrete crystals. Part c illustrates the complex surface structure of the aggregated surface where many individual crystals, thought to derive from discrete nuclei, can be seen.
Figure 3.23: Mechanistic scheme starting with the acquisition of equilibrium by gel dissolution in panel 1, followed by microstructure formation and supersaturation in panel 2, then interfacial crystallization of nuclei in panel 3, and finally propagation of the crystalline regions to yield the crystalline product in panel 4. The TEM inset in panel 2 shows the structural development of the gel surface. The branched species in the circular inset of the panel 2 TEM illustrates the beginning of order. The TEM inset in panel 3 signifies the appearance of crystalline regions. The circular inset in the panel 3 TEM illustrates the crystal structure of zeolite Y.
Figure 3.24: XRD of SAR X gels. Composition SAR 1.4 grown hydrothermally for 3hrs (a), and grown by rapid synthesis for 3 hrs (b). Composition SAR 2.1 grown hydrothermally for 4 hrs (c), and grown by rapid synthesis for 4 hrs (d). Composition SAR 2.5 grown hydrothermally for 48 hrs (e), and grown by rapid syntheis for 48 hrs (f).
Figure 3.25: Crystallization Curve for the composition SAR 2.1 showing the crystallization time scale for hydrothermally grown zeolite Y represented by the small red circles, the crystallization of co-phase zeolite P represented by the blue squares. The large red circles represent the time scale for the crystallization of SAR 2.1 under rapid synthesis conditions.
Figure 3.26: SEM of SAR 1.4 crystals. Crystalline products isolated after 6 hrs of hydrothermal growth imaged at three magnifications (a, c, and e.). Crystalline products isolated after 3 hrs of rapid synthesis imaged at the same three magnifications for comparison of the resultant crystal morphology (b, d, and f).
Figure 3.27: SEM of SAR 2.1 crystals. Crystalline products isolated after 12 hrs of hydrothermal growth imaged at three magnifications increasing from a, to c, and finally to e. Crystalline products isolated after 4 hrs of rapid synthesis imaged at the same three magnifications for comparison of the resultant crystal morphology (b, d, and f).
Figure 3.28: SEM comparison of SAR X gels. Crystalline products isolated from composition SAR 1.4 after 6 hrs hydrothermal growth (a) and after 3 hrs of rapid synthesis (b). Crystalline products isolated from composition SAR 1.5 after 8 hrs hydrothermal growth (c) and after 2 hrs of rapid synthesis (d). Crystalline products isolated from composition SAR 2.1 after 12 hrs hydrothermal growth (a) and after 4 hrs of rapid synthesis (f).
Figure 3.29: Raman of TMA$^+$ incorporation into the sodalite cages of a TMA$^+$ templated zeolite reaction replicated from the literature$^{76}$ (a), and a rapidly synthesized zeolite powder after 20 min of reaction while rehydrating with an aqueous TMAOH solution (b).
Figure 3.30: XRD of copper containing zeolite products isolated after 110 min of rapid synthesis while rehydrating with an aqueous solution of $[\text{Cu(NH}_3\text{)}_4]^{2+}$. 
Figure 3.31: SEM images of the as-synthesized membrane. SEM Image of the top view of a 300 kDa cutoff PES support (a), SEM image of the top view of rapidly synthesized nanozeolite seed layer deposited on a PES support (b), cross-setional SEM image of the rapidly synthesized membrane after 1hr of growth (c), and a close up cross-sectional SEM view of the membrane-support intergrowth layer accompanied with a color coded schematic (d).
Figure 3.32: Membrane and seed layer XRD where the support peaks are marked with asterisks. The XRD pattern of a rapidly grown membrane after 1 hr (a), and the XRD pattern of the seeded support that was used as a starting material (b). Close up views of the FAU [111] peak are seen for the membrane in part (c), and for the seed layer in part (d).
Figure 3.33: Membrane nitrogen gas adsorption analysis (a) and pore size distributions (b) for the as prepared materials. Nitrogen adsorption measurements of the bare support (purple), the seeded support (blue), and the rapidly grown membrane (red) are presented in part a. Pore size distributions derived from these measurements for the support (purple), the seed layer (blue), and the membrane (red) are contained in part b.
Figure 3.34: A close up view of the pore size distributions derived for the support (purple), the seeded support (blue), and the grown membrane (red) are contained in part a. Part b illustrates the difficulty of fitting the experimental isotherm of the membrane (blue circles) using the NLDFT method by comparing it with the model fit (red line).
Table 3.1: Comparison of physical and chemical properties of hydrothermal and rapid synthesized products.

<table>
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<tr>
<th>Synthetic Method</th>
<th>Time min</th>
<th>Diameter nm</th>
<th>Si/Al</th>
<th>S_{\text{BET}} m^2/g</th>
<th>C_{\text{BET}} x10^3 g</th>
<th>S_{\text{EXT}} m^2/g</th>
<th>V_{\text{micro}} cm^3/g</th>
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<td>601</td>
<td>6.3</td>
<td>23</td>
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</table>

* Silicon to Aluminum ratio measured by NMR  
# Surface area determined by BET method  
@ BET abscissa intercept  
** External surface area determined by t-plot method  
## Total micropore volume determined by t-plot method

Table 3.2: NOx conversion as a function of temperature for the copper containing zeolite.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>[NO$_x$] ppb *</th>
<th>Conversion %</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>820</td>
<td>99.03</td>
</tr>
<tr>
<td>300</td>
<td>190</td>
<td>99.77</td>
</tr>
<tr>
<td>350</td>
<td>204</td>
<td>99.76</td>
</tr>
<tr>
<td>400</td>
<td>30</td>
<td>99.96</td>
</tr>
</tbody>
</table>

* Feed concentration of 84ppm
CHAPTER 4 : THE CRYSTAL SIZE DEPENDENT NATURE OF IONIC CONDUCTION THROUGH POLYCRYSTALLINE ZEOLITE Y SPANNING THE NANO TO MICRON LENGTH SCALES

4.1 Introduction

The change in conductivity of ionic solids as a function of size is an active area of research. In particular, the transport across and along grain boundaries becomes relevant as the particle size decreases.\textsuperscript{1,2} There are conflicting reports in the literature of how the conductivity changes with grain size. For example, with yttria stabilized zirconia (YSZ), nanocrystalline materials exhibited an increase of conductivity by two orders of magnitude as compared to polycrystalline and single crystalline materials.\textsuperscript{3} Though, other studies have noted that conductivity of nanocrystalline (< 100 nm) YSZ is comparable to micron-sized grains or even higher than the bulk.\textsuperscript{4-6} For ceria, the activation energy for electronic conduction (76-112 kJ/mol) for nanocrystalline CeO\textsubscript{2} is lower than the micron-sized material (236 kJ/mol).\textsuperscript{7} Other studies on ceria and related materials have reported similar trends\textsuperscript{1}. The Li\textsuperscript{+} ion conductivity for a LiI/Al\textsubscript{2}O\textsubscript{3} composite is greater by a factor of 50 as compared to pure LiI, and is proposed to arise from short circuiting pathways along the grain boundary in the composite.\textsuperscript{8} Mechanical ball-milling of micron-sized BaLiF\textsubscript{3} led to ~30 nm particles, which exhibited orders of magnitude higher conductivity as compared to coarse-grained materials\textsuperscript{9}. The impact of grain boundary modifications on conductivity is manifested more strongly in nanocrystalline materials, since the fraction of ions that lie in the grain boundary region increase as particles become smaller. Other factors that can play a role in nanocrystalline materials include blocking impurities and
high defect densities at the grain boundaries. At a molecular level, surface defects can contribute to or inhibit transport pathways.

There are several technological implications of the reduction of conductivity with nanocrystalline ceramics, e.g. in solid oxide fuel cell development, where a drop in operational temperature will lead to longer device lifetimes. Also, higher conducting ceramics should provide new material opportunities in battery and sensor research. A detailed review dedicated to pushing nanoionics to the farthest limits in terms of size discusses these avenues and various prospects. Nonetheless, zeolite materials are not discussed that work. This is likely a result of the only recent growth in the understanding, and perfection of the synthesis, of nanozeolite systems.

Zeolites are crystalline aluminosilicates with typical compositions of (SiO$_2$)$_x$(AlO$_2$)$_y$zM.aH$_2$O, with M$^{n+}$ being charge neutralizing cations that can be replaced via ion-exchange. These cations are bound to the framework via electrostatic interactions and their transport through the zeolite porous structure has been the subject of many studies. Several general principles of cation conductivity on zeolites are well recognized. The activation energy relates to the disruption of cation framework electrostatic interactions, followed by cation hopping across sites, with the energetics dependent on the temperature, types and amounts of co-cations, the size of the framework windows through which the cation needs to hop (dependent on the framework structure), and presence of sorbate molecules. There is limited research exploring the role of grain boundary/interface on cation dynamics, unlike that for nanoscale ceramic materials. There is one study that reported that nano-ZSM-5 showed higher conductivity than micron-sized ZSM-5. However, these experiments were done in a hydrated environment, with the water playing an important role in the proton hopping mechanism. With a combination of growing interest in the field of nanoionics and recent progress in nanozeolite synthesis, studying the ionic conductivity of nanozeolite materials is not only within experimental reach, but builds on a wealth of existing knowledge in this research area.
In order to explore the influence of interfacial effects on conductivity, we present here an impedance spectroscopy study of faujasitic zeolites (zeolite X/Y) with particle sizes of different length scales. Thus, all studies are carried out on a framework with the same topology. Included are a zeolite Y membrane on one extreme, and nanosized zeolite Y (47 nm) particles on the other, with micron (1 μm) and sub-micron (200 nm) zeolite Y particles in between. Detailed characterization of structure, cation, and temperature-dependent impedance spectroscopy over a frequency range of 1 MHz to 0.1 Hz is reported. Our conclusion is that the role of cation transport across particle-particle interfaces becomes increasingly important as zeolite crystallite sizes approach the nanoscale.

4.2 Experimental Methods

4.2.1 Synthesis of Zeolites

4.2.1.1 Nanozeolite Synthesis

Nanozeolites were synthesized by a literature procedure\textsuperscript{17}. The following gel composition was used:

\[0.048\text{Na}_2\text{O} : 2.40(\text{TMA})_2\text{O}(2\text{OH}) : 1.2(\text{TMA})_2\text{O}(2\text{Br}) : 4.35\text{SiO}_2 : 1.0\text{Al}_2\text{O}_3 : 249\text{H}_2\text{O}\].

The aluminum source was prepared by dissolving 12.5 g of aluminum isopropoxide in an aqueous solution of 48.5 g tetramethylammonium hydroxide (25%) and 76.5 g water, while vigorously stirring at 60°C until clear (~20 min). To the clear solution 11.3 g of tetramethylammonium bromide was added with stirring at room temperature. Meanwhile, the silica source was prepared by adding 26.2 g of LUDOX HS-30 to a 10.5 g tetramethylammonium hydroxide (25% aqueous) and allowed to stir at room temperature for 30 min. The silica source was added to the aluminum source while stirring. The resulting clear sol was aged with stirring for 3 days followed by heating at 100°C in an oil bath with stirring for 4 days. The product was isolated by ultracentrifugation and washed with DI H\(_2\)O until neutral. The washed powders were calcined at 550°C for 24 hrs under a dry air stream. Upon cooling to 100°C, the powder was exposed to a
water saturated air stream until it cooled to room temperature. Calcined samples were ion exchanged by stirring zeolite powder with 0.1 M MCl (M = Li, Na, K.) for 24 hrs at a solid loading of 0.1 g/mL. The ion exchanged product was washed with water until no chloride ions were found.

4.2.1.2 Submicron Zeolite Synthesis

Submicron zeolites were synthesized from a gel with the following composition 0.037Na2O:3.13(TMA)2O.4.29SiO2.1.0Al2O3.497H2O according to reported procedures18. The aluminum source was prepared by adding 4.58 g Al(OH)3 to a solution of 53.6 g TMAOH and 152 g H2O and stirring until clear. The silicon source was prepared by adjusting the pH of a LUDOX SM-30 dispersion to ~8.1 with Dowex proton-exchange resin. 20 g of the silicon source was slowly added to the aluminum source followed by 30 mg of NaOH. The sol was aged while stirring at room temperature for 3hrs followed by heating at 100° C for 5days. The product was isolated and washed as above.

4.2.1.3 Micron zeolite synthesis

Micron-sized zeolite Y was obtained from two sources, a commercial sample from Zeolyst International, and a sample synthesized in the laboratory. Micron-sized zeolite Y was synthesized from a gel with the following composition: 17Na2O: 1Al2O3: 12.8SiO2: 975H2O19. The gel was allowed to age four hours at room temperature while stirring before being placed within a Teflon lined autoclave and heated in an oven to 100° C for 8 hrs. Zeolite Y crystals were isolated from the reaction by filtration and washed liberally with DI H2O.

4.2.1.4 Zeolite Membrane Synthesis

Zeolite membranes were synthesized using a reported procedure20. The α-alumina seeded support was submerged in a sol with a following composition: 0.037Na2O:3.13(TMA)2O.4.29SiO2.1.0Al2O3.497H2O. Hydrothermal secondary growth
of the seeded supports lasted 4 days at 98° C, with 1 day seeded side face up followed by
3 days face down.

4.2.1.5 Zeolite Surface Modification

Zeolite particles were surface modified according to a previously reported
procedure. In brief, 200 mg of calcined sodium exchanged zeolite was dehydrated at
room temperature under vacuum (10⁻³ Torr) for 3 days after which 40 μL of 1,1,3,3-
tetramethyldisilazane (TMDS) was added to the zeolite dispersion in 60 mL of dry
hexane in a dry nitrogen environment. The reaction mixture was stirred 1 hr at room
temperature. The product was isolated by ultracentrifugation after several washes with
hexane. The surface modified powder was dried under vacuum at room temperature.

4.2.2 Characterization

4.2.2.1 X-Ray Diffraction

XRD patterns for each powder sample were collected on a Bruker D8 X-Ray
diffractometer using Ni- filtered Cu Kα radiation. Patterns were collected at 0.05 degree
steps with a dwell time of 2 s with 1 mm and 8 mm entrance and scattering slits
respectively. The XRD pattern of the membrane sample was collected using a custom
build polycarbonate sample container that was compatible flat plate mode of the Bruker
D8 instrument in effort to minimize peak shifts due to height variations. The data was
collected using parameters analogous to the powder samples.

4.2.2.2 X-Ray Photoelectron Spectroscopy

XPS spectra were collected from zeolite pellets and membranes on a Kratos Axis
Ultra system utilizing monochromatic Al Kα radiation at 1486.3 eV. Samples were
prepared for XPS by first dehydrating under vacuum (~10⁻³ Torr) at 500° C for 24 hrs
followed by sample transfer into the instrument under a dry nitrogen environment.
Spectra were calibrated according to the presence of C 1s peak at 285 eV.
4.2.2.3 **Electron Microscopy**

A Philips XL30F ESEM-FEG scanning electron microscope was used to image gold coated zeolite powders and membranes. High resolution transmission electron micrographs were collected from a Techni F20 S/TEM system.

4.2.2.4 **Nuclear Magnetic Resonance Spectroscopy**

A Bruker DSX 300 MHz superconducting magnet equipped with a dual channel (H-X) MAS probe was used to collect high resolution $^{29}$Si (59.6 MHz) and $^{27}$Al (78.2 MHz) spectra. Approximately 100 mg of sample was packed into a 4 mm zirconium rotor with a Kel-F cap. The $^{29}$Si NMR spectra were acquired using a standard CPMAS pulse program with the following acquisition parameters: spinning rate of 5 kHz, CP contact time of 5 ms, 10 s recycle delay, 6k-16k scans per sample, and line broadening of 20 Hz. Si/Al ratios were calculated using a formalism developed by Engelhardt and co-workers$^{22}$

4.2.2.5 **Dynamic Light Scattering**

A Malvern Zetasizer Nano was used to collect DLS data. The intensity averaged particle size distributions of as-synthesized zeolite particles was determined by DLS. The correlation functions presented are an average of 45 accumulations of 10 s measurements collected at a backscattering angle of 273°. The method of cumulants was used to obtain an average particle size$^{23}$. The CONTIN method was used to invert correlation data to a particle size distribution$^{24}$.

4.2.2.6 **Infrared Absorption Spectroscopy**

Diffuse reflectance infrared absorption spectra (DRIFTS) were collected on modified and un-modified zeolite powders using a Perkin-Elmer infrared spectrometer Spec400. Samples were dehydrated under vacuum for 24 hrs prior to measurement. For all spectra, zeolite was diluted to 1wt% in dry KBr. When designated transmission spectra were collected by preparing a transparent pellet at a similar concentration to the above mentioned material.
4.2.2.7 Electrochemical Impedance Spectroscopy

200 mg of calcined, ion exchanged zeolite powder was pressed into a pellet under 0.3 GPa uniaxial force. These pellets were heated to 700 °C for 2 hr with a ramping and cooling rate of 5 °C min⁻¹. Electrodes were attached to pellets with two gold wires with gold conducting paste followed by curing at 600 °C for 2 hr (5 °C min⁻¹ ramp and cooling rate). The electrodes were placed in a parallel geometry on the same side of pellet and membrane. A Solartron 1260 was employed to generate the ac excitation voltage with a magnitude of 300mV. A frequency range from 0.1 Hz to 10⁷ Hz was conducted during each scan. The impedance data were analyzed by commercial software Zplot and Zview (Scribner, Inc., USA). Data analysis was also done with Origin 8 software.

4.3 Results

This study focuses on four different size ranges of zeolite Y and the characteristics of these particles are first described. Table 4.1 summarizes these characteristics.

4.3.1 Zeolite Y membrane

Figure 4.1a shows the XRD pattern of the membrane (supported on α-alumina) indicating the presence of zeolite Y signified by the characteristic pattern of Bragg reflections. Figure 4.2a shows the cross-sectional SEM image of the as-prepared membrane, indicating a thickness of ~700 nm. The relative intensities of the characteristic zeolite Y reflections are altered relative to powders due to preferential crystal orientation in the [111] plane. There does not appear to be any macroporosity or mesoporosity evident from these micrographs of the membrane indicating a high quality membrane material. Since solid state NMR could not be obtained on the membrane samples because of interference from the α-alumina support, the Si/Al ratio was obtained from XPS measurements. The Si/Al ratios of all of the zeolite powders in this study were obtained via ²⁹Si-MAS-NMR. These same samples were also analyzed for Si/Al by XPS
measurements. A calibration curve was constructed, comparing the XPS and the NMR data (Figure 4.3). Using the XPS Si/Al value of 3.08, the Si/Al ratio of the membrane based on the calibration curve was estimated to be 2.58.

4.3.2 Micron-sized zeolite particles

There were two sources of these materials: a commercial sample and a sample obtained by synthesis. The goal was to obtain two micron-sized samples with differing Si/Al ratios. The powder XRD of the commercial sample is shown in Figure 4.1b, and all of the peaks are identified as those characteristic of zeolite Y. SEM of the commercial particles shown in Figure 4.2c indicates a size range with an average diameter of one micron. The Si/Al ratio of this zeolite was measured by $^{29}$Si-MAS-NMR, and the spectrum is shown in Figure 4.4. Using the deconvoluted intensities of the different silicon environments, the Si/Al was found to be 2.5. Another sample of comparable dimension and morphology as the commercial zeolite was synthesized, but with a Si/Al ratio of 1.5 (measured by $^{29}$Si-MAS-NMR, XRD shown in Figure 4.1c). The SEM of the synthesized zeolite is shown in Figure 4.2b, with an average particle size of ~1.5 μm.

4.3.3 Sub-micron sized particles

Sub-micron zeolite Y particles were synthesized from the composition 0.037Na$_2$O:3.13(TMA)$_2$O.4.29SiO$_2$.1.0Al$_2$O$_3$.4.97H$_2$O. The XRD pattern in Figure 4.1d show that the majority phase is zeolite Y, with zeolite A impurity estimated at less than 5%. As synthesized, these crystals contained TMA$^+$ in the zeolite, which was removed by calcination, followed by ion-exchange with Na$^+$. SEM data in Figure 4.2d indicates a size of ~200 nm. Dynamic light scattering studies indicate a mean size of 187 nm, with a polydispersity of 0.1. The Si/Al measured by $^{29}$Si MAS-NMR ratio is 1.75.
4.3.4 Nano-sized particles

Nanoparticles were synthesized from the composition
0.048Na₂O:2.40(TMA)₂O(2OH⁻):1.2(TMA)₂O(2Br⁻):4.35SiO₂.1.0Al₂O₃.249H₂O. The
XRD patterns in Figure 4.1e confirm the formation of zeolite Y. As synthesized, these
crystals also contained TMA⁺ in the zeolite, which was removed by calcination, and
followed by an ion-exchange with Na⁺. Figure 4.2e shows the TEM of these particles
indicating particle sizes of ~20-50 nm. Dynamic light scattering studies show a mean
size of 47 nm with polydispersity of 0.16. The Si/Al ratio from ²⁹Si MAS-NMR was
calculated to be 1.68.

4.3.5 Impedance Spectroscopy

Impedance spectra of all five samples were recorded over a range of temperatures.
Representative data are presented for the commercial micron-sized zeolite (for the rest of
the samples, the data is included in the Supplementary Section). Figure 4.5 shows the Z''-
Z'(Nyquist/Argand, Z'' and Z' are the imaginary and real part of the impedance,
respectively) plot for the commercial micron-sized Na-zeolite at temperatures between
525-625 °C. The impedance data are characterized by a semicircle, with a tail at the low
end of the frequency. All five samples examined in this study showed this pattern (all
data shown in Figure 4.6). In order to obtain a measure of the goodness of fit of the
measured data to a true semicircle, the parameter α was calculated from the observed
data. This was done by fitting Z'', which was obtained from Z (equations 1 and 2):

\[ Z = \frac{R}{1 + A(jw)^\alpha} \quad (1) \]

\[ Z'' = \frac{-R^2 A(w)^\alpha}{1 + (RA(w)^\alpha)^2} \quad 0 \leq \alpha \leq 1 \quad (2) \]

where R is the resistance of the sample, w is the frequency and A and α are the frequency
independent parameters of the constant phase element (CPE) derived from an equivalent
circuit model fit. In fitting $Z''$, $R^2\Delta$, RA and $\alpha$ were used as the fitting parameters. It was ensured that the $R^2\Delta$/RA ratio approached the observed experimental resistance as a constraint on the fit. As the semicircle in the $Z''$-$Z'$ plot is depressed, $\alpha$ deviates from 1 ($\alpha = 1$ being a perfect semicircle)\textsuperscript{26,27}. The values of $\alpha$ are listed in Table 4.2 for the Na\textsuperscript{+} exchanged version of all the zeolite samples at 525 °C, with $\alpha$ in the range of 0.84-1. At lower temperatures (300-400 °C, data not shown), there was increased flattening of the semicircle, with the value of $\alpha$ reaching as low as 0.63 at 300 °C. Thus, at lower temperatures, other relaxation processes are occurring. This effect is recognized in the literature\textsuperscript{14}. It is likely due to water adsorption. All results in this paper are for the temperature range of 525-625 °C, where one process dominates the relaxation time ($\alpha$ approaching 1).

The impedance data were treated in various ways to help elucidate the mechanistic aspects of cation motion. Figure 4.7 shows the plot of modulus ($M''$) as a function of frequency for the commercial micron-sized Na-zeolite at temperatures from 525 to 625 °C (Figure 4.8 shows the data for the other four samples). There is only one peak observed in the modulus plot whose frequency shifts to higher values with increasing temperature. The same behavior is observed for all five samples. Symmetric peaks for the $M''$ vs. $\omega$ plot indicate Debye like behavior, consistent with the almost semicircular arcs observed in $Z''$-$Z'$ plots.\textsuperscript{26,27}

Figure 4.9 shows the plot comparing the $Z''$ and $M''$ versus frequency for the commercial micron-sized Na-zeolite sample at 525 °C. The $Z''$ and $M''$ peaks are seen to overlap at the same frequency indicating a conduction process that is long range in nature, and also indicates the absence of space charge polarization, and therefore, is indicative of ideal Debye behavior.\textsuperscript{26,27} Similar observations were made for all five samples.

The temperature dependent impedance and relaxation time changes make it possible to calculate activation energies ($E_{act}$) related to cation motion. The intercept of the impedance on the real $Z'$ axis in Figure 4.5 was used to obtain the resistance $R$, and used to calculate $E_{act}$, and the values derived from the Arrhenius plot is listed in Table
4.2. The membrane, commercial micron, submicron, nano and synthetic micron zeolite with Si/Al ratios of 2.58, 2.5, 1.75, 1.68 and 1.48 have $E_{\text{act}}$ of 93, 83, 78, 66 and 51 kJ/mol respectively, with the overall trend being that the activation energies increase with increasing Si/Al ratio as expected.\textsuperscript{14}

The activation energy for conductivity in zeolite ($E_{\text{act}}$) is the sum of activation energy for creation of the mobile carrier ($E_{\text{mc}}$) and the energy for ion hopping ($E_{\text{h}}$). The activation energy based on relaxation time (calculated from the peak frequency in the modulus plots Figure 4.7) provides the activation energy for ion hopping. Table 4.2 shows the activation energies, $E_{\text{h}} = E_{\text{act}}(w)$, for the five zeolite samples, and also increases with increasing Si/Al ratio. The $E_{\text{mc}}$ varies between 3 to 9 kJ/mol, but does not exhibit a clear trend.

The Na\textsuperscript{+} was ion-exchanged with Li\textsuperscript{+} and K\textsuperscript{+} for the membrane, commercial micron-sized, submicron and nanozeolite, and impedance measurements were subsequently performed. The $E_{\text{act}}$ follows the trend Li\textsuperscript{+} > Na\textsuperscript{+} > K\textsuperscript{+} for all samples, and these data are plotted in Figure 4.10.

### 4.3.6 Surface Modification

In order to make monolayer modifications of the surface of the zeolite crystals, the surface hydroxyl groups of the zeolite were reacted with 1,1,3,3-tetramethyldisilazane under ambient conditions. Figure 4.11a schematically represents this process. This chemistry is based on earlier work, and the functionalization of the surface hydroxyl groups is readily confirmed by the presence of C-H bands at 2800 cm\textsuperscript{-1} (data not shown).\textsuperscript{21} In preparation of the samples for the impedance measurements, the pressed pellets are heated to 700 C. This treatment leads to the loss in the organic functionality (the C-H bands in the infrared disappear). We propose that the chemistry shown in Figure 4.11b occurs with calcination of the surface derivatized samples. There can be both intrazeolitic and interzeolitic reactions, with the disilazane being converted to Si-O-Si groups. The perturbation on the zeolite surface is the addition of a single monolayer of Si-O-Si bonds.
The $Z''$-$Z'$ plots of the surface derivatized sample were similar in appearance (a nearly perfect semicircle) to the underivatized sample. However, there were differences in the activation energy (derived from the Argand plots), and this data is presented in Table 4.2. The trends are that upon surface derivatization, there is minimal effect on the micron-sized samples (within experimental error), but a marked increase in the activation energy for the submicron and nanozeolite. This effect is more pronounced at the nanoscale.

4.4 Discussion

Extensive studies exist on ion conductivity in faujasitic zeolites.\textsuperscript{13,14,29} The number of available sites for cation transport is considerably greater than the number of cations (for all Si/Al ratios). Current models propose two types of thermally activated cation motions occur, a high frequency cation hopping within the supercage, from sites SII to SIII for example, and a low frequency motion from one supercage to an adjoining supercage across the 7.4 Å window.\textsuperscript{13,29} All reported $Z'$ - $Z''$ plots for zeolites exhibit a single depressed semicircle, with a low frequency tail that arises from polarization due to ion accumulation at the interface of the sample and electrode resulting from the use of blocking electrodes.\textsuperscript{26,27} Two relaxations are observed in the modulus plots at low temperatures (<350 °C).\textsuperscript{29} At temperatures (>525 °C) which is the focus of the present study, even in the modulus plots, only a single peak is observed. At these temperatures, and based on the existing model for charge hoping in zeolite, the cation motion is long-range and of lower frequency.

The impedance/modulus plots in Figure 4.5, Figure 4.7 & Figure 4.9 all indicate that the cation migration is best represented by a process with mostly a single relaxation time ($\alpha \geq 0.9$). The activation energy for cation transport in faujasitic zeolites has also been investigated and is dependent on the nature of the cation and the Si/Al ratio of the framework.\textsuperscript{13,14,29} Typically, for a particular cation in a specific framework, a decrease in Si/Al ratio leads to a decrease in activation energy. With lower Si/Al ratios, there is a weaker Coulombic interaction, as well as there are more cations within the framework,
and the cation-cation repulsion facilitates motion. The trend of the activation energies with Si/Al ratio in Table 4.2, with the membrane, commercial micron, submicron, nano and synthetic micron zeolite with Si/Al ratios of 2.58, 2.5, 1.75, 1.68 and 1.48 with \( E_{\text{act}} \) of 93, 83, 78, 66 and 51 kJ/mol, respectively follow the expected trend. The difference between the \( E_{\text{act}} \) obtained from the conductivity and modulus (Table 4.2) is related to the energy for creating mobile cations, and is of the order of 3-9 kJ/mol.

The activation energies as a function of ion exchanging cation (Figure 4.10) follow the order Li\(^+\) > Na\(^+\) > K\(^+\), in agreement with the literature. The basis for this activation energy trend is that the ions with higher charge to radius ratios have stronger Coulombic interaction with the framework.

All of the above observations are consistent with what has been reported in the literature. The novel observation in this paper is the change in \( E_{\text{act}} \) with surface derivatization of the particles. The surface hydroxyl groups are converted to –OSiH(CH\(_3\))\(_2\), and then during sample preparation, the organic groups are burnt off, leaving a single layer of Si-O-Si on the zeolite surface. The effect on \( E_{\text{act}} \) is size dependent. For both the micron-sized zeolites of Si/Al of 2.5 and 1.48, there is minimal influence on \( E_{\text{act}} \), with the changes within the error of the measurement (Table 4.2). With the submicron particle, \( E_{\text{act}} \) increase from 78 to 83 kJ/mol. With the nanozeolite, the effect is most pronounced with \( E_{\text{act}} \) increasing from 66 to 81 kJ/mol upon surface derivatization. These results indicate that the surface of the zeolite particles, i.e. grain boundaries are posing resistance to cation motion, as the crystallite size decreases.

Conductivity of various metal oxides as a function of size is currently an active area of research. Extensive impedance spectroscopy studies have shown that with decreasing particle size, the role of the grain boundaries becomes important. Though controversial, most studies report dramatic changes in conductivity, with the defect structure proposed to provide extra pathways for ion conduction.

In the case of zeolites, earlier papers have considered that bulk and grain boundary can contribute to the impedance, but these are not manifested as two semicircles in the \( Z' - Z'' \) plots, because the time constants of the two relaxation processes
are possibly similar in the temperature range investigated (need to be greater than 100). The equivalent circuit for such a model is depicted in Figure 4.12a with two paths in series, \( R_b \) being through the bulk and \( R_{gb} \) representing the surface conduction, \( C_b \) and \( C_{gb} \) the corresponding capacitances, and \( C_g \), the geometric capacitance due to the measuring cell. In this model, the cations move through the grain and then across the grain boundary. Earlier studies on zeolites have noted that grain boundary effects are not important, but the sizes of the particles were not explicitly determined, but considering that they were from commercial sources, will have sizes approaching a micron. Based on our results, such effects are not detectable at these scales.

In order to obtain an estimate of the resistance to cation motion posed by the grain boundary, the equivalent circuit in Figure 4.12a was used, primarily with the data of the nanoparticle (47 nm). It involved fitting the Argand plot at various temperatures with \( R_b \) and \( R_{gb} \). \( R_b \) is what is expected for the bulk conductivity, and experimental data obtained from micron sized sample with a Si/Al ratio of 1.48 was used for \( R_b \) at various temperatures. Then the \( Z' - Z'' \) data were fit to provide \( R_{gb} \) (C’s were also variables for the fit). Figure 4.12b shows the quality of the fit. The microscopic environment within the zeolite and at the intergrain boundaries, especially for samples heated at 700 °C are similar and so the capacitances are not expected to be very different (Table 4.3 shows the parameters that were used for the fitting). Based on the fitting shown in Figure 4.12b, \( R_{gb} \) is greater than \( R_b \) by a factor of 2.5-3.3 for the 47 nm zeolite, depending on the temperature (higher values as temperature is lowered).

Thus, the model of cation motion that emerges can be summarized as follows. Since all impedance measurements reported in this study were carried out at temperatures > 525 °C, the cation motion is long range, involving cation hopping between the supercages and then between grains. As the crystallite size gets smaller, the cations will have to transport across a larger number of grain boundaries. Previous studies on zeolites were primarily focused on micron-sized zeolites, and grain boundary effects were not considered relevant for cation motion. For the micron-sized zeolites, surface derivatization has minimal effect on \( E_{act} \), consistent with the assumption made in the
earlier studies. Sample preparation typically involved pressing zeolite powders at high pressures (approaching GPa), and then heat treatment at 700 °C, prior to impedance measurements. Unlike ceramics, zeolites do not sinter, in that there is no grain growth. However, high temperature treatment will lead to intergrain connections via condensation of surface Si(Al)-OH groups to form Si(Al)-O-Si(Al) bonds, as observed for metal oxides. In the larger crystals, the interface between two particles is large and there are opportunities for surface reconstruction, such that cation hopping across grain boundaries find similar microscopic environment as that of the bulk (i.e. have similar \( E_{\text{act}} \)). Thus, the surface modification shown in Scheme 1b does not significantly alter the interface structure. However, as the crystals get smaller and reach the nanoscale, interparticle bonding during the heat treatment is limited to a significantly smaller interface area. Thus, we propose that there are fewer opportunities of reconstruction, and the interface is more defective in the sense that the cages are not well aligned. Under these conditions, surface modification (Scheme 1) introduces a Si-O-Si spacer, and \( E_{\text{act}} \) corresponding to cation motion increases.

### 4.5 Conclusions

Though there have been extensive studies on impedance spectroscopy of zeolites, this report is the first one to investigate as a function of size, specially focusing on the nano scale. Previous studies have noted that grain boundary effects are not important for zeolite, primarily because the focus was on large crystallites. The influence of the grain boundary is noted only with crystallite sizes below 200 nm. The cation motion that the frequency is inducing is long range motion, which involves cation hopping from one supercage to the next, and then across grains. As the grains get smaller, ions will have to transport across a larger number of boundaries. The nano-sized crystals upon high temperature heat treatment are not as effective in the surface annealing between particles, and thus transport across these boundaries have higher activation energy. By proposing a framework to understand the electrical response of nanocrystalline zeolites our findings may be important in future applications of nanometer sized microporous materials.
4.6 References


Figure 4.1: X-Ray diffraction powder patterns of a) Zeolite membrane (the strong peaks above 25° 2θ are from the alumina support), b) Micron-sized commercial powder
c) synthetic micronsized powder d) Sub-micron powder and e) nano-sized powder
Figure 4.2: Electron micrographs of a) Cross-section view of the zeolite membrane b) Synthetic micron-sized commercial powder c) Commercial micron-sized Synthetic micron-sized powder d) Sub-micron powder and e) Nano-sized powder (a TEM image).
Figure 4.3: Comparison of the Si/Al ratio obtained by $^{29}$Si MAS NMR and XPS for synthetic and commercial micron-sized (zeolite X), sub-micron sized and nano-sized zeolites.
Figure 4.4: $^{29}$Si – magic angle spinning (MAS) NMR of commercial micron-sized zeolite, along with the curve deconvoluted bands from the differently coordinated silicon.
Figure 4.5: Impedance (Nyquist/Argand) plots of commercial micron-sized zeolite at different temperatures as designated in the legend ($\Omega = \text{Ohms}$).
Figure 4.6: Impedance (Nyquist/Argand) plots for zeolite membrane (a), submicron-sized (b), nano-sized (c), and synthetic micron-sized (d) zeolites.
Figure 4.7: Modulus ($M''$) plot against frequency for commercial micron-sized zeolite at various temperatures, along with the relaxation times calculated from the peak frequency (included in the legend).
Figure 4.8: Modulus (M") plots for zeolite membrane (a), submicron-sized (b), nano-sized (c), and synthetic micron-sized (d) zeolites. Again, the relaxation times are included for each sample at each temperature (contained in the legend).
Figure 4.9: Comparison of the normalized curves for $Z''$ and $M''$ for micron-sized commercial zeolite.
Figure 4.10: Plots of activation energy trends for Li\(^+\), Na\(^+\) and K\(^+\) exchanged zeolite membrane (black square), commercial micron-sized (red dot), submicron-sized (blue triangle), and nano-sized zeolites (purple inverted triangle). On average, an error of ±1 kJ/mol was observed based on replicate measurements on the Na\(^+\) samples. No replicate measurements were made on the Li\(^+\) and K\(^+\) samples.
Figure 4.11: Surface derivatization scheme illustrating the surface modification reaction between zeolite and TMDS.
Figure 4.12: a) Equivalent circuit model b) the Nyquist/Argand plot for nano-sized zeolite at 525 °C along with fit using the parameters listed in Table 4.3.
Table 4.1: Chemical and physical properties of the zeolite samples prepared herein.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>2.58*</td>
<td>Thickness-700nm@</td>
</tr>
<tr>
<td>Micron-sized Commercial</td>
<td>2.5</td>
<td>1.0µm@</td>
</tr>
<tr>
<td>Micron-sized Synthetic</td>
<td>1.48</td>
<td>1.5µm@</td>
</tr>
<tr>
<td>Sub-micron</td>
<td>1.75</td>
<td>187 ± 1* nm</td>
</tr>
<tr>
<td>Nano</td>
<td>1.68</td>
<td>47 ± 0.3# nm</td>
</tr>
</tbody>
</table>

* obtained from XPS, rest of the samples Si/Al by SS NMR
*# from dynamic light scattering data
@ from electron microscopy data
Table 4.2: Activation Energies (kJ/mol, error ±2-3 kJ/mol) from Impedance Spectroscopy (all Na\(^+\) form).

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>(\alpha (525^\circ \text{C}))(^&amp;)</th>
<th>Fact ((\omega))(^*)</th>
<th>Fact (R)(^#)</th>
<th>Fact (R, derivatized)(^@)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>0.84</td>
<td>90</td>
<td>93</td>
<td>----</td>
</tr>
<tr>
<td>Micron-sized Commercial</td>
<td>0.89</td>
<td>76</td>
<td>83</td>
<td>81</td>
</tr>
<tr>
<td>Micron-sized Synthetic</td>
<td>1</td>
<td>43</td>
<td>51</td>
<td>53</td>
</tr>
<tr>
<td>Sub-micron</td>
<td>0.89</td>
<td>70</td>
<td>78</td>
<td>83</td>
</tr>
<tr>
<td>Nano</td>
<td>0.91</td>
<td>57</td>
<td>66</td>
<td>81</td>
</tr>
</tbody>
</table>

\(^\&\) \(\alpha\) parameter obtained from Eq 2

\(^*\) \(E_{\text{act}}\) obtained from peak frequency (Fig 5)

\(^#\) \(E_{\text{act}}\) obtained from x-axis intercept of \(Z''-Z'\) plot (Fig 4)

\(^@\) \(E_{\text{act}}\) obtained from x-axis intercept of \(Z''-Z'\) plot for surface derivatized samples
Table 4.3: The fitting parameters for the equivalent circuit model in Figure 4.12.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>525°C</th>
<th>550°C</th>
<th>575°C</th>
<th>600°C</th>
<th>625°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_e$ (F)</td>
<td>7.5962E-11</td>
<td>7.5291E-11</td>
<td>7.3954E-11</td>
<td>7.2667E-11</td>
<td>7.1106E-11</td>
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<tr>
<td>$R_b$ (Ω)</td>
<td>4746</td>
<td>3766</td>
<td>3127</td>
<td>2635</td>
<td>2244</td>
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<td>$R_{ab}$ (Ω)</td>
<td>15900</td>
<td>12051</td>
<td>9165</td>
<td>7097</td>
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<td>$C_b$ (F)</td>
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<tr>
<td>$C_{ab}$ (F)</td>
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<td>3.1476E-11</td>
<td>3.4365E-11</td>
<td>3.7404E-11</td>
<td>4.0581E-11</td>
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CHAPTER 5: EVOLUTION OF SILVER NANOPARTICLES WITHIN NANO-SIZED ZEOLITE Y MATRICES: A MECHANISTIC STUDY

5.1 Introduction

An enormous amount of novel silver nanostructures have emerged from a flurry of intense research in nanotechnology over the past decade. Noble metals are among the most important commercial catalysts and advances in nanotechnology are extending their capabilities in numerous applications. Silver metal catalysts have been studied thoroughly and remain a popular topic due to their unique catalytic, optical, and electrical properties. For example, silver nanoparticles have found widespread use as optical sensors because of their refractive index dependent localized surface plasmon resonances in the visible region of the electromagnetic spectrum.\textsuperscript{1} This unique property is commonly exploited to enhance the Raman signals of surface adsorbed molecular species through the electromagnetic surface enhanced Raman scattering mechanism.\textsuperscript{2} The medicinal application of silver salts also has a long history and recent studies implicate silver nanostructures as antibacterial agents.\textsuperscript{3,4} Growing efforts to develop novel silver structures that maximize antibacterial properties have focused on minimizing the particle size of silver nanoparticles. Evidence suggests smaller silver nanoparticles are more effective antibacterial agents as a result of the increased surface area to volume ratio and strong surface reactivity.\textsuperscript{5} The under coordinated nature of the surface atoms of nanoparticles are hypothesized to contribute to this antibacterial activity in addition to acting as catalytic active sites in chemical reactions.\textsuperscript{6}

In all cases (perhaps except in the case of SERS) smaller particles are desired, yet, smaller particles are increasingly difficult to stabilize as they become thermodynamically...
unstable according to the Gibbs-Thomson equation. There is recent evidence supporting the notion that metal particles are exceptionally unstable below some critical threshold size below which the Gibbs-Thomson equation (and ordinary thermodynamics for that matter) fail to model experimental data. For silver, this threshold size is estimated at 5 nm. Silver nanoparticles 2-3 nm are synthesized under a variety of conditions, however, they tend to dissolve or ripen into larger structures in the absence capping/stabilizing agents. Inclusion of stabilizing agents modifies the surface properties and may render them useless in some applications. Therefore, directly synthesizing these small particles while maintaining stability and an active surface is both essential to innovating current applications and synthetically challenging. Furthermore, metal nanoparticles are hard to isolate, due to their size, making their separation and recovery difficult and increasing the risk of exposure to the environment which raises concerns.

One approach to these problems is to stabilize nanoparticles on a chemically inert substrate that serves as a support preventing aggregation or dissolution. This general approach has been demonstrated for a variety of metal nanoparticles. Silver is catalytically active on solid supports. In fact, alumina supported silver nanoparticles are one of the commercial catalysis for ethylene oxide production. Recent reports have demonstrated excellent activity of alumina supported silver clusters (Ag trimers), and nanoparticles (<3.2 nm) in the epoxidation of propylene to propylene oxide for which no commercial catalyst yet exists. These catalysts exhibited high activity even at low temperatures but the active species sintered at high temperatures leading to lower activity and lower selectivity.

Developing porous metal-oxide supported catalysts has been proposed to stabilize metal clusters from sintering. Using this approach promising catalytic activities have been reported for a number of applications including VOC decomposition and selective catalytic reduction of NOx in the presence of hydrocarbons. Recently, Au nanoparticles of about 2nm were formed within the nanocages of SBA-16 by chemical reduction. This Au-SBA16 system exhibited excellent catalytic activity toward the oxidative esterification of alcohols, even with less reactive aliphatic alcohols. The Au-
SBA16 catalyst outperformed Au containing catalysts on silica supports because the SBA-16 structure stabilized the gold particles. This is in stark contrast to the silica support where the nanoparticles aggregate and deactivate after a few reaction cycles. This illustrates the potential of zeolite and related porous materials as an effective substrate to organize and stabilize noble metal nanoparticles. This example not only illustrates the ability of a supporting substrate in stabilizing catalytic metal nanoparticles but also that the structure of the substrate is an important factor influencing performance. To this end, zeolites and zeolite-like materials are promising candidates to stabilize and improve the performance of common catalytic materials.

Furthermore, it has proved to be a fairly general process applicable to a variety of metals. For instance, silver loaded mesoporous silica SBA-15 is an excellent electrocatalyst for reduction of hydrogen peroxide.\textsuperscript{16} Pd loaded zeolites have been used for catalytic Heck coupling reactions.\textsuperscript{17} Pd SBA-15 composites have shown high catalytic activity for the Heck coupling reaction and selectivity superior to conventional Pd-Al\textsubscript{2}O\textsubscript{3} catalysts.\textsuperscript{17} Interest in silver exchanged zeolite in the catalysis community is fueled mainly from their excellent performance as a de-NO\textsubscript{x} catalyst. Zeolites exchanged with copper or silver are popular de-NO\textsubscript{x} catalysts.\textsuperscript{18} Silver exchanged ZSM-5 was demonstrated as a high temperature water vapor sensor.\textsuperscript{19} This illustrates the potential of zeolite and related porous materials as an effective substrate to organize and stabilize noble metal nanoparticles in a variety of applications.

Many forms of silver have been identified inside the zeolite pore structure. It is widely acknowledged that controlling silver speciation is crucial for a given application. For example, Ag\textsubscript{n}\textsuperscript{d+} (2≤n≤4) clusters are claimed to be the active species for enhanced de-NO\textsubscript{x} reactions in silver exchanged MFI.\textsuperscript{18} Although, metal clusters Ag\textsubscript{m} (3≤m≤5) and Ag\textsuperscript{0} were also detected and showed some activity.\textsuperscript{18} Other studies report Ag\textsubscript{4}\textsuperscript{2+} as the active species.\textsuperscript{12} In contrast, Ag\textsuperscript{0} is reported as the active species on alumina supports.\textsuperscript{20} Efforts to identify and understand the formation of silver species in zeolite pores upon reduction rely largely on ultra violet visible absorption spectroscopy (UV-Vis), though, a wide range of techniques have been utilized.\textsuperscript{21–23} Bartalamu et al. provide an extensive
literature review of the UV-vis absorption features and their assignments commonly observed for numerous silver exchanged zeolite structures. $\text{Ag}_6^0$ and $\text{Ag}_3^{2+}$ have been observed in zeolite A using various analytical methods.24,25 In zeolite Y similar species have been observed though it is thought that the pore size favors $\text{Ag}_8$ clusters.23 These findings are consistent with EPR studies of silver containing zeolites indicating $\text{Ag}^0$ formed during reduction react together to form clusters of $\text{Ag}^0$ ranging in size.26 To date, silver speciation varies widely. The exact structural details of intra-zeolitic silver clusters are handled in a case specific manner. Electron microscopy is emerging as one of the primary tools for understanding the speciation of silver within zeolites despite the beam sensitivity of both silver and zeolite.27–30 Mayoral et al. have used high resolution transmission electron microscopy to image $\text{Ag}_6$ clusters at atomic resolution within the zeolite A pore structure.31 Recent investigations have identified silver clusters of ~2 nm in ETS-10 zeolite formed by mild reduction with formaldehyde.32 There has yet to be comparable studies of silver-zeolite Y systems imaging the silver species directly. Nevertheless, there are a few reports of well dispersed silver nanoparticles formed within the pores of zeolite Y.28,33 These studies qualitatively agree with trends observed in SAXS and TEM investigation of Pt-Y materials where a distribution of 0.6-1.3 nm particles were observed dispersed homogenously throughout the zeolite, in fact, they are thought to exist within the supercages.34 It is realistic to believe such clusters are composed of ~ 40 atoms per cluster. These examples highlight the novelty of the zeolite structure in stabilizing metallic clusters and small particles. In these cases the clusters formed are dependent on the pore structure of the zeolite host.

Most work in the field of Ag-zeolites has focused on identifying small few atom silver clusters that can be formed under mild conditions. These are intermediate, reactive structures and are stabilized under controlled conditions. Forming clusters and metallic silver species within zeolite requires careful consideration of the reaction conditions. Complete reduction of the Ag-zeolite often causes silver to exit the zeolite pore system. This silver migration is a common, seemingly inexplicable, observation made by many researchers using a wide range of reducing conditions.27,35–37 Often, uncontrolled
reduction of intra-zeolitic silver can result in complete destruction of the zeolite crystal structure.\textsuperscript{36} Therefore careful choice of reaction conditions is necessary in designing a reaction that goes to completion while leaving the zeolite structure intact. Solving this problem usually requires decreasing silver loadings and or reducing agent concentrations. This has traditionally been achieved by gas phase reduction of the silver by hydrogen gas.\textsuperscript{18,20,23,27} This procedure allows precise control of the reducing agent, thus, the silver evolution. Some solution phase routes have been designed but are unpopular as reflected by the low number of publications in this area as these reactions prove difficult to control.\textsuperscript{33,36,37} Radiolytic approaches using gamma radiation have been used to prepare small particles resistant against migration to the surface.\textsuperscript{35} Herein, we report on the synthesis of highly dispersed silver nanoparticles within the micropores of nanocrystalline zeolite Y prepared in solution.

Improvements in nanozeolite science and technology allow for the extension of traditional approaches and concepts to new, novel zeolite nanocrystals. It is widely recognized that particle size often plays an crucial role in heterogeneous catalysis.\textsuperscript{11,38} In many applications small crystal sizes present new challenges, and in such cases, new methodologies must be developed. Most methods for the preparation of silver clusters within zeolites rely on high temperature treatment of silver ion exchanged powders with hydrogen gas (vide supra). This is an effective method in most circumstances, though the high temperature treatment of zeolite nanoparticles often causes irreversible aggregation. As a result the particle size distribution shifts to higher values and the colloidal stability is compromised. Under these circumstances, it is necessary to devise non-thermal methods of reduction to avoid such problems. Herein we describe a rapid, solution state method for the preparation of silver clusters dispersed within pores of nano-sized zeolite Y. These composite particles can be dispersed in water forming a stable colloidal suspension that can be studied by various in-situ techniques including transmission UV-Vis spectroscopy. The kinetics of the reduction process is studied as a function of time using a variety of analytical techniques. A model for the growth of intra-zeolitic silver
particles is proposed. We explore the use of the zeolite-silver system as a colloidal SERS substrate.

5.2 Experimental Methods

5.2.1 Synthesis

Catechol, hydroquinone, resorcinol, silver nitrate, and trans-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide were purchased and used as received.

Nanozeolites were synthesized using a modified procedure similar to that found in the literature. The following gel composition was used:

\[0.048\text{Na}_2\text{O} : 2.40(\text{TMA})_2\text{O}(2\text{OH}) : 1.2(\text{TMA})_2\text{O}(2\text{Br}) : 4.35\text{SiO}_2 : 1.0\text{Al}_2\text{O}_3 : 2.49\text{H}_2\text{O}\]. The resulting clear sol was aged with stirring for 3 days followed by heating at 100 °C in an oil bath for 4 days. The product was isolated by ultracentrifugation (50,000 rpm at 200,000 relative centrifugal force) and washed with DI H₂O until neutral. Colloidal dispersions were ion exchanged first with 0.05 M NaNO₃ for 24 hours twice to remove TMA template from the super cages. The sodium nitrate exchanged product was again washed liberally with water to remove excess ions. Finally, the sodium form was ion exchanged twice with 0.05 M AgNO₃ in the dark for 24 hrs. All ion exchanges were performed at an estimated loading of 1 g zeolite per 10 mL solution. The silver ion exchanged product was washed with DI water until no reaction was observed between the zeolite supernatant and a cold, dilute HCl solution. This stable dispersion was used fresh in all subsequent experiments. Elemental analysis indicates a silver loading of 20 wt%. A complete exchange is expected to yield ~34.2 wt% of silver. The chemical formula for a unit cell is estimated as \(\text{Na}_{38}\text{Ag}_{39}[(\text{SiO}_2)_{115}(\text{AlO}_2)_{77}]250\text{H}_2\text{O}\) based on sodium as a counter ion. The chemical formula for a unit cell is estimated as \(\text{TMA}_{32}\text{Ag}_{45}[(\text{SiO}_2)_{115}(\text{AlO}_2)_{77}]250\text{H}_2\text{O}\) based on TMA⁺ as a counter ion. The completely general formula for the material studied here is \(\text{TMA}_x\text{Na}_y\text{Ag}_z[(\text{SiO}_2)_{115}(\text{AlO}_2)_{77}]250\text{H}_2\text{O}\) were \(x+y+z=77\) so it is likely something in between these two extremes. Nevertheless, between 39-45 Ag⁺ ions per unit cell can be assumed.
Silver exchanged zeolite Y dispersions were reduced using the following reagents under identical conditions: resorcinol, hydroquinone, and catechol. The reduction step used 5 mL of ~0.20 wt% zeolite Y dispersion, with a silver loading of 20 wt%, and 5 mL of 0.2 M reducing agent was added slowly while stirring at 600 rpm at room temperature in the dark. Samples were removed periodically as indicated and washed liberally with DI H₂O. Washing consisted of repetitive centrifugation and rinsing at 150,000 rpm (900,000 relative centrifugal force) for 5-10 min.

Surface enhanced Raman measurements were made on 50/50 volume mixtures of ~0.05 wt% aqueous Ag-zeolite dispersion to benzenethiol solution in a 50/50 volume mixture of water and ethanol. Ethanol was used to increase the solubility of benzenethiol and as an internal standard. Analytical Raman enhancement factors were calculated using the definition according to the literature. The concentration of benzenethiol on the SERS active surface was estimated through UV-Vis absorption measurements of the supernatant after separation by centrifugation. A linear background was subtracted before applying Beer's law.

Trans-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide (Dsm⁺, C₁₆H₁₉IN₂, CAS#: 68971-03-9) was purchased from Aldrich. Proton NMR indicated no purification was necessary. Dsm⁺ was loaded within the silver loaded zeolite Y by ion exchange at a loading of 1 dye per 100 zeolite supercages for 6 hrs followed by liberal washing with DI H₂O. The washed mixed cation system (Ag⁺-Dsm⁺-Y) was prepared as a 0.2 wt% dispersion in water. Silver reduction was performed by the drop wise addition of 0.2 M aqueous resorcinol to an equal volume of zeolite dispersion while stirring at room temperature as outlined above. Samples were periodically collected from the reaction for analysis. Samples extracted before the reduction, after 1hr, and after 2 hrs of reduction are the focus of this experiment. The entire procedure detailed above was performed in the dark.

The absorption and emission properties of aqueous stock solutions of Dsm⁺ prepared at several pH values were examined as a control. Dsm⁻ solutions at pH 1, 2, 4,
6, and 7 were prepared by dissolving Dsm$^+$ in an appropriate concentration of aqueous HCl.

5.2.2 Characterization

UV-Vis absorption and extinction spectra were collected with a Shimadzu 3600 UV-Vis-NIR spectrophotometer. Absorption spectra used for quantitation of benzene thiol concentrations were corrected for a linear background before analysis. The extinction spectra of silver containing zeolites are complex. The extinction spectra of the colloidal system were analyzed in raw form due to the complicated background.

The average particle diameter and intensity averaged particle size distributions of zeolite dispersions were determined by dynamic light scattering (DLS). The correlation functions presented are an average of 45 accumulations of 10s measurements collected at a backscattering angle of 273°. Size distributions collected at a forward scattering angle of 15° give results similar to the backscattering results. The method of cumulants was used to obtain an average particle size.$^{41}$ The non-negative non-linear least squares (NNLS) and CONTIN method was used to invert correlation data to a particle size distribution.$^{42}$ Average zeta potentials were measured by electrophoretic light scattering (ELS). Electrophoretic mobility data was converted to zeta potentials according to the Henry equation at the Smoluchowski limit.

Emission measurements were made with a Horiba Scientific FluoroLog 3. Excitation slit widths were minimized in order to minimize any photoreduction of the silver during fluorescence measurements. Corrected emission and extinction spectra were referenced to a lamp scan to eliminate intensity variations in the light source. Photographs were taken with a Cannon Power Shot A620 camera. Fluorescence images were collected with this camera while samples were illuminated with a compact 4 Watt short wave (254 nm) UV Lamp (UVP LLC. UVGL-25).

Nitrogen adsorption measurements were made using a Quantachrome NOVA 2200e surface area and pore analyzer to determine the surface and textural properties of the reaction products. Adsorption isotherms were analyzed using Brunauer, Emmett, and
Teller (BET) theory to determine surface areas.\textsuperscript{43} The external surface area and micropore volume was estimated using the t-plot method using De Boer's thickness equation for an oxidic surface.\textsuperscript{44}

Inductively coupled plasma optical emission spectroscopy was used to determine the silver content of the silver exchanged zeolite. Elemental analysis was performed by Galbraith laboratories.

XRD patterns for each sample were collected on a Bruker D8 X-Ray diffractometer using nickel filtered Cu $K\alpha_1$ radiation. Patterns were collected at 0.05 degree steps with a dwell time of 2 s with 1 mm and 8 mm entrance and scattering slits respectively. When indicated, pattern profiles were fit using a Pearson VII line shape. Crystallite sizes were calculated from the fitted peaks using Scherrer's equation in conjunction with the appropriate internal size standard (NIST SRM 640c). In most cases the NIST SRM 640c sample was used as an external standard to maintain sample integrity. The [220] reflection of the standard was used for comparison at 47.30° 2\(\theta\). This reflection most closely matches the position of the silver reflection.

Raman spectra were collected using a Renishaw microprobe spectrometer equipped with a CCD. 458 nm excitation from a Coherent innova 300 Argon ion laser was used at 1 mW. Spectra were collected with a 1600 mm\(^{-1}\) grating giving \(\sim 3\) cm\(^{-1}\) resolution. A typical SERS spectra was acquired with a 1 s acquisition time. However, 3 s spectra are shown for aesthetic reasons. Measurements were made on \(\sim 1\) mL of a 0.05 wt\% Ag-nanozeolite colloidal dispersion mixed with 1 mL dilute analyte in a quartz cuvette while stirring.

High resolution transmission electron micrographs (HRTEM), selected area electron diffraction (SAED), energy dispersive spectroscopy (EDS), and high angle annular dark field scanning transmission electron micrographs (HAADF-STEM) were collected from a Tecnai F20 field emission 200 keV S/TEM system (NCEM at Lawrence Berkeley National Laboratory and CEMAS at the Ohio State University). Fourier Transforms were executed on size calibrated images using imageJ procession software.
Particles size distributions were calculated from TEM images using imageJ processing software. Distributions resulted from 200 observations.

$^1$H nuclear magnetic resonance spectra were collected with a Bruker DPX 400 MHz spectrometer.

5.3 Results

5.3.1 Preparation of colloidally a stable silver zeolite precursor

Size analysis of the as-synthesized zeolite colloid was measured by DLS as shown in Figure 3.1. Cumulants analysis of the correlation function indicates an average size of 48 nm and a polydispersity index of 0.16. Non-linear non-negative least squares analysis of the correlation function yields a size distribution centered at 56 nm with a width of ~24 nm. CONTIN analysis of the dispersion gave an average size of 57 nm with a width of 25 nm. The size distribution shifted to larger size upon ion exchange, as expected from DLVO theory, but was recovered upon washing. The zeta potential of the colloid was -48mV indicating a charge stabilized dispersion. Important properties of the as-synthesized colloid collected from DLS and zeta potential experiments are tabulated in Table 5.1. The dispersion remains stable for weeks which is longer than the time scale of any measurement made herein. This behavior was observed over a wide pH range as shown in Figure 5.2 which plots the particle diameter and zeta potential vs. pH. Minimal change in the size or charge is observed over a wide pH range.

5.3.2 Synthesis of Intra-Zeolitic Silver Nanoparticles

Diffraction patterns corresponding to a zeolite Y standard sample, and nanozeolite Y before and after reduction with resorcinol are seen in Figure 5.3 : XRD patterns of a standard zeolite Y as simulated from the FAU structure (a), the as-synthesized nanozeolite Y (b), and silver exchanged zeolite Y after 24 hr of reduction with 0.1 M
The reflections observed in Figure 5.3 b and c are consistent with those expected for the FAU zeolite framework (by comparison with Figure 5.3 a. Upon reduction of intra-zeolitic silver, the FAU diffraction pattern remains as seen in Figure 5.3c. Additional Bragg reflections are observed in the pattern. The additional peaks are characteristic of face centered cubic (FCC) silver metal (marked with asterisks). This is in stark contrast to diffraction patterns collected from catechol and hydroquinone reduced zeolite systems. The diffraction patterns of catechol and hydroquinone reduced silver zeolite Y are shown in Figure 5.4 b and c. The FAU pattern is not observed as seen by comparison with Figure 5.4. Only a few FAU Bragg reflections signifying FCC Ag\(^0\) are observable above the broad baseline resulting from amorphous material. The diffraction pattern of FCC Ag\(^0\) represent the major crystalline features of the pattern.

From the diffraction patterns it is clear that under similar conditions, reduction with catechol and hydroquinone result in complete destruction of the zeolite framework while resorcinol does not. Only Bragg reflections characteristic of FCC metallic silver are well resolved from the amorphous background in systems reduced with catechol and hydroquinone. These data agree with the observation that addition of 0.1 M catechol or hydroquinone to a dispersion of silver exchanged nanozeolite results in an immediate color change to metallic grey. Minutes after mixing, black precipitates are observed. This suggests the immediate formation of bulk silver metal. However, reduction of silver exchanged zeolite with resorcinol leaves the zeolite structure intact as evidenced by XRD. A photograph comparing the appearance of the resorcinol reduced system with that of the catechol reduced system is shown in Figure 5.5. The yellow color of the resorcinol system signifies smaller particles, although, some of this color is likely due to reaction products. Also, there are no precipitates observed after 12 hrs.

There is a slight decrease in the signal to noise ratio in the diffraction patterns of the resorcinol systems upon reduction. This could be due to partial destruction of the framework resulting from the formation of silver clusters larger than 1.47 nm (the cage diameter) in the zeolite pore structure. The crystallite size calculated from the silver metal [111] peak was estimated to be 21 nm using Scherrer’s equation. This size exceeds the
zeolite pore dimensions. Therefore, such crystallites formed within the zeolite structure will be expected to cause some damage to the zeolite crystal structure. Silver particles of this size could also form on the surface of the zeolite crystals, in which case, no damage to the zeolite structure is expected. This problem is addressed with electron microscopy (vide infra). Considerable broadening of the FCC silver Bragg reflections is observed due to the small crystal size. The diffraction pattern of Ag\textsuperscript{+} exchanged zeolite Y in Figure 5.4a also contains noticeable intensity changes in several peaks at low degrees relative to the FAU standard. It is known that the relative intensities of zeolite Bragg peaks is dependent on the extraframework cation present within the zeolite pores\textsuperscript{45}. This explains the increase in intensity of the peak at 2\textdegree~20° in Figure 5.3b and Figure 5.4a as a result of Ag\textsuperscript{+} or TMA\textsuperscript{+} inclusion relative to the standard pattern calculated for a Na\textsuperscript{+} FAU structure in Figure 5.3a. Nonetheless, all observed peaks are expected and belong to the FAU structure, they are different only in their intensity as a result of the cationic inclusions. Diffraction patterns collected here are in general agreement with those reported in the literature.\textsuperscript{46}

Focusing on Figure 5.3c, several other observations can be made. The pattern largely resembles that of zeolite Y with a few exceptions. A new peak observed at 2\textdegree~38.1°. This peak is assigned to the [111] plane of FCC silver metal with a d-spacing of 2.4 angstroms. There is a peak at 2\textdegree~32.2° that gains significant intensity upon reduction. Unfortunately, this position corresponds to the [111] plane of AgO as well as the [555] and [751] planes of FAU. As a result, it is difficult to determine whether the intensity at this position is manifesting a change in extra-framework ion or formation of AgO. However, if the system is fully reduced using concentrated catechol and hydroquinone no AgO is formed and only metallic Ag is observed in the XRD pattern and so the 32.2° peak is assigned to the zeolite structure. We therefore conclude that upon reduction with resorcinol silver clusters of average size of 20 nm are formed after 24 hr at the expense of some zeolite crystallinity and no other phases are formed. Because of the complete destruction of the zeolite upon reduction with catechol and hydroquinone, the remainder of this communication will focus on the resorcinol reduced system.
5.3.3 Dynamics of Intra-Zeolitic Silver Nanoparticle Growth

In-situ extinction spectra in Figure 5.6 illustrate the dynamic nature of silver nanoparticle formation upon reduction. Before reduction a largely featureless spectrum is observed throughout most of the visible spectrum. The only feature in the visible region, we attribute to scattering, increases non-linearly with increasing energy. This is a common characteristic of colloidal dispersions. Changes in the extinction spectrum can be observed after 2 hrs of reduction in Figure 5.6a. Resorcinol has an absorption band below 250 nm hinders the ability to observe the Ag$^+$ 4d$\rightarrow$4s resonance. There is an intense band that appears below 280 nm that saturates the detector. This band is attributed to quinoid-like by products: oxidized resorcinol. Due to the convolution of signals in the UV region of the spectrum in-situ examination cannot be performed with absorption spectroscopy below 300 nm. Therefore, in-situ extinction spectra discussed below focus on the visible region characteristic of silver particle formation.

Silver nanoparticles are not detected after 1hr of reduction with transmission UV-Vis extinction spectroscopy. This indicates silver nanoparticle formation has not started or has not proceeded long enough to generate an observable signal. Diffuse reflectance UV-Vis absorption spectra of the 1hr sample in Figure 5.7 indicate that a small population silver particles have formed according to the broad band centered about 400 nm which is assigned to the silver surface plasmon resonance. However this measurement was taken after fluorescence measurements so some of the formation can be attributed to light exposure (i.e. radiolytic reduction). The primary features in the spectrum are silver ion and silver clusters in the region below 300 nm, therefore, most of the sample must exist as small clusters. This is reasonable given the nearly colorless appearance of the samples in Figure 5.8 which displays photographs of powder collected at 0, 1, and 2 hrs reaction time. Signals of this nature are assigned to a wide range of clusters in the literature. Two intense bands can be seen at 213 nm and 251 nm in Figure 5.7. The 213 nm band is assigned to silver ion 4d$\rightarrow$4s transition. The band at 251 nm is somewhat ambiguous but has been assigned to Ag$_m$ ($3 \leq m \leq 5$), and it is primarily believed to be Ag$_3$.[47,48] Alternatively, this band has been commonly assigned to
Ag\textsubscript{n}\textsuperscript{δ+} (2≤ n ≤ 4),\textsuperscript{18,21,27} There is a week shoulder on the red side of the 251 nm peak centered at 290 nm. The feature at 290 nm is assigned to Ag\textsubscript{8} clusters in agreement with literature reports and given its similar energy to Ag\textsubscript{8} stabilized in solid argon is observed at 319 nm\textsuperscript{49,50}. The exact structure of the cluster is hard to determine from optical spectroscopy alone. It is clear, however, that a range of metallic and ionic silver clusters are formed at this stage in the reaction. These assignments are tentative, but reasonable given the frequency of observing low nuclearity silver clusters in faujasites\textsuperscript{51}.

At 2 hrs post reduction a band develops at 340 nm assigned to the dipolar transition of Ag\textsuperscript{0} in Figure 5.6a. After 6 hrs post reduction a broad peak at 349 nm emerges in Figure 5.6b. A shoulder at 480 nm begins to distinguish itself. In Figure 5.6c, the 12 hr. spectrum clearly shows a peak at 341 nm that appears sharper than at 6 hrs. Also, shoulders at 425 nm and 480 nm become well resolved. After 24 hrs a peak at 351 nm is visible but the largest feature is a broad band peaked at 445 nm which we assign to the surface plasmon resonance band of metallic silver in Figure 5.6d. There is no significant change is the extinction spectrum after 24 hrs.

The in-situ extinction dynamics observed for free silver ions reduced in aqueous solution by resorcinol is quite different from those observed above. The kinetics of the 445 nm band, assigned to surface plasmon resonance of silver particles, is presented in Figure 5.9. There is an immediate increase in the intensity upon mixing. This agrees with the almost immediate color change observed upon mixing the reagents: the dispersion turns yellow in ~5 min. The intensity of the 445 nm band reaches a maximum at 2 hrs. and then starts to decay. The decay indicates the rapid formation of large silver nanoparticles that grow so large they begin to sediment after only 2 hrs, thus, reducing the absorption signal. This is in agreement with observations of a black precipitate on the vessel floor after a few hours. After 24 hrs nearly all the silver has precipitated as bulk silver. If the 24 hr dispersion is agitated, a UV-Vis extinction spectrum can be obtained that is essentially identical to that of the 2 hr sample. These spectra are shown in figure 10. These data assert that there is unique chemistry occurring in the silver-zeolite system in contrast to the solution silver system as evident from the different optical signals.
obtained from the two samples. The zeolite system is the focus of the remainder of this discussion.

The temporal evolution of the absorption bands in the optical spectra indicate the continuous ripening of silver particles throughout the reaction. The extinction spectra of Ag-FAU samples contain a feature at 340 nm that is only faintly visible above the scattering background (see 2hr spectrum in Figure 5.6a). This band is present throughout the experiment experiencing a slight red shift and increase in intensity with reaction time. Since most silver particles share the feature at ~340-350 nm it is difficult to directly identify the particles responsible from UV-Vis extinction measurements. Furthermore, matters are further convoluted from the change in morphology with time as evident from electron micrographs (vide infra). Nonetheless, we assign this band to absorption by small silver nanoparticles less than 25 nm. The choice of 25 nm is somewhat arbitrary though it is chosen because we estimate ~25 nm as the size at which dipolar transitions start to become size dependent according to Mie theory estimates made with a medium refractive index of 1.5. At later times, a shoulder at 500 nm grows in becoming increasingly intense until 24 hrs when it has reached its maximum intensity peaked at ~445 nm. HAADF-STEM images provide support for our assignments.

Spectroscopic analysis of the samples, albeit convoluted, provides dynamic information about the silver growth but a higher degree of resolution can be obtained using STEM imaging to follow the reaction dynamics. Images of the initial stage of the reaction indicate silver is reduced and resides within the zeolite pores. HAADF-STEM images of the sample vs. time are shown in Figure 5.11. At 1hr a large number of silver particles are observed (Figure 5.11a). The silver particles appear to be relatively evenly dispersed throughout the zeolite host crystal. It should be noted that this sample is difficult to image as reduction of the silver species occurs under the influence of the electron beam. The particle size distribution corresponding to the 1hr image is shown in Figure 5.12a. Most particles are 2 nm or below with an average particle diameter of 1.4 nm. This size closely matches the internal dimensions of the crystal micropores:
1.47 nm. Interestingly, this size is close to diameters expected for the thermodynamically stable Ag$_{55}$ (1.3 nm) "magic" number clusters.$^{52,53}$

The image at 2 hrs post reduction looks dramatically different from the 1 hr image: most particles, though similar in size, are different in their location. Upon comparison the two images it is clear the silver particles are present on the surface of the zeolite crystal at 2 hrs as shown in Figure 5.11b. The corresponding size distribution broadens and shifts to larger average particle diameter in Figure 5.12b. The average particle size at 2 hrs is 2.45 nm. This is larger than the internal dimensions of the FAU supercage. This increase in size reflects the dimensions of the silver are no longer constrained by the zeolite micropore dimensions and likely exist on the zeolite surface. This surface growth likely proceeds by migration of silver ions to the surface in exchange for protons generated upon reduction as the mobility of the reduced silver clusters in the zeolite pores is probably poor. The ion exchange process shuttles the silver ions to the surface of the crystal where the concentration of reducing agent is refreshed by convection, and therefore, the reaction is faster. Though silver particles are still formed within the zeolite micropores, kinetics favor the formation of surface particles, and thus, there is a large population of surface particles observed in the micrograph. Imaging this sample is much easier than the 1hr sample indicating a greater degree of stability as it is not significantly reduced under the electron beam.

The images at 3 hrs post reduction primarily resemble those at 1 hr post reduction. Interestingly, few particles are observed on the zeolite surface as in the 2 hr sample, rather, the silver appears to be primarily located within the zeolite crystals again as observed in Figure 5.11e. Again, silver particles appear dense and evenly dispersed throughout the zeolite host. Particle size analysis indicates a narrowing, accompanied by a shift to smaller diameters, of the distribution in Figure 5.11c. The average particle diameter at 3 hrs is 2.33 nm. Additionally, large particles are observed closely associated with the zeolite surface. A small number of larger silver particles existing independent of the zeolite were observed (data not shown). These particles could have resulted from reduction of silver on the zeolite surface. Once the surface particles are formed the zeolite
continues to feed their growth by supplying silver ions from their large internal volumes. The surface of the zeolites at 3 hrs post reduction appears largely bare of silver particles because they have since ripened into larger silver particles observed sparsely throughout the sample. It is likely these particles were able to grow large by diffusion and addition of silver ions from neighboring locations in the zeolite where charge balance is satisfied by hydrogen ions. Nevertheless, these particles are sparse and this is reflected in the agreement between the average particle diameter and the location of the maximum in the particle size distribution: they are nearly equal. This observation indicates depletion of silver from the surface and portions of the crystal in close proximity to the surface. It is concluded that silver ions in these regions were sacrificed as nutrients for the growth of the larger external silver particles.

After 6hrs large silver particles are commonly observed throughout. This fact is illustrated in Figure 5.11d. The heterogeneity of the sample becomes apparent in these images. Also, smaller particles of 5-8 nm are observed on the surface of zeolite crystals. Silver nanocrystals (~2 nm) are observed within the zeolite crystal comparable to those observed at early times. The particle size distribution within the zeolite shows a narrow distribution centered around 1.5 nm as observed at early stages of the reaction, however, the true sample average is 2.68 nm reflecting the presence of larger silver particles on the zeolite surface.

This trend continues at later stages of the reaction after 12 hrs. Subsequent images show a decreasing number of small silver particles within the zeolite host and an increasing number of large external silver particles as seen in Figure 5.11e. Interestingly, at 12 hrs silver nanoparticles (less than 2 nm) are still observed within the zeolite crystal but only in close proximity to external silver particles growing on the zeolite surface. At this point dissolution of silver nanoparticles provides silver ions to fuel the growth of external particles. A dynamic equilibrium between particle dissolution and reformation gives the appearance that silver particles are migrating to the exterior of the crystal were they coalesce with the larger silver particles. This is a reproducible result as indicated by
a survey of the sample in Figure 5.19a-d which shows several locations where groups of small intra-zeolitic silver particles can be observed surrounding surface particles.

Similar observations can be made at 24hrs. after reduction. Images at 24 hrs in Figure 5.11 f largely resemble those at 12 hrs though larger particles are more numerous. Silver particles 5-8 nm associated with the zeolite surface are observed with increasing frequency. Small 1-2 nm silver particles are observed within the zeolite crystal though their even distribution disappears and instead they are observed in close proximity to large surface silver particles (Figure 5.20 a-d). After 24 hrs, similar observations can be made though for the first time large fractal silver structures are observed independent of the zeolite (data not shown). High resolution analysis of the zeolite particles indicate most of the silver has left the zeolite crystal as only a few silver nanoparticles ~1-2 nm are observed within the structure at extended reaction times seen in Figure 5.22 f.

After 24 hrs nearly all the silver from within the zeolite has been consumed and large fractal like silver nanostructures have formed. The diffusion of silver from the zeolite interior to the exterior occurs slow enough to keep the zeolite crystal intact. This explains why after 24 hrs reaction in Figure 5.3 c the diffraction pattern collected contains Bragg reflection characteristic of FAU. The continuous growth of the large silver structures outside the zeolite at the expense of the small interior particles agrees with dynamics measured in the UV-Vis spectra in Figure 5.6 d indicating the presence of large particles (larger than the zeolite micropores). The development of silver species within the zeolite during the first few hours of reduction will be the focus of the remainder of this discussion.

Nitrogen adsorption experiments provide an additional measure of the silver development with the zeolite host. Surface areas measured during the early stages of the reaction mirror the dynamics observed by electron microscopy. Figure 5.13 contains the nitrogen adsorption-desorption isotherms for powdered products isolated at 0hrs with Na\(^+\) cations (a), 0 hrs with Ag\(^+\) cations (b), 1 hrs (c), 2 hrs (d), and 6 hrs post reduction (e). All isotherms in Figure 5.13 are similar in shape to the parent material (Figure 5.13a) which is characteristic of nanocrystalline zeolite. Again, this indicates minimal
destruction to the zeolite. The rapid uptake of nitrogen at low pressure signifies micropore adsorption as expected given the crystalline, porous nature of the material. The mesopore regime is characterized by a broad hysteresis loop reporting on the wide distribution of intercrystalline spaces due to packing of the nanocrystals. There is an obvious decrease in the volume of nitrogen adsorbed in the monolayer regime upon reduction of the intra-zeolitic silver as seen in Figure 5.13 c. This is also reflected by the BET surface area of the materials tabulated in Table 5.2. Micropore volumes and micropore surface areas listed in Table 5.2 exhibit a parallel trend while the external surface area changes only slightly during the course of the reaction. Figure 5.14 illustrates these changes as it plots the BET surface area (from BET theory) and the relative microporosity (from the t-plot method) vs. reduction time. The surface decreases by ~17 % upon silver ion exchange. This is typical. This might be due to a small amount of silver cluster formation under degassing conditions before the measurement. The surface area decreases by ~41 % after 1hr of reduction indicating micropore occupation by silver species. The surface area increases slightly from 330 to 364 m$^2$/g at 2 hrs and remains stable at up to 6 hrs reaching a value of 373 m$^2$/g indicating some silver leaves the micropores. The BET constant ($C_{BET}$) in Figure 5.3 indicates the surface areas are derived from an acceptable fit of adsorption data. Micropore volumes derived from adsorption data can be used to define a relative microporosity as listed in Table 5.2.

Photograph images of the reaction as a function of time that were shown in Figure 5.8 are repeated in Figure 5.15 a. These same samples are again imaged under 254 nm UV excitation in Figure 5.15b-e. There is a noticeable color difference between all these samples under ambient light in Figure 5.15 a. The powder before the reaction starts is white and non-fluorescent as seen in Figure 5.15 a, b and c. After 1hr reduction, the sample adopts a yellow hue and becomes highly fluorescent as seen in Figure 5.15 a, b and d. A green-yellow fluorescence is observed in Figure 5.15d when the sample is excited with 254 nm light. Interestingly, the sample fluoresces blue when irradiated with 365 nm UV light. Photographing this fluorescence is difficult and so it is not shown here. The powder isolated after 2 hr reduction adopts a metallic grey color seen in Figure 5.15
a. This powder weakly fluoresces under 254 nm excitation as seen in Figure 5.15 e. Samples isolated at extended reaction times are similar in color to the 2 hr sample, though, the sample becomes darker with time indicating metallic silver is depositing.

5.3.4 Intra-Zeolitic pH Measurements

The intra-zeolitic pH driving the Ag⁺ redox equilibrium was probed by emission from the acidochromic probe molecule Dsm⁺ (trans-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide). Dsm⁺ is a relatively small cationic dye capable of being ion exchanged within the zeolite micropores. Dsm⁺ has the following structure:

![Dsm⁺ structure](image)

This molecule was used to measure proton activativites of other porous materials. Figure 5.16 shows the UV-visible absorption spectra of Dsm⁺ as a function of pH. Dsm⁺ has a pKₐ of 3.7:[54]

\[
\text{Dsm⁺} + \text{H⁺} \rightarrow \text{DsmH}^{2+}
\]

The absorption spectrum of Dsm⁺ contains a characteristic n-π* transition centered at 450nm and another π-π* transitions at higher energy: 260, and 240 nm. Upon protonation, the Dsm⁺ band at 450 nm disappears and gives way to band centered at 330 nm characteristic of the DsmH²⁺ cation. From Figure 5.16 it is obvious the relative intensities of these two bands are sensitive to pH. Unfortunately, at such low loadings the absorption bands of Dsm⁺ and DsmH²⁺ can hardly be discerned from the scattering background of the zeolite itself in the extinction spectra. On the other hand, higher loading of dye must be avoided so perturbation of the silver evolution is minimized. Further complications arise from the overlapping absorption signals of Dsm⁺ (at 450 nm) and silver nanoparticles (400-445 nm). Therefore, the emission characteristics of the dye were utilized to report on the proton evolution as they are intense enough to detect
against the zeolite background and are well separated from signals originating from silver species.

Figure 5.17 contains the emission spectra of Dsm$^+$ as a function of pH. Emission spectra of Dsm$^+$ and pH values above its pKa are characterized by a broad, intense band centered at 610 nm. Emission spectra of DsmH$^{2+}$ present at pH values below the pKa are characterized by an emission band at 410 nm. Spectra of intermediate pH values are characterized by a combination of emission features from Dsm$^+$ and DsmH$^{2+}$ if excited below 375 nm near the isosbestic point. The emission band at 600 nm is observed if excited above 400 nm as DsmH$^{2+}$ does not absorb at these wavelengths. Selective excitation of Dsm$^+$ over DsmH$^{2+}$ can be achieved by exciting into the n-π* transition of Dsm$^+$ at 450 nm.

Emission spectra of the mixed cation zeolite dispersion (Dsm$^+$-Ag$^+$-ZY) excited at 450 nm as a function of reduction time are presented in Figure 5.18 a and b. The strong emission band centered at 570 nm is attributed to intra-zeolitic Dsm$^+$ cations by analogy to Figure 5.17. This band is significantly blue shifted relative to its position in aqueous solution. Such solvatochromism is commonly observed for cyanine dyes\textsuperscript{55}. This shift is rationalized by the higher ionic strength solvent within the zeolite pores. The intensity of this band at 570 nm decreases with increasing reaction time indicating protons are being generated. This is clearly observed by comparison of the fluorescence intensity of the 0 hr and 2 hr reaction in Figure 5.18 a and b respectively. This effect is assigned to the formation of DsmH$^{2+}$ as the pH values approach this dye's pK$_a$ value during the reduction of silver. These data indicate there is a net decrease in pH inside the zeolite micropores during the course of the reaction. This pH change is not measurable by the litmus test.

5.4 Discussion

5.4.1 Synthesis of a Colloidally Stable Silver-Zeolite Composite

It is clear from the measurements made on the resorcinol system above that 1) silver nanoparticles are formed and 2) they are formed while leaving the zeolite structure
intact. However, XRD, UV-Vis, and electron microscopy evidence suggest another level of complexity as the metallic silver formed by this reaction is larger than the dimensions of the zeolite pore structure. How does the system produce well formed metallic silver nanoparticles larger than the host pore diameters while sustaining a highly crystalline zeolite host? The answer to this question lies in the dynamic evolution of the system as analyzed with HAADF-STEM imaging and a variety of other techniques.

The reduction potential of the reducing agent relative to that of silver ion is an important factor in the quality of the silver-zeolite composite formed. Three reducing agents examined in this study were resorcinol, catechol, and hydroquinone with one electron redox potentials of 0.79, 0.53, and 0.46 mV vs. NHE respectively.\textsuperscript{57,58} The stronger reducing agents promote rapid reduction of silver ions. This coincides with destruction of the zeolite structure, and is obvious from X-ray diffraction patterns of reactions employing catechol and hydroquinone in Figure 5.4 b and c. In these systems, the driving force to form metallic silver is high and the zeolite provides little stabilization effects to the nuclei and preliminary clusters. As a result, growth of nuclei is rapid and uninhibited under the conditions studied here. This is also observed during the reaction, and in Figure 5.5, as metallic silver can be seen as black precipitate which develops almost immediately upon mixing.

Reduction of the silver-zeolite system with resorcinol gives different results. As seen in Figure 5.3 silver nanoparticles developed while leaving the zeolite structure intact despite conditions identical to the catechol and hydroquinone experiments. Under these conditions the zeolite acts like a stabilizing agent protecting the silver against further growth. This is quite close to the standard reduction potential of the silver (I) half-reaction (i.e. 0.799 V vs. NHE).\textsuperscript{59} Given the similar potentials for these reactions, it is likely the Gibbs free energy for this reaction is smaller. Indeed, poly-alcohols, including those studied here, are commonly used as mild reducing agents in the synthesis of silver nanoparticles for this reason.\textsuperscript{60} Assuming a common relationship between Gibbs free energy and reaction rate, it is concluded that the reaction proceeds slowly. This is observed experimentally during the course of the reaction as the color change is delayed
with resorcinol as compared to the catechol and hydroquinone reactions. Perhaps the rate of reduction plays a role in zeolite destruction. Nonetheless, the reaction has obviously reached completion at the time of the diffraction measurement (24 hrs) according to the experiments in Figure 5.6 d for the intra-zeolitic system. Also, there is a marked difference between the dynamics of the free solution reduction in Figure 5.9 and Figure 5.10 and the intra-zeolitic reduction in Figure 5.6. According to the evolution of the 445 nm surface plasmon band in Figure 5.9, the reduction of silver with resorcinol is complete in 2 hrs as the intensity reaches its maximum. Indeed, it is assumed the reaction products after 2 hrs are similar to the reaction products after 24 hr in this system based on the similarities in the extinction spectra contained in Figure 5.10. In contrast, the intra-zeolitic reaction is estimated to be complete after 24 hrs. since there is no further evolution in the extinction spectra in Figure 5.6 beyond this time. For this reason, simple kinetic effects due to the difference in redox potentials are ruled out. Instead, the zeolite is providing a level of protection that is unique and not observed in the free solution experiment.

The difference in results obtained with the free solution silver and silver-zeolite system can be explained in terms of pH dependent redox potential of hydroxyphenols. The one-electron redox potentials of hydroxyphenols become more positive as the pH is decreased. For resorcinol at pH 13.5 the one electron redox potential is 0.385 V vs. 0.79 V at pH 7.\textsuperscript{57} During the intra-zeolitic reduction, consumption of silver ions produces hydrogen ions as a redox by-product originating from the oxidation of resorcinol to a ketone. These protons remain in the zeolite in close proximity to the site where they were formed as required by charge balance: as a silver ion is consumed a proton must be formed to balance the zeolite's negative charge. This creates a micro-environment where the local pH is lower as a direct result of proton production. Therefore as the reaction proceeds, protons begin to mediate the reduction potential of resorcinol thereby slowing the reaction. This essentially shuts off particle growth and limits zeolite framework destruction. This is in stark contrast to the solution experiment where reduction proceeds rapidly without constraint, because protons are able to diffuse into the bulk. Therefore,
because the protons and silver ions are always confined within the same space in the case of the zeolite reaction the particle evolution can be altered compared to a bulk solution reaction where chemicals diffuse freely. Thus, the zeolite has a novel "size control" effect on products of the reaction.

In conclusion, the redox potential of the reducing agent relative to the silver ion plays an important role in determining the driving force for the reduction, thus, the crystallinity of the zeolite host during the reaction. The crystallinity is likely affected most by rapid growth of silver particles which physically break the zeolite as they grow. More negative potentials drive the reaction to the point of zeolite destruction. More positive potentials favor smaller driving forces and can be controlled by the intra-zeolitic pH resulting in a crystalline zeolite host throughout the reaction. The zeolite exhibits size control over the silver particles formed during reduction with resorcinol by sustaining high concentration of protons during the reaction which influence the particle growth equilibrium. In this way the zeolite acts as a stabilizing agent for "naked" silver nanoparticles. A mechanism describing the evolution of this system is proposed in the following section.

5.4.2 *Evolution of Silver Within Nano-Zeolite Micropores: Mechanism.*

Based on the above results, the following model is developed to describe the temporal evolution of silver nanoclusters reduced within zeolite Y.

5.4.2.1 *Silver Growth Model*

Our chemical system conforms to Finke's general model for metal nanoparticle growth but it has several unique features that require the implementation of additional pseudo-elementary steps. Simply the presence of the zeolite substrate imposes new constraints on the system which modifies the mechanism of particle evolution. For example, the zeolite pores produce a micro-environment where not just silver reduction takes place but oxidation must be considered due to the intra-zeolitic redox by-products generated and their effects on the labile redox equilibrium. Additionally, ion exchange
steps need to be considered to account for the generation and movement of ions formed during the reaction. Inclusion of these modified steps allow us to explain previous observations made in the silver-zeolite literature.\textsuperscript{27,35–37} Also, new routes to tailor silver evolution to reach a desired product can be predicted based on these modifications. The six part model is proposed based on Finke's general mechanism to explain the evolution of silver nanoparticle growth within nanometer-sized FAU zeolite as follows.\textsuperscript{61}

\begin{align*}
\text{A} & \rightarrow \text{B} \text{ (nucleation)} \quad (1) \\
\text{A} + \text{B} & \rightarrow 2\text{B} \text{ (growth in zeolite)} \quad (2) \\
\text{A}_{\text{(zeolite)}} & \rightarrow \text{A}_{\text{(surface)}} \text{ (ion exchange)} \quad (3) \\
\text{A} + \text{B} & \rightarrow 2\text{B}_{\text{(surface)}} \text{ (surface growth)} \quad (4) \\
2\text{B} & \rightarrow \text{C} \text{ (aggregation)} \quad (5) \\
\text{B} + \text{C} & \rightarrow 1.5\text{C} \text{ (ripening)} \quad (6)
\end{align*}

The first step is nucleation. This step involves the reduction $\text{Ag}^{+}$ to form $\text{Ag}^{0}$ clusters. $\text{Ag}^{0}$ will be used to simplify the notation, but it should be recognized that $\text{Ag}^{0}_{\text{m}}$ and $\text{Ag}^{\delta+}_{\text{n}}$ are a more representative of the clustered species present in this step (vide supra). These clusters consist of a small number of silver monomers (usually less than 12). The second step is autocatalytic intra-zeolitic silver nano-particle formation. This step involves further reduction of silver clusters and formation silver particles. Particles are distinguished from clusters by their larger monomer content, thus, size. For example, particles of 1.4 nm are observed in the zeolite after 1hr according to electron microscopy and these species probably contain ~55 atoms. This step likely proceeds by monomer addition to clusters, by cluster addition to neighboring clusters, or a combination of the two. It is this step where the zeolite plays a key role as the intermediate clusters or particles are stabilized. The basic assertion of this work is that processes in the zeolite favor reaction 1 over reaction 2 under these conditions; which is in stark contrast to processes outside the zeolite. The third step is ion migration to the surface by ion exchange: another key feature of the zeolite. The fourth step is surface particle growth by monomer addition. The fifth step is aggregative growth to form large surface particles.
The sixth step is Ostwald ripening. Steps 4-6 occur independent of the zeolite. Each step is described in detail below.

5.4.2.2 Specific Mechanism for Intra-Zeolitic Silver Growth

The following reactions model for early stage silver growth in zeolite Y. Essentially, this is steps 1 and 2 in the general mechanism above: nucleation and autocatalytic intra-zeolitic silver growth. These stages of the reaction are where the zeolite has the most impact.

\[
\begin{align*}
\text{Ag}^{+} (z) + \text{R}_{\text{red}} & \leftrightarrow \text{H}^{+} (z) + \text{Ag}^{0} (z) + \text{R}_{\text{ox}} \quad (a) \\
\text{Ag}^{+} (B) + \text{R}_{\text{red}} & \leftrightarrow \text{H}^{+} (B) + \text{R}_{\text{ox}} + \text{Ag}^{0} (B) \quad (b) \\
\text{Ag}^{+} (z) + \text{Ag}^{0} (z) + \text{R}_{\text{red}} & \leftrightarrow \text{H}^{+} (z) + \text{Ag}^{0}_{m(z)} + \text{R}_{\text{ox}} \quad (c)
\end{align*}
\]

where \( \text{R}_{\text{red}} \) and \( \text{R}_{\text{ox}} \) represents resorcinol in the native and oxidized form respectively. The subscripts \( Z \) and \( B \) represent species within the zeolite and within the bulk solution or on the zeolite surface respectively: basically \( Z \) represents intra-zeolitic species and \( B \) represents exo-zeolitic species. The reduction of silver requires the oxidation of resorcinol and the formation of protons according to the following half reaction:

\[
\text{nH}^{+} + \text{Quinoid species} \rightarrow \text{nH}^{+} + \text{Quinoid species}
\]

where \( n \) is 1 or 2. Oxidation of poly-alcohols to form ketones and quinoidal species is studied elsewhere\(^{57}\). The above system of equations yields the following net reaction:

\[
2\text{Ag}^{+} (z) + \text{Ag}^{+} (B) + 3\text{R}_{\text{red}} \leftrightarrow 3\text{R}_{\text{ox}} + 2\text{H}^{+} (z) + \text{H}^{+} (B) + \text{Ag}^{0} (B) + \text{Ag}^{0} (z) + \text{Ag}^{0}_{n(B)}
\]

These pseudo-elementary steps model the initial stages of the reduction process (0-2 hrs in the optical spectroscopy and microscopy data and reactions 1-2 in the above general mechanism) which results in the formation of two silver particle populations: intra-zeolitic silver and exo-zeolitic silver. To simplify the notation exo-zeolitic silver, designated with a subscript \( B \), is considered free particles existing in bulk solution and bound particles existing on the zeolite surface. A distribution of silver species are formed be these reactions the pseudo-elementary step in (c) represents the formation of \( \text{Ag}^{0}_{n(z)} \).
where \( n \) can range from 2-55 based on the analytical results discussed below. In any case, step (c) could represent over 50 elementary steps.

In reaction (a), upon addition of reducing agent, diffusive transport carries resorcinol within the zeolite pore structure where it reduces silver ions to metallic silver upon contact. Since the resorcinol has no electrostatic charge we conclude this step is driven by chemical potential gradients. Resorcinol penetrates the zeolite crystal pore structure to reach chemical equilibrium across the crystal interface reducing silver along the way. Step (b) accounts for the reduction of small amounts of surface bound silver ions. Upon reaction with resorcinol they are reduced in a similar fashion to step (a). This reaction forms zeolite surface seeds. The formation of hydrogen ions as a redox byproduct is emphasized in these initial steps according to reaction (a) and (b). Once formed, these protons must associate with the zeolite structure as necessary for charge balance. These ions could associate with the surface of silver species formed upon reduction also. In either case protons formed in this step lower the intra-zeolitic pH as indicated in Figure 5.18 a and b. These reactions can be visualized in HAADF-STEM images in Figure 5.11 a of the sample reduced after 1hr where the formation of small silver clusters of 1.4nm are observed evenly dispersed throughout the crystal. Nitrogen adsorption measurements in Figure 5.13 c indicate that pore structure is intact given its resemblance to the parent material in Figure 5.13 b. A decrease in the total BET surface area after nucleation indicates a large percentage, estimated at \(~54\%\), of the zeolite pore spaces are accommodating silver clusters present as a minimum in the surface area at 1hr in Figure 5.14. X-ray diffraction corroborates the zeolite structural integrity as FAU Bragg reflections are clear in Figure 5.3 c. The fact that the intra-zeolitic species are highly fluorescent under UV light in Figure 5.15 b-e asserts these species are small clusters and UV absorbing \( Ag^+ \) species have been consumed as supported by literature reports\(^2\). The emission and characteristics of the 1hr species reflect the broad heterogeneity of the cluster population as green fluorescence is observed under 254 nm excitation while blue emission is observed under 365 nm excitation. The heterogeneity is also verified with diffuse reflectance UV-Vis spectroscopy as in Figure 5.7 reflecting the
formation of several bands characteristic of different sized silver clusters (251, 290 nm) in addition to a small population of silver nanoparticles (410 nm). Therefore, clusters consisting of a range of atoms likely exist at this point in the reaction. This is likely due to the temporal overlap of reactions (a)-(c) in the above model causing the formation of several species. This could be promoted by a distribution of driving forces resulting from concentration gradients in the crystal. Heterogeneity may also result from a variety of local pH values within the zeolite. A net decrease in pH within the zeolite after 1 hr as proposed in the above reactions is clear from fluorescence measurements in Figure 5.18 a and b. Decreasing the pH could partially oxidize silver clusters as the redox equilibrium characteristic of the mild reducing agent in labile$^{63,64}$.

The results obtained during the initial stages of the reaction have multiple interpretations. Interpretation 1: a distribution of species is formed by a rapid, narrow, and symmetric nucleation profile leading to a large number of uniformly sized nuclei formed evenly throughout the zeolite crystal (a), followed by autocatalytic growth (c) to clusters, and finally partial oxidation due to the labile redox equilibrium in the presence of protons (reverse of c). Interpretation 2: a distribution of species is formed by a rapid but broad and symmetric nucleation profile leads to nucleation events distributed in time (a). Autocatalytic growth of these nuclei (c) is offset in time leading to a distribution of cluster sizes. In this interpretation intra-zeolitic pH plays no role. These interpretations are derived from common considerations related to cluster formation detailed in the literature$^{65}$. The primary differences between these two interpretations are the relative rates of nucleation and autocatalytic growth ($K_a/K_c$ in the model reactions a and c above), and the reversibility of autocatalytic growth ($K^{-1}_c$). Given the density and uniformity of the clusters at early times (1hr.) observed by STEM in Figure 5.11 a and b and gas adsorption measurements in Figure 5.13 c, the pH changes during the course of the reaction in Figure 5.18 a and b, and the presences of Ag$^+$ and various clusters from UV-Vis in Figure 5.7, the first interpretation is proposed. This interpretation illustrates the novelty of the zeolite in controlling the redox equilibrium, thus, forming smaller clusters. Essentially, the zeolite creates conditions were $K_a/K_c$ is greater than 1 and $K^{-1}_c/K_c$ is can
become greater than 1 as the pH changes. This is in contrast to the zeolite-free reduction behavior of this system monitored in Figure 5.9 where $K_a/K_c$ and $K^{-1}/K_c$ are less than one and the pH changes little. Of course, these conditions depend on the reduction potential reducing agent used. Since resorcinol is a relatively weak reducing agent, its redox equilibrium is facile. This allows the proton loaded zeolite to reverse reaction (c) and mediate autocatalytic evolution of the silver that occurs by step (c). This is in stark contrast to the other reducing agents used herein, with similar structures, like catechol and hydroquinone where the driving force for reduction is too strong to be reversed by the intra-zeolitic pH. In cases of catechol and hydroquinone, reactions (b) and (c) proceed rapidly and physically break the zeolite structure. This should be a general effect applicable to all strong reducing agents where $K_c$ is inherently much greater in magnitude than $K^{-1}_c$. Indeed, this has been observed with other strong reducing agents.

To account for the role of the zeolite the following reactions must be included which are in addition to the existing mechanism for noble metal nanoparticle growth. These reactions are described as follows and are meant to signify steps 2 and 3 in the general mechanism (vide supra):

\[
\text{H}^+_{(Z)} + \text{Ag}^0_{(Z)} + \text{R}_{\text{ox}} \leftrightarrow \text{Ag}^+_{(Z)} + \text{R}_{\text{red}} \tag{d}
\]

\[
\text{Ag}^+_{(Z)} + \text{H}^+_{(B)} \leftrightarrow \text{Ag}^+_{(B)} + \text{H}^+_{(Z)} \tag{e}
\]

Reaction (d) is basically the inverse of reaction (c). It is listed again here, as its own step, to emphasize its importance in the evolution of the system as it is the key feature driving cluster stabilization. Reaction (e) represents the ion exchange equilibrium between silver ions and protons than can exist between the zeolite micropores and the bulk solution/crystal interface (as written), and also between concentration gradients existing within isolated regions in the zeolite micropores. Step (e) reflects the fact that the system will work to reach equilibrium with respect to spatial chemical homogeneity.

The net reaction derived from steps (d) and (e) are described as follows:

\[
\text{Ag}^0_{(Z)} + \text{R}_{\text{ox}} + \text{H}^+_{(B)} \leftrightarrow \text{Ag}^+_{(B)} + \text{R}_{\text{red}}
\]

Basically, this reaction represents the net migration of silver from the zeolite micropores to the zeolite surface or into the bulk. In follows that the intra-zeolitic environment
should become more acidic as this reaction progresses. As the intra-zeolitic environment becomes more acidic by means of reaction (a) and (e), reaction (d) is pushed in the forward direction. As a result, silver ion migration from the zeolite micropores to the zeolite surface becomes enhanced.

The influence of these reactions becomes obvious after 2 hrs of reduction. As seen in Figure 5.11 b small silver particles (determined to be 2.45 nm according to Figure 5.12 b) are observed mostly on the zeolite surface. This is in contrast to the image seen in figure Figure 5.11 a where the silver is more populous within the zeolite micropores and not on the surface. Certainly, these results seem to support the net migration of silver ions from the micropores to the surface as described in reactions (d) and (e) in the above model. Once on the surface, silver ions can further become reduced by reaction (b) or participate in an autocatalytic reduction reaction with silver species formed as a result of (b) as outline by reaction (f).

\[
R_{\text{red}} + \text{Ag}^+_{(B)} + \text{Ag}_0^{0}_{(B)} \leftrightarrow \text{Ag}^0_{m(B)} + \text{H}^+_{(B)} + \text{R}_{\text{ox}} \tag{f}
\]

Reaction (f) leads to the accumulation of silver nanoparticles on the zeolite surface as supported by Figure 5.11 b. Further support of the migration of silver species, and subsequent surface reduction, is reflected in the nitrogen adsorption isotherms in Figure 5.13 c and d. Upon comparison of the adsorption isotherms after 1 hr and 2 hrs reduction (in Figure 5.13 c and d respectively), a slight increase in the amount of nitrogen adsorbed in the micropore regime is observed after 2 hrs. This indicates the micropores are more accessible to nitrogen after 2hrs compared to 1 hrs. The higher accessibility of the structure is likely due to the silver migration to the surface while leaving the previously occupied micropore site vacant for nitrogen to occupy during the adsorption measurement. The micropore volumes calculated for the 1 hr and 2 hrs reduced samples listed in Table 5.2 are in agreement with this hypothesis. This effect is further reflected by the increase in the BET surface area after 2 hrs relative to the 1 hr reduction as calculated in Table 5.2 and plotted in Figure 5.14. It can be seen from these data that the surface area increases as silver leaves the micropores and moves to the surface. Most of
the parameters calculated from the adsorption-desorption isotherms listed in Table 5.2 corroborate this assignment.

The onset of reactions (d), (e), and (f) coincides with the observation of surface silver species. Surface silver formed by reaction (b) or by a combination of (d), (e), and (f) continues to evolve according to the following reactions which signify steps 4 and 5 in the general mechanism (vide supra):

\[ R_{\text{red}} + 2\text{Ag}^0_{(B)} \leftrightarrow \text{Ag}^0_{m(B)} + \text{H}^+_{(B)} + \text{R}_{\text{ox}} \]  \hspace{1cm} (g)

This reaction occurs primarily during the 3-24 hrs time period. Reaction (g) describes the aggregative growth of the surface particles observed in Figure 5.11b to form larger silver particles observed on the surface in Figure 5.11d. In this figure, larger surface silver nanoparticles (greater than 10 nm) are observed. These are particles are likely a result of reactions (f) and (g). A distribution of silver particles (greater than 10 nm) is observed in the 3 hr reduced sample (data not shown) in agreement with this mechanism. Though the data is not shown, evidence for initial formation of surface silver particles by aggregation (g) is provided by comparison of Figure 5.11 b and Figure 5.11 c, where an obvious changes in the appearance of the zeolite host crystal surface is observed. The zeolite surface, which was covered with silver nanoparticles at 2hrs in Figure 5.11 b, becomes bare of silver nanoparticles at 3 hrs as seen in Figure 5.11c. This observation is assigned to the aggregative growth of the 2.3 nm particles to yield particles in excess of 10 nm by reaction (g). Particle aggregates are observed in Figure 5.11 d at six hours and also in Figure 5.11 e at 12 hr where reaction (g) begins to dominate the evolution of the system. The zeolite still acts to supply silver ions to the growing particles by reactions (d), (e) and (f) during this time. This is best illustrated by Figure 5.19 a-d and Figure 5.20 a-d where surface nanoparticles are seen being fed by intra-zeolitic silver species. In fact, these two particle populations are coupled as they are always seen in close proximity to each other in these images. These images essentially prove the coupling between reactions (d)-(g) that lead to silver migration from the zeolite to the surface. Silver migration to the zeolite surface is a common result reported in the literature\textsuperscript{27,35–37}. Little explanation of this effect is ever given. However, the results herein provide direct evidence of migration
resulting from reactions (d)-(g). This mechanism can be used to describe the literature results. These reactions continue to contribute to the evolution of the system at later times, but the zeolites role in silver growth diminishes as expected as silver ion nutrients are eventually depleted from the micropores.

The final steps in our model are detailed by the following equations which are the analogy to step 5 and 6 in the general mechanism:

\[
\begin{align*}
R_{\text{red}} + 2 \text{Ag}^0_{\text{m(B)}} & \leftrightarrow \text{Ag}^0_{\text{metal(B)}} + \text{H}^+_{(B)} + R_{\text{ox}} \quad (h) \\
R_{\text{red}} + \text{Ag}^0_{\text{m(B)}} + \text{Ag}^0_{\text{metal(B)}} & \leftrightarrow 1.5 \text{Ag}^0_{\text{metal(B)}} + \text{H}^+_{(B)} + R_{\text{ox}} \quad (i)
\end{align*}
\]

These are not true elementary reaction steps. Steps of the 1.5 coefficient in reaction (i) follows only from reaction (h). These steps represent the Ostwald ripening of the silver nanoparticles into larger silver particulates, and eventually, to bulk silver that precipitates from solution. These steps occur independent of the zeolite. However, the zeolite is expected to provide some of the growing particles silver ion nutrients as adatoms. Silver particle spheres with higher chemical potential energy give way to lower energy hexagonal disks as the reaction proceeds from 6-24 hrs. This is likely due to the relative rates of adatom deposition and diffusion across the particle surface and the rate of reduction\(^{66}\). Silver adatoms emerging from the zeolite pores are not immediately reduced upon adsorption to the seed surface. Instead they diffuse across the surface until they find the lowest energy adsorption site (e.g. a step defect) where they are subsequently reduced. In this way the crystal grows by propagating such an edge defect giving it a characteristic morphology. This is commonly observed in systems with weak/mild reducing agents\(^{63}\). The Ostwald ripening characteristics of a similar bimodal silver nanoparticle distribution was explored previously and we observe similar phenomenon in our system during the ripening phase\(^{63}\). Although, in our case, spherical particles act as adatom donors and hexagonal plates act as adatom receptors which is opposite their observation. This is justified by the larger free energy of instability of the spheres in our system as they are \(\sim10\) nm on average while the other morphologies present are large (\(>50\) nm).
It appears there exists an additional ripening pathway that results in large flower-like fractal morphologies. It is unclear from our data if they form from the hexagonal plates or vice versa. These morphologies are always observed simultaneously (data not shown). However, further exploration of these populations is outside the scope of this paper as the zeolite is expected to play little or no role in this process.

In conclusion, silver growth within nanozeolite micropores is explained using a six part mechanism based on principles developed by Finke and LeMer.\textsuperscript{61,65} The first steps (1 and 2) are rapid nucleation and autocatalytic particle/cluster growth occurring almost instantly upon mixing reagents. Nucleation involves the transformation of silver ions to silver clusters. A wide range of cluster types varying in the number of silver monomers are formed: $\text{Ag}^0_m$ ($3 \leq m \leq 5$), $\text{Ag}_n^{6+}$ ($2 \leq n \leq 4$), $\text{Ag}_8$, according to optical measurements and possibly $\text{Ag}_{13}$ and $\text{Ag}_{55}$ "magic" number clusters according to electron microscopy. The most stable of these is hypothesized to be $\text{Ag}_{55}$. Step 2 is autocatalytic growth of silver cluster nuclei by addition of silver ions. The third step is acquisition of a pH mediated redox equilibrium and subsequent oxidation of nanoparticles and clusters to form mobile silver ions. These mobile ions are dynamic as they participate in an ion exchange equilibrium. The forth step is migration of silver ions, by ion exchange, to the surface where participate in the fifth step which is a series of autocatalytic surface nanoparticle growth steps. The last step is zeolite independent ripening of the as-formed surface silver nanoparticles. The thermodynamically favored $\text{Ag}_{55}$ cluster is stable within the zeolite throughout the reaction as seen by TEM.

Interestingly, small silver nanoparticles are still observed in the zeolite even after 24 hrs as seen in Figure 5.11 f and Figure 5.21 a-c. These species likely have an added level of stability as they appear resistant to oxidation. Some of the particles observed in Figure 5.11 f are $\sim 1.4$ nm in diameter which is similar to the dimensions of the zeolite super cage. Some larger particles are observed in Figure 5.21 a-c. There dimensions are a little larger as indicated in the Figure 5.21 inset ($\sim 2-3$ nm in diameter). These particles appear crystalline. The most stable silver cluster in this size range is the "magic" cluster
Ag$_{55}$. Experiments designed to test the hypothesis that the zeolite stabilizes silver magic clusters are currently under way.

5.4.3 Application of Silver Loaded Zeolite as a SERS Substrate

Silver nanoparticles and nanosturctures are employed as surface enhanced Raman scattering substrates. Much effort in preparing innovative SERS substrates involves engineering electromagnetic "hot-spots" where the plasmons of neighboring metal particles, or surface features, constructively interact to form high electric fields. The vibrational Raman scattering from a molecule adsorbed such a region irradiated from a light source (laser) with an electric field magnitude of $E$ is proportional to $E^4$ making these "hot-spots" an attractive way to sense single molecules. Formation of electromagnetic "hot-spots" requires the metallic features to be in close contact. Large enhancements ($>10^6$) are derived from molecules just a few nanometers from the hot spot surface feature. Most synthetic approaches result in a low density of hot spots so there are constant research activities aimed at increasing the density of hot spots. Densely formed silver particles formed within the ordered 3D array of zeolite supercages could provide a method of forming high densities of hot spots. This approach is explored here, for the first time, using novel colloidal nanozeolites and benzenethiol as a probe molecule.

A scheme illustration of the colloidal nanozeolite SERS probe preparation is contained in Figure 5.22. The Raman spectra of a benzenethiol solution mixed with colloidal silver zeolite as a function of reduction time is shown in Figure 5.23. There is considerable variation of the thiol peak intensities located at 999, 1022, and 1073 cm$^{-1}$ with reduction time. The inset in Figure 5.11 shows the normalized intensity of the 999 cm$^{-1}$ peak as a function of time. The intensity increases with time reaching a local maximum at 2hrs. followed by a decrease reaching a minimum at 4 hrs. The variations in intensity follow a trend similar to that of the silver nanoparticle evolution described above. Given the correlation between the signal enhancement and the particle evolution, SERS can be used to report on the particle growth dynamics. After extended reduction times, the SERS intensity of the 999 cm$^{-1}$ peak begins to increase and the signal becomes
irreproducible. This trend continues with time. For example, highly irreproducible enhancements are obtained with the 24 hr sample. A Raman depth map of the 24 hr reduced colloidal dispersion is presented in Figure 5.24. The Raman intensity of the 999 cm\(^{-1}\) peak increases as the laser focus approaches the bottom of the cuvette. In fact, the 999 cm\(^{-1}\) band is only observed at the bottom of the cuvette in this experiment. It is concluded that large metallic silver particle precipitates are responsible for the large enhancements.

In conclusion, silver-zeolite materials formed herein are capable of enhancing Raman signals of benzenethiol through the surface enhanced Raman scattering mechanism. Due to the heterogeneity of the sample at extended reaction times, it is hard to determine the features responsible for the signal enhancement. This is a common problem when using colloidal silver SERS substrates.\(^4^0\) After 2 hrs reduction, the sample can be considered homogeneous as evident from TEM in Figure 5.11 b. This material gives the highest, most reproducible enhancements. The enhancement factor determined for the 2 hr reduced silver zeolite colloid is on the order of 10\(^4\). This is comparable to enhancement factors characteristic of silver loaded membranes and ordinary colloidal silver sols.\(^4^0,6^9\) Higher enhancements obtained at extended reaction times are likely a result of fractal silver precipitates as observed in the literature.\(^3^6\) Therefore, trapping silver particles in or on transparent colloidally stable nanozeolite is a novel approach to forming more reproducible SERS substrates without loss of signal enhancement.

### 5.5 Conclusions

This work examines the evolution of silver ions reduced within the micropores of nanozeolite Y. As expected, this reaction is highly dependent on the concentration and relative redox potentials of the reactants. Zeolite framework destruction and/or silver migration to the zeolite surface was observed in cases utilizing strong reducing agent in agreement with literature reports. However, it was found that by pairing the redox potentials of silver ions and the reducing agent appropriately, and optimizing the reaction conditions, silver can be effectively reduced to nanoparticles while maintaining a uniform
dispersion within the zeolite host. In this way undesirable framework destruction and silver migration effects are minimized even at high reductant concentrations (0.1 M). Our work provides a method to synthesize and isolate highly dispersed zeolite supported silver nanoclusters with an average size of ~2 nm. This material might be used as a colloidal SERS substrate. SERS enhancement factors are observed on the order of ~10^4.

A mechanism is proposed to describe silver growth within zeolite pores based on a series of analytical results. The results suggest rapid nucleation of Ag^+ ions occurs within zeolite upon addition of resorcinol. However, rapid autocatalytic growth within the zeolite is slowed by extraframework protons formed as redox by-products. The zeolite, by virtue of charge balancing protons, regulates the kinetics of autocatalytic growth of intra-zeolitic silver nanoparticles by maintaining a local pH that is dependent on the degree of reduction. Therefore, silver nanoparticles above ~2.6 nm cannot form because the pH of the zeolite environment prevents any further reduction and the zeolite structure is maintained. Rather, growth must occur outside the zeolite matrix where the local pH is much higher. Growth outside the zeolite is feed by silver ion exchange equilibrium that bring a steady supply of silver ions to the surface where they are subsequently reduced to form metallic silver. This simple scheme can account of the wide spread literature reports of zeolite destruction, and silver surface migration in zeolite systems. Experiments to quantitatively analyze the kinetic of intra-zeolitic silver growth are currently under way.

5.6 References


Figure 5.1: Particle size distribution of the nanozeolite dispersion obtained from DLS. The average particle size, as indicated with the red dotted line, is 48 nm.
Figure 5.2: Average particle diameter (red dots) and zeta potential (black squares) as a function of pH.
Figure 5.3: XRD patterns of a standard zeolite Y as simulated from the FAU structure (a), the as-synthesized nanozeolite Y (b), and silver exchanged zeolite Y after 24 hr of reduction with 0.1 M resorcinol (c). Peaks marked with a dot in (c) indicate intensity variations due to silver inclusion. Peaks marked with an asterisk in (c) indicate FCC silver. The inset shows the chemical structure of resorcinol.
Figure 5.4 XRD patterns of silver exchanged zeolite Y (a), silver exchanged zeolite Y reduced with 0.1 M hydroquinone (b), and silver exchanged zeolite Y reduced with 0.1 M catechol (c). The asterisks in (b) and (c) denote FCC silver. The chemical structures of catechol (top), and hydroquinone (bottom) are included next to their respective pattern.
Figure 5.5: Photographs of an aqueous 0.1 wt% silver exchanged nanozeolite dispersion reduced with 0.1 M catechol (left), and 0.1 M resorcinol (right) after 12 hrs. The chemical structures of catechol (bottom left), and resorcinol (bottom right) are included for reference.
Figure 5.6: Extinction spectra of an aqueous 0.1 wt % silver exchanged nanozeolite dispersion reduced with 0.1 M resorcinol after 2 hrs. (a), 6 hrs. (b), 12 hrs. (c), and 24 hrs. (d). No observable features were detected in the sample prior to 2 hrs. Also, no change in the extinction spectrum was observed after 24 hrs. The major features in each extinction spectrum are labeled with a dotted black line.
Figure 5.7: The diffuse reflectance UV-Vis absorption spectrum (Kubelka-Munk transformed) of the zeolite powder isolated from the resorcinol reduction after 1 hr.
Figure 5.8: Photographs of the resorcinol reduced silver zeolite after 0 hrs. (left), 1hr. (middle), and 2 hrs. (right).
Figure 5.9: Kinetics of the 445 nm surface plasmon absorption band of silver during the reduction of an aqueous AgNO₃ solution with 0.1 M resorcinol as measured by UV-Vis spectroscopy.
Figure 5.10: Extinction spectra of the aqueous silver colloid formed after reduction for 2 hrs with resorcinol (red line), and 24 hrs with resorcinol (blue line).
Figure 5.11: A collection of HAADF-STEM images showing the progress of the silver reduction after 1 hr. (a), 2 hrs. (b), 3 hrs. (c), 6 hrs. (d), 12 hrs. (e), and 24 hrs. (f). The bright spots in these images are due to silve particles.
Figure 5.12: Particle size distributions calculated from the HAADF-STEM images in figure 5.14 after 1 hr. (a), 2 hrs. (b), 3 hrs. (c), and 6 hrs. reduction with resorcinol (d). After 6 hrs., the system becomes too heterogeneous to obtain accurate size distribution with electron microscopy.
Figure 5.13: Nitrogen adsorption isotherms (red open dots) and desorption isotherms (blue crosses) for sodium exchanged nanozeolite (a), for silver exchanged nanozeolite (b), silver nanozeolite after 1 hr. (c), after 2 hrs. (d), and after 6 hrs. reduction time with resorcinol (e).
Figure 5.14: The evolution of the BET surface area (blue line, black diamonds) and the relative microporosity (red line, black dots) of the nanozeolite materials as a function of reduction time.
Figure 5.15: Photographs of powdered silver exchanged zeolite samples viewed under ambient light (a) and 254 nm UV light (b) after several designated reduction times. A close up the photo of the 0 hr (c), a 1 hr (d), and a 2 hr reduced sample (e) viewed under UV excitation.
Figure 5.16: UV-Vis spectra of the aqueous Dsm⁺ dye as a function of pH.
Figure 5.17: Emission spectra of the aqueous Dsm$^+$ dye as a function of pH excited at 450 nm.
Figure 5.18: In-situ emission spectra of the Dsm$^+$-Ag$^+$-Y mixed cation system excited at 450 nm as a function of reduction time: (a) is before the addition of resorcinol and (b) is 2 hrs after the addition of resorcinol.
Figure 5.19: HAADF-STEM images following migration of silver species through the zeolite matrix toward large surface particles in samples reduced for 12 hrs. Panel (a) gives a unified view of a large region while panesl (b-d) are magnified views of the boxes drawn in (a).
Figure 5.20: HAADF-STEM of silver nanoparticles migrating through the zeolite matrix toward large surface silver particles observed in the sample after 24 hrs. of reduction. Panel (a) give a wide field of view while (b-d) magnify each of the boxed regions in (a).
Figure 5.21 HR TEM of silver loaded zeolite after 24 hrs reaction time. Spherical silver particles of various dimensions are observed in (a). The inset shows clear lattice planes characteristic of FCC silver and measures the dimensions of one of these particles. In panels (b) and (d) magnified views of the occluded silver particles are examined. Panels (c) and (e) are the FFT images of (b) and (d) respectively.
Figure 5.22: Schematic illustration the preparation of the colloidal nanozeolite SERS substrate.
Figure 5.23: Surface enhanced Raman spectra as a function of time. The inset plots the change in the intensity of the 999 cm\(^{-1}\) band as a function of time. The enhancement factor calculated for the 2 hr reduced sample is listed in the inset (10\(^4\)).
Figure 5.24: Surface enhanced Raman spectra of the colloidal substrate as a function of cuvette depth. The depth increases toward the bottom of the cuvette as the magnitude of the data set increases from 0 to 6 on the data set axis.
Table 5.1: colloidal properties of nanozeolites determined by DLS

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<td>24#</td>
<td>57$</td>
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* Derived from Cumulants fit
# Derived from NNLS fit
$ Derived from CONTIN fit

Table 5.2: Gas adsorption properties as a function of reaction time.

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<th>Time (hr.)</th>
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<th>$C_{BET}$</th>
<th>$S_{ext}$ (m$^2$g$^{-1}$)</th>
<th>$S_{micro}$ (m$^2$g$^{-1}$)</th>
<th>$V_{micro}$ (cm$^3$g$^{-1}$)</th>
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<td>5236</td>
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<td>386</td>
<td>0.156</td>
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<tr>
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<td>373</td>
<td>3161</td>
<td>155</td>
<td>220</td>
<td>0.09</td>
</tr>
</tbody>
</table>

* Surface calculated from Braunauer Emmett Teller theory
# Abscissa intercept from BET fit
@ External surface area calculated from DeBoer's t-plot method
** Micropore surface area calculated from DeBoer's t-plot method
*# Micropore volume calculated from DeBoer's t-plot method
6.1 Introduction

There is a long history of interest in intra-zeolitic photochemistry. This large body of work stems from the main advantage of well defined three dimensional pore structures that can orient molecules in ways ordinary dense solid or amorphous particles cannot. Indeed, zeolite-organic chromophore composite systems have long been proposed as popular approach to realizing supramolecular organized photofunctional materials. Zeolite Y/X have attracted the most attention. Their well characterized, large, and accessible pore structure can readily accommodate organic and inorganic molecules of interest. The pore space can have an important role on intra-zeolitic chemistry photochemical, thermal, or otherwise. Increased photoinduced radical reactions, enantiomeric promotion, and conformational selection are a few popular examples emphasizing the zeolite-molecule interaction.

Supramolecular control of photochemical reactions provides a powerful tool to alter photochemical behavior. Molecular degrees of freedom of molecules or aggregates are often limited upon adsorption and confinement in the zeolite pores which have dimensions that approach molecular length scales. The environmental constraints imposed on guest molecules within the zeolite host has been shown to influence the photochemical properties. These properties, in combination with the crystalline order of the zeolite, have been use to organize chromophores to produce novel photofunctional electron and energy transfer systems.
Femtochemistry in zeolites is a rapidly developing field stemming from the prospects discussed above. Most spectroscopic approaches use fluorescence or diffuse reflectance. As a result, the spectroscopic examination of intra-zeolitic chemistry is usually restricted to a highly fluorescent systems or powdered solids. Organic dyes can easily be included and examined in these systems by means of ion exchange or ship in a bottle synthesis methods and have been studied extensively. Despite the successes of these approaches, there is some indication that these studies are limited in their penetration depth, thus, the amount of chemical information they obtain is not representative of the true nature of the sample deep within the micropores. Indeed, the typical average particle size of zeolite powders is on the order of microns. Making particles smaller has been proposed as an approach to obtain a more representative optical analysis from intra-zeolitic assemblies. This idea was proposed by Dutta et al. and applied by Mintova and Bein in work involving proton transfer dynamics within the nanocrystalline zeolite. Since its inception, this idea has been illustrated using organic and inorganic systems residing in the pore system of zeolite nanocrystals. Making zeolite particles on the nano-scale provide the optimal circumstances to obtain representative signals using established transmission spectroscopic configurations. Experimental attainment of this goal is challenging, but the recent acceleration of research progress focusing on nanozeolite synthesis has catalyzed its development.

Herein we report on the dynamics of a UV absorbing bipyridinium dye (BPE$^{2+}$) within nanocrystalline zeolite using ultrafast UV-Vis absorption spectroscopy in transmission mode. Steady state and time resolved measurements on electron transfer systems containing bipyridinium molecules are commonly reported in the literature. However, there are few studies focusing on the photophysics of this specific molecule. We illustrate through a series of optic spectroscopic experiments, some of the first of their kind, that even in the UV region of the electromagnetic spectrum where scattering is intense optical signals can be obtained on organic systems within nanozeolite Y micropores using transmission spectroscopy. This allows the spectroscopic analysis of
some of the fastest chemical events ever observed within the zeolite. The influence of the
zeolite structure on the photodynamics on the picosecond time scale are explored.

6.2 Experimental Methods

Pyridinium 4,4’-(1,2-ethenediy)bis[1-methyl, tetrafluoroborate (referred to as
BPE$^{2+}$, C$_{14}$H$_{16}$N$_{2}$2BF$_{4}$, [22919-72-8]) was purchased from Aldrich and used without
further purification.

Nanozeolites were synthesized using a modified procedure similar to that found in
the literature. The following gel composition was used:

0.048Na$_2$O:2.40(TMA)$_2$O(2OH):1.2(TMA)$_2$O(2Br):4.35SiO$_2$.1.0Al$_2$O$_3$.249H$_2$O. The
resulting clear sol was aged with stirring for 3 days followed by heating at 100 °C in an
oil bath for 4 days. The reaction mixture was dialyzed to remove reactants and the
products were isolated by ultracentrifugation (50,000rpm at 200,000 relative centrifucal
force) with repeated washing (with DDI H$_2$O) until neutral. Colloidal dispersions were
ion exchanged with 0.2 M MX (MX = NaNO$_3$, TlNO$_3$ or ClNO$_3$) for 24 hours twice to
remove TMA$^+$ template from the super cages. An as-prepared sample was studied with
the understanding that TMA$^+$ exists within the supercage. For TMA$^+$ exchanged samples,
the as-synthesized material was used.

0.05 wt% aqueous nanozeolite dispersions were used in transmission
spectroscopic studies. Dye exchanged nanozeolite was prepared by ion exchange with
0.2 mM dye solution at a loading of ~1 g zeolite/10 mL solution for 24 hrs in the dark.
The crystals were washed liberally with DI water until the supernatant absorbance was
less than 0.01 at 320 nm.

6.2.1 Characterization

The average particle diameter and intensity averaged particle size distribution of
zeolite dispersions were determined by dynamic light scattering (DLS). The correlation
functions measured are an average of 45 accumulations of 10 s scans collected at a
backscattering angle of 273°. Size distributions collected at a forward scattering angle of 15° give results similar to the backscattering results. The method of cumulants was used to obtain an average particle size.\textsuperscript{19} The CONTIN method was used to invert the intensity correlation functions to a particle size distribution\textsuperscript{20}. Average zeta potentials were measured by electrophoretic light scattering (ELS). Electrophoretic mobility measurements were converted to zeta potentials according to the Henry equation at the Smoluchowski limit.

XRD patterns for each sample were collected on a Bruker D8 X-Ray diffractometer using nickel filtered Cu Ka\textsubscript{1} radiation. Patterns were collected at 0.05 degree steps with a dwell time of 2 s with 1 mm and 8 mm entrance and scattering slits respectively. When indicated, pattern profiles were fit using a Pearson VII line shape. Crystallite sizes were calculated from the fitted peaks using the Debye-Sherrer equation in conjunction with the appropriate internal size standard (NIST SRM 640c).

Nitrogen adsorption measurements were made using a Quantachrome NOVA 2200e surface area and pore analyzer to determine the surface areas of the reactants and products during the reaction. Adsorption isotherms were analyzed using Brunauer, Emmett, and Teller (BET) theory to determine surface areas.\textsuperscript{21}

UV-Vis absorption and extinction spectra were collected with a Shimadzu 3600 UV-Vis-NIR spectrophotometer. Fluorescence spectra and time correlated single photon counting (TCSPC) emission decay curves were collected with a Horiba Scientific FluoroLog 3. Corrected emission spectra were referenced to a lamp scan to eliminate intensity variations in the light source. A 285 nm pulsed diode laser was the excitation source. Dilute colloidal LUDOX was used to collect the instrument response function. Lifetimes were extracted from non-linear least squares fits to a model function containing both instrument and responses. The optical configuration of our spectrometer was optimized for visible wavelengths. Therefore, an artifact originating from the instrumental response function collected from scattered light at 290 nm persists in model fits involving a convolution.
The femtosecond transient absorption spectrometer and setup is described in detail elsewhere.\textsuperscript{22} In brief, ultrashort 30 fs pulses at 800 nm from a titanium-sapphire oscillator (Coherent, Mantis) were used to seed a high-energy titanium-sapphire regenerative amplifier (Coherent/Positive Light, Legend HE USP) producing 2.5 mJ 40 fs pulses at 1 kHz. Part of the fundamental output was used to pump an OPA (OPerA Coherent) equipped with a UV-Vis optics module to generate 315 nm pump pulses. A small portion of the fundamental was used to generate a white light probe pulse in the range of 320-700 nm by focusing into a 1mm thick CaF\textsubscript{2} plate. The CaF\textsubscript{2} plate is rotated at 1.5° every 3 s to ensure stable white light continuum. The white light is collimated through an iris to select the most stable, central region of the beam profile and subsequently split into a probe and referenced pair by reflection from the front and back surfaces of a 6 mm thick CaF\textsubscript{2} plate. Pump and probe beams pass through a 2 mm quartz flow cell (Starna cells) circulating ~50 mL of sample at an angle of 5 to the 315 nm pump pulse. The pump pulse is overlapped with only the probe pulse. Rotational diffusion effects are eliminated by setting an angle of 54.7° (magic angle) between the pump and probe polarizations via a rotating λ/2 plate. The probe and reference pair pass through a pinhole blocking excess pump light before being focused on a 0.5 mm wide entrance slit of an imaging spectrometer (Triax 550 Jobin Yvon) equipped with a 150 g/mm holographic grating. The probe and reference pulses are detected separately on their own vertical region of a thermoelectrically cooled, back illuminated CCD camera chip (Symphony Jobin Yvon, chip 2048 x 512 pixels). This allows minimization of continuum fluctuations by taking a ratio of the pump pulses to the reference pulses. Pump and probe pulses are synchronized by a pair of optical choppers (New Focus 3501). A pair of shutters (Uniblitz) permit acquisition of background and emission signals while minimizing sample exposure to the pump. 250 acquisitions are averaged per delay time.

Measurements were made on ~50 mL of transparent colloidal dispersions circulated through a 2 mm quartz flow cell. The samples were prepared at a particle loading that gave an absorbance of 1.5 at the excitation wavelength of 315 nm by dilution with water.
6.3 Results

6.3.1 Nanozeolite Characterization

The average particle diameter and polydispersity index are contained in Figure 6.1. The intensity weighted size distribution obtained from NNLS fit of the intensity correlation function yields an average particle size of 56 nm. The NNLS distribution is shown in Figure 6.1b. The intensity correlation function is shown in Figure 6.1a. A cumulants fit of the intensity correlation function yields an average diameter of 47 nm. The PDI obtained from this fit is 0.165 indicating a relatively narrow particle sized distribution is synthesized. Figure 6.2 contains the identical intensity distribution (Figure 6.2a) compared to volume (Figure 6.2b) and number (Figure 6.2c) weighted distributions calculated with Mie theory. Which each successive treatment of the data the average size decreases: intensity, volume, and number distributions yield 56, 35, and 26 nm respectively. The average particle diameter obtained from the volume weighted distribution (35 nm) most closely resembled that obtained from electron microscopy (33 nm). A CONTIN fit of the same data yields 57 nm, 31 nm, and 20 nm for the intensity, volume, and number averaged distributions respectively. The average zeta potential of the dispersion was -48 mV indicating a stable sol. The dispersion appears transparent to the eye with a slight blue tinge at all particle densities studied here. The dispersion is stable for several days to a week depending on the particle concentration. Particle sediment was easily re-dispersed by sonication.

The X-ray diffraction pattern characteristic of the as-synthesized nanozeolite powder is contained in Figure 6.3. The observed pattern is characteristic of the FAU framework. Minor modification of the typical peak intensity ratios is observed. This results from the inclusion of tetramethylammonium (TMA\(^+\)) structure directing cations entrapped within the structure during synthesis. This effect is well known\(^{23}\). The peaks are certainly derived from the FAU structure. The pattern indicates a highly crystalline product is obtained as no amorphous materials or co-phases are observed. The wide peak
widths suggest small crystallite sizes. Crystallite sizes estimated from Scherrer's equation is 39 nm.

A transmission electron micrograph of the as synthesized materials is shown in Figure 6.4. The particles posses the typical pseudo octahedral morphology observed for zeolite Y. A range of particle diameters are observed. The average particle diameter based on particle counting is 33 nm. The d-spaces measured from the obvious lattice fringes is 1.4 nm. This matches the d-spacing of the FAU [111] Bragg reflection measured in the XRD\textsuperscript{1}.

The BET surface area of the as-synthesized nanozeolite was 475 m\textsuperscript{2}/g. Such a high surface area is characteristic of zeolite materials and is a good indicator of the materials microporosity. The adsorption/desorption isotherms characteristic of the as-synthesized nanozeolite is contained in Figure 6.5. This isotherm resembles a type I isotherm characteristic of microporous materials\textsuperscript{24} The hysteresis observed in the mesoporous regime is typical of nanozeolite powders and is likely due to particle packing\textsuperscript{25}.

Table 6.1 summarizes the physical and chemical properties of nanozeolite suspensions synthesized herein.

\subsection*{6.3.2 Spectroscopic Characterization of an Intra-Zeolitic Bipyridinium Dicationic Dye}

The optical properties of the aqueous dye and the dye-zeolite system were studied by UV-Vis absorption and emission spectroscopy. The pyridinium 4,4'-{(1,2-ethenediyl)bis[1-methyl, tetrafluoroborate dye will be referred to as BPE\textsuperscript{2+} throughout the text. The BPE\textsuperscript{2+} dye has the following structure:

\begin{center}
\includegraphics[width=0.2\textwidth]{bpe2+_structure.png}
\end{center}

Optical measurements made on colloidal zeolite systems should be understood as extinction measurements because absorption and scattering comprise the total signal. The absorption and emission spectra of BPE\textsuperscript{2+}2(BF\textsubscript{4})\textsuperscript{-} in water and BPE\textsuperscript{2+} ion exchanged
within the zeolite micropores are presented in Figure 6.6. Figure 6.6 c and d (dotted lines) are absorption and emission spectra of the aqueous dye solution respectively. The lowest energy absorption band of the dye is a $\pi \rightarrow \pi^*$ transition with a maximum at 315 nm with shoulders on the red edge at 335 nm and blue edge at 305 nm. This band is assigned to transitions related to the conjugated double bond system$^{26}$. There is also a high energy $\pi \rightarrow \pi^*$ transition centered at 225 nm. This feature is assigned to transitions related to the pyridinium moieties of the dye.$^{26}$ The emission maximum is at 365 nm. The vibronic structure of the emission profile is obvious with shoulders on the red edge at 383 nm and on the blue edge at 348 nm.

Figure 6.6 a and b (solid lines) are the absorption and emission spectra of the dye ion exchanged within the zeolite micropores respectively. The spectra in Figure 6.6 a and b resemble those in aqueous solution Figure 6.6 c and d. No new bands are observed. However, there are some clear differences. The bands appear broadened relative to the solution spectra. There is less evidence of vibronic structure in both the absorption and emission profiles relative to the solution spectra. A noticeable background emerges in the absorption spectrum. The background in the absorption spectra of the dye-zeolite is derived from increased light scattering from the dispersion at UV wavelengths.

Remarkably, the absorption profile of the dye is clearly resolved from this background. Weak absorption bands develop in the dye-zeolite system at 270 nm and 260 nm. These new bands are attributed to photoproducts resulting from exposure to ambient light.$^{27}$

The nanosecond dynamics of the dye in solution and the zeolite was studied by time correlated single photon counting (TCSPC). TCSPC decay traces are contained in Figure 6.7a-c. Figure 6.7a contains the fluorescence decay (blue circles), instrument response function (thin red line), best fit line (thick red line), and residuals (black line) for the aqueous dye system. A double exponential fit to the aqueous dye system was found to be satisfactory using the following equation:

$$I(t) = \sum_i \alpha_i \exp(-t/\tau_i) \otimes IRF$$
where \( I(t) \) is the intensity decay, \( t \) is time, IRF is the instrument response function, \( \alpha \) is the amplitude of the decay with a time constant \( \tau \). The cross represents a mathematical convolution of the IRF with the model decays. In this model function the index \((i)\) of 2 is used to model two decay processes. The first decay is attributed to instrument response. The second decay is attributed to a long lived electronic state of the dye. The residuals contain a significant correlation around 3 ns. This is a artifact derived from the optical configuration used to measure the instrument response function. This artifact is not present at visible wavelengths. It is not derived from the source or it would be canceled out upon convolution. It is not a trivial reflection as it appears at a time that is longer than any round trip distance in the spectrometer. This fact also rules out dynode reflections in the PMT. There is no simple solution to removing this artifact. It should be understood at an artifact and not any photophysical process. Irrespective of what the residuals indicate, the fluorescence decay of the aqueous dye clearly involves a single process because it is linear on the log scale in Figure 6.7 a. The emission lifetime determined from this fit is 8.5 ns.

In contrast, the decay curves of the dye-zeolite system in Figure 6.7 b and c are not linear on the log scale. There is a significant curvature to the decay indicating several decay processes. This is commonly observed for colloid-dye systems and indicates a more complex heterogeneous distribution of chemical environments due to surface interactions. Figure 6.7b contains the fluorescence decays, instrument response, best fit line, and residuals for the dye-zeolite dispersion fit with two exponential functions. The life time associated with the first lifetime \((\tau_1)\) is attributed to instrument response. The second lifetime \((\tau_2)\) associated with emission from the sample is determined to be 5.3 ns. Figure 6.7c contains the fluorescence decays, instrument response, best fit line, and residuals for the aqueous dye system fit with three exponential functions. The fit improves in terms of the goodness of fit, but provides little more information on the decay dynamics. Basically, including more fitting terms only affects the goodness of fit at timescales representative of the instrument response where little physical information can
be extracted. Therefore, bi-exponential fits are in the remainder of this chapter. A summary of the emission parameters determined by TCSPC are listed in Table 6.2.

The sub-nanosecond dynamics are studied by femtosecond time resolved UV-Vis spectroscopy. The time resolved transient absorption spectrum of the aqueous dye system is contained in Figure 6.8a-d. Figure 6.8a shows the evolution of the photo-excited system over the entire duration of the experiment (3 ns). An intense band at 465 nm appears immediately after excitation at 315 nm. This broad band has a shoulder at ~515 nm. There is a simultaneous appearance of a broad negative band below 400 nm attributed to a combination of ground state bleaching and stimulated emission. This band decays in unison with the 465 and 515 nm band. While these features decay, a new band at 435 nm grows in. The feature at 630 nm is second order diffraction laser scattering incompletely blocked by the pin hole.

The absorption features are split into three time periods that capture the essential process in Figure 6.8 b-c. Figure 6.8b focuses on the earliest observable times: 0-5 ps. During this time range the transient absorption bands at 465 nm and 515 nm appear along with the bleach/stimulated emission band below 400 nm. The positive signals are intense and begin to decay during this time period with a time constant of 7.2 ps. Figure 6.8c focuses on intermediate times between 5-200 ps. The transient absorption band at 465 nm, its shoulder at 515 nm, and the bleach below 400 nm decay completely during this time scale and a new band is develops at 435 nm. This band is considerably weaker than the previously observed bands. There is no observable change in the new band during this time scale. Figure 6.8d follows the development of this band out to 3 ns. There is no observable change in this band during the duration of this experiment. The growth of this band match the decay rates of the 465 and 515 nm bands as indicated by the model fits of the kinetic traces at 375, 465, 510, and 435 nm in Figure 6.11a, Figure 6.12a, Figure 6.13a, and Figure 6.14a respectively. Time constants were extracted from model fits of the absorption spectra using the following function:

\[ \Delta OD_\lambda(t) = \sum_i \alpha_i \exp\left(-\frac{t}{\tau_i}\right) \otimes IRF \]
where $\Delta$OD is the time dependent differential absorption signal at a given wavelength, IRF is the instrument response function, $t$ is time, and $\alpha$ is the amplitude of the decay function with a time constant $\tau$. The IRF should be understood to be mathematically convoluted with the model function. The index (i) in this model function is one or two as denoted in the text. A constant offset is used in some cases to improve the fit. Kinetic parameters obtained from the aqueous dye system are contained in Table 6.3. It was found that the 465 and 515 nm band decayed in 7.2 and 8.5ps respectively while the bleach/stimulated emission band at 375 nm recovered at 6.3ps. As discussed above, these three feature give way to a band at 435 nm which lives for the duration of the experiment. Based on these observations the 465 nm band is assigned to a vibrationally hot singlet excited state of the BPE$^{2+}$ dye which vibrationally relaxes in ~7 ps to become the 435 nm band that exists for the duration of the experiment. The 515 nm band, given it likeness to radical band observed in charge transfer complexes, is assigned to an excited singlet state with charge transfer character that decays non-radiatively in ~8 ps.\textsuperscript{17}

Figure 6.9a-d contains the time resolved transient absorption spectra for the colloidal dye-zeolite system. This particular system contains sodium as the co-cation. This system will be denoted by the dye, co-cation, and zeolite respectively in abbreviated notation as follows: BPE$^{2+}$-Na$^+$-ZY. Figure 6.9a contains the evolution of the transient absorption spectra for this system over the entire duration of the experiment. In contrast to the case of the aqueous dye, a broad band centered at 515 nm with a shoulder at 465 nm is observed immediately after photoexcitation at 315 nm. The relative intensities of these two bands are reversed from the aqueous dye case. Figure 6.9b contains the evolution of the system during the earliest times of the experiments (0-5 ps). The 515 and 465 nm bands are intense during this time frame. There are no other major spectral features at this time scale. Quantitative analysis of this data was not successfully performed as the baseline fluctuations are on the order of the absorption signals throughout most of the experiment. Only qualitative analysis of the spectral features was performed. In any case, the absorption band 515 nm is observable above the baseline out to about 100 ps. The bleach-stimulated band below 400 nm is unresolved in these spectra.
and so its kinetic analysis is precluded. A combination of low dye loading and light scattering complicate this signal. Figure 6.9c contains the evolution of the system during the intermediate times of the experiment (5-90 ps). This time scale is defined by further decay of the 465 and 515 nm band with no new feature development. Figure 6.9d contains spectra out to 3 ns. No clear spectral features are resolved during this time scale. Importantly, no band at 435 nm is observed as in the case of the aqueous dye.

A comparison of the absorption spectra of the dye-zeolite sample before and after transient absorption measurements is contained in Figure 6.15. The absorption signatures of the dye remain but there is a significant increase in the intensity of the photoproduct bands at 270 nm and 260 nm. This indicates there is some degree of photo-oxidation of the dye during the course of the laser experiment. Since the absorption features of the photoproduct do not overlap with the excitation wavelength used in this experiment, they are not expected to play a role in the dynamics. A detailed mechanistic study detailing the photo-induced degradation of BPE$^{2+}$ is contained elsewhere.\(^{27}\)

A summary of the kinetic fitting parameters determined from time resolved emission and absorption measurements discussed in this section are compiled in Table 6.2 and Table 6.3.

### 6.3.3 Photophysical Dynamic as a Function of Co-Cation

The UV-Vis absorption spectra for the dye-zeolite system as a function of co-cation is seen in Figure 6.15Figure 6.16a-c. Again, the primary features of the BPE$^{2+}$-M$^+$-ZY systems resemble those of the aqueous BPE$^{2+}$ system. In Figure 6.16a the lowest energy absorption band of the BPE$^{2+}$-TMA$^+$-ZY system has a maximum at 319 nm with shoulders on the red edge at 337 nm and blue edge at 305 nm. The high energy $\pi\rightarrow\pi^*$ transition is centered at 225 nm. In Figure 6.16b the lowest energy $\pi\rightarrow\pi^*$ transition for the BPE$^{2+}$-Cs$^+$-ZY system is at 320 nm with shoulders at 337 nm and 308 nm. The high energy $\pi\rightarrow\pi^*$ transition remains centered at 225 nm. Figure 6.16c contains the absorption spectra for the BPE$^{2+}$-Tl$^+$-ZY system. The lowest energy $\pi\rightarrow\pi^*$ band is centered 321 nm with shoulders at 338 nm and 307 nm. There high energy $\pi\rightarrow\pi^*$ band remains at 225 nm.
but increases drastically in intensity. In fact, for concentrations used herein the 225 nm band saturates the detector. Aside from this, the absorption spectra for these systems are similar. Since all the experiments conducted herein focus on excitation of the low energy $\pi \rightarrow \pi^*$ transition at 315-320 nm any further discussion of the 225 nm band is omitted.

Beyond this feature, it seems the ground state absorption spectrum of the dye within the zeolite micropores is independent of co-cation. Therefore, it is assumed that the ground state of the dye is identical in all cases studied herein. There is no experimental evidence supporting the formation of ground state complexes (charge transfer or otherwise) within the zeolite. Ground state complexes with various anions have been formed in other studies. They are typically signified by a charge transfer band between 350-450 nm.\textsuperscript{17,28}

TCSPC decay curves of the Cs$^+$, TMA$^+$, and Tl$^+$ systems are presented in Figure 6.17a-c. As in the cases of Na$^+$ studied above, the decay measured for each of these systems is non-linear on a log scale indicating distribution of emissive states. The lifetime of the BPE$^{2+}$-Cs$^+$-ZY system in Figure 6.17a is 3.54 ns. The parameters determined from the model fit resemble those of the TMA$^+$ system in Figure 6.17b which was determined to have a decay constant of 3.51 ns. TCSPC decay curves of the Tl$^+$ containing system are presented in Figure 6.17c. This decay curve is unique compared to the other systems. The decay is hardly resolved from the instrument response. A lifetime of 3.2 ns is determined for this system. The relative amplitude is only ~3 % for this decay contribution compared to ~10 % for all other zeolite systems. This indicates there is much less emission from the Tl$^+$ system despite similar dye loadings. A summary of the fitting parameters derived from model fits of the TCSPC data is presented in Table 6.2.

The transient absorption spectra for the BPE$^{2+}$-TMA$^+$-ZY system is contained in Figure 6.10a-d. Figure 6.10a contains absorption spectra spanning 0-3 ns. Qualitatively similar results to the Na$^+$ containing system are observed. The dye loading is higher, thus, higher absorption signals are obtained. Figure 6.10b contains the dynamics from 0-10 ps. Formation of an intense absorption band at 515 nm is observed immediately upon excitation. This band appears sharper than the Na$^+$ analogue. In contrast to the aqueous dye and the Na$^+$ system, the TMA$^+$ system is dominated by the 515 nm band. No
absorption band at 465 nm is resolved in this experiment. There is an asymmetry to the band at times less than 10 ps that suggests a contribution from a band in the 450-500 nm region albeit weak. Additionally, the negative bleach-stimulated feature recovers quickly. Kinetic model fits to this data is presented in Figure 6.11b, Figure 6.12b, and Figure 6.14b at 465 nm (singlet), 375 nm (bleach), and 510 nm (singlet CT state) respectively. The hot singlet state at 465 nm is found to decay in 11 ps accompanied by a decay in the singlet state, with charge transfer character, at 510 nm in 8.1 ps. The recovery of the ground state bleach/stimulated emission takes place in 5.4 ps. Again, no relaxed singlet state at 435 nm can be observed above the noise in this case. These kinetic parameters are summarized in Table 6.3.

Figure 6.18a-d contains the transient UV-Vis absorption spectra for the BPE$^{2+}$-Cs$^+$-ZY system. Figure 6.18a shows the evolution of the excited state absorption over the entire 3 nm duration. Very little bleach is observed in these spectra. No band at 435 nm is observed. Overall, the spectra resemble those observed in BPE$^{2+}$-TMA$^+$-ZY system except for the development of a broad positive absorption feature below 400 nm. Figure 6.18b contains the absorption spectra from 0-20 ps. During this time frame an intense band at 515 nm appears instantaneously and decays significantly within 10 ps. No negative bleach features are observed below 400 nm as in previous cases. Rather, a positive band below 400 nm grows in as the 515 nm band decays. An isosbestic point is observed in Figure 6.18a at ~425 nm. Kinetic analysis of these bands in Figure 6.20a and Figure 6.21a indicate comparable rates as listed in Table 6.3. Figure 6.18c contains absorption spectra from 50-350 ps. The 515nm band is still observed above the background. It decays little over this time scale. The excited state absorption feature below 400 nm is intense and has nearly reached its maximum at 350 ps. Consequently, the kinetic traces displayed in Figure 6.20a, Figure 6.21a, and Figure 6.22a show little change during this time scale. Figure 6.18d contains the evolution of the spectra out to 3 ns. The band at 515 nm is still evident, albeit weak. There is little change in its intensity during this time frame except for the significant fluctuations in the baseline as observed in the 1 ns spectrum. The band below 400 nm grows in intensity, but it is slight.
Interestingly the major difference in this data compared to the previous experiments is the clearly visible, and longer lived, absorption feature at 515 nm, the absence of the 465 nm feature, and the growth of a new feature below 400 nm. Kinetic data pertaining to this system are listed in Table 6.3.

Figure 6.19a-d displays the transient UV-Vis absorption spectra for the BPE$^{2+}$-Tl$^+$-ZY system. Figure 6.19a shows the evolution of the spectra over a 3 ns time range. The band at 515 nm and ~360 nm dominate the spectra. No bleach is observed. No band at 435 nm is observed. These spectra largely resemble the BPE$^{2+}$-Cs$^+$-ZY data in Figure 6.18a-d. Figure 6.19b contains the evolution of the spectra from 0-20 ps. The intense band at 515 nm forms instantaneously upon excitation. In contrast to the aqueous dye, BPE$^{2+}$-Na$^+$-ZY, and BPE$^{2+}$-TMA$^+$-ZY systems studied above, this system does not contain a significant negative feature corresponding to ground state bleach and stimulated emission. Also, no clear evidence of the 465 nm singlet absorption band is seen at early times. Instead, a band grows in below 400 nm as the 515 nm band decays forming a isosbestic point at ~430 nm visible in Figure 6.19a. Kinetic analysis of the 515 nm band in Figure 6.22b gives a 9.5 ps lifetime. Similar analysis at 375 nm in Figure 6.21b gives 9.2 ps lifetime. Figure 6.19b contains the evolution of the absorption spectra from 20-80 ps. During this time frame the 515 nm band decreases, almost completely, in intensity. Furthermore, there is noticeable growth in the absorption band below 400 nm. Figure 6.19d contains the evolution of the absorption spectra out to 3 ns. During this time period the absorption band below 400 nm reaches a maximum and remains unchanged for the duration of the experiment. The absorption band at 515 nm is still observed but is extremely weak. In fact, it appears weaker than the Cs$^+$ case. The intensity of the 515 nm band at 3 ns is at least comparable, if not weaker, than the 515 nm band in the TMA$^+$ and Na$^+$ case. The major findings from this experiment is that the intense excited state absorption feature below 400 nm is greatest in this case.

The dynamic parameters found for all the systems studied above are summarized in Table 6.3.
6.4 Discussion

6.4.1 Colloidal Nanozeolite Dispersions Designed for Transmission Spectroscopic Analysis

The chemical analysis of zeolite containing systems with traditional spectroscopic approaches is non-trivial. This is acknowledged in the literature. Consequently, three primary approaches have emerged for the spectroscopic analysis of zeolitic systems: using single zeolite crystals that are transparent to IR light, using reflectance spectroscopy, and decreasing the crystals dimension to nanometer dimensions. Most ultrafast spectroscopic investigation relies on using solid samples. Furthermore, most ultrafast investigations rely on emission measurements because the signals are easily acquired and less sensitive to scattering. Of course, this is a successful approach, but it limits the scope of investigation to molecules containing emissive states. Absorption measurements are versatile enough to encompass a wide range molecules and electronic states, however, femtosecond absorption in zeolite systems challenging. Our previous work focused on collecting time resolved reflectance absorption spectra of solid samples. This was in part due to the complications that accompany stabilizing a colloidal dispersion given the state of the art in zeolite synthesis (large particle diameters) at the time. The large the crystal diameters used in the past (>100 nm) result in faster sedimentation which causes obvious problems in signal acquisition. Another important limitation of using larger particles in spectroscopic measurements is the amount of light scattering they introduce. Scattered light often convolutes the desired optical signals; especially when it becomes comparable in intensity to the absorption signals desired. Light scattering is proportional to the particle diameter to the sixth power so even small changes the particle size can have a significant effect in the intensity of scattered light detected. The natural solution to the scattering problem is to minimize the particle size. Developments in the understanding of nanozeolite growth from Mintova and co-workers have accelerated the experimental realization of this approach.
The zeolite synthesized herein has an average diameter of $47 \pm 1$ nm as indicated by the particle size distribution in Figure 6.1b and Figure 6.2. The high quality intensity-intensity correlation function presented in Figure 6.1a indicates a satisfactory measurement was made. The size distribution derived from this function in Figure 6.1b reflects the small size of the particles and a relative uniformity in the particle size distribution. The polydispersity index (PDI) is a semi-quantitative measure of the distribution of particle sizes present and it ranges between 0 (a single particle size) and 1 (all particle sizes). The PDI was determined to be 0.165 for the sample synthesized here. This is typical for a relatively monodisperse suspension synthesized hydrothermally. The volume averaged particle size distribution in Figure 6.2c yields an average particle diameter of $35 \pm 1$ nm and is more representative of what would be seen in a TEM. Indeed, the TEM image of the nanoparticles in Figure 6.4 yields an average particle size of 33 nm which is close to that determined by DLS (47 nm) and XRD (39 nm) as summarized in Table 6.1. The shift is the size distribution from the intensity distribution to the volume and number distribution is a result of re-normalizing the data and is expected. The zeta potential of the dispersion is -48 mV indicating a charge stabilized colloid. The dispersion is stable for days to weeks depending on the particle concentration and is transparent to the eye at a weight loading of 0.2 wt%. The XRD pattern in Figure 6.3 indicates the colloidal sample is composed of pure and crystalline zeolite Y. Nitrogen adsorption analysis of the powder collected from the colloid indicates a high surface area of 479 m$^2$/g. This surface area combined with the type I shape of the adsorption isotherm in Figure 6.5 confirms the product is microporous. The results summarizing several size measurements of the as-synthesized zeolite are summarized in Table 6.1. The small particle diameter, narrow particle size distribution, and significant zeta potential characteristic of the as-synthesized particles make this system ideal for transmission spectroscopic measurements.

The optical properties of the bipyridinium dication BPE$^{2+}$ in aqueous solution and in the zeolite are similar upon ion exchange. Comparison of Figure 6.6a and c indicate minimal shift in energy of the absorption bands of BPE$^{2+}$ upon ion exchange within the
zeolite. Differences in the absorption profiles at high energies are attributed to a scattering background that increases non-linearly with wavelength and the appearance of photoproduct bands at 260-270 nm. The polynomial background in the UV region of the spectrum is unavoidable. The photoproduct results from extended exposure to ambient light as studied by others. There are no major differences observed in the absorption spectra at low energy. The π→π* band at 315 nm appears to lose some of its vibronic structural character upon inclusion within the zeolite matrix. A similar effect is observed when comparing the fluorescence spectra in Figure 6.6 b and d. This could result from signal convolution from light scattering. Despite the small particles used here, scattering is present in these measurements as evident by the background and the noise like features riding atop the emission signal. However, these effects are not detrimental to the measurements. Qualitative and semi-quantitative analysis of the signals under these conditions is feasible without the use of additional theory or mathematical transforms. To the best of the authors knowledge, this constitutes the first observation of high quality UV optical signals in a colloidal zeolite composite system of this type.

6.4.2 Spectroscopic Analysis of an Aqueous Bipyridinium Dye and its Dynamics Within Zeolite Y Micropores

The spectral consequences of inclusion of the dye within the zeolite discussed above could also result from conformational changes, adsorption interaction with the zeolite surfaces, or a combination of both. The latter explanation is likely given the change in dynamics within the zeolite as studied with time resolved emission and absorption measurements. The two major results obtained from TSCPC indicate the lifetime of BPE\(^{2+}\) is shortened upon inclusion in the zeolite, and the emission process becomes complex as indicated by the decay shape. These effects are summarized in Table 6.2.

The significant change in the shape of the TCSPC decay curve in aqueous solution (Figure 6.7a) and within the Na\(^+\) zeolite (Figure 6.7b) suggests a significant interaction with the zeolite framework. The curvature of the BPE\(^{2+}\)-Na\(^+\)-ZY decay curve
indicates a distribution of emissive states exist. A distribution of emissive states could originate from electronic interactions with the zeolite framework upon adsorption. A distribution could also be derived from a variety of conformations constrained within the zeolite pore system. It is well established that dye inclusion within zeolite can alter the emission properties of the dye, but the exact mechanism is less established due to mixed results\(^9\). Emission decay curves that are similar in shape to those measured in this study have been observed\(^{35}\). In the case of Sudan-1, conformational changes in the dye upon inclusion in the zeolite matrix have been invoked to explain similar observations\(^{36}\).

The lifetime of the BPE\(^{2+}\) molecule decreases upon inclusion within the zeolite as contained in Figure 6.7a and b. As tabulated in Table 6.2 the lifetime decreases from 8.5 ns to 5.3 ns upon inclusion within Na\(^+\) exchanged zeolite. Also, the relative amplitude of this process decreases by \(~\)50 %. These observations are attributed to the enhancement of non-radiative decay pathways from the excited singlet state through interactions with the zeolite framework or extraframework ions. This interaction could place constraints on conformation of BPE\(^{2+}\). The BPE\(^{2+}\) molecule can be easily accommodated within the FAU pore structure. Although, the conformation could be altered in order to fulfill the charge balance conditions within the negatively charged zeolite. Given the Si/Al ratio of the zeolite studied herein (1.68) it is reasonable to assume a high density of negative sites on the zeolite surface\(^{37}\). A conformational change of the BPE\(^{2+}\) molecule might be required to balance this charge. For example, a cis conformation about the ethylene backbone, where the positively charged pyridinium moieties are closer together, could allow more efficient charge balance of the zeolite surface.

A shorter emission lifetime is commonly observed for intra-zeolitic dyes relative to their solution counterparts. Conformational modifications or modification of the decay process through isomers is commonly used to explain such results.\(^9,35,38\) Similar observations have been made for stilbene in zeolite.\(^{39}\) The local environment can have significant effects on singlet excited states. A twisted internal charge transfer state with fast internal conversion has been proposed to explain the enhancement of radiationless decay processes of aminostilbazolium dyes in polar solvents.\(^{40}\) Non radiative decay
becomes a dominant relaxation mechanism in this case. Aminostilbazolium dyes could be used as a model to understand the effects in the zeolite given the structural similarities. Also, given the higher ionic strength within the zeolite micropores, it is reasonable to expect similar effects play a role in the emission decay of BPE$^{2+}$. Solvatochromic shifts of aminostilbazolium dyes are also commonly observed upon inclusion within zeolites indicating the higher polarity of the intra-zeolitic environment.\textsuperscript{41} Though solvent effects have a smaller effect on the free dye studied in this case, as explored in various solvents.\textsuperscript{17}

An alternative explanation can be formed based on host-guest electronic interactions. Extra-framework ions, Na$^+$ in this case, are present in addition to the BPE$^{2+}$ dication. These cations might play a role in modifying the electronic structure, or conformation, of the BPE$^{2+}$ co-cation. Ramamurthy and co-workers proposed olefin groups can complex to extra-framework cations.\textsuperscript{4} These structures were determined to be important intermediates that influence the stereochemistry of photochemical reactions. Sram et al. have outlined related mechanisms to explain the regioselectivity of photochemical singlet oxygen ene reactions within zeolites.\textsuperscript{42,43} In these cases, the extraframework cation plays an important role in the conformation of the adsorbed molecule, hence, the reaction products. A similar line of reasoning can be applied here to explain the photodynamics. The net decrease in the fluorescence decay lifetime indicates these interactions, whether they are conformational or electronic in nature, enhance the decay rate.

Analysis of the intrazeolitic dynamics on the picosecond time scale utilizing femtosecond transient UV-Vis absorption spectroscopy reveals evidence for electronic interactions with the zeolite framework. This is illustrated by comparison of the transient absorption spectra of the aqueous dye and that of the BPE$^{2+}$-Na$^+$-ZY systems contained in Figure 6.8a-d and Figure 6.9a-d respectively. First, there is a marked difference in the shape of the spectra collected at the earliest times (<10 ps). The maximum intensity of the band formed for the free dye in solution is at ~465 nm with a shoulder at 515 nm. In contrast, the maximum intensity of the initial band formed in the BPE$^{2+}$-Na$^+$-ZY case is

273
at 515 nm with a shoulder at 465 nm. The spectra seem inverse of each other with respect to the relative contributions of each band. This indicates significant excited state interaction between the dye and the zeolite host on an ultrafast time scale. The band at 515 nm resembles the spectral signature for the BPE$^{2+}$ radical at 516 nm observed in solution.\textsuperscript{10,17} Furthermore, this band can be enhanced by changing the nature of co-cation. This effect is clear in the case of TMA$^+$ exchanged zeolite: BPE$^{2+}$-TMA$^+$-ZY system in Figure 6.10a-d. In the case of TMA$^+$ as a co-cation, the peak at 515 nm is stronger than in the Na$^+$ system or aqueous dye case. The 465 nm peak is not clearly observed in the TMA$^+$ case but is observed in the aqueous dye and the Na$^+$ system. The 515 nm peak is the only resolved spectral feature and lives beyond 3 ns in the case of TMA$^+$. This is in contrast to the results from both the aqueous dye in Figure 6.8c and d and the BPE$^{2+}$-Na$^+$-ZY system in Figure 6.9c and d. In the aqueous dye experiment, the bands at 465 and 515 nm decay simultaneously in 7-8 ps to form a band centered at 435 nm that persists for 8.5 ns. In the BPE$^{2+}$-Na$^+$-ZY case, the 465 and 515 nm bands also decay in less than 10ps but no additional features are observable despite strong fluorescence from the hypothesized singlet state at 435 nm observed out to 5.3 ns. It seems in the case of the BPE$^{2+}$-TMA$^+$-ZY system, and probably in the BPE$^{2+}$-Na$^+$-ZY, a charge transfer state becomes stabilized. Kinetic parameters determined for these systems do not fully reflect this but the 515 nm band is clearly more pronounced and persistent in the dye-zeolite systems relative to the aqueous dye system.

Stabilization of the posited singlet excited state with charge transfer character is justified in part by the molecular structure of the BPE$^{2+}$ dye studied here. Pyridinium groups are well known intramolecular electron acceptors. Quaternary ammonium groups are readily reduced in the presence of electron donors because of their electron deficiency. Application of BPE$^{2+}$ as an electron acceptor is widely studied.\textsuperscript{27,28} For this reason the short lived state at 515 nm is assigned to a weak charge transfer complex formed between the BPE$^{2+}$ dye and a neighboring anion. This state quickly deactivates (recombines) through a non-radiative path in 8-10 ps. The S$_1$ state is assigned to the 465 nm band that relaxes in a non-radiative manner to the 435 nm peak in the transient
absorption spectrum observed until 3 ns in Figure 6.8d by comparison to other stilbene derivative excited states postulated to exist in this region. There is no electron donor in our system in contrast to systems where the 516 nm band is observed. Nevertheless, the primary band observed in the BPE\(^{2+}\)-Na\(^+\)-ZY and BPE\(^{2+}\)-TMA\(^+\)-ZY systems resemble the BPE\(^{+}\) radical.

There are several possibilities for an electron donor in our system that might explain the radical-like signatures observed above. First, the most trivial possibility is a contaminant introduced during the preparation of the sample. Every effort was used to eliminate contaminants in this study. Also, any contaminant should contribute to both the solution state and the zeolite system, as they were prepared with the same reagents, which we do not observe. Second, based on Figure 6.15 and Figure 6.16 a photochemical by product is formed upon extended excitation with UV light. This by product could act as a donor. However, this is also unlikely as this mechanism would operate in both the solution and zeolite which is not observed. Also, based on the decay mechanism proposed by Happ et al. the photoproduct should contain electron deficient pyridinium groups and continue to be a strong electron acceptor itself. The last possibility is the zeolite itself acts as a donor. This mechanism could explain the difference in the spectrum observed between the solvent and the intra-zeolitic system. Basically, the zeolite can be thought of as an ion in this system. Obviously the zeolite "anion" has a pronounced impact on the photodynamics as seen by comparison with the tetrafluoroborate anion used in solution. The BF\(_4^-\) is a quite un-reactive anion and so we can reason the charge separated state is not fully formed, or formed only in small amounts, in the aqueous case. A shoulder at 515 nm is observed, albeit weak comparatively. Similar lines of reasoning have been proposed to explain the spectra of the related halide salts of BPE\(^{2+}\) which form obvious radical-like transient spectra with a large feature at 515 nm, and chlorate salts of BPE\(^{2+}\) which doesn't form radical-like transient spectra in solution. The chlorate anion's reactivity was determined to be similar to that of tetrafluoroborate anion: relatively un-reactive. This can explain the weak intensity of the 515 nm band in the aqueous system studied here. ZeoliteY in this case,
though typically un-reactive, might play a role similar to halides in forming the radical species. In fact, zeolite X/Y can behave as a Lewis base with some electron donation capability under the appropriate conditions. Furthermore, the zeolites used in this study can be considered basic as their Si/Al ratio is relatively low (vide supra). It is unlikely the zeolite acts as a true donor in the sense it becomes oxidized, rather, it might partially donate electron density during the adsorption process.

Based on the above discussion we propose a model for the photodynamic that is represented schematically in Figure 6.23a. According to this model, two species always exist in equilibrium with each other: the aqueous dye, and the aqueous dye in a weak charge transfer complex with an anion. In solution with a tetrafluoroborate anion, the equilibrium constant for this equilibrium is small. Therefore, a larger percentage of the population exists and the free aqueous dye. This explains the relative intensities of the excited singlet state at 465 nm and the singlet with charge transfer character at 515 nm. Most of the excited state population in this case decays non-radiatively to the singlet excited state centered at 435 nm in < 8 ps. Subsequently, this population decays through fluorescence in 8.5 ns or follows a non-radiative path either to the ground state or to a photoproduct.

This model can be applied to the zeolite systems as well. However, in the zeolite case the equilibrium constant describing the formation of the charge transfer complex is larger. This explains the higher intensity of the 515 nm band in the zeolite system. This also explains the decrease in fluorescence intensity observed in the TCSPC experiments as indicated by the smaller amplitudes derived from the model decay fits in Table 6.2. Therefore, in the model developed here the zeolite plays a role in forming and stabilizing a charge transfer state by donating electron density. If this hypothesis is true the 515 nm feature can be stabilized further by using more basic zeolites with a stronger electron donating nature. This can be achieved easily through ion exchange. This possibility is explored further in the following section.
6.4.3 Co-Cation Effects on Intra-Zeolitic Photophysical Dynamics of a Bpyridinium Dye

Given the hypothesis that the zeolite influences the dynamics of the dye through electronic interactions, this effect can be enhanced by changing the basicity of the zeolite by ion exchange. For example, the Sanderson electronegativity, hence basicity, of zeolite Y can be altered by introducing larger alkali cations Cs\(^+\) in place of Na\(^+\).

Figure 6.16a-c contains the ground state absorption spectra of the BPE\(^{2+}\)-M\(^+\)-ZY system as a function of exchanged cation for TMA\(^+\), Cs\(^+\), and Tl\(^+\). It is evident from these measurements that the ground state optical properties change little. No signatures of ground state complexes are observed and so an identical ground electronic state is assumed in each system when excited at 315 nm.

Much like the TMA\(^+\) system in Figure 6.10 the BPE\(^{2+}\)-Cs\(^+\)-ZY transient absorption spectra in Figure 6.18 contains the 515 nm band as the major feature. Though it appears to be more pronounced in the Cs\(^+\) case as expected from the stronger basicity, no 465 nm band is observed in the Cs\(^+\) case. The intensity of this band decays also decays in ~8 ps according to kinetic analysis in Figure 6.20a, but it is still observable above the background out to 3 ns in Figure 6.18d. Quantitative kinetic analysis is difficult in the zeolite systems due to scattering as the errors in the model fits suggest in Figure 6.20 and Figure 6.22. For this reason, qualitative analysis of the spectra provide more useful information about the longer time scales when the signal intensities are similar to that of the baseline. These data show the most basic system, the Cs\(^+\) system, provides greater stabilization of the radical-like state at 516 nm because of its increased electron donating ability. TCSPC decay curves indicate a lifetime of 3.5 ns as indicated in Figure 6.16 and Figure 6.17 and tabulated in Table 6.3. Also, the singlet decay seems weaker based on the TSCPC model fit so a smaller population of the excited state is relaxing through fluorescence. Rather, most of the population decays non-radiatively because it exists in the charge transfer state.

A similar effect is observed in the Tl\(^+\) exchanged system in Figure 6.19a. The charge transfer state is also stabilized in this case. The 515 nm band is intense. No
465 nm band is observed. The is observed for the duration of the experiment as seen in Figure 6.19b,c and d. After 3 ns is Figure 6.19d the 515 nm peak is still present, though it is weak. The intensity of the 515 nm peak is smaller in this system than in the Cs\(^+\) case. In fact, it is similar to the TMA\(^+\) case. The bascisity could play a role here. However, it is more likely that the 515 nm band is depleted due to intersystem crossing to a triplet state. This is evident by the isosbestic point at ~425 nm as the 515 nm band gives way to the tentatively assigned triplet state at ~370 nm in Figure 6.19c and d. Triplet formation by the heavy atom effect is well known in Tl\(^+\) containing zeolite.\(^{45}\) Whitten et al. have explored triplet formation of BPE\(^{2+}\) by heavy atom effect.\(^{28}\) In those reports, an increase in the phosphorescence to fluorescence ratio is observed as heavy atoms are introduced. Triplet formation in both the Cs\(^+\) and Tl\(^+\) case can explain the emission decay dynamics observed as well. Though we have not observed any phosphorescence directly, it is clear that the fluorescence is decreased in the heavy atom systems. This is realized by examination of the relative amplitudes of the fluorescence decay to total TCSPC signal as the cation is changed in Table 6.2. Upon changing the cation from TMA\(^+\) (little spin orbit coupling) to Tl\(^+\) (most spin orbit coupling) the relative amplitude is decreased by a factor of ~4. This effect follows the atomic number trend expected for spin orbit coupling.

Coincidentally, Tl\(^+\) transient absorption spectra contain the largest contribution from the 370 nm band.

In summary, the zeolite has a significant effect on the primary photo-processes of the BPE\(^{2+}\) dye upon inclusion within the micropores via its weak Lewis base properties. The zeolites impact on the various photochemical decay processes can be tuned by changing the zeolite chemistry via ion exchange. This provides a means to alter the fundamental decay mechanisms of the BPE\(^{2+}\) molecule without changing its chemical nature. This can be further illustrated by examining the BPE\(^{2+}\)-Tl\(^+\)-ZY photophysics in Figure 6.17b and Figure 6.19a-d where a completely new photophysical decay pathway is generated that didn't exist in aqueous solution.

A model describing the dynamics of the BPE\(^{2+}\)-M\(^+\)-ZY systems as a function of co-cation is shown in Figure 6.23 b. This model is based off of the aqueous solution
model in Figure 6.23a, but with some important modifications. Upon photo-excitation of the lowest energy $\pi \rightarrow \pi^*$ transition at 315 nm the dye-zeolite system populates two excited states. The relative population of these states depends on the Lewis basicity of the zeolite as controlled by the extra-framework cations. If small alkali ions exist as the co-cation, as in the case of Na$^+$, the zeolite host behaves as a weak Lewis base. In these cases, the equilibrium constant between the free BPE$^{2+}$ dye and the BPE$^{2+}$ dye in a charge transfer complex with the zeolite is small. As a result, the 465 nm band characteristic of the free dye singlet excited state can be observed alongside the 515 nm band characteristic of the charge transfer complex. The singlet state with charge transfer character state decays within non-radiatively in 8.5 ps while the hot singlet state of the free dye relaxes in ~7.2 ps to yield a band at 435 nm that decays by fluorescence in 5 ns. Both of the states formed upon excitation can decay by forming a photoproduct that is evident after the experiment.

In systems with large alkali metals as the co-cation, as in the Cs$^+$ and Tl$^+$ cases, the zeolite possesses a stronger Lewis base character. As a result, the equilibrium constant between the free dye and the dye participating in a charge transfer complex with the zeolite is large. In this case, the 515 nm band characteristic of the singlet excited state with charge transfer character is the dominant feature in the excited state spectra. Once formed, the 515 nm band decays either non-radiatively in 8-9 ps to the ground state or by intersystem crossing to an excited triplet state as promoted by the heavy atom effect. The free singlet state is not observed in these cases but some populations exist in this state as fluorescence is observed. The fluorescence decays in ~3.5 ns and is weaker than in the Na$^+$, TMA$^+$, and aqueous systems. The TMA$^+$ containing system is an intermediate case between the two extremes. The spectroscopic observations of this system corroborate this assertion.

6.5 Conclusions

This work, supported by earlier results, has established that nanozeolite allow for the direct probing of organic ultrafast and steady state photochemical process with
A comprehensive study of the primary photochemical and photophysical events following ultrafast photoexcitation of the BPE\(^{2+}\) molecule. The zeolite matrix studied here has been shown to influence the photophysical relaxation dynamics of the dibyridinium dye pyridinium 4,4'-(1,2-ethenediyl)bis[1-methyl, tetrafluoroborate by enhancing non-radiative decay pathways. This is postulated to be driven by the existence unique conformational distributions within the zeolite micropores due to extraframework ion complexation and/or interaction with the aluminosilicate framework itself. The existence of an ultrafast charge separated state excited state is hypothesized as evidence of such interactions. This state is short lived and under populated in aqueous solution but becomes stabilized upon inclusion within the zeolite micropores resulting from partial electron donation from the framework structure. Similar results have been observed in stilbene-zeolite systems.\(^{6,46}\) This is substantiated by evaluation of Na\(^+\), TMA\(^+\), and Cs\(^+\) co-cation exchanged samples where the relative population of the singlet CT to singlet state follows the following trend: Na\(^+\)~TMA\(^+\)<Cs\(^+\). Quantization of these effects is difficult as a result of scattering but qualitative differences are clear. Furthermore, enhancement of intersystem crossing can be easily achieved through the heavy atom effect in the zeolite. A triplet excited state is observed upon ion exchange of Cs\(^+\) and Tl\(^+\). These findings are substantiated by fluorescence lifetime measurements where the relative amplitude of singlet emission decreases in the following order: TMA\(^+\)<Cs\(^+\)<Tl\(^+\).

Based on these results we conclude nanozeolite-chromophore systems provide a method of monitoring and tuning the ultrafast fast photochemical dynamics occurring on the picosecond time scale in heterogeneous systems. The application of the understanding gained through this work could be applied to photocatalyst and photofunctional material development. Recent developments in the synthesis of small, monodisperse zeolite systems will likely perpetuate research and applications of this type. The results obtained herein represent, to the best of my knowledge, the fastest non-fluorescent photophysical dynamics (<10 ps) observed within a zeolite system to date. This highlights the novelty of nanozeolite systems in studying ultrafast host-guest interactions.
6.6 References


Figure 6.1: Intensity-intensity autocorrelation function (a) and intensity weighted particle size distribution (b) of the as-synthesized nanozeolite dispersion.
Figure 6.2: Intensity weighted (a), volume weighted (b), and number weighted (c) particle size distributions calculated for the as-synthesized nanozeolite dispersion.
Figure 6.3: XRD pattern of the as-synthesized nanozeolite powder
Figure 6.4: A TEM image of the nanozeolite particles synthesized herein.
Figure 6.5: The nitrogen adsorption (red circles) and desorption (blue crosses) isotherms representative of the nanozeolite synthesized herein.
Figure 6.6: Comparison of the UV-Vis absorption spectrum of the BPE$^{2+}$-Na$^+$-ZY system (a) and its fluorescence spectrum (b) with the UV-Vis absorption spectrum of the aqueous BPE$^{2+}$ dye (c) and its corresponding fluorescence spectrum (d).
Figure 6.7 Experimental TCSPC decay curves (blue circles), instrument response functions (thin red lines), model decay curves (thick red lines) and residuals (black lines) for the aqueous dye system (a) and the BPE\(^{2+}\)-Na\(^{+}\)-ZY system fit with a double exponential model function (b) and a triple exponential model function (c).
Figure 6.8 Femtosecond transient UV-Vis absorption spectra of the aqueous dye system observed from 0-3 ns (a), 0-5 ps (b), 5-200 ps (c) and 200 ps-3 ns (d).
Figure 6.9: Femtosecond transient UV-Vis absorption spectra of the BPE\(^{2+}\)-Na\(^{+}\)-ZY system observed from 0-3 ns (a), 0-5 ps (b), 5-90 ps (c), and 90 ps-3 ns (d).
Figure 6.10: Femtosecond transient UV-Vis absorption spectra of the BPE$^{2+}$-TMA$^{+}$-ZY system observed from 0-3 ns (a), 0-10 ps (b), 10-100 ps (c), and 150 ps-3 ns (d).
Figure 6.11: Decay traces derived from the transient UV-Vis absorption measurements of the aqueous dye system (a), and the BPE$^{2+}$-TMA$^+$-ZY system (b) at 465 nm.
Figure 6.12: Decay traces derived from the transient UV-Vis absorption measurements of the aqueous dye system (a), and the BPE$^{2+}$-TMA$^{+}$-ZY system (b) at 375 nm.
Figure 6.13: Decay traces derived from the transient UV-Vis absorption measurements of the aqueous dye system at 435 nm.
Figure 6.14: Decay traces derived from the transient UV-Vis absorption measurements of the aqueous dye system (a), and the BPE$^{2+}$-TMA$^+$-ZY system (b) at 510 nm.
Figure 6.15: UV-Vis extinction spectrum of the BPE$^{2+}$-Na$^+$-ZY system before UV laser experiments (a) and after UV laser experiments (b). The spectra are offset vertically for clarity.
Figure 6.16: UV-Vis spectra before (red line) and after (blue line) UV laser experiments for the BPE$^{2+}$-Cs$^+$-ZY system (a), for the BPE$^{2+}$-Tl$^+$-ZY system (b), and for the BPE$^{2+}$-TMA$^+$-ZY system (c)
Figure 6.17: Experimental TCSPC decay curves (blue circles), instrument response functions (thin red lines), model decay curves (thick red lines) and residuals (black lines) for the BPE$^{2+}$-TMA$^+$-ZY system (a), the BPE$^{2+}$-Cs$^+$-ZY (b) and the BPE$^{2+}$-Tl$^+$-ZY system fit with a double exponential model function (c).
Figure 6.18: Femtosecond transient UV-Vis absorption spectra of the BPE$^{2+}$-Cs$^+$-ZY system observed from 0-3 ns (a), 0-20 ps (b), 20-350 ps (c), and 350 ps-3 ns (d).
Figure 6.19: Femtosecond transient UV-Vis absorption spectra of the BPE$^{2+}$-TMA$^+$-ZY system observed from 0-3 ns (a), 0-20 ps (b), 10-80 ps (c), and 500 ps-3 ns (d).
Figure 6.20: Decay traces derived from the transient UV-Vis absorption measurements of the BPE$^{2+}$-Cs$^+$-ZY system (a), and the BPE$^{2+}$-Tl$^+$-ZY system (b) at 375 nm.
Figure 6.21: Decay traces derived from the transient UV-Vis absorption measurements of the BPE$^{2+}$-Cs$^+$-ZY system (a), and the BPE$^{2+}$-Tl$^+$-ZY system (b) at 510 nm.
Figure 6.22: Decay traces derived from the transient UV-Vis absorption measurements of the BPE$^{2+}$-Cs$^+$-ZY system (a), and the BPE$^{2+}$-Tl$^+$-ZY system (b) at 465 nm.
Figure 6.23: A schematic model representing the photophysical dynamics of the aqueous dye system (a) and the BPE$^{2+}$-M$^+$-ZY system (b) where M$^+$ represents Na$^+$, TMA$^+$, Cs$^+$ and Tl$^+$. 
Table 6.1 Physical and chemical properties of nanozeolite dispersions

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<th>Diameter nm</th>
<th>Diameter nm</th>
<th>Diameter nm</th>
<th>Diameter nm</th>
<th>Diameter nm</th>
<th>Zeta potential mV</th>
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<td>56</td>
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<td>26</td>
<td>-48</td>
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</table>

* Size determined from cumulants fit
# Size determined from NNLS intensity distribution
@ Size determined from NNLS volume distribution
** Size determined from NNLS number distribution
*# Size determined from Sherrer equation
*@ Size determined from TEM
*** Zeta potential determined at the schmoulochski limit
**# BET surface area

Table 6.2 : TCSPC fitting parameters

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<th>Sample</th>
<th>λ / nm</th>
<th>τ₀ / ns</th>
<th>α₀ / %</th>
<th>τ₂ / ns</th>
<th>α₂ / %</th>
<th>χ²</th>
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<td>BPE⁺²(BF₄)⁻</td>
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<td>8.46±0.07</td>
<td>19.4</td>
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<td>91.06</td>
<td>5.3±0.2</td>
<td>9.54</td>
<td>2.367</td>
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<tr>
<td>BPE⁺-TMA⁺-ZY</td>
<td>400</td>
<td>0.26±0.05</td>
<td>88.3</td>
<td>3.51±0.05</td>
<td>11.74</td>
<td>0.8916</td>
</tr>
<tr>
<td>BPE⁺-Cs⁺-ZY</td>
<td>400</td>
<td>0.20±0.06</td>
<td>88.75</td>
<td>3.54±0.06</td>
<td>11.25</td>
<td>1.089</td>
</tr>
<tr>
<td>BPE⁺-Ti⁺-ZY</td>
<td>400</td>
<td>0.13±0.05</td>
<td>97.02</td>
<td>3.2±0.2</td>
<td>2.98</td>
<td>1.523</td>
</tr>
</tbody>
</table>

Table 6.3: Transient absorption fitting parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>λ / nm</th>
<th>τ₀ / ps</th>
<th>α₀ / %</th>
<th>C / ΔOD x 10⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPE⁺²(BF₄)⁻</td>
<td>465</td>
<td>8.5±0.1</td>
<td>2.3±0.04</td>
<td>12</td>
</tr>
<tr>
<td>BPE⁺-TMA⁺-ZY</td>
<td>465</td>
<td>1.1±3</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>BPE⁺-Cs⁺-ZY</td>
<td>465</td>
<td>7.0±0.9</td>
<td>0.021</td>
<td>0.0028</td>
</tr>
<tr>
<td>BPE⁺-Ti⁺-ZY</td>
<td>465</td>
<td>10±2</td>
<td>0.016</td>
<td>0.0006</td>
</tr>
<tr>
<td>BPE⁺-Na⁺-ZY</td>
<td>465</td>
<td>15.2</td>
<td>7</td>
<td>0.002</td>
</tr>
<tr>
<td>BPE⁺²(BF₄)⁻</td>
<td>375</td>
<td>6.3±0.2</td>
<td>9.1</td>
<td>0.5</td>
</tr>
<tr>
<td>BPE⁺-TMA⁺-ZY</td>
<td>375</td>
<td>5.4±0.7</td>
<td>0.011</td>
<td>3.8</td>
</tr>
<tr>
<td>BPE⁺-Cs⁺-ZY</td>
<td>375</td>
<td>7±4</td>
<td>-0.014</td>
<td>0.011</td>
</tr>
<tr>
<td>BPE⁺-Ti⁺-ZY</td>
<td>375</td>
<td>9±2</td>
<td>-0.15</td>
<td>0.012</td>
</tr>
<tr>
<td>BPE⁺-Na⁺-ZY</td>
<td>375</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BPE⁺²(BF₄)⁻</td>
<td>510</td>
<td>8.5±0.2</td>
<td>12.7</td>
<td>2</td>
</tr>
<tr>
<td>BPE⁺-TMA⁺-ZY</td>
<td>510</td>
<td>8.1±0.9</td>
<td>0.041</td>
<td>0.002</td>
</tr>
<tr>
<td>BPE⁺-Cs⁺-ZY</td>
<td>510</td>
<td>7±0.9</td>
<td>0.05</td>
<td>0.004</td>
</tr>
<tr>
<td>BPE⁺-Ti⁺-ZY</td>
<td>510</td>
<td>9.5±0.9</td>
<td>0.05</td>
<td>0.003</td>
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<tr>
<td>BPE⁺-Na⁺-ZY</td>
<td>510</td>
<td>15.5</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>BPE⁺²(BF₄)⁻</td>
<td>435</td>
<td>5.1±0.1</td>
<td>7.6</td>
<td>20</td>
</tr>
</tbody>
</table>
APPENDIX A: DEFINITION OF AVERAGE DIAMETER AND
POLYDISPERSITY INDEX ACCORDING TO THE METHOD OF CUMULANTS

The polydispersity index (PDI) used to describe particle size distributions in this
document is defined in the following way:

\[ PDI = \frac{\sigma^2}{Z_D^2} \]  \hspace{1cm} (a)

where \( \sigma \) is the standard deviation of a hypothetical Gaussian particle population and \( Z_D \) is
the average particle diameter derived from a cumulants fit of the intensity autocorrelation
function. According to this definition, the PDI must be more than 0. The closer the PDI is
to 0 the better the experimentally determined intensity autocorrelation function represents
a single particle diameter: it is monodisperse. The practical upper limit for this definition
is 1 after which the width of the distribution becomes larger than the mean and the fit
becomes meaningless: the sample is polydisperse. The cumulant expansion of the
correlation function is valid only for reasonably monodisperse samples: PDI < 0.3. When
the PDI becomes greater than 0.3, another fitting method designed to consider a wide
range of polydispersities should be used, e.g. non-linear non-negative least squares or
CONTIN. The PDI can be derived from the intensity autocorrelation function as outlined
below. Detailed descriptions of the cumulants expansion as applied to light scattering can
be found elsewhere\(^1\).

Essentially a DLS experiment generates a decay curve described by the following
equation for the electric field autocorrelation function \( g^1(\tau) \):

\[ g^1(\tau) = \int_0^\infty G(\Gamma) e^{-\Gamma \tau} d\Gamma \]  \hspace{1cm} (b)

where \( \Gamma \) is defined in terms of the following equations:

\[ \Gamma = Dq^2 \]  \hspace{1cm} (c)
where \( q \) is the scattering vector:

\[
q = \frac{4\pi \tilde{n}}{\lambda} \sin \left( \frac{\theta}{2} \right)
\]

and \( D \) is the diffusion coefficient:

\[
D = \frac{kT}{6\pi \eta R_H}
\]

In the above equations \( \tilde{n} \) is the medium refractive index, \( \lambda \) is the laser wavelength, \( k \) is Boltzmann's constant, \( T \) is temperature, \( \eta \) is the viscosity, \( R_H \) is the hydrodynamic radius, \( \tau \) is the delay time and \( G(\tau) \) is a distribution function that must be determined.

Methods designed to determine this function rely on Laplace transformation. In practice, the intensity autocorrelation function \( (G^2(\tau)) \) is measured rather than the electric field autocorrelation function. The intensity autocorrelation function assumes a similar form and is related to the electric field correlation function simply through the Siegert relation.

The intensity autocorrelation function is described as follows:

\[
G^{(2)}(\tau) = \langle I(t) \cdot I(t + \tau) \rangle = A[1 + B \exp(-2\Gamma \tau)]
\]

where \( I \) is the intensity at \( t \) or \( t \) plus a delay time \( \tau \), the brackets represent a time average, \( A \) is the amplitude of the autocorrelation function and \( B \) is an estimation of the baseline. This single exponential functional form accounts for a single diffusion coefficient, and therefore particle diameter according to Stokes-Einstein, which in general is physically unrealistic. In practice, the correlation function is broadened from a number of effects including a distribution of diffusion coefficients that results from some degree of polydispersity. The cumulants expansion accounts for this broadening by expanding the exponential term as shown below

\[
G^{(2)}(\tau) = A[1 + B \exp(-2\Gamma \tau + \mu_2 \tau^2)]
\]

This function is then linearized to yield the following relations:

\[
\frac{1}{2} \ln \left[ G^{(2)}(\tau) - A \right] \approx \frac{1}{2} \ln [AB] - (\Gamma) \tau + \frac{\mu_2}{2} \tau^2 = a_0 - a_1 \tau + a_2 \tau^2
\]

It is this linear form of the equation that is fit to the experimentally obtained intensity autocorrelation function. The \( a_1 \) and \( a_2 \) parameters (often termed the first and second moments) are used to estimate the average diameter \( (Z_D) \) and the distribution (PDI) according to the following equations respectively.
It is useful to note here that the strict definition of the PDI is given in equation (j). This PDI is derived in a manner that assumes no functional form of the distribution function in equation (b). However, when using the cumulants method, it is conventional to assume a Gaussian distribution. Given this assumption, the PDI can then be understood in a statistically intuitive way, in terms of a well known Gaussian distribution, as written in equation (a). Note, however, that this standard deviation is the width of a "hypothetical" Gaussian particle population chosen for convenience. Nonetheless, it serves as the conventional starting place for the analysis of light scattering data.

References

APPENDIX B: DETERMINING THE SI/AL RATIO BY SOLID STATE NMR

Solid state nuclear magnetic resonance spectroscopy of zeolite X/Y is commonly employed to determine the Si/Al ratio. All the nuclei composing the zeolite lattice have NMR-active isotopes. For the purposes of Si/Al ratio, only the $^{29}$Si MAS NMR spectra is necessary as it gives the most direct information about the framework itself ($^{29}$Si $\sim$ 4%). The features of the Si NMR spectrum are well understood. These spectra show a maximum of five peaks that are reasonably well resolved. Each peak corresponds to the distribution of aluminum around the central tetrahedral Si unit. The magnitude of the chemical shift is representative of the first coordination sphere, and so, this is also an ideal tool for probing the local structure of the zeolite lattice. No Al-O-Al bonds are permitted in the zeolite lattice according to Lowenstein's rule making calculation of the Si/Al ratio possible using the following equation:

$$\frac{Si}{Al} = \frac{\sum_{n=0}^{4} I_{Si(nAl)}}{\sum_{n=0}^{4} 0.25n[I_{Si(nAl)}]}$$  (a)

where $I_{Si(nAl)}$ is the peak intensity of the resonance corresponding to n aluminums within the central silicon bonding environment$^{1,2}$. This equation states that the total silicon concentration is proportional to the total intensity of all the peaks, while the aluminum concentration is proportional to the weighted sum and the intensities of the corresponding peaks. The intensity of each peak should be weighted by the number of aluminums in the local environment. This method of determining the Si/Al ratio is considered the most reliable as it only accounts for aluminum within the framework as extra-framework aluminum is excluded due to its different chemical shift. In contrast, elemental analysis measures the total aluminum.
References


LIST OF REFERENCES

Chapter 1 References

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18. **Zeolites in Industrial Separation and Catalysis.** (Wiley-VCH Verlag GmbH & Co. KGaA, 2010).


Chapter 2 References


**Chapter 3 References**


**Chapter 4 References**


Chapter 5 References


**Chapter 6 References**


**Appendix A References**


**Appendix B References**
