SYNTHESIS OF MICROPOROUS FAUJASITIC ZINCOPHOSPHATES IN
NOVEL ENVIRONMENTS

DISSERTATION

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By

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* * * * *

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ABSTRACT

Zeolitic microporous materials are an important part of our everyday life. They are utilized in detergents to soften water through an ion exchange mechanism and as a catalyst to crack crude oil into more desirable fuel sources as well as for a variety of other purposes. Methods for creating new microporous materials, increasing yields and the purity and understanding the mechanisms by which they form are being studied. A low temperature growth of faujasitic zincophosphate (ZnPO-X) is reported here that implicates a preexisting structure of DABCO-phosphate when the templating agent DABCO and the phosphorus-containing source (H₃PO₄) are mixed prior to adding a zinc source. DABCO-phosphate crystals have been isolated and when they are utilized for zincophosphate growth, the reaction produces nearly pure ZnPO-X crystals. Hopeite, a condensed zincophosphate, is the preferential product when the reactant species are mixed in a different order that does not combine the DABCO and phosphate sources as a precursor. Also reported is a microwave irradiated reverse micellar growth of ZnPO-X. If a short microwave burst (1 minute at 150 W) is introduced during the nucleation stages of a 48-hour synthesis procedure, P6, an impurity, is the primary product. At later stages in the growth, after the initial 4-hour nucleation stage, competition between ZnPO-X and P6 leads to a mixed product. When the short microwave pulse is added to the reaction after complete crystallization, or after about 15 hours, ZnPO-X growth is promoted and
increased yields are noted. A microwave irradiated reverse micellar gold nanoparticle
growth by the reduction of HAuCl₄ with hydrazine hydrate was studied as a model of
microwave irradiated reverse micelle growth.
Dedicated to my family
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Dedication</td>
<td>iv</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>v</td>
</tr>
<tr>
<td>Vita</td>
<td>vii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xiii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xv</td>
</tr>
</tbody>
</table>

## Chapters:

1. **INTRODUCTION** ........................................................................................................ 1

   1.1 Microporous Materials ...................................................................................... 1

      1.1.1 Zeolites.................................................................................................. 1

      1.1.2 Structural Information........................................................................... 2

      1.1.3 Difficulties in Monitoring Zeolite Growth ........................................... 4

      1.1.4 Proposed Structures of Building Units ................................................. 4

      1.1.5 Zincophosphates ...................................................................................... 5

   1.2 Surfactants and Microemulsions.................................................................... 5

      1.2.1 Surfactants.............................................................................................. 5

      1.2.2 Microemulsions ....................................................................................... 6

      1.2.3 Micelles ................................................................................................... 7

      1.2.4 Reverse Micelles ..................................................................................... 7

      1.2.5 Nomenclature Difficulties ...................................................................... 8

      1.2.6 Winsor Classification System ................................................................ 8

      1.2.7 AOT Reverse Micelles ............................................................................. 9

      1.2.8 Co-Surfactants ........................................................................................ 10

   1.3 Reverse Micelle Growth Of Microporous Materials .................................... 10

      1.3.1 Background ............................................................................................... 10

      1.3.2 Drawbacks of Reverse Micelles ............................................................... 11

   1.4 Microwaves ...................................................................................................... 12

      1.4.1 Dielectric Constant .................................................................................. 13

      1.4.2 Microwave Reverse Micelle Synthesis .................................................... 14
2. SYNTHESES OF ZINCOPHOSPHATE FAUJASITE (ZNPO-X):
   ROLE OF A DIRECTING UNIT (DABCO-PHOSPHATE) .................. 46

2.1 Introduction ................................................................................. 46
   2.1.1 Microporous Materials .......................................................... 46
   2.1.2 Synthetic Pathways and Analysis ......................................... 47
   2.1.3 Mechanistic Possibilities ..................................................... 47
   2.1.4 Focus ................................................................................. 48

2.2 Experimental ................................................................................ 49
   2.2.1 Materials ............................................................................. 49
   2.2.2 Synthesis of ZnPO-X ............................................................ 49
   2.2.3 Synthesis of DABCO-phosphate .......................................... 50
   2.2.4 Crystal Structure Determination of DABCO- phosphate ....... 50
   2.2.5 Synthesis by Mixing Reactants in the Solid State ............... 51
     2.2.5.1 Reactions Using H₃PO₄ as a Source of Phosphate Ions ... 52
     2.2.5.2 Reactions Using DABCO-phosphate as a Source of Phosphate Ions ........................................... 52
   2.2.6 Characterization ................................................................. 53

2.3 Results ......................................................................................... 53
   2.3.1 Synthesis of ZnPO-X ............................................................ 53
   2.3.2 Reactions Using Different Combinations of Reactants ....... 54
   2.3.3 Isolation and Structure of the DABCO-phosphate Salt ....... 55
   2.3.4 Synthesis of ZnPO-X by Mixing Reactants in the Solid State.. 56

2.4 Discussion .................................................................................... 57
3. INFLUENCE OF MICROWAVE RADIATION ON GROWTH OF GOLD NANOPARTICLES IN A REVERSE MICELLAR SYSTEM………80

3.1 Introduction ........................................................................................................... 80
  3.1.1 Metal Nanoparticles .................................................................................. 80
  3.1.2 Gold Nanoparticles .................................................................................. 81
  3.1.3 Synthetic Pathways .................................................................................... 82
  3.1.4 Microwave Radiation in Gold Synthesis .................................................. 83
  3.1.5 Microwaving of Reverse Micelles ............................................................. 84
  3.1.6 Focus ........................................................................................................... 86

3.2 Experimental ......................................................................................................... 86
  3.2.1 Materials ....................................................................................................... 86
  3.2.2 AOT in Heptane ........................................................................................ 87
  3.2.3 Reactant solutions ....................................................................................... 87
  3.2.4 Reverse Micelle Solutions ......................................................................... 87
  3.2.5 Non-Microwaved Growth .......................................................................... 88
  3.2.6 Microwaved Growth Varying Hydrazine Concentration ................................ 88
  3.2.7 Microwaved Growth Varying Microwave Exposure Time ......................... 89
  3.2.8 Scanning Electron Microscopy (SEM) ......................................................... 90
  3.2.9 Transmission Electron Microscopy (TEM) ................................................ 90
  3.2.10 Ultraviolet-Visible Spectroscopy (UV-Vis) ............................................. 90
  3.2.11 Dynamic Light Scattering (DLS) ............................................................. 91
  3.2.12 Atomic Force Microscopy (AFM) ............................................................ 91

3.3 Results .................................................................................................................. 92
  3.3.1 Synthetic Strategy ....................................................................................... 93
  3.3.2 Characterization of Particles ...................................................................... 94
    3.3.2.1 SEM ................................................................................................. 94
    3.3.2.2 DLS ................................................................................................. 94
    3.3.2.3 TEM of Varying Hydrazine Concentrations ....................................... 95
      3.3.2.3.1 Non-Microwaved ................................................................. 95
      3.3.2.3.2 Microwaved ........................................................................... 96
    3.3.2.4 TEM of Varying Microwave Exposure Time ..................................... 97
    3.3.2.5 Particle Size Distributions .................................................................. 97
    3.3.2.6 UV-Vis Spectroscopy ....................................................................... 98

3.4 Discussion ............................................................................................................. 100
  3.4.1 Synthesis Reaction ...................................................................................... 101
  3.4.2 Features of the Reverse Micelle System ..................................................... 101
  3.4.3 Model for Gold Growth in a Reverse Micelle ............................................. 103
  3.4.4 Proposed Model for Reverse Micelle Reaction in the
4. MICROPOROUS ZINCOPHOSPHATE-X SYNTHESIZED IN REVERSE MICELLE SYSTEMS: EFFECT OF A BRIEF PULSE OF MICROWAVE RADIATION .......................................................... 157

4.1 Introduction ........................................................................................................... 157
  4.1.1 Microporous Materials ................................................................. 157
  4.1.2 Reverse Micelles and Microporous Materials .............................. 159
  4.1.3 Microwaved Reactions ................................................................. 161
  4.1.4 Microwaved Reverse Micelle Reactions ...................................... 162

4.2 Experimental ...................................................................................................... 164
  4.2.1 Materials ......................................................................................... 164
  4.2.2 Reverse Micellar Solutions .......................................................... 164
  4.2.3 Cleaning Samples ........................................................................ 165
  4.2.4 Preliminary Microwaving .............................................................. 165
    4.2.4.1 Optimized ZnPO-X Conditions .............................................. 166
    4.2.4.2 DABCO Concentration Adjustments ....................................... 167
    4.2.4.3 NaOH Concentration Variation .............................................. 167
    4.2.4.4 Higher Concentrations of All Reactants .................................. 167
    4.2.4.5 SEM ...................................................................................... 168
  4.2.5 Microwave Versus Reaction Time ................................................... 168
    4.2.5.1 DLS ...................................................................................... 169
    4.2.5.2 Capillary XRD ..................................................................... 169
  4.2.6 Mother Liquor Testing ................................................................. 170

4.3 Results .............................................................................................................. 171
  4.3.1 Optimized ZnPO-X Conditions ..................................................... 172
  4.3.2 Increased Template ......................................................................... 173
  4.3.3 Increased Sodium Hydroxide Reactions ....................................... 174
  4.3.4 Higher Concentrations of All Reactants ....................................... 175
  4.3.5 Microwave Versus Reaction Time ................................................ 175
    4.3.5.1 Particle Size Analysis During ZnPO-X Growth .................... 176
    4.3.5.2 Microwaving Over a Longer Time Period ............................. 176
  4.3.6 Investigation of the Clear Suspension Remaining after Crystallization is Complete ...................................................................................................................... 177
  4.3.7 Implications of Microwave Radiation on Yield............................. 178

4.4 Discussion ......................................................................................................... 179
  4.4.1 Preliminary Experiments ................................................................. 180
  4.4.2 Summary of Preliminary Data ....................................................... 182
  4.4.3 Effect of Microwave Radiation on Reverse Micellar Growth of ZnPO-X ................................................................. 182
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1. Typical zeolites, their uses, and products obtained by their use</td>
<td>25</td>
</tr>
<tr>
<td>1.2. Dielectric constants of some materials relevant to the research reported in this dissertation</td>
<td>26</td>
</tr>
<tr>
<td>2.1. Hydrogen bonds for DABCO-phosphate</td>
<td>61</td>
</tr>
<tr>
<td>2.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for DABCO-phosphate. $^aU(eq)$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.</td>
<td>62</td>
</tr>
<tr>
<td>2.3. Bond lengths (Å) and angles (°) for DABCO-phosphate</td>
<td>63</td>
</tr>
<tr>
<td>2.4. Reaction sequences</td>
<td>64</td>
</tr>
<tr>
<td>2.5. Crystal data and structure refinement parameters for DABCO-phosphate</td>
<td>65</td>
</tr>
<tr>
<td>3.1. Growth parameters for the two growth systems attempted with more emphasis on the Wu et al. parameters as difficulties arose with Arcoleo and Liveri’s parameters[23, 27]</td>
<td>113</td>
</tr>
<tr>
<td>3.2. Actual parameters used for the Au growth systems analyzed here. Adjustments were made to the Wu et al. group’s system (Table 3.1) to adjust the rates of reaction</td>
<td>114</td>
</tr>
<tr>
<td>3.3. Summary of the particle size distributions determined from the transmission electron micrographs. MW in the sample name depicts microwaved samples, nMW is non-microwaved, and the number represents the concentration of the hydrazine used to reduce the tetrachloroaurate</td>
<td>115</td>
</tr>
</tbody>
</table>
3.4. Summary of the UV-Vis data from Figure 3.19.................................................. 116

4.1. Concentrations of the individual components of the four compositions
used in this study. .................................................................................................. 191

4.2. Intensity values for several prominent P6 and ZnPO-X peaks found
in the XRD patterns for the microwave versus reaction time experiments.
Notice the general trend that the P6 peaks diminish versus time whereas
the ZnPO-X peaks increase. (Baseline corrected values) ............................... 192

4.3. Columns 2-4 are peak intensity ratios for prominent P6 peaks versus
prominent ZnPO-X peaks nearby. The numbers in the top row
represent the $2\theta$ values. (Baseline corrected values) .................................. 193
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1. Various common aluminosilicate zeolite frameworks.</td>
<td>27</td>
</tr>
<tr>
<td>1.2. A simplified diagram of how various zeolite frameworks with he sodalite framework are related. The sodalite cage shown in the middle is found in all four frameworks shown. The main difference that can be seen here, is how the sodalite cages are joined to one another. For simplicity purposes, the bonded O is usually represented as a straight line as is displayed with the sodalite cage in the middle. (Adapted from [41]).</td>
<td>28</td>
</tr>
<tr>
<td>1.3. The S4R and S6R structural units of microporous materials are shown at the top and the β-cage unit that consists of 6 S4R units and 8 S6R units.</td>
<td>29</td>
</tr>
<tr>
<td>1.4. The D4R and D6R structural units of microporous materials shown at the top. Sodalite (a), zeolite A (b) and faujasite (c) structures. D4R units connect the β-cages in zeolite A and D6R units link the β-cages in the faujasite structure.</td>
<td>30</td>
</tr>
<tr>
<td>1.5. Some proposed building units for zeolites and the type of zeolite formed from each separate unit[42].</td>
<td>31</td>
</tr>
<tr>
<td>1.6. Structures of common surfactants. The AOT is anionic, DODMAC is cationic and Tween-85 is non-ionic.</td>
<td>32</td>
</tr>
<tr>
<td>1.7. Microemulsions that form from surfactants in both inorganic and organic solvents.</td>
<td>33</td>
</tr>
<tr>
<td>1.8. Top picture is that of a micelle with the surfactant’s aliphatic tails entrapping oil on the inside and the polar head groups forming the outer layer. The bottom diagram is that of a reverse micelle whose polar head groups trap water inside as the aliphatic tails are left exposed to the oil solvent.</td>
<td>34</td>
</tr>
</tbody>
</table>
1.9. Schematic of the four types of Winsor systems. ......................................................... 35

1.10. Structure of 1,4-Diazabicyclo[2.2.2]octane, a template for faujasitic microporous materials used here for ZnPO-X. ................................................................. 36

1.11. Diagram of a reverse micelle. This particular one is an AOT reverse micelle which shows different water types within the reverse micelle leading to different uptake properties. ................................................................. 37

1.12. Schematic of a reaction between two reverse micelle solutions that shows collisions of the two reactant reverse micelles and the growth of a precipitate. ................................................................................ 38

1.13. Diffraction pattern of a crystal lattice (Adapted from [43])......................................... 39

1.14. Correlation data as seen from the Brookhaven Instruments 9000AT digital correlator. This data is then transformed to the particle size of which the cumulants method is used for the size in the upper right corner of the screen. .............................................................................. 40

2.1. Growth curve (based on crystallization kinetics) for ZnPO-X synthesis using Reaction 1 of Table 1. The y-axis is the ratio of the intensity of the ZnPO-X peak at 2θ=30.7° versus an internal standard alumina peak at 2θ=37.8°. .................................................................................. 66

2.2. Growth curve of ZnPO-X synthesis using Reaction 1 from Table 1 determined by measuring diameter of particles under an optical microscope and plotting the average of their particle size distributions. Each point represents 100 measurements. ........................................ 67

2.3. Particle Size Distribution based on 100 optical microscope measurements of ZnPO-X growth by Reaction 1 from Table 1 at a) 30 seconds and b) 2 minutes. Average size of a) 1.4 microns and b) 1.9 microns. .................................................................................. 68

2.4. Particle Size Distribution based on 100 optical microscope measurements of ZnPO-X growth by Reaction 1 from Table 1 at a) 6 minutes and b) 10 minutes. Average size of a) 2.7 microns and b) 2.6 microns. .................................................................................. 69

2.5. Particle Size Distribution based on 100 optical microscope measurements of ZnPO-X growth by Reaction 1 from Table 1 at a) 15 minutes and b) 20 minutes. Average size of a) 2.7 microns and b) 2.6 microns. .................................................................................. 70
2.6. Particle Size Distribution based on 100 optical microscope measurements of ZnPO-X growth by Reaction 1 from Table 1 after 300 minutes. Average size of particles is 2.8 micron. ........................................ 71

2.7. Comparison of the diffraction patterns of products recovered from reactions one minute after mixing two reactants. (a) Reactant A = Zn(NO$_3$)$_2$ + NaOH, Reactant B = DABCO + H$_3$PO$_4$; (b) Reactant A = Zn(NO$_3$)$_2$ + H$_3$PO$_4$, Reactant B = DABCO + NaOH. (X = ZnPO-X; H = Hopeite)................................................................................. 72

2.8. (a) Asymmetric unit of the DABCO-phosphate complex. (b) Unit cell diagram of the DABCO phosphate complex. ............................................. 73

2.9. Diffraction patterns from solid-state synthesis after 50 minutes of reaction (unwashed). (a) DABCO-phosphate complex as reagent (b) DABCO and H$_3$PO$_4$ are separate reagents. (X = ZnPO-X; H = Hopeite; D = DABCO; DP = DABCO-phosphate; Z = ZnHPO$_4$; N = Zn(NO$_3$)$_2$·6H$_2$O; U = undetermined) ............................................... 74

2.10. Diffraction from solid-state synthesis after 50 hours of reaction (products washed with ethanol). (a) DABCO-phosphate complex as reagent (b) DABCO and H$_3$PO$_4$ are separate reagents. (X = ZnPO-X; H = Hopeite)................................................................................. 75

3.1. SEM images of non-thiolated gold growth samples that show a desperate need for a capping agent to reduce/eliminate the clustering of gold nanoparticles................................................................. 117

3.2. TEM images of gold nanoparticles produced in a reverse micelle system by reducing HAuCl$_4$·3H$_2$O with a 2 M hydrazine solution. .......... 118

3.3. TEM images of gold nanoparticles produced in a reverse micelle system by reducing HAuCl$_4$·3H$_2$O with a 2 M hydrazine solution in the presence of microwave radiation. ..................................................... 119

3.4. TEM images of gold nanoparticles produced in a reverse micelle system by reducing HAuCl$_4$·3H$_2$O with a 1 M hydrazine solution. ......... 120

3.5. TEM images of gold nanoparticles produced in a reverse micelle system by reducing HAuCl$_4$·3H$_2$O with a 1 M hydrazine solution in the presence of microwave radiation. ..................................................... 121
3.6. TEM images of gold nanoparticles produced in a reverse micelle system by reducing H\textsubscript{2}AuCl\textsubscript{4}·3H\textsubscript{2}O with a 0.5 M hydrazine solution .......................................................................................... 122

3.7. TEM images of gold nanoparticles produced in a reverse micelle system by reducing H\textsubscript{2}AuCl\textsubscript{4}·3H\textsubscript{2}O with a 0.5 M hydrazine solution in the presence of microwave radiation. ................................................................. 123

3.8. TEM images of gold nanoparticles produced in a reverse micelle system by reducing H\textsubscript{2}AuCl\textsubscript{4}·3H\textsubscript{2}O with a 0.2 M hydrazine solution ...................................................................................................... 124

3.9. TEM images of gold nanoparticles produced in a reverse micelle system by reducing H\textsubscript{2}AuCl\textsubscript{4}·3H\textsubscript{2}O with a 0.2 M hydrazine solution in the presence of microwave radiation. ..................................................... 125

3.10. TEM images of gold nanoparticles produced in a reverse micelle system by reducing H\textsubscript{2}AuCl\textsubscript{4}·3H\textsubscript{2}O with a 0.1 M hydrazine solution ...................................................................................................... 126

3.11. TEM images of gold nanoparticles produced in a reverse micelle system by reducing H\textsubscript{2}AuCl\textsubscript{4}·3H\textsubscript{2}O with a 0.1 M hydrazine solution in the presence of microwave radiation. ..................................................... 127

3.12. Higher resolution TEM images of a reduction of H\textsubscript{2}AuCl\textsubscript{4}·3H\textsubscript{2}O by 0.1 M hydrazine in a reverse micelle reaction system. Some faults and grain boundaries are designated with the arrows. ........................................ 128

3.13. Higher resolution TEM images of a reduction of H\textsubscript{2}AuCl\textsubscript{4}·3H\textsubscript{2}O by 0.1 M hydrazine in a reverse micelle reaction system in the presence of microwave radiation. Some faults and grain boundaries are designated with the arrows. ........................................ 129

3.14. Particle size distribution plots for gold nanoparticles produced with 2 M hydrazine. These PSD’s are based on the images shown in Figures 3.2 and 3.3. (a) is the non-microwaved PSD and (b) is the microwaved PSD. .......................................................................................... 130

3.15. Particle size distribution plots for gold nanoparticles produced with 1 M hydrazine. These PSD’s are based on the images shown in Figures 3.4 and 3.5. (a) is the non-microwaved PSD and (b) is the microwaved PSD. .......................................................................................... 131

3.16. Particle size distribution plots for gold nanoparticles produced with 0.5 M hydrazine. These PSD’s are based on the images shown in
Figures 3.6 and 3.7. (a) is the non-microwaved PSD and (b) is the microwaved PSD. ........................................................................................................ 132

3.17. Particle size distribution plots for gold nanoparticles produced with 0.2 M hydrazine. These PSD’s are based on the images shown in Figures 3.8 and 3.9. (a) is the non-microwaved PSD and (b) is the microwaved PSD. ........................................................................................................ 133

3.18. Particle size distribution plots for gold nanoparticles produced with 0.1 M hydrazine. These PSD’s are based on the images shown in Figures 3.10 and 3.11. (a) is the non-microwaved PSD and (b) is the microwaved PSD. ........................................................................................................ 134

3.19. UV-Vis spectra for 0.5 M hydrazine reductions of HAuCl₄·3H₂O, both (a) microwaved and (b) non-microwaved. Baseline corrected spectra (using a multiple point correction function from Grams-32 Spectral Notebase program) are shown as (c) and (d) respectively. .......... 135

3.20. UV-Vis spectra for 2 M hydrazine reductions of HAuCl₄·3H₂O, both (a) non-microwaved and (b) microwaved. Baseline corrected spectra (using a multiple point correction function from Grams-32 Spectral Notebase program) are shown as (c) and (d) respectively. .......... 136

3.21. TEM images of gold nanoparticles microwaved for 2 minutes at 150 W after mixing reverse micellar mixtures of HAuCl₄·3H₂O and the reducing agent hydrazine hydrate. ........................................................................................................ 137

3.22. TEM images of gold nanoparticles microwaved for 4 minutes at 150 W after mixing reverse micellar mixtures of HAuCl₄·3H₂O and the reducing agent hydrazine hydrate. ........................................................................................................ 138

3.23. TEM images of gold nanoparticles microwaved for 6 minutes at 150 W after mixing reverse micellar mixtures of HAuCl₄·3H₂O and the reducing agent hydrazine hydrate. ........................................................................................................ 139

3.24. TEM images of gold nanoparticles microwaved for 15 minutes at 150 W after mixing reverse micellar mixtures of HAuCl₄·3H₂O and the reducing agent hydrazine hydrate. ........................................................................................................ 140

3.25. PSD of the gold nanoparticles microwaved for (a) 2 minutes, (b) 4 minutes, (c) 6 minutes and (d) 15 minutes. The average sizes in each case are (a) 10.1 nm, (b) 9.4 nm, (c) 10.0 nm and (d) 10.7 nm. .......... 141
3.26. Growth curve of the nano-gold particles both microwaved and non-microwaved samples. The time shown here is of total reaction time, where the microwaved samples were actually microwaved one minute less than total reaction time. (Lines are merely to guide the eye, and have no significance.) ................................................... 142

3.27. TEM images revealing gold nanoparticle solutions that show “superstructures” can be separated through dilution and sonication. Some “superstructures” are still present but longer sonication and more dilution can separate the structures even more. This shows it is a physical connection and not chemical. ............................................. 143

3.28. Poissonian distribution depicting the distribution of reactants in a two-reactant reverse micellar reaction. ............................................................... 144

3.29. Theoretical model of a standard two reactant reverse micellar reaction and how solubilisate exchange occurs......................................................... 145

3.30. Hypothetical distribution of reactants within reverse micelles of a two-reactant system when microwave radiation is added to alter the growth mechanism. ................................................................. 146

3.31. Hypothetical solubilisate exchange process for a two-reactant reverse micellar reaction in the presence of microwave radiation. Often referred to in the text as the “explosion model.” ........................................ 147

4.1. SEM images of the optimized ZnPO-X product from a reverse micelle system. ................................................................................................. 194

4.2. SEM images of the optimized ZnPO-X product from a reverse micelle system after microwaving for 1 minute at 150 W, 2 minutes after the reaction was started. Several hours passed before the product was isolated, cleaned and analyzed. ....................................... 195

4.3. SEM images of the optimized ZnPO-X product from a reverse micelle system after microwaving for 1 minute at 150 W, 60 minutes after the reaction was started. Several hours passed before the product was isolated, cleaned and analyzed. .............................. 196

4.4. SEM images of the optimized ZnPO-X product from a reverse micelle system after microwaving for 1 minute at 150 W, 120 minutes after the reaction was started. Several hours passed before the product was isolated, cleaned and analyzed. ........................................... 197

4.5. Standard XRD of the samples from Figures 4.2-4.4 (a-c), respectively, taken by dropping a suspension of the particles in
acetone onto a glass sample holder. This leads to preferred orientation effects. .......................................................... 198

4.6. Capillary XRD pattern of the sample shown in Figure 4.4 and Figure 4.7a. As compared to the pattern in 4.7a, this pattern is not preferentially oriented and therefore the major peaks are less intense and more of the smaller peaks are elucidated. Pattern was baseline corrected. P6 peaks are marked with a P, the other phase is unknown. ............................................................................................................. 199

4.7. Reaction of the optimized ZnPO-X conditions except that the amount of template was increased. .......................................................... 200

4.8. Microwave reaction of the increased template trials. Microwaving was done 2 minutes after the reaction began and was performed at 150 W for 1 minute. ............................................................................................................. 201

4.9. Microwave reaction of the increased template trials. Microwaving was done 60 minutes after the reaction began and was performed at 150 W for 1 minute. ............................................................................................................. 202

4.10. Microwave reaction of the increased template trials. Microwaving was done 120 minutes after the reaction began and was performed at 150 W for 1 minute. ............................................................................................................. 203

4.11. SEM images of the increased NaOH reaction. .......................................................... 204

4.12. SEM images of the increased NaOH reaction that was microwaved 2 minutes after the reaction began for 1 minute at 150 W. ......................... 205

4.13. SEM images of the increased NaOH reaction that was microwaved 60 minutes after the reaction began for 1 minute at 150 W. ......................... 206

4.14. SEM images of the increased NaOH reaction that was microwaved 120 minutes after the reaction began for 1 minute at 150 W. ......................... 207

4.15. SEM images of the increase of all reactants experiments that show predominantly P6 formation in all cases ranging from (a) non-microwaved, (b) intermittent microwaving, (c) 20 seconds at 150 W, (d) 45 seconds at 150 W, and (e) 90 seconds at 150 W. ......................... 208

4.16. Dynamic light scattering (DLS) data for the non-microwaved growth of a reverse micelle system optimized for ZnPO-X growth. Four distinct regions are seen that outline the growth process......................... 209
4.17. Capillary XRD patterns for the microwave versus reaction time where the reaction time elapsed before microwaving for 1 minute at 150 W is (a) 1 hour, (b) 3.25 hours and (c) 5 hours. All patterns have been baseline corrected and the inset is of region 26-27 2θ. ZnPO-X peaks marked with X and P6 peaks marked with P. 210

4.18. Capillary XRD patterns for the microwave versus reaction time where the reaction time elapsed before microwaving for 1 minute at 150 W is (a) 10 hours, (b) 20 hours and (c) 25 hours. All patterns have been baseline corrected and the inset is of region 26-27 2θ. ZnPO-X peaks marked with X and P6 peaks marked with P. 211

4.19. Capillary XRD pattern of a non-microwaved optimized reverse micelle growth for comparison with those XRD’s in Figure 4.19 and 4.20 that have been microwaved at various times during the reaction. The pattern was baseline corrected and the inset is of region 26-27 2θ. ZnPO-X peaks are marked with an X, and the place where the P6 peak at 26.7 (2θ) is marked with a P in the inset pattern. 212

4.20. Ratio of XRD peaks 26.7 (2θ) that represents P6 and 26.3 (2θ) representing ZnPO-X. The timescale represents the time during the reaction that 150 W of microwave radiation was introduced for 1 minute. 213

4.21. XRD patterns for products formed when the clear mother liquor from above a ZnPO-X reverse micelle reaction is isolated and microwaved at (a) 7 hours, (b) 10.5 hours and (c) 16 hours. All patterns have been baseline corrected and the inset is of region 26-27 2θ. ZnPO-X peaks marked with X and P6 peaks marked with P. 214

4.22. XRD patterns for products formed when the clear mother liquor from above a ZnPO-X reverse micelle reaction is isolated and microwaved at (a) 21 hours, (b) 31 hours and (c) 43 hours. All patterns have been baseline corrected and the inset is of region 26-27 2θ. ZnPO-X peaks marked with X and P6 peaks marked with P. 215

4.23. Mother liquor analysis data where time is the point at which the mother liquor was isolated and microwaved and the ratio is of P6/ZnPO-X peak intensities (26.7/26.3). As more time elapses, the reverse micelles harbor ZnPO-X nuclei/particles and a diminished
4.24. Representation of the microwave radiation pulse sequence (brief one minute pulse) employed at various stages of the reverse micellar growth system for ZnPO-X overlaid on a DLS growth pattern. Each solid line represents a separate experiment and the microwave pulse was added for 1 minute at the time shown above the curve. XRD’s of the products from these reactions can be seen in Figures 4.19 and 4.20. Most products were then isolated after 48 hours of total reaction time so the microwave perturbation was extremely small when compared to the total reaction time.

4.25. Combination of Figure 4.18 and Figure 4.22 that shows how as the growth process of a non-microwaved sample proceeds, the amount of P6 product decreases as shown by the ratio of a P6 peak versus a ZnPO-X peak. Without microwaving, ZnPO-X is the major product. (a) is the DLS data for growth of a ZnPO-X non-microwaved reverse micelle system and (b) is the intensity ratio of a P6 peak versus a ZnPO-X peak (26.7/26.3).

4.26. Scheme proposed for the degradation of diprotonated-DABCO in the presence of water[38].

The amount of nutrient that would promote P6 growth upon microwaving.
CHAPTER 1

INTRODUCTION

1.1 Microporous Materials

1.1.1 Zeolites

Zeolites are microporous structures composed of aluminum, silicon and oxygen that play an integral part in our world. The pores of zeolites range from approximately 0.3-1.2 nm in diameter[1]. Typically they have a large internal surface area (>300 m²/g) and void volumes (>0.1 cm³/g). Due the narrow pore size distribution, zeolites can separate molecules by size and shape and are therefore sometimes referenced as molecular sieves[2]. The microporosity and reactivity make them suitable for use in a variety of industries including, but not limited to, those involved with petroleum processing, detergents, absorbents, ion exchanging and water softening. The term zeolite was coined by a Swedish mineralogist, A. Cronstedt in 1756[3], and is Greek for boiling
stone. It was employed because the mineral appeared to boil when heated due to the large amount of water that it had trapped in its framework[3].

“Zeolites, minerals with pore sizes of less than one nanometer, serve as more efficient catalysts to break down, or crack large hydrocarbon molecules to form gasoline”[4]. In 1974, nearly 95% of all oil used in the world had come in contact with zeolites (namely, faujasitic Zeolite Y) in its production stages[5]. That percentage has risen to nearly 100% in recent years. Zeolite A is added to detergents as an in-situ method of water softening[6]. The sodium ions in the zeolite ion exchange with calcium and magnesium ions found in hard water. The zeolite that is now calcium and magnesium rich is rinsed away. Some of the most common zeolites and their uses are outlined in Table 1.1.

The mechanism by which zeolites form is heavily studied, but still not well understood. Controlled growth of known zeolites, and also discovering new framework structures, may be possible if the growth and dissolution mechanisms of current zeolites are determined. The ability to form zeolites with desired structural properties is crucial in the development of more efficient systems and processes.

1.1.2 Structural Information

The aluminum and silicon combine with oxygen to form tetrahedral arrangements that then bond together to give the recognized frameworks of zeolites Figure 1.1. The tetrahedral arrangement around the Si and Al are usually perfect, but the T-O-T’ angles can take on dimensions from 130° to 180°. In this case, T is Si and T’ can be either Si or
Al. Figure 1.2 displays more detail as to how the tetrahedron fit together and shows how the different atoms are represented in Figure 1.1. Oxygen is simply drawn as a straight line, and the corners are either Si or Al.

The SiO$_4$ and AlO$_4$ tetrahedron can combine to form 4 and 6 membered rings that can be viewed as secondary building blocks. This nomenclature comes from calling the tetrahedron the primary building blocks. They are abbreviated as S4R and S6R respectively. Figure 1.3 displays models of these structures. The β-cage of the sodalite structure is a good example of these two formations. It contains 6 S4R and 8 S6R units and can be seen in Figure 1.3. In the diagram, either Al or Si occupies the corners shown and the straight edges actually represent a linking oxygen atom. There are also double 4-ring and double 6-ring secondary building units designated as D4R and D6R respectively. A sketch of them can be seen in Figure 1.4. Faujasite has several of the D6R units and Zeolite A contains the D4R units. In each of these two cases, the D4R and D6R units are located such that they link two β-cages together. These can be seen along with sodalite in Figure 1.4. The manner in which the secondary building blocks conform, determines the pore and cavity dimensions of the zeolite. As mentioned previously, zeolites have pore sizes in the range of 0.3-1.2 nm, which classifies them as microporous materials when noting that IUPAC has set the standards at:

\[
\text{micropores: } 2.0 \text{ nm} \geq d_p \\
\text{mesopores: } 2.0 \text{ nm} < d_p \leq 50 \text{ nm} \text{ and} \\
\text{macropores: } d_p > 50 \text{ nm},
\]

with $d_p$ being the pore diameter[7-9].
1.1.3 Difficulties in Monitoring Zeolite Growth

Producing zeolites is done by following a predetermined procedure of mixing varied concentrations of the appropriate reactants. One of the problems associated with determining the mechanisms of zeolite crystallization is the difficulty in monitoring the growth process. In the past, spectroscopic and scattering methods have focused on the earliest stages of crystal growth[10-15]. The growth has been thought to occur by agglomeration of nanometer-sized nuclei into certain geometries that can then either superassemble to the crystal, or incorporate small units onto a growing crystal[16-18]. However, it is difficult to prove this mechanism because typical hydrothermal zeolite synthesis goes through a gel stage that is hard to monitor in situ.

1.1.4 Proposed Structures of Building Units

Of particular interest is how the cage-like structures form, and what causes one framework to grow as opposed to another as composition of the reactant solutions is varied. Several obvious factors are known that effect the resultant framework, including reactant concentrations, templates, pH, temperature and even the order in which the reactants are mixed. Once these factors are understood better, if the building blocks that combine to form each structure can be determined, controlled synthesis of current and new microporous materials may be possible. These new structures could be synthesized with certain properties that are desirable in a given situation. Some proposed structures of building blocks are shown in Figure 1.5.
1.1.5 Zincophosphates

Instead of directly studying the aluminosilicate (zeolite) structures, sometimes the analogous framework structures of zincophosphate can be examined to elucidate certain growth processes. As the name suggests, the zincophosphate (ZnPO) structures are composed of tetrahedra of zinc and oxygen and of tetrahedra of phosphorus and oxygen. Several frameworks that are known for zeolites, can be readily synthesized with the appropriate mixture of reactants and perhaps a template. ZnPO’s ability to form the desired structures under ambient conditions is an attractive reason for choosing it as a model for the \( \text{Al}_x\text{Si}_y\text{O}_z \), which requires a high temperature hydrothermal treatment for growth in a short timeframe. Besides zinc and phosphorus, other atoms that can replace the silicon and aluminum to form similar microstructures include, but are not limited to beryllium, boron, cobalt, gallium, germanium, iron and titanium[19, 20].

1.2 Surfactants and Microemulsions

1.2.1 Surfactants

Surfactants alter the properties between phases, especially lowering the tension at the fluid surface. They are molecules with a polar, water-soluble group (head group) attached to a water-insoluble hydrocarbon chain (tail.) Typically, the tails are \( \text{C}_6 \) to \( \text{C}_{18} \) fatty acid derivatives which are either straight or branched alkanes. Surfactants can be either ionic, or non-ionic, depending on the head group. In ionic species, the charge can be either positive or negative and is balanced by an appropriate anion, or cation
respectively. Figure 1.6 shows examples of each of these three types of surfactants. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) is anionic, polyoxyethylenesorbitan trioleate (Tween-85) is non-ionic (neutral) and dioctyldimethylammonium chloride (DODMAC) is cationic. The properties of the surfactant vary greatly depending on their charge, or neutral state[21].

Zwitterionic surfactants are different because of their ability to change between charged and neutral forms by altering the pH of the hydrophilic solvent[22].

1.2.2 Microemulsions

Microemulsions are thermodynamically stable, homogenous mixtures of two liquids and either a surfactant, or a mixture of surfactants. They are isotropic, transparent or opaque and form immediately upon mixing or stirring[23]. Being thermodynamically stable and the ability to form clear solutions make microemulsions much different than macroemulsions[24]. Water and a hydrophobic organic solvent called the "oil" are usually the two liquid components used. Depending on the ratios of the liquid phases and the nature of the surfactant, normal, reverse (inverse), bicontinuous (bilayer), and laminar phase microemulsions can be formed[22, 23]. A diagram of the various types of microemulsions can be seen in Figure 1.7.
1.2.3 Micelles

Micelles are collections of surfactant molecules with their non-polar tail (long aliphatic chains) pointed inwards toward the center and their polar head group forming the outer layer of a sphere as can be seen in Figure 1.8. The term micelle is reserved for small globules with a regular geometry, for example, spheres or cylinders of less than 100 nm. Oil in water dispersions are the result of discrete water soluble globules assembling and, in the process, entrapping the non-polar solvent in their cores[22]. A couple of the most common examples of surfactants are soaps and detergents. Detergents have a polar head group and non-polar tail. Most dirt and stains found in soiled clothing are greasy/organic in nature or are held to clothing by grease. Grease can be dissolved by the non-polar tails of the detergent (hydrophobic). Water on the other hand has an affinity towards the polar head groups (hydrophilic). Since the amount of grease is so much smaller than the volume of water in a wash cycle, the detergent forms micelles with the grease entrapped in the core along with the non-polar tails. The outer shell of the micelle composed of the polar head groups is dissolved in the water. When the water is drained, the micelles, containing the grease, are rinsed away.

1.2.4 Reverse Micelles

Reverse micelles are exactly what the name implies. A reverse micelle simply reverses the direction of the surfactant molecule such that the polar head is now at the center and the non-polar tails form the outer part of the sphere. These microemulsions
can also be called water in oil microemulsions. Water is trapped inside the globule surrounded by the polar head groups and the bulk solution is an “oil”, or hydrocarbonic solution that dissolves the non-polar tail of the surfactant molecule. Figure 1.8 displays an example of a reverse micelle.

1.2.5 Nomenclature Difficulties

Nomenclature varies among different scientists. Some believe that a reverse micelle is a microemulsion with only enough water to wet the head groups[25]. If more water is present than required to moisten the head groups, it is then referred to as a "swollen reverse micelle." Still others base the naming on the size of the droplet. If the sphere is less than 5 nm, it is a reverse micelle, but if it is larger, it is labeled a “water in oil” (w/o) microemulsion. For simplification purposes, reverse micelle will be used when referring to any microemulsion with water entrapped in a surfactant sphere with an oil as the solvent.

1.2.6 Winsor Classification System

P. A. Winsor studied a four ternary phase equilibrium systems and designated four classifications for oil/water/surfactant equilibriums. They were simply Winsor type I, II, III and IV[26]. A cartoon diagram is displayed in Figure 1.9 that shows the difference in each. In Winsor type I, there is an oil in water microemulsion at equilibrium with an excess organic phase. Nearly all of the surfactant is in the water
layer with a surfactant free oil layer on top of the water layer. A Winsor type II system is the opposite with nearly all the surfactant residing in the organic layer, making a water in oil microemulsion. The water layer on the bottom does not have much if any surfactant dissolved in it. The Winsor type III system does not dissolve the surfactant in either the organic or water layer. In this case, a third layer is formed which is rich in surfactant and is located in between the organic and water layers. Winsor type IV systems are composed entirely of either a water in oil microemulsion or a oil in water microemulsion with no other phases being present.

With a reverse micelle, the center of the sphere contains water while the solvent is organic. For instance, a DODMAC reverse micelle is reported here, where the solvent is isooctane and the solution inside the micelle is a water based solution of either Zn, P or a template such as 1,4-diazabicyclo[2.2.2]-octane (DABCO). A diagram of DABCO is shown in Figure 1.10. This classifies the system as a Winsor type IV because there is only one phase present and it happens to be similar to a Winsor type II.

1.2.7 AOT Reverse Micelles

A schematic of an AOT reverse micelle is displayed in Figure 1.11. The schematic show that there are three types of water present inside the reverse micelle. The types are listed as that tightly bound to the polar headgroup, bulk-like water in the center of the reverse micelle and a layer between these two layers with intermediate properties. The amount of loading determines how much of each is incorporated into the sphere. At higher loadings, there is more of the bulk-like water that does not contact the headgroups.
Higher loading also increases the size of the sphere. Water containing reverse micelles can range in size from about 5 to 50 nm[21].

1.2.8 Co-Surfactants

Certain reverse micelle systems need an additional co-surfactant added to the system for improved results. Long, straight chain alcohols are typically used as the co-surfactant and serve two purposes. The primary duty is to increase the solubility of the surfactant in the organic phase[27]. This function makes the system hydrophobic and then directs the system to a reverse micelle solution instead of a Winsor type III system which is a surfactant rich phase[22]. The second purpose is to change the tail length and therefore volume of the reverse micelle. This changes the packing and alters the curvature of the micelle-water interface to more stable values[28].

1.3 Reverse Micelle Growth Of Microporous Materials

1.3.1 Background

Dr. Prabir K. Dutta and his research group at The Ohio State University developed a technique for growing microporous crystals in a clear solution. Since the solution is clear, the growth can be monitored by various techniques, in situ, as the crystal grows instead of removing samples at various times in the reaction and analyzing a dry sample.
Using this new technique of reagents trapped in the reverse micelles, sodalite was directly synthesized without gel formation[29]. A schematic is shown in Figure 1.12. This diagram illustrates, that as the two reverse micellar reactants are mixed, collisions occur between those reverse micelles containing reactant A and those containing reactant B. Upon colliding, the walls of the reverse micelle open up to one another and exchange of reactants takes place. As this occurs, small crystals of the product are formed and continue to grow as more collisions occur and exchange of reactant continues.

More recent in depth studies by the Singh et al. have shown that the growth environment within the reverse micelle is different from a hydrothermal synthesis and that faujasitic zincophosphate crystals synthesized in reverse micelles have a smoother surface with significantly fewer nucleation sites than a similar crystal created hydrothermally[30].

1.3.2 Drawbacks of Reverse Micelles

A major drawback of this technique is that after considerable growth, the crystals settle and may no longer be monitored by the methods chosen. After settling occurs, the crystal does not grow nearly as fast either because it is no longer completely surrounded by nutrients making the growth slow down or essentially stop. If a technique could be devised to keep the crystals in solution for a much longer period of time, perhaps a better understanding of the crystallization mechanism could be determined. Experiments in microgravity, or outer space, have shown that crystals that do not settle, can remain in contact with nutrients and may continue to grow with less defects[31]. Combining the
aforementioned reverse micelle synthesis and this microgravity effect would allow for a much more thorough analysis and may lead to a more accurate understanding of the crystal growth process. Al Sacco and coworkers have done some experiments in microgravity growing zeolites, but they were only able to study the finished product after the gel had settled and dried[32, 33]. The crystals were in fact found to be larger and less defective, which gives us the hope that eventually we can monitor the growth of these larger crystals, in-situ and in microgravity conditions.

The other most notable drawback of the reverse micelle growth system is the thermal instability of reverse micelles. Growth of zeolites requires higher temperatures than standard reverse micelles can endure, therefore making this route futile for zeolite synthesis. Reverse micelles are not stable at all temperatures and will phase separate if taken outside of their stable range. Most zeolites require temperatures in the 90-200°C range to form in a reasonable time frame. Seemingly, these two systems are incompatible, but perhaps, new surfactant systems could allow for higher temperatures to be reached, certain zeolite frameworks will be found that can be synthesized at lower temperatures, or novel heating methods could be employed to bridge these two systems.

1.4 Microwaves

Standard surface techniques of heating depend on several factors such as radiation, convection or conduction or a mix of those. Typically these methods are slow and the overall heating is dependent on specific heat, thermal conductivity and density
(collectively labeled the diffusivity or thermometric conductivity) of the material being heated[34]. The relationship is as follows:
\[ \kappa = \frac{K}{\rho c}, \]
where \( \kappa \) is the diffusivity, \( K \) is the thermal conductivity, \( \rho \) is the density and \( c \) is the specific heat. Since standard hydrothermal heating is slow, other techniques for heating are constantly being explored to improve efficiency and curtail long processes.

Microwave radiation (900 MHz or 2450 MHz) is used extensively in our daily lives to heat things quickly and easily as is reflected in the large market for microwave dinners. The key to microwaving food is to have an adequate supply of water, because the water is what absorbs the microwaves and heats from within the food. If the concept of how microwaves work to heat is understood, then it can be applied to synthesis systems to perhaps give novel synthetic routes for zeolitic materials of interest.

### 1.4.1 Dielectric Constant

Permittivity, \( \varepsilon \), of a medium is the measure of the ability of a material to resist the formation of an electric field within. The dielectric constant, \( \varepsilon_r \), specifies the relative permittivity of a material such that
\[ \varepsilon_r = \frac{\varepsilon}{\varepsilon_0}, \]
and \( \varepsilon_0 \) is the permittivity of free space. In a vacuum (free space), the permittivity \( \varepsilon \) is just \( \varepsilon_0 \), so the dielectric constant is unity:
\[ \varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = 1. \]
Substances with higher dielectric constants have a greater response (heating) when placed in microwave radiation. This is due to their dipole moments aligning with the microwaves. As the microwaves alternate, the molecules attempt to realign and are in a constant state of mechanical oscillation. Frictional forces within the molecule cause heat to evolve[35]. Some relevant dielectric constants can be seen in Table 1.2.

1.4.2 Microwave Reverse Micelle Synthesis

From what is outlined above, it is obvious that water heats readily in the presence of microwave radiation and that non-polar solvents do not heat appreciably in the same situation. This effect can work nicely for heating the water cores of reverse micelles that have a small water core inside a surfactant with the bulk of the solution being a fairly non-polar oil. Essentially, it allows for a local heating effect in the water cores and the bulk solutions temperature is not effected as dramatically. Since it is established that reverse micelles breakdown above a certain temperature, if the bulk solution remains below that temperature, even as the water cores surpass it, a reverse micelle environment could theoretically be maintained.

1.5 X-Ray Diffraction (XRD)

X-Ray diffraction is a powerful analytical technique discovered in 1912 by von Laue. It is used primarily as a qualitative technique to identify unknowns by comparing their diffraction patterns to known patterns. However, it can also be used as a
quantitative tool. In 1992, Skoog and Leary stated, "The X-ray powder diffraction method is unique in that it is the only analytical method that is capable of providing qualitative and quantitative information about the compounds present in a solid sample." They continue to say that, instead of just determining the percentage of K⁺ and Br⁻ in a sample, XRD can be used to determine the actual percentage of KBr compound. An XRD works by accelerating electrons using a high voltage. As the electrons then hit a source, they decelerate rapidly and produce X-rays. The X-rays are directed at the sample at an angle $\theta$. The sample diffracts the incident beam and the X-rays hit a detector located at $2\theta$ from the original beam.

Usually, samples for a diffraction measurement are fine homogenous powders. If the sample is not originally like that, it is then ground into a fine powder. This way, every possible orientation of crystallites in the sample is achieved. They are then usually packed into a sample holder. In this manner, when the X-ray beam hits the sample, every possible reflection can occur from each of the orientations. Reflections occur both at the surface layer, but some X-rays can penetrate further and be reflected from other planes within the crystal. Since crystals have a regular structure, the reflection pattern from the various layers becomes the diffraction pattern. In some cases, if a homogenous powder is not possible, an XRD can still be taken to confirm identity, but the data is useless for quantitative analysis, as a preferred orientation effect can make some peaks larger and some smaller which would alter the quantitative results.

The governing equation behind XRD is known as Bragg’s Law. Crystal lattice spacings can be determined from diffraction patterns. Also, diffraction patterns can be
predicted for crystals for which the lattice spacings are already known. Using the crystal lattice in Figure 1.13, we can derive Bragg’s Law as follows:

\[ AB + BC = n\lambda, \]

considering the arrows are x-ray radiation and B and E are atoms the radiation scatters off of. As long as \( n \) is an integer, the radiation will be in phase at EC. Since,

\[ AB = BC = d \sin \theta, \]

and \( d \) is the spacing between the planes, constructive interference occurs when

\[ n\lambda = 2d \sin \theta. \]

This is Bragg’s law, and the constructive interference that results from this relationship creates the diffraction pattern.

1.6 Ultraviolet-Visible Absorption Spectroscopy (UV-Vis)

UV-Vis Spectroscopy uses the wavelengths of light in the range of 180-780 nm. These wavelengths are emitted from a source and focused on the sample cuvette. The detector collects the light that has made it through the sample and then can determine the amount of each wavelength that is absorbed by the sample. The range of wavelengths desired is scanned in succession and plotted as absorbance versus wavelength. The governing equation in UV-Vis spectroscopy is Beer's Law or

\[ A=abc, \]

where \( a \) is a proportionality constant called absorptivity, \( b \) is the path length thru the sample in centimeters and \( c \) is concentration in grams per liter. When the concentration
is reported in moles per liter, the absorptivity is then classified as the molar absorptivity and is designated by $\varepsilon$, such that Beer’s law is written as:

$$A = \varepsilon bc.$$ 

One of the major limitations with UV-Vis absorption is that concentrations must be relatively low, on the order of $10^{-2}$ M. When concentrations are higher, molecule/molecule interactions can alter absorbing abilities and change the wavelengths that are absorbed. Also, if the concentration is high enough and the solution is colored, the light may be absorbed too readily and not be able to pass completely thru the sample. This type of problem is typically corrected by changing to a sample cuvette with a shorter path length.

1.7 Atomic Force Microscopy (AFM)

1.7.1 Instrumentation

Atomic Force Microscopy (AFM) is a powerful analytical technique that allows atomic level imaging of surface structures. Typically, an AFM instrument is composed of a cantilever-tip assembly, a detector that measures the cantilever displacement, and feedback electronics to maintain instrument parameters[37]. Using a (X, Y, Z) piezoelectric translation stage, a sample, supported on a solid substrate, can be scanned with angstrom precision in two-dimensions. A laser is positioned to strike the back of the cantilever from an angle and the reflected beam is collected on a photodiode detector. When the tip is deflected from the surface by a change in topography, the movement, even as small as several angstroms, is detected.
1.7.2 Contact Mode AFM

There are three major modes by which images are taken: contact (repulsive), non-contact (attractive) and tapping modes. In contact mode, the tip is in constant contact with the surface being scanned, and scanning occurs in a (X, Y) raster pattern. Rastering is a scanning technique where the tip is swept across the surface in a straight line, then returned to the starting position, shifted by a standard increment and then swept across again. This pattern is repeated until the entire surface being imaged is scanned. The Z position is usually altered during scanning to maintain a certain force constant[37]. Generally, this mode is used for hard, flat samples since the tip applies a force to the surface and can damage the surface of the sample.

1.7.3 Non-contact Mode AFM

Non-contact mode is less common and was designed to minimize the contact with the surface so as to not damage the sample. The tip floats above the surface of the sample close enough so that Van der Waals forces between the tip and the sample can be detected. The Van der Waals forces are quite weak so in order to get better resolution, the tip is oscillated slightly. Then a change in amplitude, phase, or frequency of the tips oscillations is measured. Non-contact mode is not very effective in liquids because of the weakness of the Van der Waals forces, and the fact that the liquid itself may influence the cantilever.
1.7.4 Tapping Mode AFM

Perhaps the best alternative for most situations is tapping-mode AFM. This involves oscillating the tip near resonance and then lowering the tip to the surface resulting in the tip intermittently contacting, or tapping, the sample surface. Since the tip is not dragged across the surface, essentially no lateral forces are applied and the structure of the surface can remain without defect[37].

1.7.5 AFM Tip Structure

Tips are usually made of Si or Si$_3$N$_4$, but recently, carbon is getting more attention as a viable tip. The tip must be durable, but the smaller in diameter it is, the better the resolution will be. Current tips of Si have radii of curvature in the range of 5-10 nm and Si$_3$N$_4$ have radii of curvature between 20-60 nm. Treating these tips in certain ways will reduce those radii to 5 nm for Si$_3$N$_4$ and less than 5 nm for Si. However, the tip properties are not consistent, making high-resolution imaging difficult to reproduce. Carbon nanotubes with radii of 0.35-2.5 nm are reproducible structurally and are strong enough to remain intact while in contact mode[37].
1.8 Scanning Electron Microscopy (SEM)

1.8.1 Principle

Scanning Electron Microscopy (SEM), present in the analytical world for over 30 years, is another surface imaging technique with a magnification range large enough to image both macro- and microstructures[38]. It involves rastering a beam of electrons across the sample's surface. The raster pattern is the same as described for AFM. The beam of electrons is produced by an electron gun. Detection can vary depending on what is being measured, whether it is backscattered, secondary, or Auger electrons, X-ray fluorescence or other photons of various energies[39].

1.8.2 Thermionic Electron Gun

The beam diameter depends on the type of gun used. A thermionic electron gun will supply a beam approximately 10-50 µm, and a field emission gun supplies a beam of about 10 nm in diameter. The thermionic gun usually consists of a heated tungsten filament bent to achieve a V-shaped tip. If a greater brightness is desired, a lanthanum hexaboride (LaB₆) rod is used. The cathodic tip is kept at a potential of 1 to 50 kV with respect to the anode. The filament is surrounded by a grid cap, or Wehnelt cylinder, negatively biased with respect to the filament. The induced electric field serves to concentrate the electrons into a single spot called the crossover[39].
1.8.3 Field Emission Gun

The field emission gun utilizes a tungsten or carbon cathode with a very sharp tip (100 nm or less). The cathode is held at a high potential and electrons are formed as a result of tunneling. In this case, no thermal energy is required to free the electrons as the potential barrier that usually detains them is overcome. Field emission and LaB$_6$ sources require better vacuums to maintain the purity of their sources[39].

1.9 Light Scattering

1.9.1 Static Light Scattering

There are two basic types of light scattering. Static Light Scattering (SLS), which also carries the names low-angle, multi-angle, classical and Rayleigh light scattering, is an intensity measurement to determine the molecular weight and the second virial coefficient. It is necessary to know the concentration and refractive index of the sample being measured so that the root mean square radius, also known as the radius of gyration, can be determined. For chromatographic measurements, this is the more desired technique, but for size measurements, Dynamic Light Scattering is the instrument of choice[40].
1.9.2 Dynamic Light Scattering (DLS)

DLS not only provides size related information, but information on molecular dynamics as well[5, 40]. The measurements are based on Brownian motion or the random motion of particles in solution. Larger particles move more slowly in solution than their smaller counterparts. As long as certain parameters such as viscosity and refractive index of a solution are known, this difference in speed allows for correlations to be made to determine the size of the particles. "A limited application of dynamic light scattering is to get particle size information, but it doesn't measure size. It measures mobility." Attributed to Timothy Lodge, a polymer scientist in The University of Minnesota's chemistry department, this quote accurately summarizes the technique[40]. Other names for DLS are quasi-elastic light scattering (QELS) and photon correlation spectroscopy.

1.9.3 Principles of Dynamic Light Scattering

Directing a laser beam through a sample with small particles in solution (suspended) causes the light to be scattered when it contacts the particles. The scattered photons can be captured by a detector and correlated to determine size. This is accomplished as a result of the scattered light's intensity fluctuating as the suspended particles move into and out of the laser's beam.
1.9.4 Analysis of Light Scattering Data

Software provided by Brookhaven Instruments supplies five different methods for analyzing the data collected. The methods include cumulants, double exponential fit, exponential sampling, non-negatively constrained least squares (NNLS), and CONTIN. Each of the methods uses a different transform to give the particle size. The cumulants method was determined to be the best fitting for the purposes of the ZnPO systems and is the only method reported on. For comparison, several standards were run and an example of the correlation data is shown in Figure 1.14 for 100 nm polystyrene beads. The detector was situated at a 106° angle from the incident laser beam. Cumulants calculated a diameter of 103.5 nm, while exponential sampling and NNLS gave mean diameters of 88 nm and 91 nm, respectively.

1.10 Purpose

Microporous materials are still not well understood even though they are becoming more and more of an integral part of our daily lives. Fundamentals are sometimes overlooked once applications are found that utilize the properties that result from the novel structures. Within the following chapters, several fundamentals are explored. A templated system is monitored closely to determine if mixing order is critical to forming desired products. A reverse micelle system for growing gold nanoparticles is studied to determine if microwave radiation can effect the growth
environment within the reverse micelle. This reverse micelle/microwave system is then adapted to the growth of microporous faujasitic zincophosphate.

Several analysis techniques including XRD, UV-Vis, SEM, AFM, TEM and DLS are employed to more fully analyze the properties of the gold nanoparticles and microporous materials.
<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Process</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faujasite (Zeolite Y)</td>
<td>Cracking</td>
<td>Gasoline, fuel oil</td>
</tr>
<tr>
<td>Faujasite (Zeolite Y)</td>
<td>Hydrocracking</td>
<td>Kerosene, jet fuel, Benzene, Toluene, Xylene</td>
</tr>
<tr>
<td>Mordenite</td>
<td>Hydroisomerization</td>
<td>iC₆, C₇</td>
</tr>
<tr>
<td>Mordenite</td>
<td>Dewaxing</td>
<td>Low pour point lubes</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Xylene Isomerization</td>
<td>p-xylene</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Benzene Alkylation</td>
<td>Ethylbenzene (styrene)</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Ion-exchange</td>
<td>Detergents</td>
</tr>
<tr>
<td>Zeolite X</td>
<td>Adsorption</td>
<td>Separation of gases</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Ion-exchange</td>
<td>Radioactive waste cleanup</td>
</tr>
</tbody>
</table>

**Table 1.1.** Typical zeolites, their uses, and products obtained by their use.
Table 1.2. Dielectric constants of some materials relevant to the research reported in this dissertation.

<table>
<thead>
<tr>
<th>Medium</th>
<th>$\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>1.0000</td>
</tr>
<tr>
<td>Air</td>
<td>1.0006</td>
</tr>
<tr>
<td>Heptane</td>
<td>2.0</td>
</tr>
<tr>
<td>Teflon</td>
<td>2.1</td>
</tr>
<tr>
<td>Isooctane</td>
<td>2.1-2.3</td>
</tr>
<tr>
<td>Water (100°C)</td>
<td>55.3</td>
</tr>
<tr>
<td>Water</td>
<td>81</td>
</tr>
</tbody>
</table>
Figure 1.1. Various common aluminosilicate zeolite frameworks.
Figure 1.2. A simplified diagram of how various zeolite frameworks with the sodalite framework are related. The sodalite cage shown in the middle is found in all four frameworks shown. The main difference that can be seen here, is how the sodalite cages are joined to one another. For simplicity purposes, the bonded O is usually represented as a straight line as is displayed with the sodalite cage in the middle. (Adapted from [41]).
Figure 1.3. The S4R and S6R structural units of microporous materials are shown at the top and the β-cage unit that consists of 6 S4R units and 8 S6R units.
Figure 1.4. The D4R and D6R structural units of microporous materials shown at the top. Sodalite (a), zeolite A (b) and faujasite (c) structures. D4R units connect the β-cages in zeolite A and D6R units link the β-cages in the faujasite structure.
Figure 1.5. Some proposed building units for zeolites and the type of zeolite formed from each separate unit[42].
Figure 1.6. Structures of common surfactants. The AOT is anionic, DODMAC is cationic and Tween-85 is non-ionic.
Figure 1.7. Microemulsions that form from surfactants in both inorganic and organic solvents.
Figure 1.8. Top picture is that of a micelle with the surfactant’s aliphatic tails entrapping oil on the inside and the polar head groups forming the outer layer. The bottom diagram is that of a reverse micelle whose polar head groups trap water inside as the aliphatic tails are left exposed to the oil solvent (adapted from[22]).
Figure 1.9. Schematic of the four types of Winsor systems.
Figure 1.10. Structure of 1,4-Diazo bicyclo[2.2.2]octane, a template for faujasitic microporous materials used here for ZnPO-X.
Figure 1.11. Diagram of a reverse micelle. This particular one is an AOT reverse micelle which shows different water types within the reverse micelle leading to different uptake properties.
Figure 1.12. Schematic of a reaction between two reverse micelle solutions that shows collisions of the two reactant reverse micelles and the growth of a precipitate.
Figure 1.13. Diffraction pattern of a crystal lattice (Adapted from [43]).
Figure 1.14. Correlation data as seen from the Brookhaven Instruments 9000AT digital correlator. This data is then transformed to the particle size of which the cumulants method is used for the size in the upper right corner of the screen.
References


CHAPTER 2

SYNTHESIS OF ZINCOPHOSPHATE FAUJASITE (ZNPO-X):
ROLE OF A DIRECTING UNIT (DABCO-PHOSPHATE)

2.1 Introduction

2.1.1 Microporous Materials

Microporous solids are technologically important because of their applications in petroleum, chemical and consumer industries. These materials include a large group of solids of varying chemical composition as well as porosity. The framework structure is made up of interconnecting T-O-T' bonds where T and T' can be Si, Al, P, As, Ga, Fe, Co, Zn, B and host of other elements[1, 2]. The T elements are typically bonded to four oxygen atoms in a tetrahedral geometry. The best known of these materials are aluminosilicate zeolites, and synthesis of novel frameworks has the potential to lead to new technologies. However, crystal growth of these materials is a complicated process[1].
2.1.2 Synthetic Pathways and Analysis

Typical syntheses of these materials are done via hydrothermal methods, and involve rapid formation of an insoluble gel-like material, that goes through a complex sequence of depolymerization and polymerization reactions to form nuclei that grow into crystals. Various spectroscopic studies, including Raman, NMR, small angle X-ray and neutron scattering, of starting materials, intermediates and products have been carried out to study the mechanism of zeolite nucleation and crystal growth[3-7].

2.1.3 Mechanistic Possibilities

The mechanism as to how microporosity is generated during such crystal growth processes is not yet clear. It has been proposed that in the presence of organic molecules, the organic-inorganic-water interactions are modified by electrostatic and hydrophobic forces to generate cavities, around which the inorganic structure links itself[7]. With enough knowledge at both the molecular and macroscopic level, synthesis by design will become possible. Towards this effort, we have investigated novel routes of microporous material crystallization. In particular, a method using reverse micelles as the source of reactants has been successfully employed in our laboratories for synthesis of microporous zincophosphates (ZnPO)[8-10]. Dissolution studies of ZnPO’s have also provided information on the detaching/dissolving units[11].

During the past decade, zincophosphates with both condensed and open framework structure of various topologies have been reported[12-19]. The importance of
amine-phosphates as intermediate species in the synthesis of zinc and other metal phosphate structures has been recognized[17-19].

2.1.4 Focus

In this chapter, the focus is on understanding the structure directing property of 1,4-diazabicyclo[2.2.2]-octane (DABCO) molecule in the crystallization of ZnPO-X. By systematic variation of the order of mixing reactants for the crystallization of ZnPO-X, it was found that DABCO and phosphate ions in the same reactant solution promoted crystallization of ZnPO-X. This motivated us to isolate DABCO-phosphate crystals from a typical reactant composition and determine its crystal structure. Previous studies have reported formation of DABCO-phosphate crystals, with the DABCO molecule being doubly protonated with neutralizing HPO$_4^{2-}$ groups[17, 18]. Under our synthesis conditions, a singly protonated DABCO molecule with H$_2$PO$_4^-$ crystal was isolated. We also report that upon mixing the DABCO-phosphate salt with other solid reactants promotes the formation of ZnPO-X. This result broadens the type of zincophosphates that can be synthesized by mixing reactants in the solid state, the only previous example being sodalite, a small pore framework[20].
2.2 Experimental

2.2.1 Materials

Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) (Aldrich, 98%), phosphoric acid (H$_3$PO$_4$) (AR Grade, Mallinckrodt, 85%), H$_3$PO$_4$ (Aldrich, 98%), 1,4-diazabicyclo[2.2.2]octane (DABCO) (Aldrich, 98%), sodium hydroxide pellets (NaOH) (98.8%, Baker Analyzed), and α-alumina (99.9%, Alfa AESAR) were used as received.

2.2.2 Synthesis of ZnPO-X

Synthesis reactions of ZnPO-X were carried out following a reported literature procedure[16]. In a typical experiment, 6.5345 g (58.25 mmol) of DABCO, 0.4300 g (10.75 mmol) of NaOH, and 3.32 g of 85% H$_3$PO$_4$ (28.80 mmol) were dissolved in 45 mL of water and cooled to 4 °C. To this solution was added a pre-cooled (4 °C) solution of 5.95 g (20.00 mmol) of Zn(NO$_3$)$_2$·6H$_2$O in 5 mL of water which immediately forms a gel and was maintained at 4°C. The crystallization process was stopped at specific times, the solids recovered and powder patterns were recorded. The relative amount of ZnPO-X was determined using α-alumina as an internal standard. In a typical method, 0.050 g of α-alumina and 0.250 g of a ZnPO-X sample were mixed together in a small glass vial. The vial was capped and shaken with a Vortex Genie-2 for 5 minutes to ensure homogeneous mixture and then the XRD pattern was collected.
2.2.3 Synthesis of DABCO-phosphate

The preparation of DABCO-phosphate crystals was carried out by dissolving 11.218 g (100 mmol) of DABCO and 8.0 g of 85% H₃PO₄ (69.38 mmol of H₃PO₄) in 45 mL of water, with DABCO, phosphate and water at a molar ratio of 3:2.1:75. Reaction mixture became hot due to exothermic reaction. Upon cooling to room temperature, ethanol was added with vigorous stirring to induce crystallization and kept in a refrigerator overnight. The yield was 98% based on DABCO used. To grow single crystals, microcrystalline DABCO-phosphate material was dissolved in a minimum amount of water and placed in a test tube. This solution was layered with an excess of ethanol and kept aside at room temperature (25°C). Within 3 days, single crystals of diffraction quality were observed at the interface of water solution and ethanol.

2.2.4 Crystal Structure Determination of DABCO-phosphate

Dr. Ramsharan Singh, a former post-doc completed this section of the project and his hard work is greatly appreciated. The data was collected from a colorless rectangular chunk-like single crystal. Examination of the diffraction pattern on a Nonius Kappa CCD diffractometer indicated a triclinic crystal system. Data collection was done at 200 K using an Oxford Cryosystems Cryostream Cooler. The data collection strategy was set up to measure a hemisphere of reciprocal space with a redundancy factor of 3.8, which means that 90% of the reflections were measured at least 3.8 times. A combination of phi and omega scans with a frame width of 1.0° was used.
Data integration was done with DENZO, and scaling and merging of the data was done with Scalepack[21]. Merging the data and averaging the symmetry equivalent reflections resulted in an $R_{int}$ value of 0.028. The teXsan[22] package indicated the space group to be $P\bar{1}$ based on the intensity statistics. Relevant details of the single crystal structure determination of the DABCO-phosphate are presented in Tables 2.1-2.3.

The structure was solved by direct methods in SHELXS-86[23]. The asymmetric unit consists of $\text{H}_2\text{PO}_4^-$, a singly protonated DABCO molecule, and a water molecule. Full-matrix least-squares refinements based on $F^2$ were performed in SHELXL-93[24]. The hydrogen atoms bonded to carbon atoms were included in the model at calculated positions using a riding model with $U(H) = 1.2\times U(eq)$ (attached atom). All of the other hydrogen atoms were located on a difference electron density map and refined isotropically. The final refinement cycle was based on all 2306 intensities and 147 variables and resulted in agreement factors of $R1(F) = 0.034$ and $wR2(F^2) = 0.085$. For the subset of data with $I > 2\sigma(I)$, the $R1(F)$ value is 0.030 for 2084 reflections. The final difference electron density map contains maximum and minimum peak heights of 0.25 and -0.42 e/Å$^3$ respectively. Neutral atom scattering factors were used and include terms for anomalous dispersion.

2.2.5 Synthesis by Mixing Reactants in the Solid State

Synthesis of ZnPO-X by grinding together solid reactants was performed by the following the methods described in the next two sections.
2.2.5.1 Reactions Using H$_3$PO$_4$ as a Source of Phosphate Ions

Solid ingredients, Zn(NO$_3$)$_2$·6H$_2$O, H$_3$PO$_4$, DABCO and NaOH were used as reactants. Reaction compositions were similar to those for normal solution synthesis, but with no added water. In a typical experiment 1.6336 g (14.56 mmol) of DABCO, 0.7199 g (7.2 mmol) of H$_3$PO$_4$ (98%), 0.1075 g (2.69 mmol) of NaOH and 1.4875 g (5.00 mmol) of Zn(NO$_3$)$_2$·6H$_2$O were mixed in a mortar pestle under dry N$_2$ to start the reaction, and maintained in this state for the duration of the reaction (in a glovebag). (This section performed by Dr. Ramsharan Singh.)

2.2.5.2 Reactions Using DABCO-phosphate as a Source of Phosphate Ions

In this experiment, DABCO-phosphate was used as the source of phosphate. To match the reaction composition to the H$_3$PO$_4$-based synthesis, additional mount of DABCO was needed. In a typical experiment 1.6427 g (7.20 mmol) of DABCO-phosphate, 0.8260 g (7.36 mmol) of DABCO, 0.1075 g (2.69 mmol) of NaOH and 1.4875 g (5.00 mmol) of Zn(NO$_3$)$_2$·6H$_2$O were mixed in a mortar and pestle to start the reaction and were maintained under dry N$_2$. (This section performed by Dr. Ramsharan Singh.)
2.2.6 Characterization

The X-ray powder patterns were determined with a Bruker D-8 X-ray diffractometer using nickel-filtered Cu Kα (λ = 1.5405 Å) radiation. Galbraith Laboratories (Knoxville, Tennessee) performed the elemental analysis. Optical microscopy was accomplished with a Nikon Eclipse E600 microscope equipped with a Javelin SmartCam and Boeckeler VIA-170 image analysis system.

2.3 Results

2.3.1 Synthesis of ZnPO-X

The kinetics of the crystallization of hydrothermal synthesis of ZnPO-X is shown in Figure 2.1. For this study, a series of reactions were set up. The products were isolated at certain times and XRD patterns were recorded. The sample recovered from these experiments was pure ZnPO-X as determined by comparison with literature[12, 16, 25]. Using α-alumina as an internal standard (2θ=37.8°), the increase in the amount of ZnPO-X (2θ=30.7º) in the product mixture was monitored (standard deviations of the XRD measurements using α-alumina as standard was < 2%). The choice of the 20=30.7º peak for ZnPO-X was made based on its proximity to the α-alumina standard. Crystals were found within the first minute and the growth process was complete within the first 10 to 20 minutes.

This fast reaction was also substantiated with optical microscopy. Particle size distributions were determined from 100 random particles in each of 7 samples that were
grown for 0.5, 2, 6, 10, 15, 20, and 300 minutes. The growth curve is shown in Figure 2.2, and the particle size distributions are shown in Figures 2.3-2.6. Particle size is shown to reach its maximum size within the first 10 minutes.

2.3.2 Reactions Using Different Combinations of Reactants

Reactions using different combinations of reagents split into two reactants, but with overall similar composition were set up as outlined in Table 2.4. These reactants were mixed and solid products were recovered from the solutions at periodic intervals of 1 min, 30 min, 1h and 2h. The XRD patterns of the products indicated that all six reactions produced ZnPO-X within 30 min. Thus, in order to investigate the initial rates of formation, we have focused on the products present after the first minute of reaction and are listed in Table 2.4. Figure 2.7 shows the XRD patterns of the reaction products recovered after 1 min from reactions 5 (Figure 2.7a) and 2 (Figure 2.7b). The products were not washed prior to the diffraction experiments. As exemplified by Figure 2.7, the primary products of the reactions were ZnPO-X (marked as X in Figure 2.7) and hopeite (Zn₃(PO₄)₂·4H₂O, marked as H). These assignments were based on pure compounds synthesized in the laboratory and are also consistent with literature reports[25-27]. (Hopeite is JCPDS file No. 33-1474.) It is important to note that for the weak overlapping peaks in Figure 2.7, there is some ambiguity in assignment of the peaks, since there could be slight shifts in the peaks, even though all samples were conditioned similarly.
Except for Reaction 3, in all other cases, ZnPO-X emerges as the initial major product when DABCO and phosphate are in the same reactant batch. In cases such as Reaction 2, the presence of phosphoric acid and zinc ions in the same reactant mixture led to rapid precipitation of hopeite, thus impeding the association of DABCO and phosphate. However, for Reaction 7, presence of all three components, zinc ion, phosphate and hydroxide led to a clear solution (Reactant A), which upon reaction with a DABCO solution produced ZnPO-X as the major species. In this system, the DABCO was free to associate with the phosphate species upon mixing because Reactant A was a homogeneous solution.

2.3.3 Isolation and Structure of the DABCO-phosphate Salt

From a clear solution with a molar composition of DABCO:0.7H$_3$PO$_4$:25H$_2$O, crystals were produced by inducing precipitation with ethanol at ambient temperature. A composition based on the ZnPO-X system (without Zn$^{2+}$, DABCO:0.5H$_3$PO$_4$:43H$_2$O) also produces a similar DABCO-phosphate salt, as verified by powder diffraction data (not shown). The ORTEP diagram of the asymmetric unit of DABCO-phosphate is given in Figure 2.8a and the unit cell diagram is shown in Figure 2.8b. The structure consists of a 1:1 adduct of H$_2$PO$_4$ and singly protonated DABCO molecule with one molecule of water of hydration. The structure forms a sheet with alternating phosphate and DABCO molecules linked via the water molecule. There is extensive hydrogen bonding in the crystal structure of DABCO-phosphate. The donor-H…acceptor angles are >171° indicating strong hydrogen bonding (Table 2.1). Table 2.5 compares the crystal data and
structure refinement parameters for the complex synthesized in this study with a similar complex but with doubly protonated DABCO and \( \text{HPO}_4^{2-} \)[18]. Further details on the atomic coordinates for the DABCO-phosphate complex as well as the bond lengths, angles and hydrogen bond lengths and angles are provided in Tables 2.1-2.3.

The DABCO-phosphate polycrystalline powder isolated by ethanol-induced precipitation gave the following elemental analysis: P- 14.05%, C- 33.05%, H- 7.22%, N- 12.86%, and matched best with the formula \( \text{N(CH}_2\text{CH}_2\text{)}_3\text{NH}^+ \text{H}_2\text{PO}_4^- \cdot 0.5\text{H}_2\text{O} \), whereas the formula calculated from the single crystal data suggests a structure with one molecule of water of hydration.

### 2.3.4 Synthesis of ZnPO-X by Mixing Reactants in the Solid State

Two sets of syntheses were carried out by mixing solid reactants using either \( \text{H}_3\text{PO}_4 \) or DABCO-phosphate salt as the source of phosphate ions, the other reagents being crushed \( \text{NaOH} \) and \( \text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \). Care was taken to ensure that the overall composition in both sets of reactions was identical and the reaction was done under dry \( \text{N}_2 \). After the initial grinding, the reaction was allowed to proceed undisturbed and samples were collected over a 50 h time frame and the diffraction patterns measured (under similar conditions). Figures 2.9a and 2.9b compare the XRD pattern of samples recovered from DABCO-phosphate and \( \text{H}_3\text{PO}_4 \), respectively after 50 min of reaction (samples were not washed, data collected under identical conditions). The material prepared with the DABCO-phosphate salt exhibits stronger peaks of ZnPO-X. Along with ZnPO-X (X) and hopeite (H), unreacted DABCO (D; JCPDS file no. 21-1617)[26],
(DABCO-phosphate (DP, assignment made based on this study) and Zn(NO$_3$)$_2$·6H$_2$O (N, based on this study) were also observed. In the case of the reaction with H$_3$PO$_4$, peaks at 8 and 12° are typical of ZnHPO$_4$ (JCPDS, 37-0315)[26]. Figure 2.10 compares the XRD pattern after 50 h of reaction (samples washed with ethanol and data collected under identical conditions). Ethanol was used as solvent to avoid any transformation of reactants via contact with water. Crystals obtained from the reactant using DABCO-phosphate salt (Figure 2.10a) were purer with relatively lower hopeite contribution.

2.4 Discussion

The focus of this discussion is on the role of DABCO in crystallization of ZnPO-X. The induction time for the hydrothermal synthesis of ZnPO-X in the presence of DABCO is very short, occurring in less than a minute. Indeed, the motivation for the present study was to explore how DABCO accelerates ZnPO-X crystallization under such mild thermal conditions. Single crystal structure of novel zincophosphate open frameworks using DABCO as a structure directing agent have also been reported, showing the generality of this molecule as a structure directing agent[28-30].

There were two reasons to explore if a DABCO-phosphate unit was acting as an intermediary in the crystallization process of ZnPO-X. First, a DABCO-phosphate unit has been crystallized, suggesting its stability[17, 18]. Moreover, it has also been reported that addition of the DABCO-phosphate complex to Zn$^{2+}$ did produce ZnPO phases similar to when DABCO and H$_3$PO$_4$ were added independently[19]. Also, it was found that DABCO-phosphate will react with Zn$^{2+}$ to produce frameworks under considerably
milder conditions[19, 28]. Second, as we show in Table 2.4, ZnPO-X is nucleated more rapidly when DABCO and the phosphate are in the same reactant solution at the earliest stage of the synthesis. This suggests that association of DABCO and phosphate can promote ZnPO-X nucleation.

The DABCO-phosphate unit that crystallized from the reaction composition DABCO:0.7H₃PO₄:25H₂O in this study is slightly different from the complex reported earlier[17, 18]. The crystallization was induced by addition of excess ethanol to a clear solution at ambient temperature and the crystals consisted of a singly protonated DABCO molecule with H₂PO₄⁻ as the neutralizing anion. In the previous study[17, 18], DABCO-phosphate was crystallized from a more concentrated solution (DABCO : 1-2H₃PO₄ : 5H₂O) and contained a doubly protonated DABCO with HPO₄²⁻ as the neutralizing group, and proceeded through an amorphous gel and needed to be heated to 110°C for 6 h to produce plate-like crystals. However, both units crystallize in triclinic space group P̅1 and the unit cell dimensions and volumes are comparable, with the monoprotonated DABCO species resulting in a more compact unit cell. The detailed crystal data for both systems are compared in Table 2.5.

Evidence about the role of the DABCO-phosphate unit in directing the formation of ZnPO-X is also provided by the synthesis involving the solid-state reactants, where the presence of the salt led to an acceleration of the formation of ZnPO-X as well as higher purity. Even though no water was added to the solid-state synthesis reactions and they were kept under ambient conditions, the mixtures became moist due to the hydration water present in the reactants. A similar effect was reported for the solid-state synthesis of zincophosphate sodalite[20]. In the reaction system using DABCO and anhydrous
H$_3$PO$_4$, there is the possibility of association of these two species prior to ZnPO-X crystallization, considering the moist environment (the formation of ZnHPO$_4$ as an intermediate supports this idea). However, because of the necessity of association, the rate of crystallization is slower with the individual reactants as compared to the reaction using the DABCO-phosphate salt.

For cobaltophosphate synthesis, it was proposed that the DABCO-phosphate complex may orient the H$_2$O molecules in a specific geometry[17, 18]. These H$_2$O molecules are then replaced by Co$^{2+}$ on the path to bonding with phosphate to form the framework. The exact role by which the DABCO-phosphate complex directs the formation of ZnPO-X is unclear, especially in a typical hydrothermal synthesis. It is doubtful that the amine-phosphate indeed survives as a structural unit during the reaction, as amine-phosphates are highly water-soluble. The solid-state experiments reported here indicate that presence of preexisting DABCO-phosphate structural units do promote the formation of ZnPO-X, and even loosely arranged DABCO-phosphate units in solution may be able to promote the nucleation of ZnPO-X. The other possibility is that the synthesis is mediated by zinc phosphate primary building units[31]. Attempts at isolating such units from the ZnPO-X synthesis medium were unsuccessful.

Finally, the demonstration of the synthesis of ZnPO-X open framework structure by mixing solid reactants opens up a pathway to entrap large molecules in the supercages, as has been recently reported for sulfur and CdS entrapment in sodalite[20].
2.5 Conclusions

The hypothesis tested in this chapter is that DABCO and phosphate reactants can form DABCO-phosphate units that accelerate the nucleation of ZnPO-X. It was found that DABCO and phosphate in the same reactant solution nucleated ZnPO-X faster as compared to reactions where DABCO and phosphate were in different solutions. A DABCO-phosphate salt was crystallized from reaction mixtures typical for the formation of ZnPO-X (in the absence of Zn$^{2+}$) and its structure determined by diffraction. The rate of synthesis of ZnPO-X by mixing solid reactants was faster with DABCO-phosphate salt than when phosphoric acid and DABCO were separate, further suggesting the acceleration of ZnPO-X nucleation by DABCO-phosphate structural units.
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<td>N(1)-H(1N1)…O(1)</td>
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Table 2.1. Hydrogen bonds for DABCO-phosphate.
Table 2.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for DABCO-phosphate.

$^a$U(eq) is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

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**Table 2.3.** Bond lengths (Å) and angles (°) for DABCO-phosphate.
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<td>ZnPO-X + Hopeite (minor)</td>
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<td>DABCO+NaOH</td>
<td>Hopeite + ZnPO-X (minor)</td>
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<td>3</td>
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<td>NaOH</td>
<td>Hopeite</td>
</tr>
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<td>Zn(NO₃)₂+DABCO+NaOH</td>
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<td>Amorphous + Hopeite (minor) + ZnPO-X (minor)</td>
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**Table 2.4.** Reaction sequences.
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Table 2.5. Crystal data and structure refinement parameters for DABCO-phosphate.
Figure 2.1. Growth curve (based on crystallization kinetics) for ZnPO-X synthesis using Reaction 1 of Table 1. The y-axis is the ratio of the intensity of the ZnPO-X peak at 2θ=30.7° versus an internal standard alumina peak at 2θ=37.8°.
Figure 2.2. Growth curve of ZnPO-X synthesis using Reaction 1 from Table 1 determined by measuring diameter of particles under an optical microscope and plotting the average of their particle size distributions. Each point represents 100 measurements.
Figure 2.3. Particle size distribution based on 100 optical microscope measurements of ZnPO-X growth by Reaction 1 from Table 1 at a) 30 seconds and b) 2 minutes. Average size of a) 1.4 ± 0.2 microns and b) 1.9 ± 0.7 microns.
Figure 2.4. Particle size distribution based on 100 optical microscope measurements of ZnPO-X growth by Reaction 1 from Table 1 at a) 6 minutes and b) 10 minutes. Average size of a) $2.7 \pm 0.6$ microns and b) $2.6 \pm 0.6$ microns.
Figure 2.5. Particle size distribution based on 100 optical microscope measurements of ZnPO-X growth by Reaction 1 from Table 1 at a) 15 minutes and b) 20 minutes. Average size of a) 2.7 ± 0.9 microns and b) 2.6 ± 0.8 microns.
Figure 2.6. Particle size distribution based on 100 optical microscope measurements of ZnPO-X growth by Reaction 1 from Table 1 after 300 minutes. Average size of particles is $2.8 \pm 0.4$ microns.
Figure 2.7. Comparison of the diffraction patterns of products recovered from reactions one minute after mixing two reactants. (a) Reactant A = Zn(NO$_3$)$_2$ + NaOH, Reactant B = DABCO + H$_3$PO$_4$; (b) Reactant A = Zn(NO$_3$)$_2$ + H$_3$PO$_4$, Reactant B = DABCO + NaOH. (X = ZnPO-X; H = Hopeite)
Figure 2.8. (a) Asymmetric unit of the DABCO-phosphate complex. (b) Unit cell diagram of the DABCO phosphate complex.
Figure 2.9. Diffraction patterns from solid-state synthesis after 50 minutes of reaction (unwashed). (a) DABCO-phosphate complex as reagent (b) DABCO and H$_3$PO$_4$ are separate reagents. (X = ZnPO-X; H = Hopeite; D = DABCO; DP = DABCO-phosphate; Z = ZnHPO$_4$; N = Zn(NO$_3$)$_2$·6H$_2$O; U = undetermined)
Figure 2.10. Diffraction from solid-state synthesis after 50 hours of reaction (products washed with ethanol). (a) DABCO-phosphate complex as reagent (b) DABCO and H$_3$PO$_4$ are separate reagents. (X = ZnPO-X; H = Hopeite)
References


[26] XRD Pattern Processing software (JADES) titled MDI Jade 5.0.18, Materials Data, Inc., Livermore, California (www.materialsdata.com).


CHAPTER 3

INFLUENCE OF MICROWAVE RADIATION ON GROWTH OF GOLD NANOPARTICLES IN A REVERSE MICELLAR SYSTEM

3.1 Introduction

3.1.1 Metal Nanoparticles

Metal nanoparticle research has become more important recently as many new applications have surfaced. Nanoparticles have unique properties that differentiate them from larger bulk particles. They exhibit size dependent optical, electronic, catalytic and chemical properties[1-8]. Various applications come with these unique properties. Applications include, but are not limited to sensors[9], optics[10, 11], analytical probes[12, 13] and catalysts[2, 14].
3.1.2 Gold Nanoparticles

Gold was possibly the first metal used by humans. Gold is chemically inert; atomic number 79; atomic weight 196.9665; and melting point 1,064.43 °C (1337.43 K). It is unaffected by moisture, oxygen, or ordinary acids but is attacked by the halogens[15]. Gold is as its name suggests, golden or yellow in color. The above attributes describe bulk gold but some of these properties change as gold particles become smaller and smaller.

Gold atoms are known to oxidize instantly in air[16]. Buffat and Borel reported that the melting point of gold gradually decreases as a function of particle diameter, such that when gold reaches 3-4 nm in diameter, the melting point is near 700 K[17]. Mulvaney discussed the change in color of gold particles as a function of size. He reported atomic gold (~1 Å) is colorless, <1 nm clusters are orange, 3-30 nm nanoparticles are red, 30-500 nm particles are crimson to blue, and bulk gold (>500 nm) is the characteristic gold/yellow color[16]. Gold nanoparticles have garnered high interest due to their ease of production (typically reduction of HAuCl₄), stability (with appropriate capping agent), extensive background studies and modeling abilities for other colloidal metals. They are frequently deposited as monolayers and according to Graber et al. possess features that make them attractive for both basic and applied uses, including uniform roughness, high stability and biocompatibility[18].

Gold nanoparticle size has been controlled by a variety of synthetic techniques. The most notable being: use of a template, use of capping agents and altering the concentrations of the reactants. Additionally, a couple of post synthesis techniques have
been examined to determine how they alter particle size. These procedures are discussed below.

### 3.1.3 Synthetic Pathways

Both reverse micelle (description in Introduction Chapter)[19-27] and solution-based synthesis[28-34] are used extensively in gold nanoparticle synthesis. Chiang reported how concentration of metal salt, molar ratios of reductant to metal salt, sequence of addition and size of micelle droplet alter the size (~10 nm to ~80 nm), shape (rods, triangles, spheres and cubes) and dispersity of gold nanoparticles[25, 26]. Arcoleo and Liveri reported that the resultant gold nanoparticle size was highly dependent on the water loading levels of the microemulsions[23]. Mallick et al. used successive addition of metal ions to gold seeds (15-20 nm gold particles) to control the growth of 40-80 nm sized particles[30]. In a similar successive addition manner, Jana et al. prepared gold nanoparticles in the range of 5-40 nm starting with 3.5 nm seeds[31]. Seed-mediated synthesis coupled with the right template has also been utilized to grow gold nanorods in the presence of AgNO$_3$ with aspect ratios of ~5-15[28]. Johnson et al. also used a sequential growth process to grow nano-rods of length 30 nm (aspect ratio of 2) from 10 nm seeds[29].

The use of a capping or stabilizing agent to curtail growth and resist agglomeration is widely reported. Most capping agents contain sulfur and it is the strong affinity of sulfur to metal that allows for the compound to bond to the metallic surface and protect against further growth. Also, the capping agents create spacing between the
metallic nanoparticles keeping their inherent affinity toward one another from forming larger clusters. Such agents include thiols[20-22, 32], sulfides[20], dendrons/dendrimers[2, 35], telomers[36], polymers[37], citrate[29], xanthates[38] and amino groups[20]. Digestive ripening of a polydisperse gold particle sample in the presence of thiols[22] and laser-induced fragmentation[34] are post synthesis methods described to create gold nanoparticles with a narrow size distribution. Nanoparticles in the 2-6 nm and 1.7-3.4 nm size ranges were produced, respectively. Sonolysis in the presence of 1-propanol has also been reported to control gold reduction, which also allows control of nanoparticle size from about 30-120 nm[39]. All of these methods allow control of particle size, shape and size dispersion.

3.1.4 Microwave Radiation in Gold Synthesis

Microwaves have long been used to alter growth reactions. Early on, typical microwave reactions were carried out in a normal consumer microwave oven. Now, companies design microwave systems for lab synthesis. They have developed microwaves that can monitor and vary temperature, pressure, microwave power and also add a stirring element. The reaction vessels are placed on turntables so as to try to average out the “hot spots” common to microwave heating. These systems are designed to withstand high temperatures and pressures that are not available with using a microwave geared towards home use. Many growth systems have been introduced to microwaves with mixed results. For the most part, microwaves can cut reaction times by several orders of magnitude. A primary downfall currently facing microwaved reactions
is reproducibility. Current microwaves on the market have different geometries and therefore different hot zones. Even things such as reactor geometry have proven to dramatically effect the system under analysis[40].

Liu et al. reported that both size and size distribution of a microwaved gold growth system depend heavily on reaction temperature and rate of temperature increase. They show that 90 ± 16 nm gold nanoparticles are formed at 50 ºC while at 150 ºC, the nanoparticles are in the range of 20 ± 2 nm. Also, as the temperature ramp rate increases from ~8 ºC to 80 ºC, particles range from 37 ± 10 nm to 20 ± 2 nm respectively[41]. Jiang et al. utilized microwave radiation on an alcohol reduced HAuCl₄ system to create stable 11 nm gold nanoparticles[42].

### 3.1.5 Microwaving of Reverse Micelles

Microwaving a reverse micelle system is proposed as a synthetic approach aimed at locally heating the water cores to influence the growth dynamics. Organic solvents such as hexane, heptane and octane (nonpolar) do not heat readily when exposed to microwave radiation. If a water-in-oil reverse micelle in a bulk solution of heptane is exposed to microwave radiation, theoretically, the water core should absorb the majority of the radiation, therefore increasing the temperature. With the minute quantities of water involved, and with a high-powered microwave, the water cores can heat appreciably in only a short time exposed to the radiation. Several research groups have investigated microwaving reverse micellar growth systems for synthesizing materials such as TiO₂[43] and microporous aluminophosphate materials[44]. This quick heating
cannot be achieved in bulk solutions under typical hydrothermal conditions, making microwaves an ideal way to essentially flash heat the water cores.

Spatz et al. synthesized 5 nm TiO$_2$ particles, employing microwave radiation to selectively heat diblock copolymer reverse micelle water cores[43]. They reported that no bulk solution temperature increase was seen, however, in some cases that have been reported, the bulk solution temperatures have exceeded levels at which reverse micelles are stable, and phase separation is noted[44]. D’Angelo et al. noted that at microwave frequencies, the water component of a water/AOT/n-heptane reverse micelle system, dominates the response[45].

Fletcher, Howe and Robinson performed a systematic study on the stability of AOT based reverse micelles in various alkanes at various temperatures[46]. They discuss both low- and high-temperature phase boundaries such that there is a definite temperature range in which AOT reverse micelles are stable. These values vary greatly and the report gives data for alkyl chain lengths from 5-12 and for water loading levels from $w = 0$-100 ($w = [\text{H}_2\text{O}]/[\text{AOT}]$). The report reveals that at temperatures above the phase inversion temperature (p.i.t.), phase separation actually produces a liquid-crystalline phase that is most likely lamellar in structure containing AOT and water and a conjugate oil phase[46]. This type of separation is not desirable for the reverse micelle reactions and therefore temperature control is imperative.
3.1.6 Focus

A synthetic procedure to grow gold nanoparticles in reverse micelles was modified in such a way that a pulse of microwave radiation was introduced during the nucleation/growth timeframe. Both microwaved and non-microwaved samples were analyzed and compared to evaluate the effects that a microwave pulse has on particle size. Transmission electron microscopy (TEM) was primarily used to determine particle size distributions and average particle sizing. In each case, at least 140 particles were measured to determine the size distribution. Only particles with borders visible were measured and recorded to eliminate user bias. UV-Vis was used to reinforce the TEM studies.

3.2 Experimental

3.2.1 Materials

Dioctylsulfosuccinate sodium salt (AOT) (98%, Aldrich), n-heptane (Mallinckrodt), H AuCl₄·3H₂O (Hydrogen tetrachloroaurate (III), 99.99%, 49.5% Au, Alfa Aesar), N₂H₄·xH₂O (hydrazine hydrate, Aldrich), nanopure water (resistivity 18.0 ohms) and n-hexadecanethiol (98%, Lancaster) were all utilized.
3.2.2 AOT in Heptane

The surfactant solution of 0.1 M AOT (dioctylsulfosuccinate sodium salt) in heptane was prepared by dissolving 11.113 g of AOT in enough heptane to make 250 mL solution. This type of solution is used throughout the rest of the experimental section and is often referred to as the reverse micelle solution.

3.2.3 Reactant Solutions

A 0.5 M solution of HAuCl₄·3H₂O was prepared by mixing 1.6 mL of deaerated nanopure water and 0.2745 g of HAuCl₄·3H₂O. Various concentrations of the HAuCl₄·3H₂O solution were tested initially, but 0.5 M was chosen to be the model and to change the reaction rates, the reducing agent’s concentrations were varied. Solutions of hydrazine hydrate were prepared with the following concentrations: 2 M, 1 M, 0.5 M, 0.2 M and 0.1 M. Reactions with these hydrazine concentrations will be labeled as nMWXX and microwaved samples will be labeled as MWXX, with XX representing the hydrazine concentration. Hydrazine hydrate is not very stable, therefore, the hydrazine solutions had to be prepared immediately before use.

3.2.4 Reverse Micelle Solutions

The reverse micelles reactant solutions were prepared by a simple injection of reactant solution into the reverse micelle solution. Caution was used to add only enough
reactant solution such that one phase could be attained by sonication and shaking. A ratio of 0.13 mL reactant solution to every 12 mL of reverse micelle solution was employed for the gold growth in AOT/heptane.

### 3.2.5 Non-Microwaved Growth

A 0.065 mL aliquot of each of the HAuCl₄·3H₂O and hydrazine hydrate solutions was added to separate 6 mL portions of the AOT/Heptane solution. The solutions were then shaken and sonicated for about 30 seconds in order to suspend all of the water-based solutions to be encapsulated in the AOT reverse micelles. The two solutions were then mixed and allowed to react for four minutes. After 4 minutes of reaction time, 5 drops of hexadecanethiol were added to cap the gold particles and keep them from further growth or dissolution. A reaction where 15 minutes elapsed before capping was also ran to determine if size continued to increase at longer times.

### 3.2.6 Microwaved Growth Varying Hydrazine Concentration

The reverse micelle reactants were formed by adding 0.13 mL of the HAuCl₄·3H₂O and 0.13 mL of the hydrazine hydrate solutions (0.1, 0.2, 0.5, 1 and 2 M) to separate 12 mL portions of the AOT/Heptane solution. The solutions were then shaken and sonicated in order to encapsulate all of the water-based solutions in the AOT reverse micelles. The HAuCl₄·3H₂O solution was put into a microwave vessel, and sealed off except for the small ventilation hole. The hydrazine hydrate solution was injected into
the vessel through the ventilation hole. The vessel was closed and microwaving was started within 19 seconds of mixing. The microwave operated at 300 W for 2 minutes. The sample was then removed from the vessel and 10 drops of hexadecanethiol was added after a total of four minutes had passed since the initial mixing. The microwave used was CEM Corporation’s MARS 5 model. The resulting temperature was recorded to ensure that the heating was consistent from sample to sample. The final temperatures were all in the range of 37 °C – 39 °C. Typically this difference was a result of varying starting temperatures. The pressure did not increase enough (did not reach 1 psi) to register on the meter over the two minutes of microwaving.

3.2.7 Microwaved Growth Varying Microwave Exposure Time

Several experiments were run while varying the amount of time exposed to microwave radiation. A constant power was maintained (300 W) and constant concentrations of 0.5 M HAuCl₄·3H₂O and 1 M hydrazine hydrate. Reverse micelle solutions were made by dissolving (sonicating) 0.13 mL of the reactants in two separate 12 mL aliquots of the AOT in heptane solution. The HAuCl₄·3H₂O reverse micelle solution was put in the microwave vessel and sealed off except for the small ventilation hole. The hydrazine hydrate reverse micelle solution was then injected into the vessel through the ventilation hole. The lag time between injection of the hydrazine reverse micelle solution and starting the microwave exposure was about 17 seconds. Exposure times of 2, 4, 6, and 15 minutes were employed and then immediately after removing from the microwave, 10 drops of hexadecanethiol was added to cap the gold particles.
These experiments were run without regard to maintaining the integrity of the reverse micelles, as temperatures reached levels that may cause phase separation. Maximum temperatures of 37, 47, 56 and 81 °C were reached for the exposure times of 2, 4, 6 and 15 minutes respectively.

3.2.8 Scanning Electron Microscopy (SEM)

Scanning electron micrographs were taken of the gold nanoparticles before and after capping with thiols was attempted. The images were then obtained using a JEOL JSM-5500 SEM.

3.2.9 Transmission Electron Microscopy (TEM)

A Philips Tecnai TF20 transmission electron microscope was used to acquire images at various magnifications. A beam power of 200 kV was used to obtain the images. These TEM images were done at a low resolution and the images were mostly used for size distribution analysis, but some lattice details were apparent.

3.2.10 Ultraviolet-Visible Spectroscopy (UV-Vis)

A Shimadzu UV-2501PC spectrometer was used for all UV-Vis measurements. UV-Vis spectroscopy was run on two of the five hydrazine concentration growth samples (0.5M and 2M), in order to get a sample in two size regimes, less than 10 nm and larger
than 10 nm. The samples were cleaned to remove excess thiol, surfactant, and hydrazine before running the UV-Vis to eliminate as many variables as possible. The cleaning was done by rinsing six times with ethanol and three times with acetone, before resuspending in heptane (for analysis). Each rinse cycle included adding approximately 10 mL of the solvent, sonicating and shaking, then centrifugation at 5,000 rpm for 3 minutes. The 0.5 and 2M hydrazine samples were chosen based how clean the samples appeared and also, on amount of sample that was available. Concentrations had to be precise, so if there was not enough of the sample to weigh out accurately, the samples were discarded.

3.2.11 Dynamic Light Scattering (DLS)

Dynamic light scattering was attempted on the nanogold particles utilizing a Brookhaven Instruments 9000 correlator and a Coherent Innova 90C laser at 514 nm.

3.2.12 Atomic Force Microscopy (AFM)

Dr. Michael George at The University of Alabama, Huntsville attempted AFM studies of the nano-gold, but due to the small size of the particles and the geometry of the AFM tip, they were not successful. A different tip may alleviate these troubles, but STM has been recommended as a possible alternative for analyzing surface features. Surface feature studies were discontinued.
3.3 Results

One complication encountered in the microwave synthesis, was shortening the lag time between mixing of the two reactant solutions, and actual induction of microwaves to the mixture. With a special delivery apparatus, the lag time was cut to approximately 19 seconds. However, it has been shown in previous reports that the nanoparticles can reach their final size in a matter of seconds[24]. To slow the reaction down slightly, the hydrazine concentration was varied and the results of 5 concentrations (2 M, 1 M, 0.5 M, 0.2 M and 0.1 M) will be presented throughout.

The system used here contains a water to bulk solution ratio (by volume) of nearly 1:100. When microwaved, the water heats and over a longer timeframe can transfer heat to the heptane inducing an overall heating of the bulk solution. For the reactions reported here microwaved for 2 minutes at 300 W, the change in bulk solution temperature was between 10 °C and 14 °C. This increase in bulk temperature did not lead to a phase separation and was the basis for using 300 W of microwave power for the two-minute time interval. The AOT/Heptane was heated without water cores and was determined to heat approximately 2 °C. Therefore, the water cores contribute to an 8-12 °C rise in temperature of the bulk solution. The small temperature increase is important because the reverse micelle system employed loses its integrity above temperatures of 50 °C to 60 °C. Above those temperatures, a large-scale phase separation occurs and the system is no longer technically a reverse micelle system.
3.3.1 Synthetic Strategy

Originally, a synthetic route as studied by Arcoleo and Liveri consisting of parameters found in Table 3.1 was attempted[23]. After difficulties with keeping reverse micellar solutions in one-phase (for unknown reasons), this pathway was discarded and a new strategy similar to that outlined by Wu et al. was adopted[27]. The new parameters are displayed in Table 3.1. The hydrazine concentration was varied from that used by Wu et al. and the HAuCl$_4$·3H$_2$O concentration was increased to 0.5 M in an attempt to get reaction to take longer to complete. Five drops of hexadecanethiol was added for every 12 mL of reaction solution as a capping agent to curtail further growth after a set time period of between 4 and 16 minutes. The reasoning for the capping agent are discussed in Section 3.3.2.1 below. The final concentrations for the reactions that were studied are outlined in Table 3.2.

The reduction of HAuCl$_4$·3H$_2$O by hydrazine is known to be quick, so the overall reaction time before capping was kept short (4 to 16 minutes). Due to preparation time for mixing the reactant solutions, microwaving, and removing from the microwave vessel and capping with a thiol within a 4 minute window, the actual amount of time the growth system was introduced to microwave radiation was required to be short (2 minutes). Since the introduction of radiation was so short, in order to perturb the system readily, a microwave power of 300 W was decided upon. Within the 2 minutes it was exposed, the overall solution temperature stayed below 50 °C allowing for the reverse micellar system to remain one-phase.
3.3.2 Characterization of Particles

3.3.2.1 SEM

There was obvious clustering seen in the SEM images (shown in Figure 3.1), and from this, it was determined that an agent was needed to curtail the clustering. Gold nanoparticle clustering is seen elsewhere in the literature and is caused by the attractive forces between the metal nanoparticles[2, 20-22, 29, 32, 35-37]. Once the gold nanoparticles were separated with a capping agent, the resolution of the instrument was such that further imaging with the SEM proved futile. These micrographs were taken on particles from preliminary experiments and not of the samples prepared with the hydrazine concentrations described above.

3.3.2.2 DLS

The results of the DLS experiments were inconclusive. It is relatively easy to explain why DLS does not work on this nano-gold system. A simple glance at the UV-Vis spectra shows that the gold nanoparticles absorb visible light over a fairly broad range. The range appears to be from roughly 480 nm to about 600 nm. The laser used for DLS is set at 514 nm, which falls directly in the absorption range so absorption of the incident laser will give distorted results.
3.3.2.3 TEM of Varying Hydrazine Concentrations

Certain TEM images apparently were slightly contaminated with organic matter that burned/polymerized under the intense electron beam. This shows up as a white, ghost-like film on the images.

3.3.2.3.1 Non-Microwaved

The TEM images for the nMW2, nMW1, nMW0.5, nMW0.2, nMW0.1 are shown in Figures 3.2, 3.4, 3.6, 3.8 and 3.10, respectively. The images in Figures 3.8 and 3.10 begin to show polymorphous gold nanoparticles as opposed to the mostly spherical particle displayed in Figures 3.2, 3.4 and 3.6. These lower concentrations of hydrazine (0.2 and 0.1 M) produce non-spherical particles that show up as rods, triangles and various other forms. This is seen elsewhere in the literature[17, 28, 29, 47], and mainly is visible when the average particle size gets above about 10 nm. Not only are they more polymorphous, but also appear to be much more polydisperse. The average size of each is displayed in Table 3.3. Sizes of all particles were only measured in the X direction so as to avoid user bias. The non-microwaved samples are labeled with nMW as the precursor in the sample name with the number depicting the concentration of hydrazine used to reduce the gold source.
3.3.2.3.2 Microwaved

The TEM images for samples MW2, MW1, MW0.5, MW0.2 and MW0.1 are shown in Figures 3.3, 3.5, 3.7, 3.9 and 3.11, respectively. Upon viewing those TEM images, it is apparent that there are differences in the microwaved and non-microwaved samples. The largest particles are seen in the images of microwaved samples at low hydrazine concentrations. As was seen in the non-microwaved samples, the polydispersity of the particles grown in the presence of hydrazine concentrations of 0.5 M and higher is low and the particles are spherical. At the lower hydrazine concentrations of 0.1 and 0.2 M, polydispersity was high and various non-spherical shapes are produced. A summary of the sizes is shown in Table 3.3. The microwaved samples are labeled with MW as the precursor in the sample name with the number depicting the concentration of hydrazine used to reduce the gold source.

In every case, comparing the microwaved and non-microwaved samples of a given hydrazine concentration, the microwaved sample had larger particle sizes. The size increase became larger at lower hydrazine concentrations, but the percent increase in size did not follow a particular trend.

Higher resolution TEM images of the nMW0.1 and MW0.1 are displayed in Figures 3.12 and 3.13. Upon viewing the higher resolution TEMs, it is apparent that phase boundaries, fault lines and/or twinning is seen in both microwaved and non-microwaved samples. Some, but not all, of the boundaries are depicted with white arrows for clarification in Figures 3.12 and 3.13.
3.3.2.4 TEM of Varying Microwave Exposure Time

TEM images of the gold nanoparticles grown (with 1 M hydrazine) at increasing exposure time to the microwave radiation are shown in Figures 3.21 through 3.24. The particles look to be mostly spherical and show numerous grain boundaries or fault lines. There are also noticeable “superstructures” that seem to show a connectivity between particles. Extreme dilution and sonication for several hours was shown to break up these chainlike structures, showing that it was not an effect of the microwaving, but was due to entanglement of the hexadecanethiol capping agent. TEM images of the separated gold nanoparticles are shown in Figure 3.27. The same superstructures were seen in all of the gold samples from previous experiments. Complete separation was not observed, but adequate separation was seen to acknowledge that the superstructures were not stable. Perhaps a shorter chain thiol would work better, but it is difficult to find a balance between adequate gold-gold separation and thiol chain length that minimizes entanglement.

3.3.2.5 Particle Size Distributions

Particle size distribution graphs of the microwaved versus non-microwaved samples with various hydrazine compositions ranging from 2 M to 0.1 M, are presented in Figures 3.14 through 3.18. They were obtained from the TEM images and show how microwaving increases the particle size. With each decrease in hydrazine concentration, the difference in particle size becomes larger but percentage increase does not follow are
particular trend. A summary of the PSD’s including average size of particles and the median size of particles is available in Table 3.3. Also, particle size distributions for the variable microwave times are shown in Figure 3.25. They were taken from the TEM images in Figures 3.21 through 3.24 and each PSD is a culmination of 250 particles. A graph showing the average size and standard deviation, for non-microwaved growths that were halted after 4 and 15 minutes and microwaved growths that were microwaved for 2, 4, 6 and 15 minutes and then halted 1 minute later, can be seen in Figure 3.26. (The overall bulk temperature in the variable microwaving time experiments was 37, 47, 56 and 81 ºC, respectively.) This shows a steady particle size of approximately 10 nm and a fairly consistent standard deviation of about 1.9 nm, no matter how long the sample is microwaved. Without microwaving, the sample continues to grow over time, and as it grows, the size distribution broadens. After 4 minutes, the particle size is approximately 4.8 ± 0.85 nm and at 15 minutes, 8.1 ± 2.6 nm.

3.3.2.6 UV-Vis Spectroscopy

Interpretation of UV-Vis spectroscopy of Au colloids requires theory developed by Mie in 1908 and discussed at length by Born and Wolf[48], Kerker[49], and Bohren and Huffman[50]. The theory will not be discussed here as it is lengthy and complex. The raw spectra taken of nMW0.5 and MW0.5 and their baseline corrected equivalents are displayed in Figure 3.19. The spectra of nMW2 and MW2 samples are shown in Figure 3.20 along with their baseline corrected spectra. The baseline correction was done
in Grams-32 Spectral Notebase using multiple points. For ease of presentation, the important information from these spectra are presented in Table 3.4.

The obvious thing to note upon microwaving is that the UV-Vis spectra appear to red shift, from 536.5 to 547.2 nm for 2 M hydrazine and from 551.7 to 555.7 for 0.5 M hydrazine, as particles become larger in both cases (size regimes larger than 10 nm and smaller than 10 nm.) Liz-Marzan and Mulvaney explain that the exact position and intensity of the plasmon band is extremely sensitive to particle size and shape and the properties of the medium the particles are in[51]. The red shift correlates well with Mie theory and with other research performed on silver nanoparticles[52] and gold nanoparticles[47, 53].

The intensities within a certain hydrazine concentration also illustrate that larger particles have a higher absorbance intensity. This relationship however cannot be seen from concentration to concentration because the Mie theory simply works for spherical particles, and begins to break down when different geometries are present[47]. For this reason, the results of the slower reaction (0.5 M hydrazine) were separated from the faster reaction (2 M hydrazine.) In the faster reaction, most particles appear to be spherical and can therefore be compared to each other using the Mie theory. In the slower reaction, the particle shapes become less uniform and therefore do not necessarily adhere to the Mie theory.
3.4 Discussion

Both the UV-Vis spectroscopy data and the TEM images support that the microwaved samples produce larger gold nanoparticles than samples not introduced to microwave radiation. The red shift in UV-Vis spectra, from 536.5 to 547.2 nm and from 551.7 to 555.7 nm, as particles increase in size from 4.2 to 5.8 nm and from 7.9 to 10.6 nm, for the 2 M hydrazine and 0.5 M hydrazine samples respectively, is consistent with Mie theory and of other reports[47, 52, 53]. While the intensity increases seen in the UV-Vis data of 0.094 (nMW2) to 0.096 (MW2) and 0.018 (nMW0.5) to 0.051 (MW0.5) are consistent with other gold nanoparticle reports[47, 53], this increase has not been directly linked to particle size. Bloemer et al. proposed that the intensity increase is more likely due to shape changes or defects than to size differences[47], which would explain the larger difference seen in the 0.5 M hydrazine samples since the particle shapes are starting to become less spherical as viewed by the TEM images. The TEM images allow us to see that particle shapes are different, especially at lower hydrazine concentrations, and therefore comparing intensities between hydrazine concentrations is not advisable.

As was mentioned earlier in this chapter, Liz-Marzan and Mulvaney report that particle shape is detrimental in determining peak shape, intensity and position by UV-Vis spectroscopy[51]. A discussion of possible reasons for the differences in a microwaved and non-microwaved gold growth reverse micelle system is presented below.
3.4.1 Synthesis Reaction

Several research groups give the generic equation for the reduction of HAuCl$_4$ with hydrazine[24, 26, 27] as:

$$4\text{HAuCl}_4 + 3\text{N}_2\text{H}_5\text{OH} \rightarrow 4\text{Au} + 16\text{HCl} + 3\text{N}_2 + 3\text{H}_2\text{O} \quad (1).$$

The form of hydrazine (extent of hydration) used initially may differ, but it typically exists as N$_2$H$_5$OH in solution.

3.4.2 Features of the Reverse Micelle System

The approximate size of the reverse micelles within the system can be calculated based on the ratio of [H$_2$O]/[AOT]. For AOT, there are slight discrepancies in a general equation as Eastoe et al. reported[54]:

$$R \ (\AA) = 1.8w,$$

where $R$ is the radius of the water core and $w$ is [H$_2$O]/[AOT]. Pileni however reported the relationship to be (using the same variables)

$$R \ (\AA) = 1.5w[55].$$

Also, Nicholson and Clarke reported a different relationship such that:

$$R \ (\text{nm}) = 0.175w + 1.5[56].$$

Utilizing these equations and the $w$ value of 6 that was used, the average diameter of the reverse micelles is approximately 18, 22 or 26 Å, respectively.

As the two reverse micelle solutions mix, one containing the metal source and the other containing the reducing agent, a distribution of concentrations develops in the
reverse micelles. The reaction rate is highly dependent on the “solubilisate exchange rate” between reverse micelles. Fletcher, Howe and Robinson define this as inter-droplet transfer of reacting species and determined it to be governed by the second order rate constant of \(10^6 - 10^8\) \(\text{dm}^3\) \(\text{mol}^{-1}\) \(\text{s}^{-1}\), which is 2-4 orders of magnitude slower than the droplet encounter rate predicted from diffusion theory[46].

If two separate reactant species dissolved in reverse micelles are mixed, a distribution or reactant species within the water cores has to be established. Early fluorescence quenching work by Bridge and Fletcher supported a Poisson distribution being established as the system approaches steady state[57].

The size of the reverse micelles in the growth system can also alter the size of the synthesized particles. Typically size and water loading levels are used interchangeably to represent the size of the water pool. Higher water loading levels represent larger reverse micelle diameters as is discussed above. Chiang reported sizes of particles grown in reverse micelles with loading levels of 4, 8 and 20 as 11.9 nm, 22.3 nm and 33.0 nm respectively, using a \([\text{N}_2\text{H}_5\text{OH}]/[\text{HAuCl}_4]\) of 1[25]. With a similar ratio of \([\text{N}_2\text{H}_5\text{OH}]/[\text{HAuCl}_4]\), and a loading level of 6, the sizes reported in this study are slightly smaller at 7.9 and 10.6 nm for nMW0.5 and MW0.5, respectively. In a separate report, Chiang demonstrated that increasing the \([\text{N}_2\text{H}_5\text{OH}]/[\text{HAuCl}_4]\) in a reverse micellar system for gold growth, led to a decrease in particle size such that as \([\text{N}_2\text{H}_5\text{OH}]/[\text{HAuCl}_4]\) increases from 0.2 to 20, particle size decreases from 78.6 to 10.5 nm[26]. This report observed that as \([\text{N}_2\text{H}_5\text{OH}]/[\text{HAuCl}_4]\) increases from 0.2 to 4, particle size decreases from 15.5 to 4.2 nm for the non-microwaved and 21.6 to 5.8 nm for the microwaved samples. Water loading level differences, overall reactant
concentrations and the use of a co-surfactant could explain the noted size differences between this report and Chiang’s.

3.4.3 Model for Gold Growth in a Reverse Micelle

Whetten et al. reveals that gold nanoparticles tend to be face-centered cubic (fcc) gold lattices with a truncated-octahedral morphology[58]. Bloemer et al. agrees, but concedes that under low resolution imaging, they would appear rounded and have slightly distorted geometries instead of the perfect geometry predicted by crystal growth theory. He also reports that twin boundaries are evident in the samples prepared by reducing a commercially available gold source[47]. Link et al. show multiple twinning and stacking faults of 15 nm gold nanoparticles by HRTEM[59]. Buffat and Borel reported that particles smaller than 10 nm have practically spherical shapes[17]. All of these reports show that for larger nanoparticles, ~10 nm and larger, intergrowth and growth of nanogold seeds proceeds in a way that many imperfections are observed, much like those seen in this study. Chiang reported that when the hydrazine to HAuCl₄ ratio was below unity, that anisotropic gold nanoparticles, such as cylinders, polyhedrons and trigons were obtained[26]. This same effect is shown here when the hydrazine to HAuCl₄ ratio is 0.4 and 0.2 for both microwaved and non-microwaved samples. Figures 3.8, 3.10 and 3.12 are TEM images of the aforementioned 0.4 and 0.2 ([N₂H₅OH]/[HAuCl₄]) samples and clearly show rods, triangles and larger non-spherical particles and average particle size is 15.5 nm in both cases. When the [N₂H₅OH]/[HAuCl₄] is 1 or more, the spherical
particles seen in Figures 3.2, 3.4 and 3.6 whose average particle sizes are 4.2, 4.8, and 7.9 respectively, are produced.

Figure 3.28 shows a Poissonian distribution such as that predicted by Bridge and Fletcher for reactant species in a reverse micelle system[57]. A cartoon of the solubilisate exchange process is shown in Figure 3.29. Figure 3.29a represents the two-reactant system and just before micellar collision. Figure 3.29b and 3.29c shows post collision with the walls open to one another and solubilisate exchange occurring. Figure 3.29d represents the splitting of the coupled micelles and the new distribution of particles. After millions of these solubilisate exchange collisions and a steady state established, the reactants should attain a Poissonian distribution within the reverse micelles as reported by Bridge and Fletcher[57].

In the samples at low hydrazine concentrations (nMW0.2 and MW0.1, [N₃H₅OH]/[HAuCl₄] of 0.4 and 0.2 respectively), an evident bi-modal PSD is observed. In Figure 3.17a, for nMW0.2, distributions centered around 9 nm and about 18.5 nm are observed. For nMW0.1, represented in Figure 3.18a, the distributions seem to be centered around 7 and 16 nm. Whetten et al. that reported that there are certain dimensions that gold nanoparticles favor leading to multi-modal distributions depending on the procedure followed[58], however, their report looked at particles between about 1.4 and 2.7 nm. However, it is not certain if this same effect would be seen at larger sizes.

The faster reactions (nMW2, nMW1 and nMW0.5, [N₃H₅OH]/[HAuCl₄]) = 4, 2 and 1), TEM images in Figures 3.2, 3.4 and 3.6 and size distributions in Figures 3.14a, 3.15a and 3.16a, have a relatively narrow distribution indicating they are basically one
size with the slight broadening coming from the Poissonian distribution. Chiang observed this same effect and rationalized that increasing the reducing agent while keeping all other concentrations constant leads to an increased average amount of reducing agent per reverse micelle. This promotes fast nucleation which produces numerous, smaller particles[26]. The reactions with $[\text{N}_2\text{H}_5\text{OH}]/[\text{HAuCl}_4]$ of 0.4 and 0.2 M have very broad distributions and are polymorphous. The TEM images of these can be viewed in Figures 3.8 and 3.10, and size distributions are given in Figures 3.17a and 3.18a. In another study Chiang observed a polydispersity at ratios of $[\text{N}_2\text{H}_5\text{OH}]/[\text{HAuCl}_4] \leq 1$. He rationalizes that both growth and nucleation occur simultaneously resulting in both large particles and new nuclei[25] whereas at higher $[\text{N}_2\text{H}_5\text{OH}]/[\text{HAuCl}_4]$ ratios, the nucleation step is predominant, leading to a large population of small particles. Since the system reported here is similar but not the same as Chiang reported, small discrepancies with the $[\text{N}_2\text{H}_5\text{OH}]/[\text{HAuCl}_4] = 1$ can be expected as his particles were on average larger than those reported here. The particle sizes observed in the two cases are 22.3 nm for Chiang’s report and 7.9 nm in this study, one being above the 10 nm spherical particle divide and the other below.

Figure 3.26 shows that the particle size increases from about 4.8 ± 0.85 nm to 8.1 ± 2.6 nm when allowing the reaction to proceed for 15 minutes instead of 4 minutes. This increase in growth is consistent with the Poissonian model because section II of Figure 3.28 has the right nutrients for nucleation and growth. Within the reverse micelles represented by section I of Figure 3.28, the $\text{Au}^{3+}$ concentration is high and the concentration of hydrazine is low. Since there is not enough hydrazine to reduce all of the $\text{Au}^{3+}$, the resultant gold particles will be small with excess $\text{Au}^{3+}$ remaining in
solution. In section III of Figure 3.28, there is a high concentration of hydrazine and low concentration of Au$^{3+}$, which Chiang reported leads to small gold particles because the high hydrazine concentration causes fast nucleation, separating it from the growth phase, and then the supply of Au$^{3+}$ for the impending growth phase has been depleted[25]. As those nutrients get depleted, more collisions and exchange of nutrient will continue and as the Au rich or hydrazine rich reverse micelles from sections I and III (Figure 3.28) continue to collide, nutrient is exchanged into reverse micelles that contain nuclei, but not enough nutrient to grow. This growth process is gradual as is shown by the gradual rise in average particle size in Figure 3.26. The polydispersity also increases at longer growth times as collisions of reverse micelles continue to collide and exchange nutrients creating reverse micelles that are conducive to nucleation and those that are adequate for growth of preexisting nuclei.

3.4.4 Proposed Model for Reverse Micelle Reaction in the Presence of Microwaves

The ability to selectively heat the inner water core is utilized here to alter the growth environment of gold nanoparticles. At no time in the preliminary experiments does the temperature of the bulk reverse micelle solution exceed 40 °C. Later, when microwave time was increased, the bulk solution temperature did rise as high as 79 °C, but the PSD analysis (Figure 3.25) shows that the particles grow to a certain size, ~10 nm in this case, and then level off at longer microwave times (see Figure 3.26). This is indicative that the reaction is completed (expended all the nutrients) at the shorter
microwaving times, and therefore heating longer has no effect on the growth of the particles.

The TEM results presented in the form of particle size distributions (Figures 3.14-3.18), show that microwaving a reverse micelle system designed to grow gold, produces larger particles than what are produced in the non-microwaved control samples. When microwaved for 2 minutes at 300 W, 17 seconds after mixing the H\textsubscript{AuCl\textsubscript{4}} and the hydrazine encapsulated reverse micelles, the 2 M hydrazine sample increased from 4.2 to 5.8 nm, the 1 M hydrazine sample increased from 4.8 to 7.6 nm, the 0.5 M hydrazine from 7.9 to 10.6 nm, 0.2 M hydrazine from 15.5 to 20.6 nm and the 0.1 M hydrazine increased from 15.5 to 21.6 nm. The bi-modal distribution that was obvious in nMW0.2 and nMW0.1 M hydrazine disappears when microwave radiation is employed. The distribution is still broad, but that can be attributed to the first 17 seconds of reaction before the microwave radiation is introduced. During this time, nucleation and growth occur simultaneously and then when the microwave radiation is added, the nucleation is halted and growth is dominant. This type of effect seems contrary to what Liu et al. reported for a standard (not reverse micellar) microwaved hydrothermal gold growth. They report that higher temperatures grow smaller particles, but they do not compare to a non-microwaved sample[41].

There are numerous examples in the literature of nano-metals sintering in less than 20 seconds[60, 61] and at temperatures as low as 200 °C[62]. Upon viewing the earliest results, it appeared as if the nano-sized gold particles were perhaps sintering under the intense heating of the water cores by the microwaves. However, the later results from longer microwave heating samples would disprove the sintering mechanism
because particle size and polydispersity does not increase at longer microwaving times. If sintering were occurring, disappearance of smaller particles would be evident as would the overall increase in average particle size. This is not seen in the particle size distributions. The data suggests a rapid growth that overpowers the nucleation step such that fewer nuclei are formed, allowing the nuclei that are formed to grow to a larger size than their non-microwaved counterparts. The polydispersity is consistent regardless of the time exposed to microwave radiation. The temperature increases at longer times, but since the reaction is completed, no changes are seen in the TEM images, or the PSD’s. The polydispersity is larger than in the case of the 4 minute reaction discussed in the Model for Gold Growth in a Reverse Micelle section, but smaller than the 15 minute reaction discussed in the same section. The natural Brownian motion that leads to the broader size distribution at longer reaction times no longer governs the reverse micelle reaction when microwave radiation is utilized as the growth is much quicker due to faster exchange of nutrient since collisions are no longer necessary for nutrient exchange.

The phenomena that causes growth of non-spherical particles in nMW0.2 and nMW0.1 systems is also seen in MW 0.2 M and MW0.1 M gold growth systems. The TEM images shown in Figures 3.9, 3.11 and 3.13. This is discussed in the Model for Gold Growth in a Reverse Micelle section of this report. Figure 3.7 shows TEM images of the microwaved growth with [N₂H₅OH]/[HAuCl₄] equal to 1 (MW0.5) whose particle size is approximately 10.6 nm. The nMW0.5 had an average particle size of 7.9 nm and TEM images are shown in Figure 3.6. Some of the particles from MW0.5 shown seem to be already showing signs of becoming rod-like whereas nMW0.5 appears to contain only spherical particles.
Figure 3.30 is a hypothetical distribution for the reactant species within a microwaved reverse micellar system and Figure 3.31 displays a cartoon diagram for the perceived solubilisate exchange mechanism. The distribution does not have the long tails that are noted for a Poissonian distribution because the microwave radiation is believed to present a different solubilisate exchange mechanism.

It is important to realize that since the water content in the reverse micellar reactions is extremely small (0.26 mL of water for every 24 mL of AOT/Heptane solution), and the microwaves heat water more readily than the oil surrounding it, it is highly likely that the water temperature is above boiling. Figure 3.31a represents the two reactant species encapsulated in reverse micelles and mixed before microwave radiation is introduced. After microwaving starts, the water boils and expands, breaking the surfactant shell surrounding it and violently expelling the water from the core (Figure 3.31b). When two or more reverse micelles are close to one another, their enclosed species intermingle (Figure 3.31c). As the vapor enters into the bulk solution (max bulk temperature is ~39 ºC), it cools enough that reverse micelles can reform, encapsulating any solubilized species in the vicinity (Figure 3.31d). Also, with this type of system, direct collisions are not necessary for solubilisate exchange.

This turbulent environment leads to a higher degree of solubilisate exchange and deters the distribution from the Poisson model seen for the non-microwaved sample. With the “explosion model,” collisions are not required, so the typical slower exchange of solubilisate is not followed. With the environment constantly undergoing explosions and re-encapsulation while being microwaved, the proper mix of nutrients for nucleation becomes less likely as the proper concentrations need time to form nuclei once the
nucleation concentration threshold is surpassed. The disorder brought about by the microwave radiation makes remaining at or above the nucleation threshold, long enough to form viable nuclei, less likely and promotes the growth of the already existent nuclei. During the first 17 seconds of reaction, before microwave radiation is introduced, the standard reverse micellar reaction is occurring as described in the Model for Gold Growth in a Reverse Micelle section. In this first 17 seconds, nucleation is occurring rapidly MW2, MW1 and MW0.5. Nucleation is not occurring as rapidly for the reactions of MW0.2 and MW0.1 during the first 17 seconds before microwaving. In the latter two reactions, nucleation and growth are simultaneous during this period. When the microwave radiation is finally introduced, MW2, MW1 and MW0.5 have numerous nuclei, that begin to grow with the addition of microwave radiation because of enhanced exposure to nutrients. The MW0.2 and MW0.1 have a smaller number of nuclei, and some that have already began growth. When the microwave radiation is employed, these nuclei/particles begin to grow and no new nucleation is occurring, thus eliminating the smaller population seen in the non-microwaved samples. This decrease in the number of nuclei/smaller particles provides an increase in the overall size. The growth effect seen can be attributed to the sharp rise in water temperature and novel turbulent environment. A temperature jump of the magnitude seen in these trials cannot be imitated through normal hydrothermal synthesis, therefore making the microwaved systems unique.
3.4.5 Other Potential Methods of Localized Heating

Acoustic cavitation has been reported as another means of synthesis where extremely high local temperatures are achieved[39]. The temperatures reached by this means are orders of magnitude larger, 5,000-100,000 K, and extremely short lived, mere picoseconds[63, 64]. Utilizing acoustic cavitation would drastically shorten any delay time associated with the microwaving, but the dynamics behind the system are not well known, and the temperatures reached are significantly higher than ideal for the system studied. Therefore, the reverse micelle with microwave radiation system is more ideal for the localized heating phenomenon at more manageable temperatures.

3.5 Conclusions

Microwave radiation was employed to increase the local temperature in the water cores of the reverse micelles. This was accomplished since the bulk solution, n-heptane, is relatively microwave inactive. Microwave radiation proves to be a viable way to alter the size of gold nanoparticles grown in reverse micelles by altering the growth environment. In every case, when microwave radiation was introduced to reverse micelle systems using various ratios of \([\text{N}_2\text{H}_5\text{OH}]/[\text{HAuCl}_4]\) (from 0.2 to 4) to reduce \(\text{HAuCl}_4\), the particle size was increased, by between 33 and 58%. When the hydrazine concentration was held constant at a \([\text{N}_2\text{H}_5\text{OH}]/[\text{HAuCl}_4]\) of 1, increasing the microwave reaction time, from 2 minutes to 15 minutes, had no effect on final particle size or polydispersity which could be attributed to the reaction being rapid enough that
completion was reached in the shortest microwaved reaction since the system is no longer
governed by Brownian motion. This is contrasted to a non-microwaved system with the
same reactant ratios that increases in size from 4.8 to 8.1 nm when the reaction time is
increased to 15 minutes from 4 minutes. The polydispersity of the 4 minute sample was
smaller than the microwaved samples, but the 15 minute sample had a larger
polydispersity than the microwaved sample. With a well-devised strategy incorporating a
reverse micelle system, appropriate molar ratios and concentrations of reactants (gold
source and reducing agent), changing order of addition, seeding, micellar loading
levels[23, 25, 26, 28-31] and the addition of microwave radiation, a wide range of nano-
scaled gold particles could be grown rapidly. The use of microwaved reverse micellar
systems can also be adapted for use in the synthesis of a variety of other nanoparticles.
<table>
<thead>
<tr>
<th></th>
<th>Arcoleo and Liveri</th>
<th>Wu et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[AOT]</td>
<td>0.295 M</td>
<td>0.1 M</td>
</tr>
<tr>
<td>[HAuCl₄]</td>
<td>0.0103 M</td>
<td>0.1 M</td>
</tr>
<tr>
<td>[Hydrazine]</td>
<td>0.0624 M</td>
<td>1 M</td>
</tr>
<tr>
<td>w*</td>
<td>2.23 - 14.7</td>
<td>6</td>
</tr>
</tbody>
</table>

* w=[H₂O]/[AOT]

**Table 3.1.** Growth parameters for the two growth systems attempted with more emphasis on the Wu et al. parameters as difficulties arose with Arcoleo and Liveri’s parameters[23, 27].
Table 3.2. Actual parameters used for the Au growth systems analyzed here. Adjustments were made to the Wu et al. group’s system (Table 3.1) to adjust the rates of reaction.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Avg. Size (nm)</th>
<th>Median Size (nm)</th>
<th>Δ Average (% Increase)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nMW2</td>
<td>4.2</td>
<td>4.1</td>
<td>+1.6 nm (39%)</td>
</tr>
<tr>
<td>MW2</td>
<td>5.8</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>nMW1</td>
<td>4.8</td>
<td>4.9</td>
<td>+2.8 nm (58%)</td>
</tr>
<tr>
<td>MW1</td>
<td>7.6</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td>nMW0.5</td>
<td>7.9</td>
<td>7.9</td>
<td>+2.7 nm (33%)</td>
</tr>
<tr>
<td>MW0.5</td>
<td>10.6</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>nMW0.2</td>
<td>15.5</td>
<td>15.6</td>
<td>+5.1 nm (33%)</td>
</tr>
<tr>
<td>MW0.2</td>
<td>20.6</td>
<td>18.1</td>
<td></td>
</tr>
<tr>
<td>nMW0.1</td>
<td>15.5</td>
<td>15.1</td>
<td>+6.1 nm (39%)</td>
</tr>
<tr>
<td>MW0.1</td>
<td>21.6</td>
<td>20.4</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.3.** Summary of the particle size distributions determined from the transmission electron micrographs. MW in the sample name depicts microwaved samples, nMW is non-microwaved, and the number represents the concentration of the hydrazine used to reduce the tetrachloroaurate.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavelength of max (nm)</th>
<th>Max Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>nMW2</td>
<td>536.5</td>
<td>0.094</td>
</tr>
<tr>
<td>MW2</td>
<td>547.2</td>
<td>0.096</td>
</tr>
<tr>
<td>nMW0.5</td>
<td>551.7</td>
<td>0.018</td>
</tr>
<tr>
<td>MW0.5</td>
<td>555.7</td>
<td>0.051</td>
</tr>
</tbody>
</table>

**Table 3.4.** Summary of the UV-Vis data from Figure 3.19.
Figure 3.1. SEM images of non-thiolated gold growth samples that show a need for a capping agent to reduce/eliminate the clustering of gold nanoparticles.
Figure 3.2. TEM images of gold nanoparticles produced in a reverse micelle system by reducing HAuCl$_4$·3H$_2$O with a 2 M hydrazine solution.
Figure 3.3. TEM images of gold nanoparticles produced in a reverse micelle system by reducing H Au Cl₄·3 H₂O with a 2 M hydrazine solution in the presence of microwave radiation.
Figure 3.4. TEM images of gold nanoparticles produced in a reverse micelle system by reducing HAuCl₄·3H₂O with a 1 M hydrazine solution.
Figure 3.5. TEM images of gold nanoparticles produced in a reverse micelle system by reducing HAuCl$_4$·3H$_2$O with a 1 M hydrazine solution in the presence of microwave radiation.
Figure 3.6. TEM images of gold nanoparticles produced in a reverse micelle system by reducing HAuCl$_4$·3H$_2$O with a 0.5 M hydrazine solution.
Figure 3.7. TEM images of gold nanoparticles produced in a reverse micelle system by reducing HAuCl₄·3H₂O with a 0.5 M hydrazine solution in the presence of microwave radiation.
Figure 3.8. TEM images of gold nanoparticles produced in a reverse micelle system by reducing HAuCl$_4$·3H$_2$O with a 0.2 M hydrazine solution.
Figure 3.9. TEM images of gold nanoparticles produced in a reverse micelle system by reducing HAuCl$_4$$\cdot$3H$_2$O with a 0.2 M hydrazine solution in the presence of microwave radiation.
Figure 3.10. TEM images of gold nanoparticles produced in a reverse micelle system by reducing HAuCl$_4$·3H$_2$O with a 0.1 M hydrazine solution.
Figure 3.11. TEM images of gold nanoparticles produced in a reverse micelle system by reducing HAuCl$_4$·3H$_2$O with a 0.1 M hydrazine solution in the presence of microwave radiation.
Figure 3.12. Higher resolution TEM images of a reduction of HAuCl₄·3H₂O by 0.1 M hydrazine in a reverse micelle reaction system. Some faults and grain boundaries are designated with the arrows.
Figure 3.13. Higher resolution TEM images of a reduction of HAuCl₄·3H₂O by 0.1 M hydrazine in a reverse micelle reaction system in the presence of microwave radiation. Some faults and grain boundaries are designated with the arrows.
Figure 3.14. Particle size distribution plots for gold nanoparticles produced with 2 M hydrazine. These PSD’s are based on the images shown in Figures 3.2 and 3.3. (a) is the non-microwaved PSD and (b) is the microwaved PSD.
Figure 3.15. Particle size distribution plots for gold nanoparticles produced with 1 M hydrazine. These PSD’s are based on the images shown in Figures 3.4 and 3.5. (a) is the non-microwaved PSD and (b) is the microwaved PSD.
Figure 3.16. Particle size distribution plots for gold nanoparticles produced with 0.5 M hydrazine. These PSD’s are based on the images shown in Figures 3.6 and 3.7. (a) is the non-microwaved PSD and (b) is the microwaved PSD.
Figure 3.17. Particle size distribution plots for gold nanoparticles produced with 0.2 M hydrazine. These PSD’s are based on the images shown in Figures 3.8 and 3.9. (a) is the non-microwaved PSD and (b) is the microwaved PSD.
Figure 3.18. Particle size distribution plots for gold nanoparticles produced with 0.1 M hydrazine. These PSD’s are based on the images shown in Figures 3.10 and 3.11. (a) is the non-microwaved PSD and (b) is the microwaved PSD.
Figure 3.19. UV-Vis spectra for 0.5 M hydrazine reductions of HAuCl₄·3H₂O, both (a) microwaved and (b) non-microwaved. Baseline corrected spectra (using a multiple point correction function from Grams-32 Spectral Notebase program) are shown as (c) and (d) respectively.
Figure 3.20. UV-Vis spectra for 2 M hydrazine reductions of HAuCl₄·3H₂O, both (a) non-microwaved and (b) microwaved. Baseline corrected spectra (using a multiple point correction function from Grams-32 Spectral Notebase program) are shown as (c) and (d) respectively.
Figure 3.21. TEM images of gold nanoparticles microwaved for 2 minutes at 150 W after mixing reverse micellar mixtures of H₄AuCl₄·3H₂O and the reducing agent hydrazine hydrate.
Figure 3.22. TEM images of gold nanoparticles microwaved for 4 minutes at 150 W after mixing reverse micellar mixtures of HAuCl₄·3H₂O and the reducing agent hydrazine hydrate.
Figure 3.23. TEM images of gold nanoparticles microwaved for 6 minutes at 150 W after mixing reverse micellar mixtures of HAuCl$_4$.3H$_2$O and the reducing agent hydrazine hydrate.
Figure 3.24. TEM images of gold nanoparticles microwaved for 15 minutes at 150 W after mixing reverse micellar mixtures of HAuCl₄·3H₂O and the reducing agent hydrazine hydrate.
Figure 3.25. PSD of the gold nanoparticles microwaved for (a) 2 minutes, (b) 4 minutes, (c) 6 minutes and (d) 15 minutes. The average sizes in each case are (a) 10.1 nm, (b) 9.4 nm, (c) 10.0 nm and (d) 10.7 nm.
Figure 3.26. Growth curve of the nano-gold particles both microwaved and non-microwaved samples. The time shown here is of total reaction time, where the microwaved samples were actually microwaved one minute less than total reaction time. (Lines are merely to guide the eye, and have no significance.)
Figure 3.27. TEM images revealing gold nanoparticle solutions that show “superstructures” can be separated through dilution and sonication. Some “superstructures” are still present but longer sonication and more dilution can separate the structures even more. This shows it is a physical connection and not chemical.
Figure 3.28. Poissonian distribution depicting the distribution of reactants in a two-reactant reverse micellar reaction.
**Figure 3.29.** Theoretical model of a standard two reactant reverse micellar reaction and how solubilisate exchange occurs.
Figure 3.30. Hypothetical distribution of reactants within reverse micelles of a two-reactant system when microwave radiation is added to alter the growth mechanism.
Figure 3.31. Hypothetical solubilisate exchange process for a two-reactant reverse micellar reaction in the presence of microwave radiation. Often referred to in the text as the “explosion model.”
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CHAPTER 4

MICROPOROUS ZINCOPHOSPHATE-X SYNTHESIZED IN REVERSE MICELLE SYSTEMS:
EFFECT OF A BRIEF PULSE OF MICROWAVE RADIATION

4.1 Introduction

4.1.1 Microporous Materials

Microporous materials are discussed at length in the Introduction (Chapter 1). There has been a robust effort over the last couple of decades to not only understand the nucleation and growth mechanisms involved, but also to develop new methods of synthesis that allows for size control and also alteration of elemental ratios and framework structure. Many techniques are used to alter structures with some of the most common simply being, templating or adjusting concentration of reactants or reaction time. Temperature plays a vital role in synthesis, as typically high temperatures, in the range of 90-200 °C, are necessary for synthesis of aluminosilicate zeolites. However,
much milder conditions (even below room temperature) can be used for synthesis of microporous zincophosphate frameworks.

Molecular-level investigation of the overall growth environment is stepping to the forefront of crystalline growth studies. One novel environment that has been studied recently is microgravity. It has been employed to better understand the mechanism of a variety of zeolites, including, but not limited to A and X[1, 2], ZSM-5[3, 4], and Beta[5], as well as for realizing new morphologies. Coker et al. also presented a review of earlier microgravity work that reveals a slower growth in microgravity due to a reduction in convection, but the possibility of growing larger crystals due to the crystals being suspended longer in solution, remaining in close contact with the growth nutrients[6].

Ghobarkar et al. has attempted to produce zeolites by simulating their natural formation conditions. They have synthesized zeolites in the millimeter to nanometer size range with temperatures in the range of 120-400 °C and pressures as high as 1 kbar over a 60 day time period[7]. Solid-state synthesis of a faujasitic zincophosphate has been achieved as well[8]. A review of the Chinese literature on microporous materials shows that Meng et al. and Song et al. have grown a variety of microporous materials, including NaA, NaX, AlPO4-C, AlPO4-5, Beta and ZSM-5, using microwave radiation[9].

Dutta and Robins grew zeolite A starting with their precursors entrapped in reverse micelles[10]. Microemulsions and pseudophase reverse micelles have been employed in the growth of silicalite-1[11], silica[12], and AlPO4-5 molecular sieve[13]. However, none of these studies have taken caution to ensure the integrity of the reverse micelles. At the temperatures zeolites require for growth, most reverse micelle systems are not stable and phase separation occurs.
4.1.2 Reverse Micelles and Microporous Materials

Reverse micelles have been studied for over 35 years but only in the past decade has a reverse micelle system been adapted to synthesize microporous materials[14]. Earlier growth studies of faujasitic zincophosphate (ZnPO-X) via an sodium bis(2-ethylhexyl) sulfosuccinate (AOT) in hexane reverse micelle system were unsuccessful[15]. Attempts were made to produce ZnPO-X from a system with a reactant composition identical to that necessary to prepare ZnPO-X by a conventional hydrothermal synthesis, to no avail. The core water in the reverse micelle, as studied by infrared spectroscopy, showed that there were three different types of water[15]. The structure of water contained within the reverse micelles was important in realizing that the environment was not conducive to synthesize open framework microporous materials[16]. Differences in water structure in reverse micelles has been realized elsewhere as well[17-19]. Goto et al. have utilized calorimetry to show that water in an AOT reverse micelle exists in at least three states[17]. Nickolov et al. employed FTIR-ATR to show that water in the core of reverse micelles has different spectral characteristics than bulk water due to confinement in nano-sized domains and interaction with the head group of the surfactant[18]. Kitano et al. showed that zwitterionic surfactants do not significantly disturb the water structure by studying the O-H stretching vibration with a polarized Raman scattering technique[19]. A simplistic cartoon of a reverse micelle composed of AOT with general layers drawn (not to scale) is shown in Figure 1.11.
Castagnola and Dutta determined that the sodium ion concentration was important in determining the type of zincophosphate synthesized[15]. Each AOT molecule contributes a sodium ion to the water phase. It was estimated that each reverse micelle would contain about 400-600 AOT molecules leading to a Na\(^+\) concentration of nearly 4 M. Such a high concentration of Na\(^+\) favors the growth of sodalite, no matter what the concentrations of the other reactants are. Phase separation occurs at high intramicellar concentrations of crown ether-type Na\(^+\) complexing agents, or it may have been possible to eventually form ZnPO-X in the AOT/hexane system.

Using a dioctyldimethylammonium chloride (DODMAC) based reverse micelle and tetramethylammonium (TMA\(^+\)) as a template, Castognola and Dutta, reported the synthesis of ZnPO-X[16]. DODMAC is a cationic surfactant and infrared studies show that the entrapped water resembles that of bulk water more than in the AOT reverse micelles reported above. DODMAC does not have sodium ions that would guide the products to the sodalite framework thus making DODMAC a more suitable surfactant.

An optimized system for the growth of ZnPO-X in DODMAC/isoctane reverse micelles and employing 1,4-diazabicyclo[2.2.2]octane (DABCO) as a template has been reported by Singh et al.[20]. In a study aimed at further understanding the growth mechanism of zeolite like materials in reverse micelles, Singh et al. used that optimized system to compare surface structures of ZnPO-X crystals grown via reverse micelles with those grown in a standard hydrothermal synthesis[21]. The reverse micellar grown crystals showed fewer nucleation sites on the surface, signifying a slower, more controlled growth.
4.1.3 Microwaved Reactions

Microwaves have long been used to alter crystal growth processes. Early on, typical microwave reactions were carried out in a normal consumer microwave oven. Now, companies design microwave systems for lab synthesis. They have developed microwaves that can monitor and vary temperature, pressure, microwave power and also add a stirring element. The reaction vessels are placed on turntables so as to try to average out the “hot spots” common to microwave heating. These systems are designed to withstand high temperatures and pressures. Many growth systems have been introduced to microwaves with mixed results. For the most part, microwaves enhance growth and can cut reaction times by orders of magnitude. A primary downfall currently facing microwave-induced reactions is reproducibility. Current microwave reactors on the market have different geometries and therefore different hot zones. Even things such as reactor geometry have proven to dramatically effect the system under analysis[22].

Synthesis of several microporous materials with microwave radiation has been reported. Cundy’s review summarizes most of the advances in the field before 1998[23], but many articles have been published since in regards to microporous materials and microwave radiation. Among the frameworks grown in a microwaved atmosphere are zeolite Y[24, 25], ZSM-5[24, 26], and a titanium rich titanium silicate (TS-1)[27]. In most reported cases, the crystallization time for zeolites is drastically reduced when synthesized in the presence of microwave radiation.

However, since microwave ovens vary from lab to lab, it is often difficult to get consistent, reproducible data. Arafat claims to have created a pure zeolite Y in the
presence of microwave radiation in only 10 minutes after a ripening period of about 24 hours and ZSM-5 with only about 30 minutes of microwaving after digesting at 40 °C for one hour[24]. Katsuki et al. increased the rate of crystallization of zeolite Y by 3 to 4 times, synthesizing zeolite Y in 1 to 3 hours in a microwaved hydrothermal synthesis as compared to a similar conventional hydrothermal synthesis that required nearly 5 hours to achieve equivalent yields[25]. Somani et al. demonstrated growth of ZSM-5 both with microwave radiation and conventional hydrothermal heating. After a 17 hour aging period, ZSM-5 was collected after 18 hours of microwaving and 36 hours of conventional heating with nearly identical crystallinity[26].

In the case of titanium-rich titanium silicates (TS-1), it was found that synthesis time was decreased from 3-7 days for conventional hydrothermal synthesis to approximately 30 minutes with the assistance of microwave radiation[27].

4.1.4 Microwaved Reverse Micelle Reactions

Microwaving a reverse micelle system is proposed as a synthetic approach aimed at locally heating the water cores to influence the growth dynamics. Organic solvents such as hexane, heptane and octane (nonpolar) do not heat readily when exposed to microwave radiation. If a water-in-oil reverse micelle in a bulk solution of heptane is exposed to microwave radiation, theoretically, the water core should absorb the majority of the radiation, therefore increasing the temperature. With the minute quantities of water involved, and with a high-powered microwave, the water cores can heat appreciably in only a short time exposed to the radiation. Several research groups have
investigated microwaving reverse micellar growth systems for synthesizing materials such as TiO$_2$[28] and microporous aluminophosphate materials[29]. This quick heating cannot be achieved in bulk solutions under typical hydrothermal conditions, making microwaves an ideal way to essentially flash heat the water cores.

Spatz et al. synthesized 5 nm TiO$_2$ particles, employing microwave radiation to selectively heat diblock copolymer reverse micelle water cores[28]. They reported that no bulk solution temperature increase was seen, however, in some cases that have been reported, the bulk solution temperatures have exceeded levels at which reverse micelles are stable, and phase separation is noted[29]. D’Angelo et al. noted that at microwave frequencies, the water component of a water/AOT/n-heptane reverse micelle system, dominates the response[30].

Fletcher, Howe and Robinson performed a systematic study on the stability of AOT based reverse micelles in various alkanes at various temperatures[31]. They discuss both low- and high-temperature phase boundaries such that there is a definite temperature range in which AOT reverse micelles are stable. These values vary greatly and the report gives data for alkyl chain lengths from 5-12 and for water loading levels from $w = 0-100$ ($w = \frac{[\text{H}_2\text{O}]}{[\text{AOT}]}$). The report reveals that at temperatures above the phase inversion temperature (p.i.t.), phase separation actually produces a liquid-crystalline phase that is most likely lamellar in structure containing AOT and water and a conjugate oil phase[31]. This type of separation is not desirable for the reverse micelle reactions and therefore temperature control is imperative.
4.2 Experimental

4.2.1 Materials

Bardac LF-80, which is 80% dioctyldimethylammonium chloride (DODMAC), a surfactant, was donated by Lonza, Inc. (Fair Lawn, NJ). It was concentrated by evaporation at a reduced pressure and then dried under vacuum at an elevated temperature. Zinc nitrate hexahydrate (Aldrich, 98%), 1-decanol (Alfa Aesar, typically 99%), sodium hydroxide pellets (Baker Analyzed), phosphoric acid (Mallinckrodt, N.F. Food Grade, 85%) and isooctane (Fisher, HPLC grade) were all used without modifications. The purification of 1,4-diazabicyclo[2.2.2]octane (DABCO)(Aldrich, 98%) was done by recrystallization in hexane. The structure of DABCO can be seen in Figure 1.10.

4.2.2 Reverse Micellar Solutions

A previously reported procedure for preparing the reverse micellar solutions, was followed[20]. This method involves injecting the aqueous reactant species into a surfactant in oil solution and shaking/sonicating to create a clear, single-phase solution. The surfactant solution was 0.33 M 1-decanol and 0.19 M DODMAC in isooctane. Typically, two reverse micelle solutions were prepared and then mixed to initiate the reaction. One solution contains sodium hydroxide, the template DABCO and phosphoric acid, while the second reactant solution contains the zinc nitrate hexahydrate. The preparation of these two reverse micelle solutions was done by injecting 0.2 mL of the
aqueous reactant species for every 10 mL of the surfactant solution and then shaking until the solution was clear. With this ratio, the reaction can be scaled to fit any of the experiments done throughout this chapter. The $[\text{H}_2\text{O}]/[\text{DODMAC}]$ ratio is approximately 6, which is consistent with the water loading levels in the Gold Growth chapter (Chapter 3). However, the concentration of DODMAC in nearly double that of the AOT in Chapter 3, and therefore the amount of water injected is nearly double as well. In most cases, the solution was then set aside overnight to ensure that a single phase was maintained and no phase separation was obvious.

4.2.3 Cleaning Samples

Before analysis on any of the products occurred, a cleaning procedure was used. Rinses consist of adding ~5-10 mL of ethanol to the sample, sonicating in a Branson 3510 bath for about 30 seconds to redisperse the sample and then centrifuging at 10,000 rpm (~11,000 g) for 3 minutes in a Beckman L-8M ultracentrifuge with a 70 Ti rotor. After decanting the ethanol solution, 5-10 mL ethanol was added and the process repeated. Five rinse cycles were used for samples to be imaged, and three rinse cycles were used for the powder diffraction samples.

4.2.4 Preliminary Microwaving

Microwave radiation was employed to alter the growth environment within the reverse micelle system. A MARS 5 system from CEM Corporation was utilized.
Various microwave programs were created that have different introduction times, microwave power and overall exposure time. The highest power used was 300 W and the lowest power used was 3 W. The exposure time varied from 20 to 90 seconds. Some samples were heated intermittently for 30 seconds and then a delay of about 15 minutes and endured 3 cycles such as this. Finally, some samples were mixed, and then the microwaving was introduced at later times such that anywhere from a couple minutes to several hours of time elapsed from mixture of reactants until the microwaves were introduced. The majority of the reactions reported here were microwaved at 150 W for 1 minute unless otherwise noted. When discussing the reactions, the time involved is the amount of elapsed reaction time before the 1 minute microwaving at 150 W.

### 4.2.4.1 Optimized ZnPO-X Conditions

The reverse micelle reactant solutions shown in previous works[20] to optimally give ZnPO-X were reproduced and employed for microwave reverse micelle experiments. The concentrations of the optimized ZnPO-X growth system reported for Zn(NO$_3$)$_2$·6H$_2$O, NaOH, H$_3$PO$_4$, and DABCO are 0.16 M, 0.11 M, 0.27 M, and 0.58 M, respectively. As was mentioned before, the Zn(NO$_3$)$_2$·6H$_2$O was prepared by itself and the other three reactants were combined in a second reactant solution. This is labeled as Comp1 in Table 4.1.
4.2.4.2 DABCO Concentration Adjustments

DABCO concentration is important in the growth of ZnPO-X. DABCO acts as the template, so, at low concentrations, other frameworks of ZnPO can compete for nutrient, and diminish the growth of ZnPO-X. Different concentrations of DABCO were used in the range of 0.60 M to 1.22 M. This composition is listed as Comp2 in Table 4.1.

4.2.4.3 NaOH Concentration Variation

The NaOH concentration can play a key role in inhibiting the nucleation of certain open framework microporous materials. Castagnola and Dutta determined that high concentrations of sodium ions are not conducive to growth of faujasite like ZnPO[15]. Sodium ion concentrations of 0.11 M and 0.14 M were explored. The concentration of DABCO was also increased to 1.13 M after initial experiments did not produce ZnPO-X with the 0.14 M NaOH solution. Comp3 in Table 4.1 outlines the concentrations used here.

4.2.4.4 Higher Concentrations of All Reactants

The concentrations of all reactant species from the optimized system outlined in section 4.2.4.1 were increased. Solutions of each reactant were made such that the Zn(NO$_3$)$_2$·6H$_2$O concentration was 0.26 M, NaOH was 0.17 M, H$_3$PO$_4$ was 0.43 M and
the DABCO was at 0.93 M. Table 4.1, Comp4 summarizes the concentrations discussed in this section.

4.2.4.5 SEM

Analysis of the products for each of the reactions outlined in preliminary microwaving was performed with a JSM-5500 scanning electron microscope (SEM).

4.2.5 Microwave Versus Reaction Time

After the preliminary work, concentration was shifted to a microwave power of 150 W and a microwave duration of 1 minute. This combination allowed for the perturbation of the system, but also kept the bulk solution temperature under 50 °C. Comp1 was used throughout these reaction time experiments. At this point, the variable tested is timeframe at which the microwaves are introduced to the growing system. Times ranging from 60 minutes to 43 hours were utilized to develop a curve representing ratio of the two major products seen, ZnPO-X and P6. Shorter times, between 2 and 45 minutes were tested, but in each case, showed similar results to the 60-minute trials. The microwaved systems were then compared to a non-microwaved growth.
4.2.5.1 DLS

Dynamic light scattering (DLS) was used to monitor the growth versus time of a non-microwaved sample grown over 22 hours. A Brookhaven Instruments 9000 digital correlator with detector positioned at 90° from the incident laser was employed. The Coherent Innova 90c argon ion laser was operating at 200 mW and at a wavelength of 514.5 nm. The quadratic term of a cumulant analysis algorithm was selected to represent the particle size.

4.2.5.2 Capillary XRD

Once the preliminary work was done, the analysis for microwaving versus reaction time products were accomplished with X-ray diffraction (XRD). X-ray diffraction was used to determine crystal structure and to determine the peak intensity ratios between ZnPO-X and P6. Several peaks were compared including the 6(2θ), 26.3(2θ), and 31.6(2θ) peaks associated with ZnPO-X and the 11.4(2θ), 26.7(2θ) and 31.9(2θ) peaks of P6. The X-ray diffractometer used was a Bruker D8 Advance equipped with a copper anode X-ray tube. A capillary unit was installed that allows for analysis of extremely small samples and the tube output was filtered with a Ge monochromater to produce pure Kα₁ radiation. A Braun PSD (position sensitive detector) was utilized. The capillary unit is necessary because the yields of reverse micelle synthesis systems are much smaller than a standard hydrothermal synthesis. All capillary XRD work was baseline corrected using Galactic’s Grams Spectral Notebase 7.0, employing a multipoint
correction to correct for a drift in baseline starting at 4 2θ and extending to about 11 2θ. For this reason, the peaks located at 26.3 and 26.7 2θ were used for future comparisons.

4.2.6 Mother Liquor Testing

The mother liquor left behind once the growth has started was removed from the precipitate, centrifuged for 10 minutes at 20,000 rpm (~40,000 g) in a Beckman L-8M ultracentrifuge with a 70 Ti rotor. The centrifuging was to remove remaining crystals and then the sample could be microwaved at 150 W for 1 minute. The precipitate generated after microwaving was isolated and washed with several ethanol rinses and XRD patterns were collected. The mother liquor was collected and analyzed in this manner at 7, 10.5, 16.5, 21, 31 and 43 hours of reaction time.

4.2.7 Microwave Radiation’s Effect on Yield

Two identical reverse micellar growth systems designed to grow ZnPO-X as outlined above were allowed to grow for 48 hours. At that point, one of the systems was microwaved for 1 minute at 150 W. That system was removed, and both were allowed to continue growth for 48 additional hours. The products of each were isolated, cleaned, dried and weighed.
4.3 Results

The current scale of the reverse micelle reactions does not produce very much product (only about 2-5 milligrams). For that reason, analysis has been almost solely done with scanning electron microscopy and capillary XRD. The SEM is however, an excellent analytical technique when it comes to microporous materials because they all have fairly distinctive morphologies. ZnPO-X crystals adopt an octahedral morphology and can easily be identified (example shown in Figure 4.1). Sometimes the shape is slightly modified and may not form perfect octahedrons, but the characteristic features are always present. The major impurity with a system designed for ZnPO-X is P6, a dense form of ZnPO that adopts primarily a hexagonal bipyramidal structure and is therefore quite distinguishable when viewed under SEM.

The intention of the following experiments is to develop a reverse micellar synthetic procedure for ZnPO-X in the presence of microwave radiation. Much work has been done by the Dutta research group at The Ohio State University in developing reverse micellar growth systems for microporous ZnPO-X and ZnPO-sodalite. Initially, the hope was that microwave radiation would increase the reaction rate and thus decrease the amount of time necessary for reverse micellar growth of microporous ZnPO-X. The average temperature increase was about 22 ºC by the end of the 1-minute microwave pulse and most of that increase results from the water at the core of the reverse micelles. The water loading level for these experiments is about $w = 6$ where $w = \frac{[H_2O]}{[\text{DODMAC}]}$. This is the same water loading level that was used in Chapter 3 for the gold growth, but the overall concentration of DODMAC is almost double the
concentration of AOT in heptane from the gold growth study. Therefore, the amount of water used in this study is nearly double the amount of water used in the gold study and perhaps is the biggest reason for the difference in bulk temperature heating. The following results reveal that microwaving adds complexity to the growth system, but proved instrumental in increasing the overall yield.

4.3.1 Optimized ZnPO-X Conditions

The reverse micelle reactant solutions shown in previous works[20] to optimally give ZnPO-X were reproduced and employed for microwave reverse micelle experiments. The water loading level for these experiments is about \( w = 6 \) where \( w = \frac{[H_2O]}{[DODMAC]} \) and the brief microwave pulse (1 minute) increased the bulk solution temperature from room temperature to approximately 47-48 °C. Comp1 in Table 4.1 represents the concentrations mentioned above. The SEM images in Figures 4.1-4.4, display the results of those experiments. Figure 4.1 is of a mixture of the reactant solutions that was allowed to react to completion under ambient conditions. Figure 4.2 is of the same reaction, but was microwaved for 1 minute at 150 W immediately after mixing. Figures 4.3 and 4.4 allowed a lag time of 1 hour and 2 hours respectively after mixing before microwaving for 1 minute at 150 W and will henceforth be called the 1 and 2 hour experiments, respectively. As can be seen in these images, in Figure 4.1, the ZnPO-X product is seen, but the structures seen in Figures 4.2-4.4 are not the faujasite framework.
The hexagonal bipyramidal structures seen in Figure 4.2 are indicative of P6 crystals, which are a condensed form of ZnPO-X. The other layered-type structures have not been reported previously. XRD’s of these three samples are shown in Figure 4.5, and appear to be the same material (P6) even though their morphologies look quite different. Capillary XRD was used to elucidate the XRD better and is shown in Figure 4.6 for the sample shown in Figure 4.5(a). The P6 peaks are marked with a P, and the other phase present is not identified or discussed further.

### 4.3.2 Increased Template

Since the microwaved samples of the optimized growth conditions do not produce ZnPO-X crystals, an attempt was made to essentially force the reaction to ZnPO-X crystals by elevating the concentration of the templating agent, DABCO. The concentration of each reactant is listed as Comp2 in Table 4.1. The results of the reactions with a DABCO concentration nearly double that of the previous experiments led to the crystals shown in Figures 4.7-4.10. From Figure 4.7 it is abundantly clear that ZnPO-X is the major product even though a fairly polydisperse size distribution is indicated. However, when comparing the images from the microwaved samples Figures 4.8-4.10 with Figure 4.8 being microwaved at 150 W immediately after mixing, Figure 4.9 and Figure 4.10 introduced to 150 W of microwave radiation for 1 minute at 1 and 2 hours, respectively, it is obvious that ZnPO-X is not the major product. While there is undoubtedly ZnPO-X in all of the microwaved samples, the major product in each case is
P6, the hexagonal bipyramidal structure. Typically the P6 crystals are larger and have a larger aspect ratio when comparing tip-to-tip length versus hexagonal diameter.

The experiment was attempted again at the same time intervals as the original, immediate, 1 hour and 2 hours and the results were very similar to those shown above, therefore those images are not shown here.

### 4.3.3 Increased Sodium Hydroxide Reactions

Increasing the sodium hydroxide concentration on its own does not readily produce good ZnPO-X crystals, however, increasing both NaOH and DABCO does. The DABCO concentration was increased from 0.58 M to 1.13 M. The overall concentrations are displayed as Comp3 in Table 4.1. The SEM results from the experiments that saw the sodium hydroxide concentration raised from 0.11 to 0.14 M are shown in Figures 4.11-4.14. Essentially the same results that occur in the previous experiments with 0.11 M NaOH are seen, where ZnPO-X is the major product of the non-microwaved sample and P6 is the major result of the microwaved samples. The sample shown in Figure 4.12 was microwaved at 150 W for 1 minute immediately after mixing the reactant species and those displayed in Figures 4.13 and 4.14 are microwaved at 150 W for 1 minute at 1 and 2 hours, respectively. Since the ZnPO-X crystals grown here in the non-microwaved sample do not seem to be superior as determined by SEM the optimized concentration of NaOH, 0.11 M, was used for later experiments.
4.3.4 Higher Concentrations of All Reactants

The SEM images for the experiments that were run on the more concentrated reactant solutions (Comp4, Table 4.1) are shown in Figure 4.15. Figure 4.15a, is what occurs when the reverse micelle solutions with nutrients are mixed and allowed to fully react with no intervention at ambient conditions. Figure 4.15b-e shows the same reaction, but that was altered by introduction of microwaves. Figure 4.15b shows the results from a microwave program that exposes the sample to microwaves for 30 seconds at 300 W, allows cooling for 15 minutes, and then repeats that cycle twice more. The maximum bulk temperature achieved was 54 °C after the last burst of microwave radiation. Figure 4.15c represents a sample that was exposed to 150 W of microwaves for 20 seconds (maximum temperature 31 °C), Figure 4.15d, 150 W for 45 seconds (maximum temperature 40 °C) and Figure 4.15e to 150 W for 90 seconds (maximum temperature 55 °C). None of these trials produced a product that was primarily ZnPO-X, so these concentrations and microwave programs were discontinued.

4.3.5 Microwave Versus Reaction Time

The microwave radiation seemed to be disrupting the system and not leading to the synthesis of ZnPO-X. An experiment that reacted longer than intended, 2.5 hours instead of 2 hours, before microwave radiation was introduced seemed to show a small amount of ZnPO-X, not previously seen at the shorter digestion periods. This intriguing discovery led to introducing microwave radiation after longer digestion periods to
determine if ZnPO-X can be made at later stages with the assistance of microwave radiation.

4.3.5.1 Particle Size Analysis During ZnPO-X Growth

The experiments thus far laid the ground work for the following. Appropriate concentrations of reactants were found and reaction conditions were determined for a more in depth study of the reaction over time. Figure 4.16 shows the DLS data of how the ZnPO-X reverse micelle growth system (Comp1) grows over a 22 hour time period. Notice that for about the first 4 hours, little to no growth occurs (nucleation stage). Then growth occurs for about 4 hours at which point, growth continues, but precipitation of larger particles leads to the declining particle size over the next 4 hours. After about 12 hours, growth is essentially halted, but the size of the entities are about an order of magnitude larger (68 nm) than in the nucleation stage (6.7 nm). From 12 to 22 hours, the system is fairly stable and the reaction is considered to be complete. The mother liquor from above the precipitate can be removed after approximately 22 hours and it remains stable with no precipitation or other noticeable reaction for at least 2 months.

4.3.5.2 Microwaving Over a Longer Time Period

X-ray diffraction patterns for the products of microwaved samples, using Comp1, at various lag times are shown in Figure 4.17-4.18. The figures show diffraction patterns for reactions where microwave radiation was introduced briefly for 1 minute after 1, 3.25,
5, 10, 20 and 25 hours, respectively. The products of each reaction were isolated after 48 hours of total reaction time, cleaned with ethanol and dried with N\textsubscript{2} gas. The sample was then put in a glass capillary tube and sealed. The XRD pattern of ZnPO-X is well known and the remaining peaks are attributed to P6. For comparison, Figure 4.19 is the same growth system, but has not been microwaved and shows a relatively pure ZnPO-X pattern. When viewing the patterns as lag time increases between 4 hours and 20 hours, there are obvious differences in many of the peak intensities. ZnPO-X peaks located at 2\theta values of 6, 26.3 and 31.6 are increasing and P6 peaks with 2\theta values of 11.4, 26.7 and 31.9 are decreasing. The values for the peak intensities are outlined in Table 4.2. Likewise, ratios of the P6 peak intensities to the ZnPO-X intensities closest to one another (2\theta) are displayed in Table 4.3. In general, the P6 peaks diminish at longer times and the ZnPO-X peaks grow in intensity thus making the ratio of P6/ZnPO-X peaks decrease versus time. Figure 4.20 shows the ratio of the 26.7 peak of P6 versus the 26.3 peak of ZnPO-X against the time during the reaction when microwaves were introduced. The other peak ratios taken show the same trend.

### 4.3.6 Investigation of the Clear Suspension Remaining after Crystallization is Complete

The mother liquor remaining when a standard reverse micelle system has reacted and precipitated (Comp1) was studied. The DLS studies show that after about 8 hours, growth is halted and after about 12 hours, the entities left in solution are about 67 nm as opposed to the approximately 7 nm reverse micelles in the nucleation phase at earlier stages of the growth. The mother liquor is removed from the reacting solution at various
points, centrifuged for 10 minutes at about 40,000 g, and introduced to microwave radiation for 1 minute to determine if the microwaves disturb the growth, increase the growth, or do not disturb the system. XRD’s are displayed in Figures 4.21 and 4.22 at the times the mother liquor was removed, centrifuged and microwaved (7, 10.5, 16, 21, 31 and 43 hours). The products were isolated and cleaned with ethanol after approximately 48 hours of total reaction time. The signature ZnPO-X peaks grow larger and the peaks of P6 decrease in size at latter points in the curve. Figure 4.23 takes the ratio of a characteristic P6 peak (26.7, 20) versus a ZnPO-X peak (26.3, 20) in the same vicinity. Other peak ratios followed the same trend and therefore are not shown.

4.3.7 Implications of Microwave Radiation on Yield

The introduction of microwave radiation increased the yield of the reverse micelle reactions. In situations where the mother liquor was removed and microwaved, additional precipitate was formed. In one extreme case, when microwave radiation was added to a typical reverse micellar growth system and compared to a system that was not microwaved, a nearly five-fold increase was seen in yield from about 2 mg to about 10 mg. However, doubling the yield was more typical when microwave radiation was employed.
4.4 Discussion

Most literature suggests that zeolites are formed much more rapidly when a standard hydrothermal type synthesis system is microwaved[23, 25, 26, 32]. However, it is important to note that while zeolites (aluminosilicates) typically require elevated temperatures in the range of about 80 °C to 200 °C to form readily, the zincophosphate system studied here readily forms at room temperature[16, 20].

The most bewildering information gathered, is how drastically a short period (1 minute) of microwave radiation effects the reverse micellar ZnPO-X growth system. The 1-minute pulse of microwave radiation is introduced to a reverse micelle growth system at various points along its growth curve over a period of about 22 hours. Figure 4.24 shows the pulse sequence for 5 experiments that were briefly introduced to microwave radiation and then allowed to react for approximately 48 hours total. The pulse sequences are overlaid on a representative growth curve of the ZnPO-X reverse micelle system which shows that pulses were introduced in various regions throughout the growth of ZnPO-X including the nucleation stage, growth stage and after completion is attained. The 1-minute pulse is extremely small in comparison to the 48-hour total reaction time, but the positioning of the pulse is detrimental in determining the product collected. The mother liquor left behind after crystallization is complete is studied over a longer period, up to 43 hours. It is understood that the water core temperatures will heat extremely fast, and to a high temperature, with the introduction of microwave radiation. The bulk solution temperature increase is about 21-23 °C and most of the heating is attributed to microwave absorption by the water cores. However, it is not easy to justify
the production of P6 when microwaves are introduced in the early stages of nucleation and growth (about the first 4 hours of reaction). Later in the synthesis, after product formation has ceased, microwave radiation promotes the further growth of ZnPO-X, the intended product. This change in product formed under the influence of microwave radiation at various points in the reaction is discussed below.

4.4.1 Preliminary Experiments

Concentrations of reverse micelle reactant solutions from previous work[20] provided interesting data, but ZnPO-X was not grown in the microwaved system. Some microwaving programs resulted in small amounts of P6 and all of the microwaving attempted provided a phase not previously seen. It appears to be an alternate state of P6 since the XRD’s in Figure 4.5 and 4.6 have many of the characteristic peaks of P6, with Figure 4.6 also showing another phase present that was not identified. Kooli et al. performed a series of experiments that showed several phases of a microporous silica formed with the same reactant concentrations, but a change in reaction temperature[33]. The XRD’s shown in Figure 4.5 were however taken on samples prepared by dropping a suspension of the crystals in ethanol on an XRD plate and allowing the solvent to evaporate. This type of sample preparation usually results in preferred orientation effects and therefore the intensities are not to be used for any quantitative data and some less intense, but characteristic peaks that could be used to identify a product may be too small to differentiate. However when the capillary XRD was taken (Figure 4.6), to eliminate
the preferential orientation, the characteristic pattern for P6 is recognized along with another unknown impurity.

As was mentioned previously, the template concentration was increased to try to provide enough structure to force the growth of ZnPO-X during the microwaving. Microwave radiation is introduced at various times in the reaction process as before with the optimized system with half the amount of template. For the samples that are introduced to the microwaves, the overwhelming product becomes P6 and not ZnPO-X. In that regard, it supports the earlier data that P6 is the preferred structure and microwaving overcomes the effects of increasing the template, trying to force ZnPO-X to form. The microwave introduction period is brief, only 1 minute, and therefore not in effect throughout the growth process (>24 hours) as most samples took a couple hours at least to show signs of product formation.

No real advantage was seen when the NaOH concentration was raised from 0.11 M to 0.14 M (and DABCO was increased from 0.58 M to 1.13 M), so this line of experiments was discontinued and the optimum value of 0.11 M (and 0.58 M for DABCO) was used for the duration. The same effects were seen, in that microwaving promoted the formation of P6 crystals.

The stringy fiber-like crystals seen when the concentrations of all reactants were raised, were thought to be hopeite. Hopeite is a condensed form of ZnPO, that is kinetically favored and would form without the use of a template. Studies were performed that showed that when certain frameworks such as ZnPO-X and ZnPO-sodalite dissolve and re-precipitate, that hopeite is the major product[34]. However, the amount of product produced was small enough that conventional XRD patterns could not
be collected. Regardless of the identity of the stringy product, upon microwaving, the appearance of P6 becomes obvious and the fiber-like crystals disappear. The formation of P6 in this case further bolsters the claim that the microwaved reverse micelle environment is more conducive to the growth of P6.

4.4.2 Summary of Preliminary Data

It is noted that the amount of time necessary to get ZnPO-X crystals to precipitate from a similar reaction was approximately 8 hours[20]. That 8 hour timeframe includes mixing, nucleation and then precipitation of larger particles. The microwaves introduced were almost entirely absorbed by the aqueous reactants at the core of the reverse micelles. The water loading level for these experiments is about \( w = 6 \) where \( w = \frac{[\text{H}_2\text{O}]}{[\text{DODMAC}]} \) and 0.6 mL of water was the total volume of water added. For this reason, the minute quantity of water would have risen significantly in temperature. Currently there are no good ways to monitor or predict the water temperature.

For a brief burst of microwaves to completely distort the product as it did in all of the cases presented above, one has to suspect the nucleation step was the point of disturbance. If nucleation of ZnPO-X was complete, then heating would theoretically mainly contribute to the growth phase. Cundy et al. demonstrates how thermal effects can alter the growth rates such that higher temperatures often lead to faster growth[35]. Since P6 is the primary product if microwaves are added during the nucleation phase, interest was taken in the growth process after nucleation is completed and growth begins.
4.4.3 Effect of Microwave Radiation on Reverse Micellar Growth of ZnPO-X

The DLS growth curve of ZnPO-X versus time shows four very distinct regions. The first region, Region I in Figure 4.16, covering about the first 4 hours is referred to as the nucleation stage and the reverse micelles show a constant size during this stage of about 7 nm. Growth then starts and occurs for about 4 hours before the particles begin to precipitate (Figure 4.16, Region II). At that point, growth continues, but precipitation of larger particles leads to the declining particle size over the next 4 hours (Figure 4.16, Region III). After about 12 hours, growth discontinues and the solution stabilizes with the particles remaining in solution approximately an order of magnitude larger (67.2 nm) than in the nucleation stage (Figure 4.16, Region IV). The solution from above the precipitate (mother liquor) can be removed and it remains stable for at least 2 months with no precipitate forming or other reactions occurring that are visible.

X-ray diffraction was employed to determine the predominant phase (ZnPO-X or P6) that was formed in the various samples. When comparing the diffraction patterns, taking the ratio of predominant peaks known for each of the frameworks involved will help determine which phase is prevalent. Figure 4.20 shows that as more reaction time elapses before the brief microwave radiation pulse is added, the lower the ratio of P6 to ZnPO-X, or more of the product is shifted towards ZnPO-X. The original goal was to synthesize ZnPO-X from reverse micelles and this shows that with the system outlined here, that microwaving early in the reaction forces the product to P6, an undesired product.
When DLS and XRD results are combined as is shown in Figure 4.25, an interesting dynamic is exposed. The two plots, the growth of ZnPO-X non-microwaved (Figure 4.25a) and the ratio of P6 to ZnPO-X (Figure 4.25b) seem to intersect at about 6 hours. If the 1 minute pulse of microwave radiation is introduced during the nucleation phase (first 4 hours of Figure 4.25a), the major product is P6. This seems to indicate that the radiation pulse is forcing the system to P6 and that the ZnPO-X nuclei that form are overwhelmed by the P6 growth and never really have the opportunity to grow. However, once growth of the ZnPO-X initiates after 4 hours of reaction, ZnPO-X begins to be observed by XRD although the microwaving still induces the growth of P6 so there are competing products. Eventually as the reaction proceeds further, introducing a microwave pulse does not have as large of an effect on the product composition. After about 15 hours of reaction time, ZnPO-X is the major product and the microwave pulse at later points does not lead to the formation of P6. Moreover, a microwave pulse after about 12 hours promotes more ZnPO-X growth and will be discussed in the next section.

After the growth of ZnPO-X is completed, as shown in Figure 4.16 to be around 12 hours, it was noted that the size of the particles remaining in the solution were much larger than during the nucleation phase, 67 nm as compared to about 7 nm. This remaining clear solution however proved to be stable for periods of more than 2 months, with no new precipitate forming. At various times after growth has started in the non-microwaved system, the mother liquor was removed, centrifuged and briefly microwaved (1 minute) to identify the product if new precipitate was formed. The temperature of the system typically rose from room temperature to ~48 °C during the minute of microwaving. Figure 4.21-4.22 shows the capillary diffraction patterns and Figure 4.23
exposes the ratio of the 26.7 2θ peak of P6 to the 26.3 2θ peak of ZnPO-X. At later periods (after 20 hours), when a microwave pulse is introduced, the major product is ZnPO-X and the nucleation concentration necessary for P6 is not as easily obtained in the reverse micelles and P6 shows up as a minor impurity. As more time elapses, the reverse micelles harbor ZnPO-X nuclei/particles and a diminished amount of nutrient that would promote P6 growth upon microwaving.

When performing early versions of the microwaved reactions, it was noted that the yield seemed to increase when microwave radiation was introduced. In instances where the mother liquor was removed and microwaved after approximately 48 hours of reaction time, the clear mother liquor produced more precipitate indicating the microwaves were causing the reaction to proceed even after it had seemed to conclude under reverse micellar reaction conditions (Brownian motion). In most cases, without using microwave radiation, 2-3 mg of product was recovered. Introduction of microwave radiation after about 48 hours of total reaction time would increase that yield to between 7-10 mg. Removing the mother liquor, and microwaving typically lead to yields of 2-4 mg. The yield was noted to improve by as much as five-fold, but was typically not that dramatic.

4.4.4 Hypotheses for the Early Stages of Reaction

The results displayed in Chapter 3 support an explosion type growth environment for a reverse micelle growth system influenced by microwave radiation described in Figure 3.31. A typical Brownian motion driven reverse micelle reaction presents a slow
nutrient exchange environment that allows for nucleation and eventual growth of the ZnPO-X product that is desired in this study. In the early stages of the ZnPO-X reverse micelle growth system, if microwave radiation is utilized in a short 1-minute pulse, the growth environment appears to no longer promote the growth of ZnPO-X, but a more condensed product identified as P6 is favored. With the gold growth system described in Chapter 3, the microwave radiation induced explosions introduce more nutrient to the growing nuclei faster than if Brownian motion were the driving force. With the explosions in the ZnPO-X microwaved system at early stages in the growth (first 4-8 hours), the compositions within each reverse micelle are changed more rapidly and do not allow the nucleation of ZnPO-X, but favors the nucleation and growth of P6. The temperature increase of approximately 22 °C is mostly attributed to heating of the water cores and their dissipation of heat into the bulk solution.

The microwave radiation appears to be promoting the nucleation and growth of P6 at all stages of the reverse micelle reaction aimed at producing ZnPO-X. The ZnPO-X nuclei formed before the brief microwave pulse remain intact, but the microwave pulse induces the nucleation and growth of P6. The full nucleation stage does not occur naturally for ZnPO-X (by the Brownian motion model in Figure 3.29) and the solubilisate exchange is effected such that proper conditions are not present to nucleate ZnPO-X. The DABCO concentration is crucial to direct the synthesis to the faujasite framework, and without it in adequate supply or distributed properly, the major product with the Zn and P concentrations as they are would be P6. The brief one minute pulse of microwave radiation causes the reaction to proceed without the slow solubilisate exchange nucleation stage for ZnPO-X, creating an environment that is more conducive to the formation of
P6. Rani et al. suggested that the nucleation phase for colloidal zeolites should perhaps be split into two parts: a prenucleation step for formation of primary particles (not nuclei), followed by a period over which those primary particles evolve into nuclei[36]. The microwave radiation supplied in this study disrupts the required pre-nucleation and nucleation steps, for ZnPO-X, and replaces it with nucleation and growth of P6. However, since the XRD patterns still show traces of the ZnPO-X peaks regardless of when the microwave radiation is introduced, it does not seem as if the ZnPO-X are actually being destroyed. Those nuclei can grow, but the opportunity for new nucleation of ZnPO-X diminishes as the P6 grows and reduces the nutrient concentrations.

If the prenucleation/nucleation scenario proposed by Rani et al. [36] exists within the reverse micelle system studied here, perhaps the microwave radiation applied in the early stages of the reaction are destroying these ZnPO-X pre-nuclei structures. If the ZnPO-X pre-nuclei are destroyed by the microwave radiation, the actual nucleation of ZnPO-X would not occur and the growth of P6 would dominate because it is the preferred structure. The occurrence of ZnPO-X in the products after the brief microwave pulse in the prenuclei timeframe could be due to the system returning to a Brownian motion driven system. If this occurs, it might be feasible for a small portion of the reverse micelles to attain the proper nucleation compositions for ZnPO-X before the system is depleted by P6 growth. Also, if the nucleation stage is attained before the microwave pulse, those nuclei may be stable enough to withstand the violent environment caused by the microwave radiation and those nuclei could grow along with the P6.
A third scenario in the early stages of the reaction is that the microwave radiation increases the temperature sufficiently to decompose the template DABCO. As mentioned above, the DABCO concentration is crucial to growth of ZnPO-X as the DABCO occupies the cages allowing for the open framework of faujasite and not the denser framework of P6. The melting point of DABCO is about 158-160 °C. It is conceivable that with the small quantity of water entrapped in the reverse micelle and the fact that most of the 150 W of microwave power is being absorbed by the water core, that the temperature is exceeding the melting point. Two separate reports state that DABCO has decomposed under reaction conditions of 180 °C. One suggests that the DABCO decomposes into NH$_4^+$ ions in 14 days at 180 °C[37], while the other suggests decomposition of diprotonated DABCO in the presence of water by the scheme presented in Figure 4.26 after 2 days at 180 °C[38]. Arafat et al. reports the Hoffman degradation of TPABr template occurs in 3 minutes in the presence of microwave radiation[24]. Although the degradation process would be different for DABCO, than TPABr, quick degradation in the presence of microwaves is possible.

### 4.4.5 Hypotheses for the Later Stages of Reaction

Microwave radiation employed after the first 8-12 hours of reverse micellar reaction time no longer favored the product P6, but resulted in a mixture of the two products. After about 12 hours of reaction time, microwave radiation actually seemed to promote additional growth of ZnPO-X as a 2 to 5-fold increase in yield was noted. This increase in yield and increased formation of ZnPO-X, instead of P6, can also be
supported by the model for a microwaved reverse micelle system reported in Chapter 3 and described by Figure 3.31.

When a reaction is “complete” in a reverse micelle system, there are still reactants encased in the reverse micelles, but concentrations are not high enough to continue growth on a short time scale (through Brownian motion). At extremely long times, growth may be visible as the random mixing would eventually provide nutrients to the nuclei/seeds. Singh and Dutta found that as the remaining clear suspension (after crystallization) from a reverse micellar system aimed at growing ZnPO-X was added to a nutrient system that was not conducive to growing ZnPO-X. ZnPO-X crystals grew, as ZnPO-X nuclei had remained in the reverse micelle solution and were used as seeds by the nutrients provided[20].

With the proposed microwaved reverse micelle growth mechanism from Chapter 3 (Figure 3.31), the mixing of the remaining reactants is accelerated, leading to continued growth of the leftover ~67 nm particles/nuclei that are observed by DLS after 12 hours of growth. The slower Brownian motion driven model (Figure 3.29) is replaced by the faster “explosion” driven model in Figure 3.31. The Brownian motion model would require extremely long timeframes as the remaining reverse micelles contain much lower concentrations of nutrients. It appears that the microwave radiation promotes better mixing and introduces the more of the remaining nutrient left to viable nuclei in the reverse micellar solution. This promotes further growth (yield improvements), an effect similar to what Singh and Dutta reported when they add nutrient to the remaining clear suspension after crystallization was complete[20].
4.5 Conclusions

A 1 minute pulse of microwave radiation introduced during the nucleation phase (first 4 hours of reaction) of a water in oil micellar reaction designed to grow the faujasitic form of a zincophosphate, induces the production of a more dense and stable product, P6 after 20 hours. At later phases of the growth system (4 hours to about 15 hours), after ZnPO-X has had a chance to nucleate and begin growth, the brief microwave pulse still leads to P6 growth, but the ZnPO-X crystals are robust, and enough have formed that they begin to appear in the diffraction patterns. At later periods, after actual growth of ZnPO-X has ceased, the microwave pulse actually promotes the growth of the already formed ZnPO-X nuclei. At this point, enough ZnPO-X nuclei have formed that the nucleation concentration threshold for P6 in the remaining reverse micelles is barely attainable and therefore most of the remaining nutrients, in the reverse micelles, contribute to the growth of the ZnPO-X nuclei.

The initial goal of this project was to expedite the process of making ZnPO-X in a reverse micelle system. When the optimized conditions for a non-microwaved reverse micellar growth formed primarily P6 after microwaving, several variations in concentrations of the reactants were attempted to no avail. Eventually, latter phases of the reaction were studied and suggest that perhaps the nuclei formed in the nucleation phase were not being destroyed, that they simply were overwhelmed by the nucleation and growth of P6, but when given enough time to fully form and grow, the ZnPO-X nuclei eventually will direct a microwave synthesis to the formation of more ZnPO-X than forms in the non-microwaved reactions.
Table 4.1. Concentrations of the individual components of the four compositions used in this study.

<table>
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<tr>
<th></th>
<th>[Zn(NO$_3$)$_2$·6H$_2$O]</th>
<th>[NaOH]</th>
<th>[H$_3$PO$_4$]</th>
<th>[DABCO]</th>
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<td>Time (hours)</td>
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<td>11.4 (P6)</td>
<td>26.3 (X)</td>
<td>26.7 (P6)</td>
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<td>970.19</td>
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<td>1007.9</td>
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**Table 4.2.** Intensity values for several prominent P6 and ZnPO-X peaks found in the XRD patterns for the microwave versus reaction time experiments. Notice the general trend that the P6 peaks diminish versus time whereas the ZnPO-X peaks increase. (Baseline corrected values)
<table>
<thead>
<tr>
<th>Time (hours)</th>
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<th>31.9/31.6</th>
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<td>2.71</td>
<td>1.54</td>
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<td>5</td>
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<td>2.01</td>
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</tr>
<tr>
<td>6</td>
<td>0.95</td>
<td>1.43</td>
<td>1.31</td>
</tr>
<tr>
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<td>0.85</td>
<td>1.37</td>
<td>1.21</td>
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<tr>
<td>10</td>
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<td>0.77</td>
<td>0.96</td>
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<td>15</td>
<td>0.18</td>
<td>0.38</td>
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**Table 4.3.** Columns 2-4 are peak intensity ratios for prominent P6 peaks versus prominent ZnPO-X peaks nearby. The numbers in the top row represent the 2θ values. (Baseline corrected values)
Figure 4.1. SEM images of the optimized ZnPO-X product from a reverse micelle system.
Figure 4.2. SEM images of the optimized ZnPO-X product from a reverse micelle system after microwaving for 1 minute at 150 W, 2 minutes after the reaction was started. Several hours passed before the product was isolated, cleaned and analyzed.
Figure 4.3. SEM images of the optimized ZnPO-X product from a reverse micelle system after microwaving for 1 minute at 150 W, 60 minutes after the reaction was started. Several hours passed before the product was isolated, cleaned and analyzed.
Figure 4.4. SEM images of the optimized ZnPO-X product from a reverse micelle system after microwaving for 1 minute at 150 W, 120 minutes after the reaction was started. Several hours passed before the product was isolated, cleaned and analyzed.
Figure 4.5. Standard XRD of the samples from Figures 4.2-4.4 (a-c), respectively, taken by dropping a suspension of the particles in acetone onto a glass sample holder. This leads to preferred orientation effects.
Figure 4.6. Capillary XRD pattern of the sample shown in Figure 4.2 and Figure 4.5a. As compared to the pattern in 4.5a, this pattern is not preferentially oriented and therefore the major peaks are less intense and more of the smaller peaks are elucidated. Pattern was baseline corrected. P6 peaks are marked with a P, the other phase is unknown.
Figure 4.7. Reaction of the optimized ZnPO-X conditions except that the amount of template was increased.
Figure 4.8. Microwave reaction of the increased template trials. Microwaving was done 2 minutes after the reaction began and was performed at 150 W for 1 minute.
Figure 4.9. Microwave reaction of the increased template trials. Microwaving was done 60 minutes after the reaction began and was performed at 150 W for 1 minute.
Figure 4.10. Microwave reaction of the increased template trials. Microwaving was done 120 minutes after the reaction began and was performed at 150 W for 1 minute.
Figure 4.11. SEM images of the increased NaOH reaction.
Figure 4.12. SEM images of the increased NaOH reaction that was microwaved 2 minutes after the reaction began for 1 minute at 150 W.
Figure 4.13. SEM images of the increased NaOH reaction that was microwaved 60 minutes after the reaction began for 1 minute at 150 W.
Figure 4.14. SEM images of the increased NaOH reaction that was microwaved 120 minutes after the reaction began for 1 minute at 150 W.
Figure 4.15. SEM images of the increase of all reactants experiments that show predominantly P6 formation in all cases ranging from (a) non-microwaved, (b) intermittent microwaving, (c) 20 seconds at 150 W, (d) 45 seconds at 150 W, and (e) 90 seconds at 150 W.
Figure 4.16. Dynamic light scattering (DLS) data for the non-microwaved growth of a reverse micelle system optimized for ZnPO-X growth. Four distinct regions are seen that outline the growth process.
Figure 4.17. Capillary XRD patterns for the microwave versus reaction time where the reaction time elapsed before microwaving for 1 minute at 150 W is (a) 1 hour, (b) 3.25 hours and (c) 5 hours. All patterns have been baseline corrected and the inset is of region 26-27 2θ. ZnPO-X peaks marked with X and P6 peaks marked with P.
Figure 4.18. Capillary XRD patterns for the microwave versus reaction time where the reaction time elapsed before microwaving for 1 minute at 150 W is (a) 10 hours, (b) 20 hours and (c) 25 hours. All patterns have been baseline corrected and the inset is of region 26-27 2θ. ZnPO-X peaks marked with X and P6 peaks marked with P.
Figure 4.19. Capillary XRD pattern of a non-microwaved optimized reverse micelle growth for comparison with those XRD’s in Figure 4.17 and 4.18 that have been microwaved at various times during the reaction. The pattern was baseline corrected and the inset is of region 26-27 $\theta$. ZnPO-X peaks are marked with an X, and the place where the P6 peak at 26.7 ($\theta$) is marked with a P in the inset pattern.
Figure 4.20. Ratio of XRD peaks 26.7 (2θ) that represents P6 and 26.3 (2θ) representing ZnPO-X. The timescale represents the time during the reaction that 150 W of microwave radiation was introduced for 1 minute.
Figure 4.21. XRD patterns for products formed when the clear mother liquor from above a ZnPO-X reverse micelle reaction is isolated and microwaved at (a) 7 hours, (b) 10.5 hours and (c) 16 hours. All patterns have been baseline corrected and the inset is of region 26-27 °θ. ZnPO-X peaks marked with X and P6 peaks marked with P.
Figure 4.22. XRD patterns for products formed when the clear mother liquor from above a ZnPO-X reverse micelle reaction is isolated and microwaved at (a) 21 hours, (b) 31 hours and (c) 43 hours. All patterns have been baseline corrected and the inset is of region 26-27 $\theta$. ZnPO-X peaks marked with X and P6 peaks marked with P.
Figure 4.23. Mother liquor analysis data where time is the point at which the mother liquor was isolated and microwaved and the ratio is of P6/ZnPO-X peak intensities (26.7/26.3). As more time elapses, the reverse micelles harbor ZnPO-X nuclei/particles and a diminished amount of nutrient that would promote P6 growth upon microwaving.
**Figure 4.24.** Representation of the microwave radiation pulse sequence (brief one minute pulse) employed at various stages of the reverse micellar growth system for ZnPO-X overlaid on a DLS growth pattern. Each solid line represents a separate experiment and the microwave pulse was added for 1 minute at the time shown above the curve. XRD’s of the products from these reactions can be seen in Figures 4.17 and 4.18. Most products were then isolated after 48 hours of total reaction time so the microwave perturbation was extremely small when compared to the total reaction time.
Figure 4.25. Combination of Figure 4.16 and Figure 4.20 that shows how as the growth process of a non-microwaved sample proceeds, the amount of P6 product decreases as shown by the ratio of a P6 peak versus a ZnPO-X peak. Without microwaving, ZnPO-X is the major product. (a) is the DLS data for growth of a ZnPO-X non-microwaved reverse micelle system and (b) is the intensity ratio of a P6 peak versus a ZnPO-X peak (26.7/26.3).
Figure 4.26. Scheme proposed for the degradation of diprotonated-DABCO in the presence of water[38].
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**Chapter 3**


Chapter 4


