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Synthesis and spectroscopy of zeolite-encapsulated metal complexes

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The Ohio State University, 1990
SYNTHESIS AND SPECTROSCOPY OF ZEOLITE ENCAPSULATED METAL COMPLEXES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of the Ohio State University

By

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*****

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# TABLE OF CONTENTS

ACKNOWLEDGMENTS .......................................................... ii
VITA ................................................................................ iii
LIST OF TABLES .................................................................. vii

LIST OF FIGURES ........................................................... iix

CHAPTER  PAGE

I.  INTRODUCTION TO ZEOLITE ENCAPSULATED  PAGE
   METAL COMPLEXES ...................................................... 1
   References ................................................................. 22

II. INFRARED STUDY OF Fe(CO)\textsubscript{5} ABSORBED  PAGE
   ONTO ZEOLITE Y ....................................................... 24
   Introduction ............................................................... 24
   Experimental ............................................................. 27
   Results ................................................................... 29
   Discussion ............................................................... 61
   Conclusions ............................................................. 81
   References ............................................................... 85

III. OLEFIN OXIDATION BY ZEOLITE  PAGE
    ENCAPSULATED Mn(SALEN) ......................................... 89
    Introduction ............................................................ 89
    Experimental .......................................................... 94
    Results .................................................................. 98
    Discussion ............................................................ 113
    Conclusions ........................................................... 124
    References ............................................................. 125
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1.</td>
<td>IR Band Assignments for Fe( CO)\textsubscript{5}/NaY</td>
</tr>
<tr>
<td>3.1.</td>
<td>Reactivity of Olefins</td>
</tr>
<tr>
<td>3.2.</td>
<td>Relative Reactivity of Olefins versus Cyclohexene</td>
</tr>
<tr>
<td>5.1.</td>
<td>Effect of Ethanol Upon Zeolite Crystallization</td>
</tr>
<tr>
<td>5.2.</td>
<td>Effect of HMPA Upon Zeolite A Crystallization</td>
</tr>
<tr>
<td>5.3.</td>
<td>Effect of DMSO Upon Zeolite A Crystallization</td>
</tr>
<tr>
<td>5.4.</td>
<td>Comparison of Effect Upon Zeolite A Crystallization of Cosolvents Present in Equal Molar Quantities</td>
</tr>
<tr>
<td>5.5.</td>
<td>Effect of Hydroxide Concentration Upon Zeolite A Crystallization</td>
</tr>
<tr>
<td>5.6.</td>
<td>Effect of Cosolvent Addition Upon Zeolite A Crystallization with Constant [OH\textsuperscript{-}]/[H\textsubscript{2}O]</td>
</tr>
<tr>
<td>5.7.</td>
<td>Effect of Varying Si/Al with DMSO as a Cosolvent</td>
</tr>
<tr>
<td>5.8.</td>
<td>Effect of [OH\textsuperscript{-}] Concentration Upon Zeolite Formation with DMSO as a Cosolvent</td>
</tr>
<tr>
<td>5.9.</td>
<td>Effect of Addition of TMA\textsuperscript{+} to Zeolite Y Reaction Mixture</td>
</tr>
<tr>
<td>FIGURE</td>
<td>PAGE</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>1.1. Structure of the sodalite cage</td>
<td>2</td>
</tr>
<tr>
<td>1.2 Structure of Zeolite A</td>
<td>4</td>
</tr>
<tr>
<td>1.3 Structure of Zeolite Y</td>
<td>5</td>
</tr>
<tr>
<td>2.1 Infrared spectra of Fe(CO)$_5$ on dehydrated Na-Y</td>
<td>32</td>
</tr>
<tr>
<td>2.2 Infrared spectra of Fe(CO)$_5$ on dehydrated Na-Y at different loadings at room temperature: (a) 1 Fe(CO)$_5$ per ~250 supercages, 0.01 Torr of Fe(CO)$_5$, 5 s of contact; (b) 1 Fe(CO)$_5$ per ~25 supercages, 0.3 Torr of Fe(CO)$_5$, 5 s of contact; (c) 1 Fe(CO)$_5$ per ~2 supercages, 0.3 Torr of Fe(CO)$_5$, 10 s of contact; (c') spectrum obtained by subtracting (a) from (b); (d) Fe(CO)$_5$ on amorphous aluminosilicate, 0.01 Torr of Fe(CO)$_5$, 5 s of contact</td>
<td>34</td>
</tr>
<tr>
<td>2.3 Infrared spectra of Fe(CO)$_5$ on dehydrated Na-Y as a function of increasing loading (a-e) at ~77 K. (f) Spectrum obtained by subtracting (b) from (c) (10 Torr of Fe(CO)$_5$; contact times (a-f) 5 s, 5 min, 10 min, 15 min, and 45 min)</td>
<td>36</td>
</tr>
<tr>
<td>2.4 Infrared spectra of Fe(CO)$_5$ on (a) dehydrated Na-Y, 0.3 Torr of Fe(CO)$_5$, 5 s, (b) dehydrated Na-Y with pyridine (25 Torr, 10 min), (c) dehydrated Na-Y with PMe$_3$ (25 Torr, 10 min). All loadings at room temperature</td>
<td>41</td>
</tr>
<tr>
<td>2.5 Infrared spectra of Fe(CO)$_5$ (0.3 Torr, 5 s) on dehydrated Na-Y (a) exposed to O$_2$ (1 atm, 10 s), (b) exposed to C$_2$H$_4$ (75 Torr, 10 s), (c) heated with CO at 60°C for 40 min. All loadings at room temperature</td>
<td>43</td>
</tr>
</tbody>
</table>

viii
2.6. Infrared spectrum of (a) Fe(CO)$_5$-NaY (0.3 Torr, 5 s) and (b) exposed to PMe$_3$ (25 Torr, 1 min). All loadings at room temperature. ............................... 46

2.7. Infrared spectra of Fe(CO)$_5$-PMe$_3$-NaY exposed to increasing amounts of CO. The weak bands due to PMe$_3$ have been subtracted out by comparison with a PMe$_3$-NaY sample, the 1425 cm$^{-1}$ peak of PMe$_3$ (Samples prepared according to the caption in Figure 2.6.) .................. 48

2.8. Infrared spectra of (a) Fe(CO)$_5$-Na-Y (0.3 Torr, 5s) exposed to increasing amounts of NH$_3$ (b-d), 0.25 Torr, 0.5 atm, 1 atm, respectively. Contact times were for 30 s at room temperature. .......................... 49

2.9. Infrared spectra of (a) Fe(CO)$_5$-Na-Y (0.3 Torr, 5 s) exposed to increasing amounts of pyridine (b and c), 25 Torr, 10 s, 30 s, respectively. The bands due to pyridine have been subtracted out by comparison with a pyridine- Na-Y sample, by using the 1440-cm$^{-1}$ peak of pyridine. Loadings were at room temperature. ............................... 53

2.10. Infrared spectrum of (a) Fe(CO)$_5$-Na-Y (0.3 Torr, 5 s) (b) exposed to acetylene (1 atm, 10 s) at ~77 K. .......................... 55

2.11. Infrared spectra of Fe(CO)$_5$-Na-Y (0.3 Torr, 5 s) exposed to water vapor as a function of time (a) initial spectrum, (b) 20 Torr, 15 min, (c) 20 Torr, 30 min, (d) 20 Torr, 1 h. Loadings were at room temperature. ............................... 57

2.12. Infrared spectra (a) of high loaded Fe(CO)$_5$-Na-Y (10 Torr, 10 s) samples and (b) upon its exposure to O$_2$ (1 atm, 10 s). Loadings were at room temperature. ............... 60

3.1. Diffuse reflectance spectra of Mn$^{11}$(salen) encapsulated in zeolite Y (Kubelka-Munk with reference to NaY). ................................. 100

3.2. Diffuse reflectance spectra of Mn$^{11}$ (salen)-Y.. 101
3.3. Transmission infrared spectra of Mn^{III} (salen)-Y ........................................... 103
3.4. GC trace of the products formed upon cyclohexene oxidation with catalyst A [Mn^{III} (salen)]. .................................. 105
3.5. Determination of turnover number. .............. 110
3.6. Determination of rate of reaction. .............. 111
3.7. Structure of Mn(salen)OH. ...................... 115
3.8. Proposed reaction scheme for olefin oxidation. 116
4.2. IR spectra of J-en and Co(J-en). .............. 137
4.3. Diffuse reflectance spectra of Co(J-en)-Y. Kubelka-Munk with reference to NaY. .......... 138
4.4. X-ray absorption spectrum of Co(J-en). ...... 141
4.5. X-ray absorption spectrum of Co(J-en)-Y. .. 142
4.6. Normalized EXAFS spectrum of Co(J-en). ..... 143
4.7. Normalized EXAFS spectrum of Co(J-en)-Y. .. 144
4.8. PRDF of (a) Co(J-en)-Y and (b) Co(J-en) .... 145
4.9. EPR spectra of Co(J-en)-Y. ..................... 149
4.10. EPR spectra of dehydrated NaY. ............... 151
4.11. EPR spectra of dehydrated CoY. .............. 153
4.12. EPR spectra of J-en heated at 300°C with NaY. 155
4.13. Room temperature EPR spectra of Co(J-en)(pyridine)-Y exposed to oxygen. .............. 157
4.14. Low temperature EPR spectra of Co(J-en)(pyridine)-Y exposed to oxygen. .............. 159
4.15. Comparison of UV-VIS spectra of Co(tetren) in solution and encapsulated in zeolite Y. .... 161
4.16. X-ray absorption spectrum of Co(tetren). ..... 162
4.17. X-ray absorption spectrum of Co(tetren)-Y. ... 163
4.18. Normalized EXAFS spectrum of Co(tetren). ..... 164
4.19. Normalized EXAFS spectrum of Co(tetren)-Y. ... 165
4.20. PRDF of (a) Co(tetren)-Y and (b) Co(tetren). .. 166
4.21 Room temperature EPR spectra of Co(tetren)Y. .. 167
4.22 EPR spectrum of Co(tetren)-A (air dried). ... 169
4.23 EPR of Co(tetren)-A (evacuated). ............... 171
4.24. EPR spectrum of Co(tetren)-A evacuated at 100°C. 173
4.25. Diffuse reflectance UV-VIS spectra of Co(tetren) encapsulated inside zeolite A. .... 175
4.26. Room temperature EPR of Co(tetren) formed in LiCo-A. ................................. 177
4.27. Room temperature EPR spectra of Co(tetren) formed in KCo-A. .......................... 179
4.28. Room temperature EPR spectra of Co(tetren) formed in CsCo-A. .......................... 181
4.29. Determination of the $K_{obs}$ for oxygen binding by Co(tetren). ....................... 184
5.1. XRD patterns of zeolite crystals after three hours. ......................................... 212
5.2. XRD patterns of zeolite crystals after four hours. .......................................... 213
5.3. XRD pattern after three hours heating. ........ 214
5.4. XRD pattern after four hours heating. ........ 215
5.5. Comparison of XRD pattern to determine Si/Al ratio of zeolite Y product. .............. 219
5.6. XRD pattern of mazzite. ....................... 220
A1. XRF calibration curve for the determination of iron in zeolite matrix. Standards prepared by ion exchanging with FeCl$_3$·6H$_2$O solution. Excitation using a Ge target at 20 kV and 2.0 mA for 100 seconds. ............... 234

A2. XRF calibration curve for the determination of manganese in zeolite matrix. Standards prepared by ion exchange with MnCl$_2$·4H$_2$O solutions. Direct excitation at 13 kV and 0.01 mA for 100 seconds was used. ........... 235

A3. XRF calibration curve for the determination of cobalt in zeolite matrix. Standards prepared by ion exchanging with Co(acetate)$_2$·4H$_2$O. Direct excitation at 11 kV and 0.01 mA for 100 seconds was used. ...... 236
Zeolites are microporous crystalline materials made up of tetrahedrally bonded silicon and aluminum atoms connected by bridging oxygens.\(^1\) The composition of zeolites can be given by the following formula.

\[ M^{n+} \frac{y}{n} [(SiO_2)_x(AI_2O_2)_y] zH_2O \]

The aluminosilicate framework has a repetitive three dimensional structure which contains a precise and repetitive network of channels and cavities. The presence of the aluminum results in a negative charge on the framework and the loosely held cations are present as charge compensators. Normally the void volume of the zeolite is filled with water which can be removed reversibly by heating.

Zeolites A, X, and Y are made from a common building unit, the sodalite cage. The sodalite cage, sometimes called the B cage, is made up of four and six-membered rings and is shown in Figure 1.1. The central cage of this unit has a diameter of 6.5Å, and access to this cage is gained through one of the six-membered rings which have diameters of 2.2Å.
Figure 1.1. Structure of the sodalite cage.
The zeolite A structure is made up of sodalite cages connected at the four membered rings by bridging oxygen atoms. This arrangement results in a cubic symmetry. Connection of these cages in this manner results in a central cage with a diameter of 11.5Å which is accessible through eight-membered rings with a diameter of 4.2Å. A schematic of the zeolite A structure is shown in Figure 1.2.

Zeolites X and Y have identical structures and differ only in the Si/Al ratio of the material. The mineral faujasite is also isostructural with zeolites X and Y. In the faujasite structure, the sodalite cages are connected in a tetrahedral manner. The sodalite cages are connected through their six-membered rings and enclose a cavity with an internal diameter of 12.5Å which is accessible through twelve-membered rings with a free aperture of 7.5Å (Figure 1.3). This cavity is commonly referred to as the supercage, as it is the largest void present in a zeolite structure. This large cavity makes zeolite Y a favorite support for metal complexes.

The unique features of zeolites make them important materials in industry in the production of products as diverse as detergent and gasoline. The presence of loosely held cations gives zeolites a cation exchange capability. This property has been exploited in the softening of water as calcium and magnesium in the water are exchanged for sodium in the zeolite. For similar reasons zeolites, are often ingredients in laundry detergents. The cation exchange
Figure 1.2. Structure of Zeolite A.
Figure 1.3. Structure of Zeolite Y.
The ability of zeolites also provides a means of introducing metal ions into the zeolite. The introduction of a metal into the zeolite support allows the production of useful catalysts.

Removal of the water from the zeolite channels allows the zeolite to act as a unique absorbent. There are over 150 different zeolites with pore sizes that range from 3-13Å. The zeolites can selectively absorb only those molecules physically small enough to enter the pore structure. This phenomenon is what gives zeolite the name molecular sieves. The elemental composition of the zeolite framework also affects the absorption properties of the zeolite as this determines whether the zeolite is hydrophilic or hydrophobic. Zeolites with lower Si/Al ratios contain more cations; therefore, the interior of the zeolite is quite polar. Such zeolites are often used to preferentially remove water from organic solvents. In contrast, zeolites with very low aluminum content are hydrophobic and can be used to remove trace quantities of organics from water. The molecular sieving properties of zeolites have also been exploited in the separation of gas mixtures.

Zeolites have also found considerable use as catalysts, especially in the petroleum industry. The acidity of the zeolites make them very useful as cracking catalysts. Use of metal doped zeolites as cracking catalysts represents the largest volume of any manufactured catalyst. Much effort is continually spent in the attempt to synthesize new zeolites
which will be more efficient in the production of gasoline. ZSM-5, a high silica zeolite synthesized by Mobil, is a catalyst in the production of gasoline from methanol.\textsuperscript{3,4} The key to zeolite usefulness as catalysts is the combination of acidity and shape selectivity which arises from the fact that the active catalyst sites are inside the pores of the zeolite. Also of importance is the thermal stability of the zeolites which allows reactions and regeneration processes to be carried out at elevated temperatures. Zeolite Y, for instance, is stable up to temperatures in excess of 1000K.

Zeolites contain both Brønsted and Lewis acid sites. The Brønsted sites are due to protons attached to lattice oxygen atoms, while the Lewis sites can be due to the charge compensating cations or incompletely coordinated framework aluminum atoms. The number and strength of acid sites in the zeolite can be varied either by the zeolite synthesis process or by subsequent ion exchange treatments. These acid sites are critical for virtually all the industrially important uses of zeolites as catalysts. The most important industrial applications of zeolites are in catalytic cracking, hydroisomerization, selective forming, hydrocracking and transformations of aromatic hydrocarbons.\textsuperscript{2}

Catalytic cracking, and all other large scale industrial uses of zeolites as catalysts, takes advantage of the unique properties of zeolites to form a useful product in a manner more efficient than is possible without the zeolite. These
reactions could be run using different catalysts, but the greater selectivity of zeolites often makes them the preferred catalyst. Because the active site of the catalyst is inside the zeolite pores, the framework of the zeolite exerts control over the reaction from start to finish. Only molecules which are of an appropriate size to diffuse into the cavities of the zeolite can become reactants. The steric restraints of the zeolite framework can exert an influence over the structure of any reaction intermediates. Finally, only products of an appropriate shape can diffuse out of the zeolite. Any other products are trapped and are susceptible to further reaction while trapped in the zeolite cavity.

The unique pore structure of the zeolite, coupled with its thermal stability, makes it a novel and useful support for other catalysts. Now rather than the zeolite itself acting as a catalyst, it is simply the host for a catalyst. This idea has also been put into practice on an industrial scale in the hydroisomerization of paraffins to isoparaffins. The catalyst in this case is a noble metal highly dispersed on a very acidic zeolite with a low sodium content. The acidic zeolite is playing a promoting role in the chemistry in this example, but the difference here is that the dispersed metal is not a part of the zeolite. The zeolite is an active support for the catalyst, not only promoting the reaction due to its acidic nature, but also introducing size selectivity due to its molecular sieving ability.
Once zeolites themselves became viable replacements for homogenous catalysts the next logical step was to examine if the zeolite could act as a host for other homogeneous catalysts, effectively heterogenizing them. In addition, the cavity of the zeolite can be looked upon as a beaker of approximately molecular dimension and there would be interest in how encapsulation would affect the spectroscopy, reactivity, catalytic activity and other physical and chemical properties of the enclosed materials. There was particular interest in encapsulating metal complexes which were known catalysts in solution.

Supporting of a metal complex inside a zeolite would produce a catalyst which was intermediate between the two limiting cases of molecular catalysts in solution ("homogeneous catalyst") and metal surfaces ("heterogeneous catalysts"). As an intermediate between these two extremes a supported metal complex could be expected to have characteristics of both, giving it a unique set of properties which have made it the best catalyst for a particular job. By comparing the advantages and disadvantages of homogeneous and heterogeneous catalysts one can get an idea of the possible benefits of supporting a metal complex inside a zeolite.

Separation of the catalyst from the reaction mixture at the conclusion of a reaction is often a difficult or expensive step when using homogeneous catalysts. Due to the homogeneous
nature of the system the separation must involve a very efficient distillation, ion exchange or solvent extraction. Distillation is often the choice of commercial processes catalyzed by homogeneous reactions. This is feasible, for instance, in the Monsanto process for the production of acetic acid, due to the relatively low boiling point (117.9°C) of the product. This is in contrast to a heterogeneous catalytic system where filtration is sufficient to remove the catalyst. The ease of removal of the catalyst in a heterogeneous system compared to a homogeneous system is often the crucial factor in determining which process is most feasible on a large scale.

Because all of the metal centers are accessible in a homogeneous system the resulting efficiency and activity will be higher. However, dimerization or other bimolecular decay modes can work to limit this advantage. A properly designed supported catalyst can be as accessible as a homogeneous catalyst with the added benefit that bimolecular decay can be prevented by encapsulation of the complex which prevents two catalyst molecules from encountering each other. This could result in a longer life and higher efficiency for the supported metal complex. Due to the molecular nature of a homogeneous catalyst with its unique stoichiometry and structure there is total reproducibility in catalyst preparation. Such reproducibility should result in the higher specificity inherent to homogeneous catalysis. This
reproducibility should be approached in a supported metal complex system, but complicating factors like pore blockage preventing ligands from reacting with the metal ion will often result in a less than perfectly uniform catalyst.

Heterogeneous catalysts often have several available active sites which can result in several competing reactions being catalyzed. A homogeneous catalyst will usually have one active site and so will generally be more specific toward catalyzing one reaction. With care, supported metal complexes with specificity as high as a homogeneous catalyst can be produced. It should be noted that with complex reaction mixtures such as petroleum fractions the catalysis of several reactions may be desirable. The specificity of a homogeneous catalyst can be varied controllably by changing the ligands present to alter the electronic or steric properties of the active site. This can also be done with supported metal complexes.

The thermal stability of metal complexes, either supported or unsupported, is generally lower than that of a typical heterogeneous catalyst. This allows a heterogeneous catalyst to operate at higher temperatures which would be expected to result in greater reactions rates. Supporting a metal complex can also result in reduced sensitivity to oxidative degradation. This advantage, along with the prevention of bimolecular decay modes, often results in longer life for supported metal complex catalysts.
The choice of an appropriate solvent for use with a homogeneous metal catalyst is limited by the solubility of the complex. This is, of course, not a limitation with a heterogeneous catalyst. This will also not be a consideration for a zeolite encapsulated metal complex. The choice of the solvent can be made strictly on the basis of cost, convenience and other factors specific to the reaction of interest.

Consideration of the effects of supporting a metal complex in a zeolite suggests that a combination of the advantages of both homogeneous and heterogeneous catalysis could result. Specifically, the advantages of homogeneous catalysts such as selectivity and controllability which are a result of the catalyst's molecular nature can be combined with ease of separation inherent to a heterogeneous system. There is also the possibility of other benefits due to the presence of a zeolite support.

The zeolite may take an active role in selecting the substrate upon which the catalyst acts. The molecular sieving capability of the zeolite may come into play as certain molecules can more easily reach the active site in the interior of the zeolite. Also, as mentioned earlier, catalyst life can be prolonged by preventing catalyst molecules from encountering each other. These possible benefits, along with interest in obtaining more fundamental understanding of the effect of supports on metal complexes, made this a promising field.
Early work concentrated upon the synthesis and characterization of metal complexes inside the supercages of zeolites X and Y. Usually the metal complex was formed by adding the ligand to a dehydrated zeolite which has had the desired metal ion exchanged in. It is also possible to study the effect of zeolite encapsulation upon complexes formed outside the zeolite. These complexes can be added to the zeolite either by absorption from the gas phase or by ion exchanging a cationic complex into the zeolite.

A wide variety of techniques are available for the characterization of zeolite encapsulated metal complexes and the nature of the metal complex can determine which technique is best suited to obtain the desired information. Paramagnetic compounds are often examined via EPR due to its great sensitivity. EPR is also the obvious technique for the determination of the oxygen binding constant for reversible oxygen binding metal complexes. Because of its ability to get detailed structural information from a dispersed material, EXAFS can be used on virtually any zeolite encapsulated metal complex. The limitation to the use of this technique is access to a synchrotron radiation source. The use of infrared spectroscopy is usually limited to metal carbonyls supported upon zeolites as the zeolite matrix does not interfere in the carbonyl stretching region. Vibrational information is often more conveniently obtained using resonance Raman spectroscopy as this avoids problems due to interference from the zeolite.
matrix.\textsuperscript{12} Spontaneous Raman has also been used to obtain information in compounds in which resonance could not be achieved.\textsuperscript{13} If the complex is colored, diffuse reflectance UV-VIS spectroscopy is a useful characterization tool and can also aid in the choice of an excitation wavelength for resonance Raman spectroscopy.\textsuperscript{14} Finally, for complexes which contain an appropriate nucleus, solid state NMR can be a very useful characterization tool.\textsuperscript{15}

When these metal complexes are formed, the zeolite may take upon the function of a ligand, an anion or a solvent. It is possible for the zeolite to take upon more than one role at a time. It has been generally found that the oxide ions of the zeolite lattice are fairly weak ligands and neutral molecules can easily replace them to form more stable complexes. Encapsulation inside the zeolite can allow the formation of unusual symmetries which would not occur in a homogeneous solution. The cation, extent of hydration of the zeolite and the effect of the zeolite as a ligand are all factors which can cause results which are different from that seen in solution. It is also possible that size restraints in the zeolite supercage can prevent a dimerization which would normally occur.

Even when the zeolite is simply acting as a solvent for a metal complex it can exert an influence which causes a change in the molecule’s spectroscopy. Dutta et al. examined the influence of cations and the extent of hydration upon the
resonance Raman spectra of the cobalticinium ion in zeolite Y. By examination of the C-H stretching region it was determined that cobalticinium cation forms stronger hydrogen bonds in the hydrated zeolite cavities than in solution. When the zeolite was dehydrated under mild conditions the bond between the cobalt and the ring became polarized. The electrostatic fields of the cations were responsible for this polarizing effect and the effect increased as K⁺ ions were replaced by Ca⁺² ions and experienced a further increase when La⁺³ ions were used. It is seen that the interior of the zeolite is a quite polar environment and that this polarity can be varied by changing the extent of hydration and the type of cation present.

An interesting example of the type of effects that the zeolite can exert is seen in a bipyridine complex with cobalt in zeolite Y. The interesting feature of the Co(bpy)₃⁺² complex encapsulated in the supercage of zeolite Y is that it exhibits a spin equilibrium. That is, as the temperature is raised from 77K the complex goes into the high spin state. The equilibrium between the high and low spin states of the complex is temperature dependent. Such spin equilibria are known for systems outside the zeolite, but this is the first report of the phenomena with a metal complex encapsulated inside the cavity of zeolite Y. In addition this situation was in contrast to the Co(bpy)₃⁺² complex outside the zeolite where it does not exhibit any spin equilibrium. It was
hypothesized that the zeolite may be stabilizing the low spin form of the complex as the complex and the supercage are of comparable size. Thus it is seen that even fairly subtle interactions with the zeolite can result in profound changes in a metal complexes' properties.

With the ability to synthesize and characterize zeolite encapsulated metal complexes with a variety of techniques well established, interest next arose in determining how the chemical properties of these complexes was affected by encapsulation.\textsuperscript{18} Examining systems where zeolite encapsulation offers a solution to a problem associated with that particular system was a common theme.

Synthesis of a robust reversible oxygen carrier in solution is fraught with difficulties associated with bimolecular decomposition of the complex. Not only could one oxygenated complex oxidize the ligand of another complex, but dimerization which resulted in the formation of the stable irreversible oxygen binding $\mu$-peroxo dimer was also a competing process. Zeolite encapsulation of a complex too large to dimerize inside the zeolite supercage could provide a means of avoiding these problems. Zeolite encapsulation has been shown to prevent dimerization and prolong the lives of reversible oxygen binders.

The search for a practical oxygen carrier encapsulated in a zeolite has been so wide ranging that it has resulted in the synthesis of the first large negative ion within a zeolite
cavity. Drago et al. synthesized a complex identified as \( \text{Co(CN)}_4^{2-} \) inside the supercage of zeolite Y.\(^{19} \) This material was found to act as a reversible oxygen binder and shows particular stability in its resistance to moisture which is often the cause of degradation of the oxygen binding ability of supported metal complexes.

An early example of catalysis by a transition metal complex in a zeolite is the reduction of NO by \( \text{NH}_3 \) to \( \text{N}_2 \) and \( \text{H}_2\text{O} \).\(^{20} \) This process would have the practical application of removing NO from stack emissions. The catalyst in this case was a cobalt ammonium complex formed by absorbing \( \text{NH}_3 \) onto a cobalt exchanged zeolite Y sample. One disadvantage of zeolite supported metal complexes is that the pores or active sites of the catalyst have a tendency to become clogged or blocked from various products of the reaction. It is sometimes possible to remove these blockages by treating the catalyst by heating gently while pulling a vacuum.

Oxidation catalysts would be expected to benefit greatly from zeolite encapsulation, as the useful life of a homogeneous catalyst is often limited by decomposition of the complex. Placement inside the supercage of a zeolite would prevent any bimolecular decay modes from occurring by preventing two catalyst molecules from encountering each other. In addition, the shape selectivity of the zeolite catalyst would allow a certain degree of selective oxidation to occur. Herron et al. have examined the oxidative ability of iron
phthalocyanine encapsulated inside zeolite Y.\textsuperscript{21} The synthesis of this complex inside the zeolite Y supercage results in a ship-in-a-bottle type situation with the metal complex, once formed, being too large to exit through the supercage windows. They indeed saw an improvement in catalyst life and shape selectivity due to zeolite encapsulation.

The photochemical properties of zeolite encapsulated metal complexes have also been studied. Both \( \text{Ru(bpy)}_3 \)\textsuperscript{2} and \( \text{Rh(NH}_3)_5 \text{I} \)\textsuperscript{2} have been the subject of studies on the effect of zeolite encapsulation upon their photochemistry.\textsuperscript{22-23} In the case of \( \text{Rh(NH}_3)_5 \text{I} \), the quantum efficiencies of the zeolite encapsulated complex were lower than when the complex is in solution. One factor in this is that the steric restraints of the zeolite were hindering the necessary rearrangements during the photochemical process. Also, the highly scattering nature of the zeolite particles causes a certain percentage of the light to be lost without doing any useful work.

Although there are certain inherent difficulties associated with doing catalysis with a zeolite encapsulated metal complex, there remains considerable interest in this area. It remains to be seen if a system can be designed which would allow a metal complex encapsulated inside a zeolite to compete favorably on a large scale with a commercial process. However, there is still promise that the size and shape selective capabilities of the zeolite based complexes will outweigh any associated problems for certain systems.
Herron has championed the zeolite encapsulated metal complex as having the potential to be an inorganic analog to an enzyme with the zeolite framework acting as the protein. Herron compares zeolite encapsulated Co(salen) to hemoglobin as they are both reversible oxygen binders. The zeolite protects the active site from decomposition and increases its life when compared to its behavior in solution. Unlike hemoglobin the zeolite encapsulated Co(salen) shows a negative cooperativity when binding oxygen as it becomes progressively more difficult to add oxygen to the complexes inside the zeolite. This example demonstrates the ability of zeolites to act like enzyme proteins in controlling the interaction of active sites with each other and also affecting the thermodynamics of the reactions at those sites.

A comparison can also be drawn between the cytochrome P450 monoxygenase enzyme and a zeolite supported oxidation catalyst. Again the key to this comparison is the role that the zeolite plays. It acts like an enzyme protein and controls access to the active site of the catalyst. Using a material composed of 2 wt% Fe and 1 wt% Pd supported upon zeolite A, selective oxidation of octane over cyclohexane could be obtained. The same catalyst supported on amorphous aluminosilicate showed a slight (55:45) preference toward the oxidation of octane while the zeolite A based system almost excluded the oxidation of cyclohexane (<200:1). It was also seen that the yield of products from terminal methyl group
oxidation was considerably higher in the zeolite A system. The molecular sieving ability of the zeolite causes both the substrate and product distributions to be affected.

Another attempt at mimicking nature involved the synthesis of an iron-sulfur protein analogue.\textsuperscript{27-28} These materials are essential cofactor enzymes in the cytochrome P450 network which provide electrons to reduce iron and/or oxygen to generate the active oxidant. CdS was prepared inside the cavities of zeolite Y and its photooxidation chemistry was examined. The CdS clusters reside in the small cages of zeolite Y and so the large cages are available for the absorption of olefin substrate molecules. It was found that when irradiated at 365 nm this material was capable of oxidizing olefins and that some size selectivity, when compared to solution behavior, was noted.

Due to the inherent difficulties with using zeolite encapsulated metal complexes as catalysts, perhaps the area of greatest future promise for zeolite encapsulated metal complexes lies in the preparation of unique electronic or optical materials. Quantum size effects in small semiconductor particles have been known for some time and zeolites provide a promising support for the preparation of semiconductor clusters of a known size. Herron et al. have examined the structure of clusters of CdS, PbS, and CdSe inside zeolites by EXAFS and XRD studies.\textsuperscript{27,29-30} It was found that it was possible to synthesize well defined clusters of
the semiconductors in the pores of zeolite Y. At lower loadings there were distinct clusters in the sodalite cages. As the loadings were increased the amount of interconnection increased. The optical properties of these materials were studied with diffuse reflectance UV-VIS and emission studies. The ultimate aim of such research is the production of optical computer elements such as optical transistors, spatial light modulators, and phase conjugate materials.

In this work we are interested in comparing the properties of zeolite encapsulated metal complexes to their solution counterparts. There is a particular interest in how the spectroscopy, especially infrared, of a metal complex is affected by encapsulation inside a zeolite supercage. In addition the possibility of combining the advantages of homogeneous and heterogeneous catalysis via encapsulation of metal complexes inside zeolite is explored. In the area of zeolite encapsulated reversible oxygen carriers work has been done in an attempt to improve upon the oxygen binding ability of previously reported zeolite bound oxygen carriers. Finally, there has been work in the area of zeolite synthesis, both in order to obtain greater understanding of the process and also in an attempt to synthesize novel zeolitic materials.
REFERENCES


CHAPTER II

INFRARED STUDY OF Fe(CO)₅ ABSORBED ONTO ZEOLITE Y

INTRODUCTION

The structure and reactivity of metal carbonyls supported on high surface area metal oxides, zeolites, and polymers continues to be of considerable interest, stemming from their potential use as heterogeneous catalysts. One method of preparation of supported metal clusters is the decomposition of metal carbonyls absorbed onto the supports. The possibility of controlling the decomposition to enable the preparation of metal particles of a uniform and controllable size is a great attraction toward such systems.¹ There is an interest in preparing particles with a narrow size range in order to explore the effect of particle size upon catalytic activity. The high surface area of the support and the fact that the clusters are highly dispersed may offer certain catalytic advantages over metal surfaces.

Zeolites are interesting supports for such systems due to their unique properties.² The ion exchange capability of zeolites is both a means of loading metal ions onto the support as well as varying the polarity of the medium. The metals are ion exchanged into the zeolites and then reduced
to produce small clusters of the metal. The internal electrostatic fields of the zeolite may exert certain unique effects on the catalytic ability of the metal cluster. The microporous nature of zeolites allows the absorption of metal complexes which can also be used as a source for neutral metal atoms. The well defined pore system of zeolites allows for the possibility of size or shape selectivity in catalysis and for the production of metal clusters of an uniform size.

Supported clusters of metallic iron are known catalysts in such processes as Fischer-Tropsch catalysis and the water gas shift reaction, both of which are of great significance.\(^3\) In addition the absorption of Fe(CO)_5 into zeolites is a convenient method of getting neutral iron onto the support. Fe(CO)_5 is the source of choice due to its size and vapor pressure which makes loading it into the zeolite pores quite easy. This is especially advantageous as there are considerable practical problems with ion exchanging Fe^{42} into the zeolite and subsequently reducing it reproducibly without contamination.\(^4,5,6\)

In addition to the interest in metal carbonyls on supports due to their potential as catalysts, there are fundamental questions associated with such systems. Any changes in the thermal decomposition processes due to the support are of both fundamental and practical interest in the preparation of metal cluster catalysts. The effect of supports upon the photochemistry of metal carbonyls is another
area of interest associated with this system. Understanding of these effects is also important in order to allow the preparation of uniform metal particles in a reproducible manner. Detailed knowledge of the identity and structure of the metal carbonyl species present is necessary in order to better understand the subsequent decomposition processes.

There is an interest in the effect of the support upon the vibrational spectra of metal carbonyls. The vibrational spectra will give a measure of the strength of the interaction between the metal complex and the support. Such studies allow for the investigation of ligand substitution reactions of the immobilized metal carbonyl. Also the absorption, desorption and any chemical reactions between the metal carbonyl and the substrate can be probed.

Infrared spectroscopy is the most obvious technique by which to examine Fe(CO)₅ absorbed onto zeolite Y. The zeolite matrix itself does not absorb in the carbonyl stretching region and this allows the vibrational spectra to be obtained. These studies can be done in a transmission mode if thin self supporting pellets of zeolite and low loadings of Fe(CO)₅ are used. Bein and Jacobs concluded that the seven peaks observed between 1800 and 2200 cm⁻¹ were due to a single species of composition Fe(CO)₅ which has had its symmetry lowered by the interaction with the zeolite. Lowering of the molecular symmetry causes new peaks to become allowed in the infrared region. The major difficulties with this tentative assignment
is that Fe(CO)$_5$ with its symmetry completely lowered can only account for five fundamental C-O stretching peaks and seven are observed. Also according to the assignment given, the peak with the highest intensity is assigned to $^{13}$C. The major difficulty with any such assignment is the limited amount of information upon which it is based. It is very unlikely that a novel species can be identified simply on the basis of an IR spectra in the region of 2200-1800 cm$^{-1}$. To address this problem, we have used infrared spectroscopy to examine low temperature behavior and the reactivity of the absorbed carbonyls toward a variety of ligands.

**EXPERIMENTAL**

**Materials.** Na-Y (Union Carbide) was washed with 0.1M NaCl and then rinsed with water until chloride free. Pyridine (Fischer), Fe(CO)$_5$ (Alfa), and trimethylphosphine (Aldrich) were degassed by freeze-evacuate-thaw cycles prior to use. Ammonia, acetylene, ethylene, carbon monoxide, and oxygen were all used as received.

**Infrared Measurements.** All infrared spectra were obtained on a Mattson Cygnus FT-IR equipped with a MCT detector. A 10-20 mg self-supporting pellet of Na-Y (diameter=13 mm) was placed into a cell with NaCl windows. The zeolite was activated in the cell by heating at 250°C for 2 hours under 10$^{-4}$ torr. Higher activation temperatures (400°C) produced the same IR data upon absorption of Fe(CO)$_5$,.
as observed in this study. So it appears that the residual water upon 250°C dehydration does not interfere with the reactivity of Fe(CO)₅. The cell was equipped with a valve that allows evacuation or the addition of gas. To take IR spectra at low temperatures, the aluminum cell body was wrapped with copper tubing that was connected to a coil placed inside a Dewar of liquid nitrogen. By flowing nitrogen gas through the tubing, the temperature of the pellet was lowered. The exact temperature of the pellet was not determined, but the body of the cell reached temperatures close to 77 K. The sample cell was heated resistively by a heating coil, with the approximate control of ±2 °C.

Preparation of Iron Carbonyl Compound. To obtain a loading of iron carbonyl appropriate for infrared measurements, the cell was opened and the pellet was allowed to contact 0.3 torr of Fe(CO)₅ vapor for 5 s. The extent of loading could be varied by changing the pressure of Fe(CO)₅.

Addition of ligands to the Fe(CO)₅-zeolite sample was accomplished on a vacuum line. The pressure of gas put into the cell was monitored by a manometer on the vacuum line. Pyridine, trimethylphosphine, and water were degassed in a separate flask, and the vapor was allowed to enter the IR cell and contact the zeolite for a given time.

X-ray Fluorescence (XRF) Measurements. The loading of iron on the zeolite was obtained via XRF. A calibration curve was constructed by ion exchanging a known amount of iron(III)
chloride into the zeolite. The IR spectra of a zeolite loaded with Fe(CO)$_5$ was taken, and the same pellet was placed into the XRF spectrometer. With a Ge target and excitation conditions of 20 kV and 2.0 mA, the weight percent of iron corresponding to a particular loading of Fe(CO)$_5$ was obtained and could be correlated with the infrared spectra.

**RESULTS**

**Adsorption of Fe(CO)$_5$ on Zeolite Y.** As noted earlier, the IR spectra in the C-O stretching region of Fe(CO)$_5$ absorbed onto zeolite Y is considerably more complex than the molecule in its liquid and gas phase. This spectra is shown in Figure 2.1 and it can be seen that at least seven peaks are present. This leads one to suspect that absorption onto the zeolite is causing either a rearrangement of the molecule's symmetry or that some sort of chemical reaction is occurring when Fe(CO)$_5$ is contacted with the zeolite.

The infrared spectra of Fe(CO)$_5$ adsorbed onto dehydrated Na-Y at different loadings at room temperature is shown in Figure 2.2. At the lowest loadings, which correspond to 1 Fe(CO)$_5$ molecule per every 250 available supercages (Figure 2.2a), bands at 2060, 2043, 2015, 1984, 1960, and 1945 cm$^{-1}$ are observed. On increasing the loading levels by an order of magnitude, all of these bands along with a band at 2122 cm$^{-1}$ are observed (Figure 2.2b). Scaling of Figure 2.2a and subtraction from Figure 2.2b indicates that a broad band centered at 2000 cm$^{-1}$ has also grown in as the loading level
is increased (Figure 2.2c'). In Figure 2.2b, this band accounts for 60% of the observed intensity. Increasing the loading by another order of magnitude produces Figure 2.2c, in which all of the bands observed in Figures 2.2a and 2.2b are observed. Subtraction of Figure 2.2c from Figure 2.2a after scaling shows a spectrum similar to that observed with Figure 2.1b minus Figure 2.1a, consisting of a broad band at 2000 cm\(^{-1}\) and a sharper band at 2034 cm\(^{-1}\). However, in Figure 2.2c, these bands are responsible for 73% of the total intensity. It appears, therefore, that at low loadings, a species characterized by bands at 2122, 2060, 2043, 2015, 1984, 1960, and 1945 cm\(^{-1}\) is observed (referred to as species I). Upon increase in loading, the intensity of bands due to species I increases slightly, and bands due to a different species at 2000 cm\(^{-1}\) and 2034 cm\(^{-1}\) (species II) are observed. At the higher loadings, most of the infrared intensity arises from species II. The products of the adsorption of Fe(CO)\(_5\) onto Na-Y are tightly held to the zeolite and cannot be removed by pulling a vacuum (10\(^{-4}\) torr) on the sample.

Since the loading levels are so low, we investigated the possibility that Fe(CO)\(_5\) could be adsorbing onto some impurities or amorphous material in the zeolite. Figure 2.2d shows the adsorption of Fe(CO)\(_5\) on a dehydrated sample of amorphous aluminosilicate made by destroying the framework on Na-Y with 0.1M HCl. At the low loading levels, only bands due
Figure 2.1. Infrared spectra of Fe(CO)$_5$ on dehydrated Na-Y.
Figure 2.1
Figure 2.2. Infrared spectra of Fe(CO)$_5$ on dehydrated Na-Y at different loadings at room temperature: (a) 1 Fe(CO)$_5$ per ~250 supercages, 0.01 Torr of Fe(CO)$_5$, 5 s of contact; (b) 1 Fe(CO)$_5$ per ~25 supercages, 0.3 Torr of Fe(CO)$_5$, 5 s of contact; (c) 1 Fe(CO)$_5$ per ~2 supercages, 0.3 Torr of Fe(CO)$_5$, 10 s of contact; (c') spectrum obtained by subtracting (a) from (b); (d) Fe(CO)$_5$ on amorphous aluminosilicate, 0.01 Torr of Fe(CO)$_5$, 5 s of contact.
Figure 2.2
to physiosorbed Fe(CO)$_5$ at 2034 and 2015 cm$^{-1}$ are observed. Clearly the bands due to species I are observed only on zeolite Y surfaces and not from any impurities present in the sample.

To investigate this process further, we studied the adsorption of Fe(CO)$_5$ onto dehydrated Na-Y at temperatures approaching 77K. Figure 2.3 shows the data as a function of increasing loading. It was not possible to do XRF measurements on these samples to estimate the Fe content since facilities were not available for doing such measurements in situ at low temperature. At the lowest loadings (Figure 2.3a), bands at 2075, 2033, and 2001 cm$^{-1}$ were observed along with bands at 2171, 2136, and 2120 cm$^{-1}$. This set of peaks is assigned to absorbed CO and was removable upon evacuation. Upon further loading of Fe(CO)$_5$, the intensity of these bands between 2000 and 2080 cm$^{-1}$ increased (Figure 2.3b), along with the appearance of a band at 1945 cm$^{-1}$. Additional loading increased the intensity of the 1945 cm$^{-1}$ band along with the appearance of a shoulder at 2043 cm$^{-1}$ (Figure 2.3c). Upon subtraction of Figure 2.3c from Figure 2.3b, such that the intensity of the bands at 2001, 2033, and 2075 cm$^{-1}$ were minimized, Figure 2.3f was obtained. The bands in this spectrum at 2065, 2043, 2013, 1985, 1960, and 1945 cm$^{-1}$ are characteristic of species I obtained at room temperature. This can be seen by comparing Figure 2.3f with Figure 2.1. Increased loading leads to an increase in intensity of bands
Figure 2.3. Infrared spectra of Fe(CO)$_5$ on dehydrated Na-Y as a function of increasing loading (a-e) at ~77 K. (f) Spectrum obtained by subtracting (b) from (c) (10 Torr of Fe(CO)$_5$; contact times (a-f) 5 s, 5 min, 10 min, 15 min, and 45 min).
Figure 2.3

Absorbance

Wavenumber

2100

2000

1900

0.4

15x

3x

15x

a

b

c

d

e

f
due to species I (Figure 2.3d) and finally to the appearance of new bands at 2033 and 2013 cm\(^{-1}\) (Figure 2.3e). These bands at 2033 and 2013 cm\(^{-1}\) are characteristic of free Fe(CO)\(_5\). So it appears that at low temperature, upon adsorption of Fe(CO)\(_5\), a new species characterized by bands at 2075, 2033, and 2001 cm\(^{-1}\) (species III) is followed by the appearance of species I and finally unperturbed Fe(CO)\(_5\). All of these species can coexist as seen in Figure 2.3e.

Nature of Species I, II, and III. Summarizing the above observations, it appears that at low temperatures an increase in loading levels causes the appearance of species III to be followed by I and finally Fe(CO)\(_5\). At room temperature, on the other hand, species I followed by II is observed. The structure of species III was deduced from comparison of its IR spectra with published data on iron carbonyls. However, the complexity of the spectrum of species I and II necessitated a study of their reactivity to assign a structure, and these studies are also described below. Species I and II were distinguished experimentally by adjusting the loading levels. Species I was considered to be the primary constituent at loading levels of \(1\) Fe(CO)\(_5\) per 50-100 supercages and species II at loading levels greater than \(1\) Fe(CO)\(_5\) per 3 supercages. After appropriate loading, reactivity studies were carried out on these materials.

Formation of I. Species I is characterized by infrared bands at 2122, 2060, 2043, 2015, 1984, 1960, and 1945 cm\(^{-1}\).
This spectrum is considerably more complicated than free Fe(CO)₅, which typically contains two infrared bands. The maximum number of CO stretching bands possible for Fe(CO)₅ is five. Considering the fact that at least seven bands are observed, it is clear that Fe(CO)₅, upon interaction with the zeolite, must be undergoing rearrangement and/or chemistry.

To elaborate on the role that the zeolite may be playing in the formation of I, dehydrated samples of Na-Y zeolite were treated with pyridine or trimethylphosphine (PMe₃), evacuated, and then exposed to a loading of Fe(CO)₅. Pyridine and trimethylphosphine are Lewis bases and will interact strongly with any Lewis acid sites within the zeolite, effectively blocking access to them. Figure 2.4 compares the IR spectra of the untreated and treated samples. For the PMe₃ sample, the bands at 2122, 2060, 2015, 1984, and 1960 cm⁻¹ have decreased considerably in intensity relative to the 2043 and 1945 cm⁻¹ bands. In the pyridine-exposed sample, only bands at 2033 and 2013 cm⁻¹ typical of free Fe(CO)₅ are observed, and no bands due to species I are observed. Both pyridine and PMe₃, because of their Lewis basicity, are blocking any Lewis acid sites and therefore it is seen that such sites must be responsible for the observed IR spectra.

Reactivity of Species I. A. CO, O₂, and C₂H₄. The reaction of species I with CO, O₂, C₂H₄ was studied. Figure 2.5 shows the spectra observed in the presence of these ligands. No change was observed in the presence of 3 atm of
Figure 2.4. Infrared spectra of Fe(CO)$_5$ on (a) dehydrated Na-Y, 0.3 Torr of Fe(CO)$_5$, 5 s, (b) dehydrated Na-Y with pyridine (25 Torr, 10 min), (c) dehydrated Na-Y with PMe$_3$ (25 Torr, 10 min). All loadings at room temperature.
Figure 2.5. Infrared spectra of Fe(CO)$_5$ (0.3 Torr, 5 s) on dehydrated Na-Y (a) exposed to O$_2$ (1 atm, 10 s), (b) exposed to C$_2$H$_4$ (75 Torr, 10 s), (c) heated with CO at 60°C for 40 min. All loadings at room temperature.
Figure 2.5
CO. Upon heating species I with CO to 60°C all bands due to species I decreased in intensity with no new bands appearing. This decomposition was accelerated at higher temperatures. We studied this process up to 150°C. No reactivity of species I was observed with O₂ or C₂H₄ as evidenced by the lack of any changes in the IR spectra.

B. Trimethylphosphine. Figure 2.6 shows the changes in IR spectra that take place upon exposure of species I to PMe₃. The peak at 2122 cm⁻¹ loses approximately one-half of its intensity and shifts to 2116 cm⁻¹. The peaks at 2060, 2015, 1984, and 1960 cm⁻¹ all lose their intensity. The peaks at 2043 and 1945 cm⁻¹ remain. New sharp peaks at 2033, 1996, and 1940 cm⁻¹ appear. This also leads to broadening of the 1945 cm⁻¹ band. The spectrum remains unchanged upon further addition of excess PMe₃.

The reaction of the Fe(CO)₅-PMe₃ adduct on zeolite Y with CO at room temperature is shown in Figure 2.7. At first, there is the appearance of a band at ~2010 cm⁻¹, which gradually grows in intensity as more CO is added. Along with it, there is also the appearance of a band at 2035 cm⁻¹. The final spectrum shows bands at 2043 and 1945 cm⁻¹ due to species I and the new bands at 2035 and 2012 cm⁻¹, which are similar to that for gaseous Fe(CO)₅. The other bands of species I at 2060, 2015, 1984, and 1960 cm⁻¹ have disappeared.

C. NH₃. Upon the addition of NH₃ to species I (Figure 2.8), a band at 1990 cm⁻¹ appears, along with the appearance
Figure 2.6. Infrared spectrum of (a) Fe(CO)$_5$-NaY (0.3 Torr, 5 s) and (b) exposed to PMe$_3$ (25 Torr, 1 min). All loadings at room temperature.
Figure 2.6
Figure 2.7. Infrared spectra of Fe(CO)$_5$-PMe$_3$-NaY exposed to increasing amounts of CO. The weak bands due to PMe$_3$ have been subtracted out by comparison with a PMe$_3$-NaY sample, the 1425 cm$^{-1}$ peak of PMe$_3$ (Samples prepared according to the caption in Figure 2.6.)
Figure 2.8. Infrared spectra of (a) Fe(CO)$_5$-Na-Y (0.3 Torr, 5s) exposed to increasing amounts of NH$_3$ (b-d), 0.25 Torr, 0.5 atm, 1 atm, respectively. Contact times were for 30 s at room temperature.
of a weak band at \(\sim 2170 \text{ cm}^{-1}\) due to free CO. The bands at 2122, 2060, 2015, 1984, and 1960 cm\(^{-1}\) all lose intensity, similar to the case discussed for PMe\(_3\). However, in contrast to the reaction with PMe\(_3\), as the amount of NH\(_3\) is increased, there is a rapid decrease in the intensity of all the bands, with the increase in the CO peaks. Finally, complete decarbonylation of species I occurs at high loading of NH\(_3\).

D. Pyridine. Pyridine appears to react with species I in the same way as NH\(_3\) (Figure 2.9). Incremental addition of pyridine brings about the loss of infrared bands due to species I. Unlike the PMe\(_3\) and NH\(_3\) reactions, no distinct bands due to any intermediate species were observed, just a decrease in intensity.

E. Acetylene. In contrast to ethylene, acetylene reacts readily with species I to form new bands at 2020, 2002, and 1990 cm\(^{-1}\). The strong band at 1957 cm\(^{-1}\) is due to physisorbed acetylene. Figure 2.10 shows the IR spectrum obtained on exposure to \(\text{C}_2\text{H}_4\) at 77K. A weak band due to adsorbed CO is seen at \(\sim 2170 \text{ cm}^{-1}\).
Figure 2.9. Infrared spectra of (a) Fe(CO)$_5$-Na-Y (0.3 Torr, 5 s) exposed to increasing amounts of pyridine (b and c), 25 Torr, 10 s, 30 s, respectively. The bands due to pyridine have been subtracted out by comparison with a pyridine-Na-Y sample, by using the 1440-cm$^{-1}$ peak of pyridine. Loadings were at room temperature.
Figure 2.8
Figure 2.10. Infrared spectrum of (a) Fe(CO)$_5$-Na-Y (0.3 Torr, 5 s) (b) exposed to acetylene (1 atm, 10 s) at -77 K.
Figure 2.10
F. H₂O. The IR spectrum of species I exposed to H₂O is shown in Figure 2.11. The reaction with H₂O, unlike the other ligands discussed above, is slow. After 15 min, there is a general decrease in intensity of all bands along with the appearance of a band at 1990 cm⁻¹. This band shifts to 2002 cm⁻¹ and gradually broadens. This final spectrum (after a period of 60 minutes) shows broad bands at 2030, 2000, and 1960 cm⁻¹.

Reactivity of Species II. At high loadings (1 Fe(CO)₅ molecule/2-3 supercages), the IR spectrum is dominated by a broad peak at 2000 cm⁻¹ and a sharper peak at 2030 cm⁻¹ (Figure 2.2c'). The spectrum of this species can be seen clearly upon subtracting out the bands due to species I that ride on top of this band. Unlike species I, species II is very reactive with O₂. As Figure 2.12 shows, exposure to O₂ is followed by instant decarbonylation with strong bands at 1315, 1578, and 2353 cm⁻¹ due to CO₂ and 2140 cm⁻¹ due to CO. In the carbonyl stretching region, bands due to species I are observed indicating, as noted before, its unreactive nature with O₂. Exposure of species II samples to pyridine or PMe₃ results in formation of bands at 2033 and 2013 cm⁻¹ due to free Fe(CO)₅.
Figure 2.11. Infrared spectra of Fe(CO)$_5$-Na-Y (0.3 Torr, 5 s) exposed to water vapor as a function of time (a) initial spectrum, (b) 20 Torr, 15 min, (c) 20 Torr, 30 min, (d) 20 Torr, 1 h. Loadings were at room temperature.
Figure 2.11
Figure 2.12. Infrared spectra (a) of high loaded Fe(CO)$_5$-Na-Y (10 Torr, 10 s) samples and (b) upon its exposure to O$_2$ (1 atm, 10 s). Loadings were at room temperature.
Figure 2.12
DISCUSSION

Structural Assignment of the Low Temperature Species III. Species III is characterized by bands at 2075, 2033, and 2001 cm\(^{-1}\) and is formed on the zeolite at low loadings of Fe(CO)\(_5\) at \(-77\)K (Figure 2.3). Along with this species, bands at 2171, 2136, and 2120 cm\(^{-1}\) are also observed. These latter bands can be assigned to CO physisorbed on the zeolite and can be readily removed by evacuation. Angell reported that CO adsorption on dehydrated Na-Y exhibited bands at 2172 and 2122 cm\(^{-1}\).\(^1^4\) The frequency of CO vibration in the gas phase is 2143 cm\(^{-1}\). Interaction with Lewis acid sites, such as with cations, should bring about an increase in CO frequencies, whereas the opposite would be expected for basic sites. The bands observed between 2100 and 2180 cm\(^{-1}\) upon initial adsorption of Fe(CO)\(_5\) at low temperatures can be assigned to CO interacting with the framework Lewis acid sites (Al\(^{3+}\), Na\(^+\)) and oxygen/hydroxyl groups.

The formation of free CO indicates that decarbonylation is occurring upon interaction of Fe(CO)\(_5\) with dehydrated Na-Y. Ballivet-Tkatchenko and Coudurier noted a slight evolution of CO during the absorption of Fe(CO)\(_5\) onto dehydrated H-Y.\(^1^5\) After evacuation for 1 hour at 60°C, approximately 1 mole of CO per mole of Fe(CO)\(_5\) was evolved. The IR spectra obtained upon the initial room temperature absorption was assigned to a mixture of Fe(CO)\(_5\) and Fe(CO)\(_4\)-O\(_2\), where O\(_2\) is an oxygen from the zeolite acting as a ligand. Since our loadings were
very low (absorptivities ~0.05 units), we did not attempt to estimate manometrically the amount of CO evolved. The absorptivity for free CO at 77K has been reported (~400 M\(^{-1}\) cm\(^{-1}\)),\(^{16}\) but Angell\(^{14}\) has shown that the molar absorptivity for CO adsorbed on zeolite sites shows a strong temperature dependence and therefore the value of 400 M\(^{-1}\) cm\(^{-1}\) for free CO may not be applicable upon absorption onto the zeolite. So, from the infrared data, it is difficult to estimate the CO evolved on adsorption of Fe(CO)\(_5\). The decarbonylated species III has bands at 2075, 2033, and 2001 cm\(^{-1}\). These peaks are assigned to a single species, because the three bands grow at the same rate as the loading is increased (Figure 2.3a and 3b).

The simplest and most obvious assignment for III is that it is due to an Fe(CO)\(_x\) (x = 2, 3, or 4) species trapped in the zeolite matrix. Vibrational spectra of such species have been reported upon the photodecomposition of Fe(CO)\(_5\) in rare-gas matrices at low temperatures and in the gas phase. On the basis of studies involving isotopic CO, Poliakoff and Turner showed that, in rare-gas matrices, Fe(CO)\(_4\) produced by photolytic dissociation of Fe(CO)\(_5\) adopts a C\(_{2v}\) geometry with infrared bands at 2088(A\(_1\)), 1995 (A\(_1\)), 1988 (B\(_1\)), and 1973 cm\(^{-1}\) (B\(_2\)).\(^{17}\) Upon prolonged photoirradiation, Fe(CO)\(_3\) is produced, and bands at 2040 (A\(_1\)) and 1936 cm\(^{-1}\) (E) have been assigned to it on the basis of a C\(_{3v}\) geometry.\(^{18}\) Gas phase photolysis of Fe(CO)\(_5\) produced Fe(CO)\(_4\) (bands at 2000 (A\(_1\), B\(_1\))
and 1985 cm\(^{-1}\) (B\(_2\)) and Fe(CO)\(_3\) (2060 (A\(_1\)) and 1950 cm\(^{-1}\) (E)).\(^{19}\)

The bands due to Fe(CO)\(_x\) (x=2,1) are observed at 1905 cm\(^{-1}\) in an Ar matrix and 1920 cm\(^{-1}\) in the gas phase.\(^{16}\) Species III has infrared bands in the region discussed above for Fe(CO)\(_x\) (x= 3,4) species, but no direct correlation can be made. This is not surprising because the zeolite must be acting as a ligand toward the unsaturated iron carbonyl species and therefore direct comparison with a species which is isolated in a rare gas matrix is not possible. The zeolite oxygen is a weak ligand, however its presence is affecting the IR spectra.

More appropriate comparisons are, therefore, the photochemical dissociation studies of Fe(CO)\(_5\) reported on silica,\(^{20,21}\) in Vycor glass,\(^{22}\) and in polymers,\(^{23}\) since in all these cases the matrix has been shown to play a significant role. Adsorption of Fe(CO)\(_5\) onto Vycor glass results in a material with an IR spectra almost identical to unperturbed gas phase Fe(CO)\(_5\). A weak band appears at 2115 cm\(^{-1}\) which indicates that there is some distortion of the Fe(CO)\(_5\) upon adsorption into the glass. The amount of interaction is much lower than in the zeolite as evidenced by the IR spectra and also by the fact that unlike in the zeolite the absorption of Fe(CO)\(_5\) is reversible with the signal due to Fe(CO)\(_5\) disappearing upon evacuation for five minutes. Photolysis of Fe(CO)\(_5\) in Vycor glass led to the formation of two sets of bands, one with peaks at 2073 and 2048 cm\(^{-1}\) and another with
a single peak at 2062 cm\(^{-1}\). These bands were assigned to H-Fe(CO)\(_4\)-OSi and H-Fe(CO)\(_4\)OH and were thought to form by oxidative addition of Fe(CO)\(_4\) with surface groups.

Absorption of Fe(CO)\(_5\) into a matrix of polytetrafluoroethylene (PTFE) results in an unperturbed Fe(CO)\(_5\) IR spectra with peaks at 2074 and 2005 cm\(^{-1}\). Ultraviolet irradiation of Fe(CO)\(_5\) trapped in a PTFE matrix produced new bands at 2120 (w), 2074 (w), 2040 (w), 2030 (w), 1992 (w), 1973 (s), and 1950 (m) cm\(^{-1}\) (s, m, and w are indications of the intensity of the infrared bands and specify strong, medium, and weak, respectively). The authors, based primarily on the previous photolysis studies in Ar matrix, assigned these peaks to two different species Fe(CO)\(_4\) (2074, 1992, 1973, 1950 cm\(^{-1}\)) and Fe(CO)\(_3\) (2040, 2030, 1950 cm\(^{-1}\)).

The photolysis study performed on silica absorbed Fe(CO)\(_5\) shows that the support can act as a ligand toward unsaturated metal carbonyls. It was proposed that silica surface hydroxyl groups or siloxane bridging oxo groups participate as weak ligands and actually alter the products formed in the photolysis. The photolysis of Fe(CO)\(_5\) in the gas or liquid phase or in solution yields mainly Fe\(_2\)(CO)\(_9\) while the photolysis of Fe(CO)\(_5\) on SiO\(_2\) results in the formation of Fe\(_3\)(CO)\(_{12}\). Weak bands at ~1960 and 1940 cm\(^{-1}\) were observed upon photolysis on a SiO\(_2\) surface at temperatures between 100 and 150K. These bands were assigned to a Fe(CO)\(_4\)-SiO\(_2\) complex. Above 2000 cm\(^{-1}\) there were strong bands due to unphotolyzed
Fe(CO)$_5$ and the photoproduct Fe$_3$(CO)$_{12}$, so the higher frequency bands of Fe(CO)$_4$-SiO$_2$, if any, could not be observed.

The bands for III at 2077, 2033, and 2001 cm$^{-1}$ bear resemblance to the photolytic species generated in both Vycor glass and polymer matrices. We assign species III to Fe(CO)$_4$ bound to the zeolite. The mechanism of formation of such an unsaturated species would require the presence of a strong Lewis acid site with which the CO of Fe(CO)$_5$ could interact. This interaction will lead to the weakening of the Fe-CO bond, and a zeolite framework oxygen could act as a ligand to the Fe, resulting in a nucleophilic displacement of the Lewis acid bound CO and formation of a zeolite O-Fe(CO)$_4$ complex. The oxygen atoms of the zeolite framework are weak nucleophiles and this necessitates the strong Lewis acid-CO interaction for this reaction to occur. The structure of the zeolite-Fe(CO)$_4$ complexes (in which L is a base), would be a C$_{3v}$ complex, with the zeolite oxygen in the axial position. Three infrared bands are expected (2A$_1$ + E). For strongly coordinating ligands such as PPh$_3$ and tetrahydrofuran, these bands appear at 2059, 1984, 1946 cm$^{-1}$ and 2040, 1970, 1940 cm$^{-1}$, respectively.\textsuperscript{25,26} It is not surprising that in the zeolite complex, these bands are all shifted to higher frequencies, since the nucleophilicity or the electron-donating power of the framework oxygens is considerably lower, thus donating less electrons into the CO $\pi^*$ orbitals.

Further evidence that this is a weak interaction with the
zeolite oxygen is also supported by the fact that species III is unstable at higher temperatures and is not observed in the room-temperature study. $\text{Fe(CO)}_4$ is very unstable and reactive at temperatures higher than 77K and the zeolite is unable to stabilize it. As noted earlier Ballivet-Tkatchenko and Courdier tentatively identified a $\text{Fe(CO)}_4$ species stabilized on $\text{H-Y}$ at room temperature. This is not necessarily inconsistent with our observations because the protons in the $\text{H-Y}$ could be acting as ligands to satisfy the coordination of the iron. The number of Lewis acid sites that lead to the formation of zeolite-$\text{Fe(CO)}_4$ adduct are also small, since it is observed only at the lowest $\text{Fe(CO)}_5$ loadings. The nature of these sites is unclear, at present. They could be arising from defect sites within the zeolite crystal, such as incompletely coordinated $\text{Al}^{13}$ atoms. Also, it is likely that these sites, at least the ones that we are observing, are on the surface, since at these lowest loadings and low temperatures diffusion of $\text{Fe(CO)}_5$ into the pores is unlikely. So it is concluded that at low temperatures there are a number of sites inside the zeolite which are able to stabilize $\text{Fe(CO)}_4$.

Structural Assignment of Species I. Species I, which is characterized by bands at 2122, 2060, 2043, 2015, 1984, 1960, and 1945 cm$^{-1}$, is observed at both low-temperature and room temperature loadings of $\text{Fe(CO)}_5$ onto dehydrated $\text{Na-Y}$ (Figures 2.2 and 3). At room temperature, even at the lowest possible
loadings (1 Fe(CO)₅ per 250 supercages), bands due to species I are observed. This is in contrast to the ~77K loadings which exhibit bands due to III at low loadings with the subsequent appearance of species I as more Fe(CO)₅ is absorbed (Figure 2.3).

A spectra identical with that of species I has been reported previously by Bein and Jacobs.¹⁰ The authors assigned this spectra to Fe(CO)₅ with the additional peaks becoming allowed due to symmetry lowering because of interaction with the zeolite (Table 2.1). There are two problems with this assignment. First, the assignment of the strong peak at 1945 cm⁻¹ due to a naturally occurring isotope (¹³C) is unreasonable. Second, even complete symmetry lowering can account for only a maximum of five fundamental C-O stretching bands. Symmetry lowering in this system could be due to the interaction of a carbonyl oxygen with the zeolite. The irreversibility of the adsorption of Fe(CO)₅ is evidence that the interaction between the support and the metal carbonyl is strong and so symmetry lowering is not unexpected.

Ballivet-Tkatchenko and Courdier observed a similar spectrum upon adsorption of Fe(CO)₅ on dehydrated H-Y and assigned the bands to a mixture of Fe(CO)₅ and a zeolite oxygen-Fe(CO)₄ adduct (bands at 2040, 1985, and 1350 cm⁻¹).¹⁵ They noted a slight evolution of CO upon absorption of Fe(CO)₅ onto the dehydrated H-Y. Such a species is more likely to be stabilized on a H-Y zeolite rather than Na-Y due
to the presence of protons to act as ligands toward the iron.

Table 2.1

IR Band Assignments for Fe(CO)$_5$/NaY$^{10}$

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$\text{cm}^{-1}$</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>2122 (w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2060 (s)</td>
<td></td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>2044 (s)</td>
<td></td>
</tr>
<tr>
<td>$\nu_6$</td>
<td>2012 (s)</td>
<td></td>
</tr>
<tr>
<td>$\nu_{10}$</td>
<td>1960 (sh)</td>
<td></td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>1945 (s)</td>
<td></td>
</tr>
</tbody>
</table>

In addition to the expected instability of such a species at room temperature the other difficulty with such an assignment is the lack of reactivity with CO as shown in Figure 2.5. All of the examples in the literature involving unsaturated metal carbonyls on supports, including Mo(CO)$_5$, Mo(CO)$_3$, and Ni(CO)$_2$ on alumina, are characterized by the fact that in the presence of CO, they rapidly revert to the parent carbonyls.$^{27,28}$ In the case of species I, no formation of Fe(CO)$_5$ was observed at pressures of CO of 3 atm or temperatures of 150°C in the presence of CO. Clearly, species I is not reactive toward CO. If species I did contain an unsaturated Fe(CO)$_4$ fragment, this reaction would have been facile, since Fe(CO)$_5$ is known not to be labile toward substitution as compared to other metal carbonyls, such as Ru, Mo, and V.$^{29}$ This is especially so,
and as such should be readily displaced. Also, as we have indicated before, the zeolite-Fe(CO)₄ adduct that is formed at ~77K is unstable and not observed at room temperature, in agreement with the above findings. It therefore appears that species I does not contain Fe(CO)₄ but must be due to Fe(CO)₅ interacting with the zeolite. It has been shown that there is considerable basicity in the oxygen atom of a metal carbonyl and there are numerous examples of the interactions between carbonyl oxygen and Lewis acids⁷,₃⁰ \( \text{pK}_a(\text{Fe(CO)}_5) \sim -8 \).

To assign a structure to species I, we studied its adsorption on pretreated zeolites and its reactivity with various ligands (Figures 2.4-2.11). If pyridine is preabsorbed on the zeolite, the resulting spectrum upon Fe(CO)₅ adsorption is similar to that of gaseous Fe(CO)₅ (Figure 2.4b). Clearly pyridine is blocking sites on the zeolite that are responsible for formation of species I. Pyridine is a Lewis base and is expected to block any accessible Lewis acid sites in the zeolite. So it appears that interaction with Lewis acid sites within the zeolite are responsible for the symmetry lowering which is causing the new peaks to appear in the IR.

The effect of preabsorbed PMe₃ is different. The peaks at 2122, 2060, 2015, 1984, and 1960 cm⁻¹ have decreased greatly in intensity relative to the 2043 and 1945 cm⁻¹ bands, indicating that PMe₃ may be blocking some of the sites
will act as a Lewis base toward any Lewis acid sites which it can access and block any possible interaction between such a site and adsorbed Fe(CO)₅. In both the pyridine and PMe₃ samples, the samples were extensively evacuated (10⁻⁴ torr for 1 h) prior to Fe(CO)₅ adsorption. This removes any weakly held or physisorbed base and leaves only the base interacting strongly with the Lewis acid sites. Since pyridine and PMe₃ are both strongly basic with pKₐ's of 5.2 and 8.7, respectively, the difference in their ability to block the responsible sites in the zeolite could stem from their ability to access the acid sites in the zeolite. The cone angle intercepted by PMe₃ is 136°, whereas pyridine is a planar molecule with an angle of 114° (both calculated for an approach distance of 2.3 Å), thus making it more difficult for PMe₃ to access restricted sites.

The interaction of Fe(CO)₅ with sites on the zeolite would lower its symmetry and depending on the nature of this interaction, three to five carbonyl bands would become IR active. In M(CO)₆ (M = Cr, Mo, W), adsorbed on alumina, the interaction with Lewis acid sites leads to the formation of five infrared bands as compared to one in the gas phase. Seven bands are observed in spectrum of Fe(CO)₅ on zeolite Na-Y. This requires that more than one type of adsorption site must exist on the zeolite. The reactivity of species I with a variety of ligands sheds light on the nature of the adsorption sites.
Reaction with PMe₃. Upon addition of PMe₃ to species I, the peak at 2122 cm⁻¹ decreases in intensity and a peak at 2116 cm⁻¹ is observed. Also, the peaks at 2060, 2015, 1984, and 1960 cm⁻¹ are all decreasing without any apparent effect on the 2043 and 1945 cm⁻¹ peaks (Figure 2.6). As we have noted before, Fe(CO)₅ adsorbed on zeolite with preabsorbed PMe₃ showed a significant decrease in intensity of this same set of peaks (Figure 2.4c). These observations are critical in allowing us to make any conclusions about the species present. Due to the number of bands observed it was believed that I was actually a mixture of two or more iron carbonyl species, but conditions to preferentially form or remove one over another were not known. Having a reactant like PMe₃ which preferentially reacts with one species allows us to separate the bands observed into two sets. On the basis of these observations, we propose that species I is made up of Fe(CO)₅ molecules adsorbed on two different zeolite sites. Species IA has bands at 2122, 2060, 2015, 1984, and 1960 cm⁻¹, whereas species IB has bands at 2116, 2043, and 1945 cm⁻¹. Species IA is reactive toward PMe₃, whereas species IB is not.

New bands are observed at 2033, 1996, and 1940 cm⁻¹ upon reaction of PMe₃ with species IA (Figure 2.6b). It is well known that O bonding of metal carbonyls to strong Lewis acids in the homogeneous phase favors CO elimination in the presence of coordinating ligands.29 We propose that species IA reacts with PMe₃ leading to replacement of a CO and formation of
Fe(CO)_4PMe_3. Normally such a displacement would require thermal or photochemical activation, but in the zeolite-bound case, the M-C bond is weakened enough by interaction with the Lewis acid site to allow the reaction to occur at room temperature. Fe(CO)_4PMe_3 is expected to have a trigonal bipyramid structure, with PMe_3 in an axial position with a C_3v symmetry. Group theory predicts that such a structure should have three allowed CO stretching peaks (2A_1 + E), and the peaks at 2033, 1996, and 1940 cm\(^{-1}\) are assigned to such a species. Fe(CO)_4P(C_2H_5)_3, prepared photo-catalytically, exhibits three bands at 2032, 1966, and 1948 cm\(^{-1}\), in reasonable agreement with those observed on the zeolite. The two most likely mechanisms for ligand substitution are given in schemes I and II. It has been shown that pure Fe(CO)_5 will not undergo substitution below 90°C. Ru(CO)_5 is more reactive and undergoes substitution with PPh_3 by scheme I.

While the dissociation mechanism is the most likely route in solution, it may not be so in the zeolite. Because of the unique situation of having the Fe(CO)_5 held in a site with a Fe-C bond weakened, a diffusion-controlled cage combination as outlined in scheme II may be preferable in the zeolite.

The formation of the species Fe(CO)_4PMe_3 is also supported by its reactivity with CO. As shown in Figure 2.7, upon reaction with CO the peaks at 2033, 1996, and 1940 cm\(^{-1}\) disappear and are replaced by bands at 2030 and 2010 cm\(^{-1}\). These peaks are readily assigned to Fe(CO)_5, which is the
expected product as the $\sigma$-donor ligand is replaced by CO, a preferred reaction.$^{27,28}$ The Fe(CO)$_5$ produced does not exhibit the spectrum characteristic of species IA, since the zeolite sites responsible for this species are now occupied by PMe$_3$. Peaks due to the other Fe(CO)$_5$ species (IB) remain largely unperturbed (2043, 1945 cm$^{-1}$).

Reaction with Nitrogenous Bases. Upon addition of NH$_3$, the infrared spectrum appears to be similar to the one discussed above for PMe$_3$ (Figure 2.8). Peaks due to species Ia disappear, and bands at ~2030, 1990, and 1940 cm$^{-1}$ appear, which are assigned to Fe(CO)$_4$NH$_3$. Species IB appears unperturbed. However, unlike the PMe$_3$ ligand, further
addition of NH\textsubscript{3} leads to decarbonylation of all iron carbonyl, and a band due to free CO is observed at 2170 cm\textsuperscript{-1}. A similar reaction takes place with pyridine, though the intermediate product Fe(CO)\textsubscript{4}-pyridine is not clearly observed. There is just a general increase in intensity in the \textasciitilde2000 cm\textsuperscript{-1} region. It appears, therefore, that with these nitrogenous ligands, both Fe(CO)\textsubscript{5} species (IA and IB) react, and this leads to total decarbonylation and proceeds through the intermediate Fe(CO)\textsubscript{4}L species. This is in contrast to Fe(CO)\textsubscript{4}PMe\textsubscript{3}, which is stable in the presence of excess PMe\textsubscript{3}. It is well recognized that amine ligands react with metal carbonyls to produce valency disproportionation of the metal.\textsuperscript{33,34} However, the mechanism of this reaction requires the reaction of a Fe(CO)\textsubscript{4}L with another Fe(CO)\textsubscript{5} molecule. Considering the fact that our loadings correspond to 1 Fe(CO)\textsubscript{5} molecule per 50 supercages, the probability of 2 Fe(CO)\textsubscript{5} molecules in the same cage is very low. In the absence of this route for the disproportionation reaction, rapid decarbonylation appears to be taking place. It is unclear if the final product upon decarbonylation is iron atoms stabilized in the zeolite or if iron nitrides are formed.

Reaction with \textit{\textgamma} Ligands. Ethylene exhibits no reactivity toward I. Acetylene, on the other hand, reacts rapidly with IB, and new bands at 2020, 2003, and 1990 cm\textsuperscript{-1} are observed (Figure 2.10). These bands can be assigned to Fe(CO)\textsubscript{4}-C\textsubscript{2}H\textsubscript{2} on the basis of comparison with Fe(CO)\textsubscript{4}-C\textsubscript{2}H\textsubscript{4}, which exhibits bands
Typically, acetylene will not react with Fe(CO)$_5$ unless activated by ultraviolet radiation, again indicating an enhancement of reactivity of the adsorbed Fe(CO)$_5$. Also, in solution, acetylene will yield polymeric complexes unlike the LFe(CO)$_4$ product with the zeolite.$^{36}$ A peak at ~2170 cm$^{-1}$ due to the displaced CO is clearly observed since this reaction was carried out at low temperature (~77 K). In the case of PMe$_3$ substitution at room temperature, no peaks due to the displaced CO were observed.

Reaction with Water. The reaction of I with water is complicated. At the initial stages (Figure 2.11b), the spectrum (2030, 2000, 1960 cm$^{-1}$) very closely resembles that reported for adsorption of Fe$_2$(CO)$_9$ and Fe$_3$(CO)$_{12}$ on partially dehydrated Na-Y (60$^\circ$C),$^{37}$ which were assigned to HFe$_3$(CO)$_{11}$$. Salts of this anion exhibit bands at 2073 (w), 2012 (vs), 2004 (vs), 1980 (s), and 1949 (m).$^{38}$ The fact that the spectrum requires tens of minutes to evolve indicates that because of the low loadings iron carbonyl units have to migrate toward each other. The complex formed is also not evacuable in support of its anionic nature. The structure of the intermediates involved in the formation of this species is unclear. A weak broad band at 1460 cm$^{-1}$, which can be assigned to CO$_3^{2-}$, is also observed upon reaction with water. The formation of HFe$_3$(CO)$_{11}$ from Fe(CO)$_5$ in basic solution involves the loss of CO as CO$_2$$^{39}$ and is supportive of the formation of HFe$_3$(CO)$_{11}$- on the zeolite surface. However, on the basis of
the IR data alone, the assignment of this species to HFe$_3$(CO)$_{11}$ is tentative.

**Nature of Species I.** On the basis of the evidence discussed above, it is clear that species I consists of Fe(CO)$_5$ adsorbed on two different sites in the zeolite. These sites are Lewis acid sites, which interact strongly with the Fe(CO)$_5$. The two sites are distinguished by their infrared spectra: Fe(CO)$_5$ adsorbed at IA exhibits bands at 2122, 2060, 2015, 1984, and 1960 cm$^{-1}$, whereas IB exhibits bands at 2116, 2043, and 1945 cm$^{-1}$. Such phenomena have recently been reported for M(CO)$_6$ (M= Cr, Mo, W) on alumina, in which four different sites for adsorption were noted.

Fe(CO)$_5$ exists in a D$_{3h}$ trigonal bipyramidal configuration. In the gas phase, bands at 2118 (a$_1''$, Raman), 2045 (a$_1'$, Raman), 2034 (a$_2''$, IR) and 2013 (e', IR) are observed. The trigonal bipyramid Fe(CO)$_5$ can interact with the zeolite through an equatorial carbonyl (symmetry C$_{2v}$) or an axial carbonyl (C$_{3v}$). In the former case five IR bands will be allowed, and in the latter three IR bands are allowed. On the basis of the observation of five peaks for species IA, we assign it to Fe(CO)$_5$ bound through an equatorial CO to the sites on the zeolite. A bonding justification can also be made for binding through an equatorial site. In the absence of any steric considerations, the position of a particular ligand in LFe(CO)$_4$ is determined by electronic factors. For a d$^8$ complex, if L is a strong $\pi$-accepting ligand, it will
prefer an equatorial position (e.g. \( \text{C}_2\text{H}_4\text{Fe( CO)}_4 \)), whereas for \( L \) being a \( \sigma \)-donor ligand, the axial position will be preferred (e.g. \( \text{(pyridine)Fe( CO)}_4 \)). In the particular case under discussion, \( L \) is a CO Lewis acid type ligand. Due to the interaction with an electron deficient site, it can be expected that the \( \pi \)-accepting ability of this particular CO will be enhanced. It is expected then that the interaction of \( \text{Fe( CO)}_5 \) with the acid site in the zeolite will be favored through an equatorial CO. The infrared spectrum also supports such an interaction with Lewis acid sites, because even though it is difficult to correlate the normal modes observed for gaseous \( \text{Fe( CO)}_5 \) with species IA in the lowered symmetry because of considerable mixing between all modes, the trend should be that the normal modes involving the CO's interacting with Lewis acid sites should decrease in frequency at the expense of other noninteracting CO's from which the electron density is pulled. Bands of IA at 1985 and 1960 cm\(^{-1}\) are considerably lower than gas-phase frequencies, whereas bands at 2120 and 2060 cm\(^{-1}\) are at higher frequency. On the basis of these observations, we are excluding the presence of trigonal bipyramidal \( \text{Fe( CO)}_5 \) bonding to the zeolite through axial CO's.

The other type of \( \text{Fe( CO)}_5 \) on the zeolite is characterized by three bands at 2116, 2043, and 1945 cm\(^{-1}\) (IB). Another limiting structure of \( \text{Fe( CO)}_5 \) is a square pyramid. It is of only slightly higher energy (~5 kcal/mol) than the trigonal
bipyramid form, as evidenced by the fact that on the NMR time scale only one CO is observed due to scrambling of all the CO's. This scrambling is proposed to go through a Berry mechanism in which the intermediate is a square pyramidal structure.\textsuperscript{42,43} For such a structure interacting with the Lewis acid site through the apical carbonyl, three bands are allowed in the infrared. For example, W(CO)\textsubscript{5} produced by UV irradiation of W(CO)\textsubscript{6} exhibits three bands at 2075 (w), 1936 (s), and 1912 (m) cm\textsuperscript{-1} and is typical of a square pyramidal M(CO)\textsubscript{5} group.\textsuperscript{44} So, we assign species IB whose infrared bands are observed at 2116 (w), 2043 (s), and 1965 (s) cm\textsuperscript{-1} to a square pyramidal Fe(CO)\textsubscript{5} bonded to the zeolite through the apical CO. The stronger $\pi$ acceptor in square pyramidal complexes is expected to be in the apical position.\textsuperscript{40,41}

**Structural Assignment of Species II.** Species II is characterized by a broad band at -2000 cm\textsuperscript{-1} (Figure 2.1c'). It is observed at high loadings of Fe(CO)\textsubscript{5} onto dehydrated zeolite. Upon addition of pyridine or PMe\textsubscript{3} to it, bands characteristic of gaseous Fe(CO)\textsubscript{5} are observed. We assign this species as Fe(CO)\textsubscript{5} in the supercages of the zeolite. The considerable broadening of the 2013 cm\textsuperscript{-1} band is attributed to interaction of the carbonyl groups with Na\textsuperscript{+} ions in the zeolite, analogous to the recent report of Ni(CO)\textsubscript{4} on zeolite Y.\textsuperscript{45} Upon addition of pyridine or PMe\textsubscript{3} to it, bands characteristic of gaseous Fe(CO)\textsubscript{5} are observed. Because the cations act only as weak Lewis acid sites, no ligand
replacement for CO is observed in contrast to Fe(CO)₅ bound at site I. The rapid decarbonylation reaction with O₂ also supports the presence of Fe(CO)₅ in the cages. For this reaction to take place, loading levels have to be high since multiple Fe(CO)₅ molecules are required, similar to the disproportionation reaction.

Sites on the Zeolites. Our studies indicate that at least four types of iron carbonyl species exist on the zeolite, indicating a heterogeneity of sites. It is also clear from our experiments (Figure 2.2d) that these sites are not due to amorphous impurities that are usually present in zeolite samples. This is not unexpected, since there is no compelling driving force for Fe(CO)₅ to seek out the few impurity sites as compared to the predominant zeolitic sites. The iron carbonyls on the zeolite include a zeolite-ligated Fe(CO)₄, which is unstable at temperatures over -77 K (species III). Fe(CO)₅ at low loadings exists in two forms (IA), a trigonal bipyramidal structure, an equatorial CO interacts with a Lewis acidic site. The other form is assigned to a square pyramidal structure, with the apical CO interacting with the zeolite framework (IB). At high loadings, the adsorbed species is principally Fe(CO)₅ in the supercages interacting weakly with the cations leading to a broadening of the infrared bands that are typically observed in the gas phase.

The reactivity patterns of species IA and IB are
different. IA reacts with ligands such as NH₃, PMe₃, C₂H₂, and pyridine to form L-Fe(CO)₄ complexes. However, IB is unreactive toward PMe₃, and both IA and IB completely decarbonylate in the presence of excess NH₃ and pyridine. There are two related questions about species I: first, why is there the difference in geometry, and second, what is the cause for a difference in reactivity. We propose that Lewis acid sites on the zeolite that are responsible for formation of I are defect sites on the surface arising from coordinatively unsaturated Al³⁺ and that is the reason they appear at the lowest loading levels. There is obviously a distribution of these sites considering the heterogeneous character of the surface of the zeolite. These sites are distinguished by steric factors. The sites responsible for the trigonal bipyramidal structure are easily accessible, whereas those for the square pyramidal structure are buried in grooves. Such buried sites stabilize the pyramidal form, presumably due to steric reasons. This also explains the differences in reactivity toward PMe₃. The cone angle of PMe₃ is 136°, thus limiting its approach to sterically restricted sites. Pyridine, NH₃, and C₂H₂ all will be more effective at interacting with these sites. The ease of elimination of CO and formation of L-Fe(CO)₄ for species IA also indicates that the interaction of the CO with the Lewis acid site is strong. The inaccessibility of site IB toward PMe₃ is also confirmed by the fact that it does not block this site upon
preadsorption on the zeolite, prior to Fe(CO)₅ adsorption (Figure 2.4c). The Fe(CO)₅ molecule with a Oₓ₋Oₑ distance of 4.1 Å, is still able to access these IB sites.⁴⁷

CONCLUSIONS

The original motivation for this research was to characterize the iron carbonyl initially present after adsorption onto the zeolite to be able to better understand subsequent photochemical decomposition. Previous experience in our group had shown that the vibrational spectra of a metal complex inside a zeolite was virtually identical to the free molecule.⁴⁸,⁴⁹,⁵⁰ As shown, this is not the case with Fe(CO)₅ absorbed onto dehydrated zeolite Y and there are two possible explanations for the uniqueness of the system. The technique for observing the vibrational spectra in the previous studies in our group was resonance Raman while IR was used to examine Fe(CO)₅. The other important difference is that this was a metal carbonyl while the previous studies in the group were other types of metal complexes. Therefore any unique interactions due to the carbonyl ligand may be causing the changes in the vibrational spectra.

The infrared spectra of other metal carbonyls on zeolite supports have been examined and changes from the spectra of the free molecule are usually noted. Abdo and Howe examined the infrared spectra of Mo(CO)₆ absorbed onto dehydrated Na-
Y and H-Y.\textsuperscript{51} Gas phase Mo(CO)\textsubscript{6} has only one allowed C-O stretching band. Upon absorption onto either Na-Y or H-Y four C-O stretching bands are observed. These bands are assigned to two species: a chemisorbed Mo(CO)\textsubscript{6} and a physically absorbed Mo(CO)\textsubscript{6}. Other investigators have looked at the absorption of Co\textsubscript{2}(CO)\textsubscript{8} onto zeolite X or Y and saw vast changes in the IR spectra upon adsorption.\textsuperscript{52,53} Several new species were formed and identified as Co(CO)\textsubscript{4}, and Co\textsubscript{4}(CO)\textsubscript{12} among others. So it is seen that metal carbonyls can be expected to undergo changes, either physical or chemical, upon absorption onto zeolites which result in changes in the observed IR spectra.

Similar changes would be expected in the Raman spectra as well. The Raman spectra, like the infrared spectra, would be sensitive to changes in the symmetry of a molecule upon absorption onto supports. However due to the difference in sensitivity between IR and Raman, much higher amounts of metal carbonyl must be present in order to obtain a Raman spectra. This will be significant if the number of sites responsible for the observed IR spectra are limited in number. If this is true as the loading level is increased the metal carbonyl subsequently added is not perturbed in a significant manner from the free molecule. So it may be possible that at saturation the species observed at low loadings in the IR actually account for only a few percent of the total iron carbonyl present. Therefore a technique which requires a high
loading of iron carbonyl will detect Fe(CO)₅ which is unperturbed compared to the free molecule.

This can be tested by examining Fe(CO)₅ absorbed onto Na-Y with techniques less sensitive than infrared spectroscopy and determining if the signal observed is similar to free Fe(CO)₅. It should be pointed out that the difficulty with doing this with laser Raman spectroscopy is the unavoidable photodecomposition of Fe(CO)₅ which would occur. Nagy et al. used ¹³C NMR to examine Fe(CO)₅ absorbed onto dehydrated Na-Y. This shows a signal which was slightly shifted from that observed for the neat compound. The shift seen was comparable to a shift due to a solvent such as CDCl₃. This study also showed somewhat restricted mobility of the Fe(CO)₅, but the overall conclusion was that the interaction between the Fe(CO)₅ and the zeolite was quite weak. Mossbauer studies of this system have also assigned the initial species to be Fe(CO)₅ absorbed onto the zeolite.¹⁵⁵,¹⁵⁶

The combination of these factors makes Fe(CO)₅ a unique probe molecule to examine the surface of the zeolite when IR spectroscopy is used as the characterization technique. When the zeolites are saturated with Fe(CO)₅ molecules the majority of them are in the supercages interacting weakly with each other and with the sodium cations. These molecules are not much different from Fe(CO)₅ in a liquid state. At lower loadings the Fe(CO)₅ molecules seem to preferentially seek out sites with which they interact much more strongly. We assign
both of these sites to be Lewis acid sites present in the zeolite. The exact nature of these sites is somewhat unclear, but they are now believed to be due to defects in the crystal. These defects are most likely due to incompletely coordinated aluminum on the surface of the zeolite. The two sites differ simply due to steric considerations. Site IA is more accessible to potential ligands and is therefore more reactive while site IB must be blocked to some extent preventing bulkier molecules from being able to interact with them.
REFERENCES


CHAPTER III

OLEFIN OXIDATION BY ZEOLITE ENCAPSULATED MN(SALEN)

INTRODUCTION

The development of a catalyst which is able to selectively oxidize organic compounds to yield desirable products would be a great achievement. Ideally one wants to mimic biological systems in which highly selective oxidations are done at ambient conditions. The cytochrome P450 enzymes are responsible for the oxidation of hydrocarbons in living systems, using $O_2$ as the oxidant. These enzymes are monooxygenases where one oxygen atom of the dioxygen is added to the substrate and the second is reduced to water. The development of a synthetic catalyst similar in properties to these enzymes could not only have great industrial applications, but may also provide insight into the mechanism of the selective oxidation by the cytochrome P450 enzymes.

The processes for the partial oxidation of organic compounds which are of commercial importance are normally carried out at high temperatures, generally above 150°C. These reactions proceed via a radical chain mechanism and the elevated temperature is necessary in order to make the oxidation proceed at a reasonable rate. Overall the process is exothermic and this helps explain why the loss of a certain
percentage of the products to CO and CO₂ is inevitable. The P450 enzymes follow a quite different catalytic cycle and this accounts for the greater reaction control with this system.

The desire to more closely mimic the enzymatic system has prompted the examination of metal porphyrin complexes. Generalizing further, other macrocyclic ligands in which a square planar array of nitrogen and oxygen atoms are coordinated to the metal have been examined. Using a variety of terminal oxidants these metal complexes are capable of epoxidation and oxidation of olefins at ambient conditions. Oxidation of alkanes had also been reported in a number of cases. This is quite intriguing as the C-H bonds in alkanes are quite strong and resistant to reaction. The ability to controllably oxidize alkanes brings these synthetic catalysts one step closer to fully reproducing the ability of the biological systems.

A further improvement in the performance of these catalysts may be seen by encapsulating them inside zeolite cavities. It has been suggested that zeolite encapsulated metal complexes have the potential to act as inorganic enzymes. The steric constraints placed upon the active catalytic site by encapsulation inside the zeolite could cause the zeolite framework to play a role similar to that of the protein of the P450 enzymes. In the case of the zeolite encapsulated metal complex, substrate selectivity would be on the basis of size with small molecules enjoying an advantage
over larger ones.

The catalytic properties of transition metal complexes encapsulated in zeolite cavities have recently become of considerable interest.\(^2\) These materials hold the promise of combining the advantages of homogeneous and heterogeneous catalytic systems. The active transition metal site differs from the solution species only by the constraints placed upon it by the zeolite, allowing reactions to occur under mild conditions. Also, as the catalyst is trapped inside the zeolite, the products can be readily separated. Other influences, arising primarily from the architecture of zeolites, include reactant and product selectivity due to size constraints in the zeolite cages.\(^3\) In addition, the lifetime of the catalyst can be influenced by its encapsulation since degradation pathways involving reactions such as dimerization of catalysts can be prevented.

Previous work in the area of zeolite encapsulated metal complexes has included the use of metal carbonyls for the water-gas shift reaction, carbonylation of methanol and aromatic compounds, and hydroformylation.\(^4,5,6,7\) Studies on oxidation catalysts have been more limited. These include the synthesis of iron phthalocyanine in zeolite Y and oxidation of saturated hydrocarbons.

Tolman, Herron and Stucky have examined a number of zeolite encapsulated oxidation catalysts to determine the advantages and disadvantages associated with placement of the
metal complex inside the zeolite. Iron phthalocyanine was synthesized inside zeolite X and Y and its ability to oxidize a number of different alkanes was determined. The turnover number in the oxidation of methylcyclohexane increases by a factor of five upon zeolite encapsulation when compared to iron phthalocyanine in solution. The increased lifetime of the catalyst upon encapsulation is due to the fact that bimolecular self destruction, which is the primary decomposition mode in solution, is prevented by zeolite encapsulation. Size or shape selectivity was shown by the preference for cyclohexane to be oxidized in a solution containing it and cyclododecane. The molecular sieving properties of the zeolite cause there to be a preference for the smaller substrates. This effect can be enhanced by ion exchanging larger cations such as ammonium or Rb⁺ into the zeolite in place of the Na⁺ ions. This alters the zeolite pore size and improves the selectivity from a 65:35 ratio to a 90:10 ratio. In addition to these benefits there is the added advantage of the ease of separation of the catalyst from the reaction mixture for reuse.

The rate of the oxidation of the alkanes was considerably slower when the catalyst was encapsulated inside the zeolite when compared to the reaction in solution. Also the performance of the catalyst degraded over time as the pores became blocked by products of the reaction and decomposition of the catalyst. The catalytic activity can be restored by
drying the spent catalyst in a vacuum oven to remove the species responsible for plugging the zeolite pores. In addition, the presence of the catalyst itself restricts mobility through the zeolite pore system and this results in limited access to the catalytic sites deeper in the crystal. A final disadvantage of this system is that the zeolite cage size places a limit on the size of the metal complex which can be built inside the zeolite.

Kochi et al. have studied a number of metal salen complexes and found that generally they are useful as epoxidation catalysts with olefins as substrates.\textsuperscript{9,10,11,12,13} There was an interest to determine how zeolite encapsulation would affect the catalytic performance of these compounds. The size of the salen ligand is such that while the uncomplexed ligand is able to move into the zeolite supercage, once it is complexed to a metal ion its size and rigidity prevents it from migrating through the zeolite. Iodosylbenzene is a terminal oxidant which is used in many such systems and is a convenient choice for the zeolite encapsulated system. It can be used in an organic solvent and therefore allows the entire system to be in one phase. Hypochlorite would be a cheaper and more convenient terminal oxidant, but its insolubility in organic solvents makes the presence of a phase transfer catalyst mandatory and greatly complicates the process when the catalyst is inside a zeolite. We set out to explore the catalytic behavior of metal salen
complexes encapsulated in the zeolite using iodosylbenzene as a terminal oxidant. Also, the insolubility of PhIO in the solvent allows it to be easily separated from the reaction products. In addition, quantitative analysis of the PhI formed allows for the direct measurement of the oxygen transferred to reactants.

EXPERIMENTAL SECTION

Materials. Zeolite Y (NaY, Union Carbide) was ion exchanged with 0.1M NaCl for 16 hours prior to its use. The iodosylbenzene (PhIO) was prepared via literature methods from its diacetate (Aldrich).14 The styrene (Gold Label), salen, cis-stilbene, trans-stilbene, styrene oxide, cis-stilbene oxide, trans-stilbene oxide, cyclohexene oxide, iodobenzene, and 1-octene were purchased from Aldrich and used as received. The acetonitrile, chlorobenzene, cyclohexane and cyclohexanol were from Mallinkrodt and were used without further purification. The cyclohexene (E/M Science), MnCl₂·4H₂O (Baker), Cr(NO₃)₃·9H₂O (Baker), Ni(CH₃CO₂)₂·4H₂O (Aldrich), FeCl₂·4H₂O (Baker) were used as received. The hexafluorophosphate salt of ferrocenium was prepared from ferrocene (Strem) and NaPF₆ (Alfa).

Synthesis of Metal Salen Complexes inside Zeolite Y. One gram of NaY is shaken overnight in an aqueous solution containing the desired amount of the metal cation. At these low levels of approximately 1 mM it can be assumed that all
the metal cation is exchanged from the solution into the zeolite. The zeolite is then filtered and washed with deionized water to remove any chloride ions present. Next the MnNaY is heated up to 400°C under vacuum or flowing dry nitrogen to dehydrate the zeolite. The zeolite is then cooled and ground with 0.1 gram of salen in an inert atmosphere glove box, the solid is then sealed into a tube and heated to 120°C for one half hour. After heating the manganese complex is a bright yellow color, the nickel a golden color, the chromium a yellow-green color, and the iron an orange color. The catalysts are then Soxhlet extracted with CH$_3$CN overnight to remove any surface bound complex and any excess ligand.

**Treatment of the Manganese Complex.** The Mn(II)(salen) complex initially formed is air sensitive and three different methods of handling these samples and converting them to the stable Mn(III)(salen) complex were used. All the samples were treated identically up to the point of the formation of the bright yellow Mn(II)(salen) complex. Catalyst A was then Soxhlet extracted with CH$_3$CN, ion exchanged with 0.1M NaCl for twelve hours and upon filtering the solid had turned a brown color indicative of Mn(III)(salen). Catalysts B and C were reacted with a solution of ferrocenium under an inert atmosphere. Upon the addition of ferrocenium the catalyst turns from a bright yellow color to a brown color. Catalyst B was then ion exchanged with 0.1M NaCl for one hour and the catalyst C sample was simply washed with acetonitrile.
Instrumentation. Gas chromatography was done on a Varian Aerograph Series 1400 using a 2m 10% Carbowax 1540 column. The apparatus was equipped with a flame ionization detector. The column temperature was programmed to go from 100 to 160°C at 6°C/minute. Generally 1 μL aliquots were injected. The HPLC analysis was done on an Alltech Econosil column using a 75/25 mixture of methanol and water. Ultraviolet detection was used.

The elemental analysis was done on a Kevex 0700 X-ray fluorometer. The X-ray diffraction patterns were taken on a Rigaku D/Max 2B diffractometer. The diffuse reflectance UV-VIS spectra were taken on a Shimadzu UV-265 equipped with a Harrick diffuse reflectance attachment. The infrared spectra were taken of self-supporting wafers of the catalyst samples on a Mattson Cygnus 25 FT-IR. All inert atmosphere manipulations were performed in a Vacuum Atmospheres glove box.

Oxidation and Analysis of Products. All oxidations were done in 5 mL CH₃CN with ~0.2 mmol of olefin, ~0.2 mmol chlorobenzene (internal standard), 25 mg PhIO and 100 mg of catalyst. In the study of the effect of an axial base the conditions were identical with the appropriate amount of pyridine added to the solution. Unless otherwise noted the reaction time was sixteen hours. GC analysis was performed on the solution before the addition of the PhIO and the catalyst. After the desired reaction time the solution was
centrifuged and subjected to another GC analysis. The initial and final GC analysis were done three times and the peaks were ratioed to the internal standard. This procedure was used for all trials, however for solutions containing cis- or trans-stilbene HPLC analysis was also necessary to quantitate the stilbenes. To obtain appropriate sample concentrations it was necessary to dilute a 10μL aliquot to 2 mL. The relative reactivity experiments were done in a similar manner. The products were identified by comparison of retention times from authentic samples.

Relative Reactivities of Different Olefins. The relative reactivities of olefins in competition with each other was checked for catalysts A, B, and C with cyclohexene and styrene. Additionally for catalysts A cis-stilbene and trans-stilbene were compared to cyclohexene. The relative reactivity was calculated from the equation $k_x/k_y \times \log(X_f/X_i)/\log(Y_f/Y_i)$ where $X_i$ and $Y_i$ are the initial concentrations of the olefins $X$ and $Y$ and $X_f$ and $Y_f$ are the final concentrations of these olefins.

Determination of Maximum Turnover Number. The reaction was carried out in 5 mL of CH$_3$CN containing 1 mmol cyclohexene, 1 mmol chlorobenzene, 1.5 mmol of PhIO and 100 mg of catalyst. The solution was periodically sampled via GC to determine the amount of PhI formed as a function of time.

Quantification of Mn in Catalysts. The amount of manganese in the various catalysts was determined by XRF. A
calibration curve was set up by ion exchanging a known amount of manganese into a weighed amount of NaY. These samples were placed into the sample chamber which was then evacuated. The samples were analyzed with direct excitation for 300 seconds at 13 kV and 0.01 mA. The standard samples were used to set up a calibration curve which was used to determine the manganese content of the catalyst samples. The calibration curve could be set up using absolute manganese intensity or by ratioing the manganese peak to the silicon peak. Both methods gave straight lines for the calibration curve and the final results generally agreed to within 5%.

RESULTS

The reaction that forms the focus of this investigation is the oxidation of olefins by the terminal oxidant PhIO in the presence of a zeolite encapsulated metal complex to produce oxidation products and iodobenzene. No reaction occurred if PhIO was excluded from the reaction system or if Na-exchanged zeolite Y was used as the catalyst. It is clear that PhIO interacting with the transition metal zeolite forms the active oxygenating species. The ratio of olefin that reacts to the quantity of PhI formed provides a direct measure of the amount of olefin that is interacting with the catalyst.

Salen Complexes. In an effort to screen the various metal salen complexes to determine which held the most promise as an encapsulated oxidation catalyst the four metal salen
complexes were compared in their ability to oxidize styrene. Using the quantity of products recovered ratioed to the amount of iodobenzene formed as a measure of the yield of the reaction, Mn(salen) showed the most promise. The yield for the metal salen complexes were: Cr(salen) 2%, Ni(salen) 4%, Fe(salen) 7% and Mn(salen) 46%. Because of its higher yields the manganese complex was studied in greater detail.

Mn(salen) in Zeolite Y. Three catalyst preparations were examined. All of these were made from Mn(II)(salen)-zeolite Y. This was a bright yellow solid, and its diffuse reflectance spectrum is shown in Figure 3.1, with characteristic bands at 270 and 407 nm. Soxhlet extraction of this material with CH$_3$CN in an aerobic environment led to the formation of a brown solid. Ion exchange with a 0.1M NaCl solution to remove unreacted Mn$^{2+}$ ion led to the preparation of the first catalyst sample (catalyst A). Catalyst A was found to contain 1.7 mg Mn/ g zeolite, while the starting MnNaY used to make this catalyst contained 7 mg Mn/ g zeolite. The diffuse reflectance and infrared spectrum of catalyst A are shown in Figures 3.2 and 3.3. The bands in the electronic spectrum at 231, 283, 314, 350, 382 and 500 nm are in fairly good agreement with the solution spectrum of Mn(salen)PF$_6$.$^9$ The IR spectra, with bands at 1609, 1583, 1512, 1468, 1448, 1414, 1396, 1290, 1232 and 1182 cm$^{-1}$, are also in fair
Figure 3.1. Diffuse reflectance spectra of Mn$^{II}$(salen) encapsulated in zeolite Y (Kubelka-Munk with reference to NaY).
Figure 3.2. Diffuse reflectance spectra of Mn$^{III}$(salen)-Y.
Figure 3.3. Transmission infrared spectra of Mn^{III}(salen)-Y
Figure 3.4. GC trace of the products formed upon cyclohexene oxidation with catalyst A [Mn$^{III}$(salen)].
Figure 3.4

A. cyclohexene
B. acetonitrile
C. cyclohexene oxide
D. chlorobenzene
E. cyclohexenol
F. iodobenzene
agreement with the published data. The reactions of various olefins with catalyst A were examined and are shown in Table 3.1. The total amount of catalyst in these experiments corresponds to 0.003 mmoles of Mn(III)(salen). In the case of cyclohexene, the amount of olefin that reacts is comparable to the PhI formed. About 24% of the olefin could be accounted for in terms of the products cyclohexene oxide and cyclohexenol. The color of the solution was yellow after the reaction, indicating the presence of some other product, which was not evident in the GC or HPLC traces. A typical GC trace of the products is shown in Figure 3.4. Styrene is also oxidized by this catalyst, forming two major products: styrene oxide and phenylacetaldehyde. Unlike cyclohexene, only 60% of the styrene reacts with the oxygenated catalyst. It is possible that the initial products of the oxidation are reacting with the catalyst rather than with styrene. In order to examine this possibility, styrene oxide and cyclohexene were reacted with the catalyst. It was found that while cyclohexene was oxidized, styrene oxide could be recovered quantitatively, indicating that the oxide is fairly inert to oxidation in the presence of olefin.

Because the source of the yellow color which the solution develops upon reaction is unknown, there was the possibility that it was due to manganese leaching into the solution from decomposition of the complex. Examination of the zeolite catalyst for manganese content via XRF after reaction with
### Table 3.1

Reactivity of Olefin

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Olefin</th>
<th>Olefin reacted mol</th>
<th>Phi formed mol</th>
<th>Ratio (olefin/Phi)</th>
<th>Products, mol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-Y</td>
<td>cyclohexene</td>
<td>0.058</td>
<td>0.096</td>
<td>0.6</td>
<td>0.009 (16%) cyclohexenol</td>
</tr>
<tr>
<td></td>
<td>styrane</td>
<td>0.049</td>
<td>0.084</td>
<td>0.58</td>
<td>0.013 (27%) styrene oxide</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.002 (4%) PhCH₂CHO</td>
</tr>
<tr>
<td>Mn(salen)-Y A</td>
<td>cyclohexene</td>
<td>0.11</td>
<td>0.11</td>
<td>1</td>
<td>0.015 (14%) cyclohexane oxide</td>
</tr>
<tr>
<td></td>
<td>styrane</td>
<td>0.057</td>
<td>0.092</td>
<td>0.6</td>
<td>0.011 (19%) styrene oxide</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.015 (26%) PhCH₂CHO</td>
</tr>
<tr>
<td></td>
<td>trans-stilbene</td>
<td>0.048</td>
<td>0.090</td>
<td>0.5</td>
<td>0.01 (20%) trans-stilbeneoxide</td>
</tr>
<tr>
<td></td>
<td>cis-stilbene</td>
<td>0.019</td>
<td>0.085</td>
<td>0.2</td>
<td>cis-stilbene oxide</td>
</tr>
<tr>
<td></td>
<td>1-octene</td>
<td>0.009</td>
<td>0.082</td>
<td>0.1</td>
<td>no products were identified</td>
</tr>
<tr>
<td></td>
<td>cyclohexene</td>
<td>0.043</td>
<td>0.082</td>
<td>0.5</td>
<td>cyclohexanone, cyclohexanol</td>
</tr>
<tr>
<td></td>
<td>no olefin</td>
<td>-----</td>
<td>0.10</td>
<td>-----</td>
<td>-------</td>
</tr>
<tr>
<td>B</td>
<td>cyclohexene</td>
<td>0.066</td>
<td>0.095</td>
<td>0.7</td>
<td>0.007 (11%) cyclohexene epoxide</td>
</tr>
<tr>
<td></td>
<td>styrane</td>
<td>0.026</td>
<td>0.105</td>
<td>0.2</td>
<td>styrene oxide</td>
</tr>
<tr>
<td>C</td>
<td>cyclohexene</td>
<td>0.012</td>
<td>0.088</td>
<td></td>
<td>products too small to be quantified</td>
</tr>
<tr>
<td></td>
<td>styrane</td>
<td>0.014</td>
<td>0.110</td>
<td>0.1</td>
<td>0.007 (50%) styrene oxide</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.009 (50%) PhCH₂CHO</td>
</tr>
</tbody>
</table>

* 0.110 mmol of Phi0

+ X - relative to olefin reacted.
PhIO and cyclohexene showed a decrease in manganese level of about 20%. This indicates that over time a certain amount of ligand degradation and manganese leaching can occur, it is not known if this fully accounts for the color of the solution.

Table 3.1 also shows the results from the oxidation of other larger olefins. It also shows that even in the absence of an olefin substrate there is a formation of Phi as the PhIO reacts with the metal complex. What is being oxidized in this case will be examined later.

One possible effect of placing the active catalyst site inside the zeolite is that there will be an introduction of size or shape selectivity due to the molecular sieving properties of the zeolite. To determine the selectivity properties of this catalyst, the relative reactivity (defined in the experimental section) of the olefins were compared with cyclohexene. The results from these trials are summarized in Table 3.2. From these results it can be seen that cyclohexene more readily reacts and this is probably due to its smaller size which allows it to encounter the active site of the catalyst more readily.

The Mn(III)(salen) complex in solution can undergo about thirty cycles on average before it loses its effectiveness. The zeolite encapsulated complexes maximum turnover number was determined as described in the experimental section. A plot of the number of cycles through which an average complex has gone as a function of time is given in Figure 3.5. It is seen
Table 3.2

Relative Reactivity of Olefins versus Cyclohexene

<table>
<thead>
<tr>
<th>Mn Catalyst</th>
<th>Olefin, initial final (mmol)</th>
<th>Olefin, initial final (mmol)</th>
<th>Relative Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>cyclohexene 0.247, 0.175</td>
<td>styrene 0.218, 0.184</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>cyclohexene 0.247, 0.180</td>
<td>trans-stilbene 0.286, 0.257</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>cyclohexene 0.247, 0.205</td>
<td>cis-stilbene 0.140, 0.132</td>
<td>0.31</td>
</tr>
<tr>
<td>B</td>
<td>cyclohexene 0.247, 0.167</td>
<td>styrene 0.218, 0.179</td>
<td>0.50</td>
</tr>
<tr>
<td>C</td>
<td>cyclohexene 0.247, 0.219</td>
<td>styrene 0.218, 0.193</td>
<td>0.83</td>
</tr>
</tbody>
</table>
Figure 3.5. Determination of turnover number.
Figure 3.6. Determination of rate of reaction.
that the complex loses its efficiency over time and its maximum value is approximately sixty. So zeolite encapsulation seems to be responsible for extending the catalyst life.

A similar trend is seen on a shorter time scale when the amount of Phi formed is plotted as a function of time during the oxidation of cyclohexene (Figure 3.6). The rate drops dramatically as the reaction proceeds. This could be due to pore clogging by products of the oxidation reaction. This mechanism could also be causing some of the loss of catalyst effectiveness over longer times.

Catalyst samples B and C were prepared from Mn(II)(salen)-Y by oxidation with ferricenium ion. This procedure was similar to that for homogeneous solutions. Catalyst B and C contained 6 and 12 mg Mn/g NaY which corresponds to one ion per 4 and 2 supercages respectively. In general, the reactivity of these catalysts were lower than that of catalyst A. Both these samples were not Soxhlet extracted to remove excess salen ligand, and only sample B was ion-exchanged with 0.1M NaCl to remove unreacted Mn\(^{2+}\) and ferricenium cation. The lower reactivity of these systems could be due to pore plugging in the zeolite and the inability of olefin molecules to reach the active sites. The only point of interest appears to be the increase in the relative reactivity of styrene over cyclohexene from 0.5 for catalysts A and B to 0.83 for sample C. This is most likely due to the
reaction in sample C occurring on the zeolite surface which lowers discrimination in size selectivity.

Mn-Y. Mn$^{2+}$ exchanged zeolite Y (13mg/g zeolite, 1 Mn$^{2+}$ per 2 supercages) exhibits catalytic activity in the oxidation of cyclohexene and styrene. The amount of manganese in the zeolite corresponds to 0.023 mmoles. In both cyclohexene and styrene, about 60% of the PhIO reacts with the olefin. Cyclohexenol and phenylacetaldehyde are the major products, with conversions of 16 and 27% as compared to the total olefin that has reacted. No epoxide was detected in the cyclohexene case, whereas only a small amount (4%) of styrene oxide was formed.

**DISCUSSION**

When taking note of the metal salen's reactivity in solution it is not surprising that the Mn(salen) complex shows the greater ability to oxidize olefins. The Ni(salen) complex and other similar compounds have been shown to be active catalysts for the decomposition of terminal oxidants such as iodosylbenzene.$^{9,10,11}$ The oxo-nickel(IV) complex thus formed displays a very high reactivity so many competing side reactions interfere. The formation of the $\mu$-oxo nickel dimers is observed, but encapsulation inside the zeolite should prevent this. More important for the zeolite encapsulated case is the ease with which the oxidation of the ligand and
solvent proceeds. It was concluded that the oxo nickel salen complex is essentially too reactive and therefore not selective toward olefins.\textsuperscript{10}

In contrast, the Cr(salen) complex gives a 40\% yield of styrene oxide in solution.\textsuperscript{11} However, in obtaining this yield N-pyridine oxide was present and acting as an axial base. The presence of this donor ligand was shown to be critical in the formation of the oxidation products. This could explain the lower yields seen in the zeolite encapsulated case as there was no axial base present.

The behavior of the Mn(salen) complex in solution is generally similar to its behavior when encapsulated inside the zeolite.\textsuperscript{9} The addition of an axial base was shown to have an effect on the yield of oxidation products, but it is not as critical as in the case of Cr(salen). The effect in the zeolite encapsulated case is even smaller as the addition of pyridine had no observable effect upon the products of the reaction. This lack of influence due to the presence of an axial base could be due to crowding in the zeolite cages which either prevents or limits the ability of the axial base to bind to the metal complex.

The electronic spectra of the Mn(II)(salen) complex confirms that it is being formed in the zeolite. This complex is unstable in air and the Mn(III) complex is the catalytically active species. The aerobic oxidation of Mn(II)(salen) complexes in solution is very complicated.
Based on magnetic measurements, a complex set of products has been proposed. These include Mn(II)(salen)OH, as well as oxybridged structures and polymeric forms represented by [Mn(salen)O]n.\textsuperscript{15,16} In the zeolite, there is no room in the supercages for polymerization of the Mn(salen) species. Also, the mobility of Mn(salen) through the zeolite is restricted because of the 7Å ring openings of the supercage. It is proposed that the oxidation product is of the form Mn(salen)OH (shown below) based on the spectroscopic properties and constraints of the zeolite. It is important to point out that the zeolite architecture is responsible for stabilizing the Mn(III) monomeric complex, in contrast to solution studies.

![Structure of Mn(salen)OH](image)

**Figure 3.7.** Structure of Mn(salen)OH.
Based on the oxidation of olefins by a Mn(salen) in solution, the following scheme has been proposed.

\[
\begin{align*}
Mn^{IV} & - O - Mn^{IV} \\
\downarrow & \quad \uparrow \\
\text{PhiO} & \quad \text{OMn}^{V} \quad \text{C} = \text{C} \\
\Phil & \quad \text{Mn}^{III} \\
\end{align*}
\]

Figure 4.8. Proposed reaction scheme for olefin oxidation.

In the zeolite, the size of the supercage prevents the formation of the \( \mu \)-oxodimer. This is also supported by the lack of any spectral changes upon addition of PhIO to Mn(III)(salen)-\( \gamma \), unlike the appearance of the 530 nm band in solution. Other than the prevention of the dimerization pathway it is believed that the catalytic behavior is identical whether the metal complex is in solution or encapsulated inside the zeolite.

It is useful to contrast the trends in reactivities of the encapsulated Mn(salen)-zeolite and the complex in solution. Reaction conditions are similar in both cases, except that the amount of catalyst in the zeolite sample was
differences between the catalytic behavior of the zeolite encapsulated Mn(salen) and its solution properties will be examined.

In the presence of olefin in the homogeneous system, the catalyst Mn(salen) preferentially reacts with the olefin rather than the solvent. Typically, this reaction is complete within 30 minutes. However, the reaction with the zeolite encapsulated complex is considerably slower, being complete only after 16 hours of reaction. The slower overall rate for the zeolite system as compared to solution is similar to observations made for alkane oxidation by zeolite encapsulated iron phthalocyanine. It appears that diffusion through the zeolite network may cause the overall lower reaction rate.

To quantify the role of diffusion inhibition in the reaction rate, the Weisz-Prater criterion has often been used.\textsuperscript{17,18} According to this criterion, if the modulus \( \phi = k(R^2 /D) \) exceeds 2, the reaction is diffusion inhibited. In the equation, \( k=(dn/dt)(1/C) \) is the observed rate constant, \( R \) is the radius of the zeolite particles, and \( D \) is the diffusion coefficient in the system. For the oxidation of cyclohexene, we calculated an initial first-order rate constant of \( 1.4 \times 10^{-4} \text{ s}^{-1} \) (for the first 2000 seconds) and estimate an average radius for the zeolite particles of \( 5 \times 10^{-4} \text{ cm} \). So, for the reaction to be diffusion inhibited, the diffusion coefficient must be less than or equal to \( 1.75 \times 10^{-11} \text{ cm}^2/\text{s} \).
The diffusion coefficients for the olefins used in this study could not be found in the literature. However, diffusivities of similar sized molecules from the liquid phase into NaY has been reported.\textsuperscript{19} For example, cumene and 1,3,5-trimethyl, triethyl- and triisopropylbenzene with minimum molecular diameters of 6.8, 8.4, 9.2, and 9.4 Å have diffusion coefficients of \(7 \times 10^{-11}\), \(0.68 \times 10^{-11}\), \(0.0065 \times 10^{-11}\), and \(0.00028 \times 10^{-11}\) \(\text{cm}^2/\text{s}\), respectively. The olefins used in this study include cyclohexene, styrene, and trans- and cis-stilbene. The comparability in size of these molecules and those described above indicates that the reaction is indeed operating in a region of diffusion-controlled rate inhibition. The diffusivity of cyclohexene is expected to be higher than the diffusivities of the other olefins and is probably comparable to that of cumene; therefore, its reactivity is on the borderline for diffusion inhibition. The relative rates for diffusion of cyclohexane, p-xylene, o-xylene, and mesitylene into zeolite Y have been reported by Chester and coworkers as 1, 0.25, 0.20, and 0.16.\textsuperscript{20} This would indicate that for the olefins examined in this study, besides cyclohexene, the reaction rates are definitely in the diffusion controlled inhibition regimes.

Referring to Table 3.1, the major difference in performance between the complex in solution and in the zeolite is the amount of olefin which reacts compared to the amount of PhI formed. In the case of cyclohexene these numbers are
nearly identical, but for the other olefins under study the amount of olefin which disappears is one half or lower of the amount of Phi formed. The formation of Phi from PhIO necessitates that some other species in the system is gaining an oxygen and there are several possibilities as to where this oxygen could be going. As mentioned earlier, styrene oxide is inert to oxidation in the presence of cyclohexene and this seems to rule out the possibility of oxidation products being oxidized further. This would be a valid assumption in the solution reaction, but in the zeolite special circumstances make consideration of another point important. If styrene is being oxidized then the styrene oxide would be formed at an active site within a zeolite crystal. It is possible that this styrene oxide would be more likely to undergo further reaction due to its proximity to the catalyst. That is, the oxidation of an olefin is preferred to the further oxidation of an epoxide if they are both in solution, but if the epoxide is caught in the zeolite pore system near the catalyst its oxidation could proceed at a competing rate.

It is also possible that the salen ligand could be undergoing oxidation, especially since such effects have been observed with Cr(salen) in solution. It is important to note that due to encapsulation of the Mn(salen) complexes in the zeolite supercages and the low loading levels, any direct interaction between Mn(salen) complexes is highly unlikely. There are $3.1 \times 10^{-6}$ moles of Mn(salen) in a sample of catalyst
A in a typical reaction. To fully account for the PhIO that
does not react with styrene, each salen ligand would have to
be oxidized eleven times on the average. Clearly this cannot
be the case for it would lead to rapid deactivation of the
catalyst. The analysis of the manganese content of the
catalyst after reaction did reveal that approximately 20% of
the manganese leached into the solution which indicates that
some decomposition of the catalyst is taking place. Due to the
small quantity of catalyst present, this process is not
important in explaining the formation of PhI without the
corresponding loss of olefin.

Another possibility is that the solvent molecules
(acetonitrile) may be undergoing oxidation. The ability of
the catalyst to oxidize unactivated C-H bonds was confirmed
by the oxidation of cyclohexane to cyclohexanone and
cyclohexanol. It was found that PhI is formed in the
catalytic system in the absence of any hydrocarbon. These
facts indicate that olefin molecules are competing with
oxidation of the solvent. This has been observed in solution
using Ni(salen) as a catalyst. In the case of styrene,
however this electron-rich substrate is considerably more
favored than acetonitrile to undergo oxidation. The
competition must arise from the restricted diffusion of
styrene through the zeolite pore system and considerably
higher concentration of the solvent molecules. This is also
confirmed by the study of larger olefins, such as 1-octene and
trans- and cis-stilbene. In the case of stilbenes, only 50 and 20% of PhIO molecules go toward the oxidation of trans- and cis- olefins, respectively. In both cases, formation of the oxides was noted from the HPLC traces. The yield for cis-stilbene oxide was too small to be measured accurately. From these data, however, it is clear that as the olefin increases in size (cyclohexene, 6.7 x 7.4 Å; styrene, 6.7 x 9.5 Å; trans-stilbene 6.7 x 13.9 Å; cis-stilbene, 8.0 x 10.3 Å), and there is the corresponding decrease in the diffusion coefficient for the molecule inside the zeolite, the competition with solvent oxidation rises.

Encapsulation of the metal complex brings about an increase in the average lifetime of the catalyst. The lifetime over which a catalyst retains its activity can be expressed in terms of a turnover number which gives a value as to the number of times each molecule of Mn(salen) has been oxygenated. In this case the turnover number was written as the ratio of iodobenzene formed to the quantity of catalyst present. As seen in Figure 3.5 the catalytic activity decays over time and the maximum turnover number is approximately sixty. This is twice the value observed in solution as Kochi et al. found that the catalyst could go through thirty cycles before activity was lost. Encapsulation is directly responsible for longer catalyst life as any bimolecular degradation pathways are blocked. In solution one catalyst molecule can oxidize the ligand of another catalyst,
eventually causing a loss of activity. The formation of the stable \( \mu \)-peroxo dimer, another decomposition pathway, is also prevented by encapsulation of the metal complex which prevents two Mn(salen) molecules from encountering each other. The observed loss of catalytic activity in the zeolite encapsulated case could possibly be due to clogging of the zeolite pores with products of the oxidation reaction. The catalyst itself may still be active, but olefins may be prevented from encountering it by pore blockage.

The oxidation products formed from the olefins in the zeolite-encapsulated material were comparable to those formed in the homogeneous system, though the yields were different. The total products identified in homogeneous Mn(salen) reactions with cyclohexene, styrene, and trans-stilbene as reactants were 58, 48, and 47% of the total olefins reacted in each case. Analogous figures for the zeolite system were 24, 44, and 20% for cyclohexene, styrene, and trans-stilbene. The identity of the unrecovered products is unclear. In the homogeneous system, polymeric materials have been proposed as reaction products. Cyclohexene oxidation by the zeolite encapsulated Mn(salen) resulted in formation of equal amounts of cyclohexene oxide and the allylic oxidation product cyclohexenol, whereas in the solution system, the epoxide was the dominant product. In the oxidation of styrene, the ratio of phenylacetaldehyde to styrene oxide was 1.36 in the zeolite system, as compared to 0.25 in the homogeneous phase. The
oxidation reaction has been proposed to follow a radical pathway in the solution system. The different ratios of products in the zeolite as compared to solution could result from several factors. The catalyst in the zeolite undergoes some degradation over the 16 hour reaction period, as evidenced by the 20% loss of Mn content of the zeolite. As indicated in Table 3.1, uncomplexed Mn-Y also catalyzes the oxidation of olefins, forming mainly cyclohexenol and phenylacetaldehyde. Part of the products in the zeolite system could arise from Mn-Y formed by the degradation of Mn(salen) complexes. The polar zeolitic environment may also promote the stabilization of charged species that are proposed to form from the radicals as intermediates in the formation of phenylacetaldehyde.

The final observed difference between the catalytic behavior of zeolite encapsulated Mn(salen) with the complex in solution is another manifestation of the fact that diffusion of the olefin into the zeolite is a critical factor in the determination of the rate of oxidation. The relative reactivity data shown in Table 3.2 shows that with the zeolite encapsulated complex cyclohexene is the most readily oxidized olefin, styrene is less reactive and the stilbenes are even less readily oxidized. This is a reversal of the trend seen in solution as the electron rich stilbenes are 1.4 times more reactive than both styrene and cyclohexene which have identical reactivities in solution. This reversal of the
trend seen in solution can be explained readily when the sizes of the molecules are examined. The bulky stilbene molecules have smaller diffusion coefficients in the zeolite and are at a competitive disadvantage with cyclohexene in being able to encounter the catalyst molecules. Exploitation of this phenomenon would have potential application as the catalyst is size or shape selective due to placement of the active site inside the zeolite pore structure. This selectivity can probably be increased by ion exchanging larger cations into the zeolite to decrease the pore diameter and increase the steric hinderance larger molecules would encounter.

CONCLUSIONS

This study has shown that zeolite encapsulated Mn(salen) is capable of catalyzing the oxidation of olefins using iodosylbenzene as a terminal oxidant. Encapsulation of the catalyst inside the zeolite greatly enhances the importance of diffusion as the active catalytic site is within the zeolite pore structure. This diffusion inhibition can be used to explain not only the slower rates seen for the zeolite encapsulated catalyst, but also the size selectivity that the catalyst shows. The encapsulated catalyst has two advantages over its solution counterpart: longer life and size selectivity. It is possible that in certain situations these benefits will overcome the disadvantage of slower oxidation rates.
REFERENCES


CHAPTER IV

ZEOLITE ENCAPSULATED REVERSIBLE OXYGEN CARRIERS

INTRODUCTION

Tsumaki reported the first reversible cobalt-oxygen carrier in 1938. It was shown that the darkening of the red-brown crystals of Co(salen) when exposed to the atmosphere was due to the reversible absorption of molecular oxygen. Due to this discovery that Schiff base complexes of Co(II) can act as oxygen carriers there has been continued interest in this type of complex. These materials are of interest because they may shed light on the manner in which dioxygen is bound in metal complexes. This is an interesting problem because the ligation of dioxygen to a metal complex is significantly more complex than the reaction between a metal center and a simple neutral or anionic species. The addition of molecular oxygen to a metal complex can involve a formal oxidation of the metal with the corresponding reduction of the coordinated dioxygen. The reaction of the dioxygen with the metal center can result in the transfer of zero, one or two electrons from the metal to the coordinated dioxygen.

The potential applications for a synthetic dioxygen carrier are quite diverse. Some research is geared toward
eventually using these synthetic oxygen carriers as possible sources for temporary whole blood substitutes. The complexes were used for a short period of time during World War II by the U. S. Navy for the production of pure dioxygen for use in portable devices in military aircraft.² There continues to be an effort made to develop these materials as oxygen sources for high performance aircraft or as a means of generating an underwater oxygen supply.³ Synthetic oxygen carriers could also be used to provide oxygen enriched atmospheres for relief in such ailments as emphysema.⁴ One major attraction of such systems is that the oxygen binding constants for known metal complexes span twelve orders of magnitude and this allows for flexibility in obtaining the desired affinity.

In addition to smaller scale specialized uses of synthetic oxygen carriers there is a need for more efficient means of separating oxygen from the atmosphere for the production of dioxygen. Dioxygen is a commodity chemical whose United States production exceeds eighteen million tons per year. The usual means of production is based upon the liquefying and distillation of air. The thermodynamic efficiency of this process in practice is approximately twenty percent. A novel approach is needed to significantly improve this and reversible oxygen binders may offer an answer.

As usual, nature has developed some highly effective means of performing the process that we are interested in. There is interest in mimicking important biological oxygen
binders such as hemoglobin, myoglobin, hemerythrin and hemocyanin not only to better understand how these molecules work, but also to possibly gain insight into the requirements for a practical reversible oxygen binder.

The two major categories of synthetic oxygen carriers are the porphyrins and Schiff bases. The porphyrins can be natural, when derived directly or with modification from metalloporphyrin complexes observed in nature, or obtained from a totally synthetic route. Schiff bases are macrocyclic ligands obtained from the Schiff base condensation reaction of a ketone with an amine. The Schiff base ligand can be either tetra- or pentadentate with at least two of the ligating atoms being nitrogen atoms and the others are usually oxygen. A tetradentate Schiff base will cause the metal complex to acquire a square planar configuration. Various substitutions can be made upon the ring of the ligand to alter the complex's electronic properties and this may allow for the tailoring of a complex's oxygen binding ability.

The most significant problem associated with synthetic oxygen carriers is decomposition via autoxidation due to the bound dioxygen. This is a process which even hemoglobin suffers from. If the use of synthetic oxygen carriers is ever to proceed to be of large scale importance the problem of autoxidation will have to be solved satisfactorily. As Busch has pointed out this is a good area for basic research as there is little chance of controlling the process of
autoxidation until the mechanisms of degradation are well understood through basic research. Once these mechanisms are understood, synthesis of complexes which are capable of resisting them need to be synthesized.

The formation of peroxo bridged dimers of reversible oxygen carriers is one mechanism of deactivation in solution. In many systems the dimer is so stable that its formation is irreversible and the system quickly loses all oxygen carrying capacity. Also irreversible oxidation of the ligand or of the central metal may cause the oxygen carrier to lose its activity. Much effort has gone into designing molecules in which these mechanisms can be prevented.

In their quest to synthesize the optimal dioxygen carrier Busch et al. have attempted to design ligands which would be expected to hinder the major degradation mechanisms. They have relied upon the concept of inclusion chemistry which involves molecules containing permanent voids. They have concentrated on macrocycles or macrobicycles because of the advantage these ligands lend in binding to the metal ion. In addition these ligands offer a distinct molecular chamber where the dioxygen can be bound.

The second theme of their research has been the use of ligand superstructure. Ligand superstructure is the term applied to structural features added to a ligand which do not play an active role in binding the metal ion. The purpose of the superstructure is to provide an enclosure around the
active site of the carrier to protect it. The size of the enclosure could be varied, for instance, to allow dioxygen to enter but prevent anything larger from entering. Synthesis of ligands which provide protection around the oxygen carriers active site would be expected to greatly reduce irreversible dimer formation. In addition, if the oxygen is sheltered from other molecules it would be unable to oxidize the ligand of another oxygen carrier. This approach to the problem of autoxidation has shown much promise, but there remain doubts if these types of complexes will ever be robust enough to meet some of the more extreme demands that will be placed upon these systems. For this reason it is sensible to explore how zeolite encapsulation affects the performance of reversible dioxygen carriers.

Ideally encapsulation of a metal complex will offer the protection from autoxidation by preventing any contact between oxygen carrier molecules. Generally Schiff base ligands such as salen are of an appropriate size to diffuse through the windows of the zeolite Y supercage when uncomplexed. Upon reaction with the metal ion the complex takes a rigid square planar structure and no longer has the flexibility to fit through the supercage window. When synthesized inside a zeolite supercage the complexes are prevented from encountering each other. This encapsulation prevents the formation of the \( \mu \)-peroxo dimer and reduces the possibility of irreversible ligand oxidation.
Because of these possible benefits, several attempts have been made to synthesize reversible oxygen carriers encapsulated in the supercage of zeolite Y. Lunsford et al. synthesized both the \([\text{Co}^{\text{II}}(\text{terpy})_2]^{+2}\) and the \([\text{Co}^{\text{II}}(\text{bpy})(\text{terpy})]^{+2}\) complexes (bpy = 2,2' bipyridine; terpy = 2,2',2''-terpyridine) in zeolite Y.\(^7\)\(^8\) It was found that in the presence of a pressure of oxygen the five coordinate complex \([\text{Co}^{\text{II}}(\text{bpy})(\text{terpy})]^{+2}\) reversibly forms the oxygen adduct \([\text{Co}^{\text{III}}(\text{bpy})(\text{terpy})\text{O}_2^+]^{+2}\). The complex was found to be quite thermally stable in the presence of oxygen at 343K, but was susceptible to deactivation from water absorption. A later study showed that this material had a \(P_{1/2}\) of 0.34 torr at 298K and was capable of separating oxygen from a dry mixture of oxygen and nitrogen.\(^8\) The performance of this zeolite encapsulated metal complex could not be compared to its solution counterpart because only the binuclear complex can be synthesized in solution.

Herron synthesized zeolite encapsulated Co(salen) and found that upon the addition of pyridine to act as an axial base, this complex could reversibly bind oxygen.\(^9\) However its value of 305.5 torr for \(P_{1/2}\) at 293K was considerably larger than the value of 10.5 torr for free Co(salen) in a pyridine solvent. It was hypothesized that this reduction in oxygen binding propensity was due to crowding in the zeolite cage. The steric constraints of the zeolite supercage served to hinder the binding of the axial base pyridine and the
dioxygen.

The synthesis of an anionic cobalt(II) cyanide complex inside zeolite Y is another example of a zeolite encapsulated reversible oxygen binder. This complex is stable in the presence of water and can continue to act as a reversible oxygen binder in the presence of water vapor. The active complex in this system was identified as a square planar Co(CN)₄⁻² ion which had a P₁/₂ value of 9 torr. The major difficulty with this system is that the active oxygen binding component represents only 1% of the total cobalt content.

In this work two new zeolite encapsulated cobalt complexes are prepared and their ability to reversibly bind oxygen is evaluated. As an attempt to improve upon the oxygen binding ability of zeolite encapsulated Co(salen) a similar, but smaller ligand, 3,3'-[ethylenebis(iminomethylidyne)]di-2,4 pentanedione (J-en), was used. The structure of the Co(J-en) complex is shown in Figure 4.1. The smaller size of the ligand may improve the binding of the required axial base and increase the complex's oxygen binding ability. Jäger type ligands have shown resistance to oxidation due to the presence of the acetyl groups and this makes them a promising class of ligands. The other ligand studied here is tetraethylenepentaamine (tetren). Because this ligand is pentadentate there is no need for an axial base and this simplifies the system. In addition, Co(tetren) is among the strongest dioxygen binders known, but in solution this always
results in the formation of a very stable μ-peroxo dimer. Perhaps zeolite encapsulation would prevent this dimerization and allow for the preparation of the mononuclear cobalt dioxygen complex.

Figure 4.1. Structure of Co(J-en).
EXPERIMENTAL

Materials. NaA and NaY samples were shaken overnight in 0.1 M NaCl, filtered and rinsed until chloride free. CoNaA and CoNaY zeolites were prepared via ion exchange with a solution of cobalt acetate. J-en was prepared from triethyl orthoformate, 2,4-pentanedione and ethylenediamine according to literature methods. Tetraethylenepentaamine was obtained from Aldrich and used without further purification.

Instrumentation. The diffuse reflectance UV-VIS spectra were taken on a Shimadzu UV-265 equipped with a Harrick diffuse reflectance attachment.

The EXAFS experiments were carried out at the X-9A beamline at the National Synchrotron Light Source with a stored electron energy of 2.5 GeV at currents between 90 and 120 mA. The samples were prepared into pellets diluted with boron nitride and the spectra were run with the samples at liquid helium temperatures. Data analysis was performed using the UWEXAFS software package.

EPR spectroscopy was performed on a Bruker ESP300 in the X band region. The spectra were obtained on powdered samples and unless noted otherwise the Co(J-en) samples were run at 77K and the Co(tetren) samples at room temperature. The microwave power was 2.00 mW with a resonance frequency of 9.30 GHz and 100 kHz modulation.

Preparation of Co(J-en)-Y. One gram of CoNaY was heated at 400°C under vacuum for two hours and allowed to cool. This
dehydration results in a color change from light pink to blue. The activated zeolite material is then ground with the J-en ligand in an inert atmosphere glove box. The zeolite and ligand mixture is placed inside a sealed tube and heated at 300°C for ten hours and this results in an orange brown material. This material is Soxhlet extracted with pyridine overnight to remove excess ligand, surface bound complex and to add the axial base to the Co(J-en) complex.

Preparation of Co(tetren)-Y or Co(tetren)-A. One gram of the appropriate cobalt zeolite is added to 20 mL of a 1 M tetren solution in water and stirred for three hours. This material is then filtered and air dried.

RESULTS

Co(J-en). Synthesis of the J-en ligand was confirmed by checking its infrared spectra. This is shown in Figure 4.2 along with the spectra of the free Co(J-en) complex which was used as a standard in the EXAFS experiments. There is close agreement between these spectra and previously published results. The infrared spectra of the zeolite encapsulated complex is not informative as the loading level of the complex is fairly low and absorption due to the zeolite matrix interferes.

The diffuse reflectance UV-VIS spectra of Co(J-en)-Y is given in Figure 4.3. An ethanolic solution of the complex has peaks at 207, 240, 280, 345(sh) and 395 nm. Any peaks below
Figure 4.2. IR spectra of J-en and Co(J-en).
Figure 4.3. Diffuse reflectance spectra of Co(J-en)-Y. Kubelka-Munk with reference to NaY.
approximately 210 nm due to the complex are obscured by the rising background due to absorption and scattering by the zeolite. The peaks at 250 and 310 nm are both red shifted from their solution counterparts. As the zeolite encapsulated Co(J-en) sample was exposed to the air it would be expected that the complex is solvated by water. The red shift in these \( \pi + \pi^* \) bands could be due to the different solvating ability of ethanol and water.

The X-ray absorption spectra of Co(J-en) and Co(J-en)-Y are given in Figures 4.4 and 4.5. The EXAFS portion of the X-ray absorption spectrum of Co(J-en) and Co(J-en)-Y is obtained by subtracting out a smooth edge jump and this function is termed \( \chi \). In Figures 4.6 and 4.7 \( \chi \) is shown and the energy scale has been converted from eV to the photoelectron wave vector scale (\( \text{Å}^{-1} \)), \( k \).

Fourier transform of \( \chi(k) \) produces the Pseudo Radial Distribution Function (PRDF) and these are compared in Figure 4.8. The peaks in the PRDF correspond to different radial coordination shells about the cobalt. The distances are shifted down from their actual values, but they give a picture of the local environment of the cobalt atom.

The first two peaks in the PRDF can be assigned to nitrogen and oxygen with their position relative to each other determined by their phase shift. Without other similar compounds to act as standards it is impossible to determine if the first peak is due to backscattering from the nitrogens
or the oxygens of the ligand. The third broad peak is due to the carbons, both on the ethylenediamine portion of the ligand as well as the other carbons attached to the oxygens and nitrogens of the ligand. Finally the peak at approximately 3Å in the zeolite encapsulated sample is probably due to backscattering from the silicon and aluminum in the zeolite framework.

Using the PRDF simply as a fingerprint, it is seen that there are structural differences between Co(J-en) and Co(J-en)-Y. In the zeolite encapsulated sample the intensities of the first two peaks relative to the third peak are diminished. These observed differences could be due to steric restraints of the zeolite, incomplete complexation of the cobalt in the zeolite, or spectral differences due to interaction with the zeolite framework. The lower intensities in the nitrogen and oxygen shell peak could be an indication that complexation inside the zeolite is not complete. Also it is probable that the complex formed outside the zeolite contains some dimer which is prevented from forming upon zeolite encapsulation. In the absence of additional standards for use in the determination of other structural parameters all that can be concluded at this point is that zeolite encapsulation changes the EXAFS spectra of the Co(J-en) complex.

The EPR spectra of the Co(J-en) complex encapsulated inside zeolite Y is given in Figure 4.9. The cause of the strong peak at \( g \approx 2 \) which shows no hyperfine splitting due
Figure 4.4. X-ray absorption spectrum of Co(J-en).
Figure 4.5. X-ray absorption spectrum of Co(J-en)-Y.
Figure 4.6. Normalized EXAFS spectrum of Co(J-en).
Figure 4.7. Normalized EXAFS spectrum of Co(J-en)-Y.
Figure 4.8. PRDF of (a) Co(J–en)–Y and (b) Co(J–en).
to interaction with cobalt is not obvious. The EPR spectra of dehydrated NaY and CoY are shown in Figures 4.10 and 4.11 and while each shown a similar peak in this region their intensities are respectively 64 and 8 times smaller. Heating the J-en ligand with NaY also results in an EPR peak in this region (Figure 4.12) but its intensity is 16 times less than the peak shown in Figure 4.9. Whatever is responsible for the EPR peak is formed in substantially greater numbers when J-en is heated in the presence of Co-Y.

Figure 4.13 shows the room temperature EPR spectra of Co(J-en)-Y which has been exposed to pyridine and air and it shows hyperfine splitting due to interaction with cobalt. Cooling the sample to 77K results in the production of the spectra shown in Figure 4.14. The eight hyperfine lines can be assigned to superoxide bound to cobalt ($^{59}$Co, spin = 7/2). This pattern is most likely due to superoxide interacting with the cobalt complex and points out the necessity of the presence of an axial base in order for the complex to bind oxygen. The observed splitting is 16 G which is characteristic of cobalt superoxide complexes. There are several possible explanations for the broad peak observed in Figure 4.14. This peak appears to have no observable hyperfine splitting which indicates a lack of interaction with a cobalt atom. It is possible that this peak is actually due to a Co(J-en)(pyridine) superoxide species and its hyperfine splitting is not resolved due to line broadening. This peak
would be in the appropriate position to be assigned to $g_\perp$. If this is the case the set of eight peaks could be assigned to $g_{||}$ with the splitting due to interaction with the cobalt.

The large unsplit peak is similar in appearance to the peak observed for zeolite encapsulated Co(J-en) before the addition of pyridine (Figure 4.9). This suggests the possibility that this peak is due to the same species in both cases and that it is simply an interference from a superoxide formed upon heating CoY with J-en. This leads to the possibility that the hyperfine pattern is isotropic due to free rotation of the complex inside the zeolite cage. This explanation requires that the free motion is occurring even at 77K. This seems somewhat unlikely, but if it is true it is an indication that the molecules inside the zeolite are not acting as they would in a bulk solution and are not forming a rigid glass even at 77K.

**Co(tetren).** Combining tetren and cobalt acetate in water and bubbling oxygen through the solution causes the immediate and irreversible formation of the $\mu$-peroxodimer, $\text{Co}_2(\text{tetren})_2\text{O}_2$. The UV-VIS spectra of this solution species is compared with the diffuse reflectance UV-VIS of Co(tetren) prepared inside zeolite Y in Figure 4.15.

The EXAFS spectra for Co(tetren) and Co(tetren) encapsulated inside zeolite Y are given in Figures 4.16 - 4.20. The similarity between the PRDF of the complex inside and outside of the zeolite is evidence that the complex is
Figure 4.9. EPR spectrum of Co(J-en)-Y.
Figure 4.10. EPR spectrum of dehydrated NaY.
Figure 4.11. EPR spectrum of dehydrated CoY.
Figure 4.12. EPR spectrum of J-en heated at 300°C with NaY.
Figure 4.12

16X

100G
Figure 4.13. Room temperature EPR spectrum of Co(J-en)(pyridine)-Y exposed to oxygen.
Figure 4.14. Low temperature EPR spectrum of Co(J-en) (pyridine)-Y exposed to oxygen.
present as a \(\mu\)-peroxo dimer inside the zeolite supercages. Additionally the EPR spectra of the complex encapsulated in zeolite Y (Figure 4.21) has a very weak EPR signal indicating that the majority of the cobalts have reacted to form the EPR silent \(\mu\)-peroxo dimer.\(^{13}\)

The ability of the Co(tetren) complex formed inside zeolite A to bind oxygen is apparent from its EPR spectra (Figure 4.22). The observed spectra can readily be assigned to a superoxide species interacting with a cobalt atom. The material whose spectra is shown in Figure 4.22 was obtained by simply filtering the reaction mixture and allowing the powder to air dry. As seen in Figure 4.23, evacuation of the material for one hour does not result in the removal of the oxygen. Examination of a sample evacuated for four hours shows that upon the addition of oxygen the signal increases by a factor of ten. Evacuation of the sample at 100°C results in an EPR spectra with a single peak at the position of a free superoxide (Figure 4.24).

The diffuse reflectance UV-VIS spectra of the oxygen adduct of Co(tetren) formed inside zeolite A is given in Figure 4.25. The similarity of the spectra of this mononuclear superoxide complex and the spectra of the \(\mu\)-peroxo dimer is of interest. Based upon comparison with other cobalt oxygen complexes the peak at ~310 nm in all three spectra can be assigned to a ligand to metal charge transfer transition. A peak in this region has been observed and given this
Figure 4.15. Comparison of UV-VIS spectra of Co(tetren) in solution and encapsulated in zeolite Y.
Figure 4.16. X-ray absorption spectrum of Co(tetren).
Figure 4.17. X-ray absorption spectrum of Co(tetren)-Y.
Figure 4.18. Normalized EXAFS spectrum of Co(tetren).
Figure 4.19. Normalized EXAFS spectrum of Co(tetren)-Y.
Figure 4.20. PRDF of (a) Co(tetren)-Y and (b) Co(tetren).
Figure 4.21. Room temperature EPR spectra of Co(tetren)Y.
Figure 4.22. EPR spectrum of Co(tetren)-A (air dried).
Figure 4.23. EPR of Co(tetren)-A (evacuated).
Figure 4.24. EPR spectrum of Co(tetren)-A evacuated at 100°C.
Figure 4.25. Diffuse reflectance UV-VIS spectra of Co(tetren) encapsulated inside zeolite A.
assignment in both cobalt superoxo and \( \mu \)-peroxo complexes.\(^\text{14, 15} \) This emphasizes the fact that the electronic spectrum has limited usefulness in the identification of the superoxo or peroxo complex. Another possible explanation for the similarity of the spectra is that the majority of the cobalt is present in a \( \mu \)-peroxo dimer form in either case, but encapsulation inside zeolite A allows a sufficient quantity of the superoxo complex to form for the EPR to detect its presence.

The effect of the cation present with cobalt in the zeolite was examined. The EPR spectra of Co(tetren) formed in LiY, KY and CsY are shown in Figure 4.26-4.28. The hyperfine splittings are not as well resolved as in the sodium zeolite, but otherwise the spectra are quite similar. The changing of the cation present seems to have a very small effect upon the formation of the Co(tetren) superoxide complex.

As noted above the oxygen binding is not readily reversed by brief evacuation of the sample. More extensive treatments such as storage of the sample under an oxygen free environment for 24 hours does result in a decrease in the EPR peak intensity. In order to determine the value of the oxygen binding constant \( K_{\text{obs}} \) (eq. 4-1) the EPR intensity as a function of applied oxygen pressure was determined.

\[
K_{\text{obs}} = \frac{[\text{Co(tetren)O}_2]}{[\text{Co(tetren)}]} \frac{p\text{O}_2}{1} \quad (4-1)
\]
Figure 4.26. Room temperature EPR of Co(tetren) formed in LiCo-A.
Figure 4.27. Room temperature EPR spectra of Co(tetren) formed in KC\textsubscript{o}-A.
Figure 4.27
Figure 4.28. Room temperature EPR spectra of Co(tetren) formed in CsCo-A.
The total concentration of active cobalt \([\text{Co(tetren)}]_T\) is the sum of \([\text{Co(tetren)O}_2]\) and \([\text{Co(tetren)}]\) and substitution into equation 4-1 yields

\[
[\text{Co(tetren)O}_2] = [\text{Co(tetren)}]_T - K_{\text{obs}}^{-1}[\text{Co(tetren)O}_2]/pO_2 \quad (4-2)
\]

A plot of \([\text{Co(tetren)O}_2]\) versus \([\text{Co(tetren)O}_2]/pO_2\) should yield a straight line with a slope of \(-K_{\text{obs}}^{-1}\). Such a plot is shown in Figure 4.29 and its nonlinearity is a manifestation of the sieving ability of the zeolite. This sieving effect at lower oxygen partial pressures is a result of the absorption characteristics of the zeolite which tends to cause the oxygen pressure inside the zeolite pores to be greater than the applied pressure.\(^9\) This results in an increase in \(K_{\text{obs}}\) and a decrease in slope. Using the three points corresponding to the higher pressures resulted in a value of \(3 \times 10^{-3}\) torr\(^{-1}\) for \(K_{\text{obs}}\) while for the lower pressures \(K_{\text{obs}}\) was measured to be \(1 \times 10^{-2}\) torr\(^{-1}\).
Figure 4.29. Determination of the $K_{obs}$ for oxygen binding by Co(tetren).
DISCUSSION

The quantity of the zeolite encapsulated complex Co(J-en)(pyridine)(O_2) prepared is limited by the multistep nature of its synthesis. The complex Co(J-en) must first be formed, followed by the addition of pyridine to form Co(J-en)(pyridine) and the subsequent addition of O_2 to form the oxygen adduct of Co(J-en)(pyridine). The yield of each step limits the total amount of the final product formed and leads to limited superoxo formation.

Lunsford et al. have found that a major limitation of [Co(terpy)(bpy)]^{2+} as an oxygen carrier is the limited quantity of the complex which can be formed inside the zeolite.\(^7\)\(^-\)\(^8\) The formation of the [Co(terpy)(bpy)]^{2+} complex is somewhat more complicated than the formation of the Co(J-en) complex because of the competing formation of [Co(bpy)_3]^{2+} and [Co(terpy)_2]^{2+}. Using a variety of different cation exchanged zeolites with various reaction temperatures and times a maximum of fifty percent of the cobalt ions in the zeolite react to form any of the possible complexes. Increasing the cobalt exchange level caused the percent yield based upon cobalt to decrease, although the total amount of complex formed increased.

The formation of zeolite encapsulated CoL where L is the ligand of interest can be limited by two major factors. The dehydration of the zeolite to make it more reactive with the ligand would be expected to result in the migration of the
cobalt ions into the sodalite cages.\textsuperscript{16,17} In the sodalite cages the cobalt ions would be inaccessible to ligands the size of bpy, terpy, or J-en and thus would have to migrate back into the supercages in order for the reaction to occur. The migration of the cobalt ions from the sodalite cage to the supercage may not be complete in a dehydrated zeolite and the formation of the complex may be limited.

The other major difficulty in the formation of CoL is the mobility of the ligand inside the zeolite. The size of the ligands of interest are such that their diffusion inside the zeolite is restricted, reducing their encounters with cobalt ions. The formation of a complex inside a zeolite supercage will result in a "dead end" as a ligand molecule will no longer be able to pass through that supercage. Any unreacted ligand will also serve to restrict diffusion through the zeolite. Herron found that even with extensive washing excess ligand was still found inside the zeolite, indicating that molecules could become trapped inside the zeolite pore structure.\textsuperscript{9}

The reaction with the ligand J-en is further complicated by the low volatility of the ligand. The melting point of the ligand is 293°C and it was necessary to heat the ligand to above this temperature in order for the reaction to occur at a reasonable rate.\textsuperscript{18} The lower volatility of the J-en ligand compared to salen or bpy and terpy would be expected to cause the mobility of the ligand to be a significant factor in the
decreased formation of zeolite encapsulated Co(J-en).

Once the Co(J-en) complex has been formed an axial base such as pyridine must be added in order for the complex to bind oxygen. The function of the axial base seems to be to localize the odd electron into the $d^2_z$ cobalt atomic orbital and increase the nucleophilicity of the cobalt atom. This facilitates binding of dioxygen and the partial transfer of the $d^2_z$ electron to the oxygen. Herron found that the binding of pyridine to the Co(salen) complex was essential to observe oxygen adduct formation, but that this binding did not readily occur. In a later paper it was stated that no oxygen binding was observed unless the pyridine was preabsorbed into the zeolite before the addition of the salen ligand. Factors discussed earlier such as diffusion through the zeolite and pore blockage from the cobalt complexes and excess ligand all restrict the ability of the pyridine to encounter the cobalt complex. The formation constant for the Co(J-en)(pyridine) complex is $10^{2.13}$ M$^{-1}$ and so the limited extent to which it is forming must be due to difficulties associated with the pyridine encountering the Co(J-en) complex. The necessity of the addition of an axial base in order for the complex to become an active oxygen binder is a serious limitation upon this zeolite encapsulated system.

The formation of the superoxide complex Co(J-en) (pyridine)O$_2$ is limited by all the above factors. First the amount of the complex Co(J-en) formed is limited by diffusion
of the Co\(^{2+}\) into inaccessible sites and the size and volatility of the ligand which determines its mobility inside the zeolite. The ability of this zeolite encapsulated Co(J-en) complex to then bind pyridine is restricted by the ability of the pyridine molecule to diffuse into the zeolite in order to encounter the metal complex.

The cause of the large EPR peak (Figure 4.9) which does not show any hyperfine coupling due to interaction with cobalt is also of interest. Due to the high temperatures required to insure sufficient mobility of the J-en ligand the possibility that an organic radical was being formed due to decomposition of the ligand was explored. Lunsford had noted the formation of an organic radical which was stable at room temperature when bpy, terpy, and CoY were heated at 703K.\(^8\) However, when J-en was heated at 300°C with NaY rather than CoY the characteristic EPR peak was of a much smaller intensity. From this result the possibility that the peak was due to decomposition of the ligand was eliminated.

Another possibility for an assignment of the EPR peak in question is that it could be due to an uncoordinated superoxide radical formed in the process of heating J-en with CoY. These superoxide radicals could be the result of trace amounts of oxygen interacting either with the zeolite or the Co(J-en) complex.

Habgood et al. had noted the thermal formation of oxygen radicals on various Y zeolites.\(^{21}\) It was found that two types
of oxygen radicals were formed upon NaY. The first superoxide ion \( \text{O}_2^- \) was similar to that formed upon \( \gamma \) irradiation.\(^{22}\) It was formed by heating the NaY up to 200°C and was destroyed completely by heating to 300°C. The second radical was formed at temperatures greater than 200°C and was stable even at 500°C. It was hypothesized that \( \text{Fe}^{+2} \) and \( \text{Cu}^{+2} \) ions are acting as electron donors in the formation of \( \text{O}_2^- \) on the zeolite. It was observed that only the low temperature radical could be formed when KY was used in place of NaY. The use of KCoY in place of NaCoY had no effect upon the EPR spectra of the zeolite when heated with J-en and so it was concluded that the superoxide peak being observed was not due to superoxide being formed by this mechanism. Additionally the intensity of the peak observed for \( \text{Co(J-en)-Y} \) is too large to be accounted for solely by this mechanism, but the peaks seen upon the dehydration of CoY and NaY may be due to superoxide formation via this mechanism.

Dutta and Zaykoski noted the formation of superoxide ions upon oxygenation of CoMY (M = Na, K, or Cs) after heating to 250°C.\(^{23}\) They found that as the iron content of the zeolite decreased due to cobalt ion exchange treatment the signal due to the superoxide ion increased. The addition of ethylenediamine results in the disappearance of this superoxide peak and the proper treatment results in the formation of a superoxide bound to cobalt.

In the case of the formation of zeolite encapsulated
Co(J-en) all of these mechanisms are probably playing some role in the production of the observed signal. The difficulty associated with determining the oxygen binding ability of the complex comes about because the uncoordinated superoxide peak is present even after the formation of the Co(J-en)(pyridine)(O$_2$) complex. With interference from this peak it is difficult to determine the oxygen binding ability of the Co(J-en)(pyridine) complex.

In an effort to avoid some of the problems associated with the formation of oxygen adducts of zeolite encapsulated Co(J-en) another much different approach was explored. The use of tetraethylenepentaamine (tetren) as the ligand for a zeolite encapsulated cobalt complex could be expected to avoid many of the problems associated with ligands like salen and J-en. Tetren is a pentadentate ligand and its use would eliminate the need for the addition of an axial base. This would make the synthesis of an active oxygen binder a one step process as the Co(tetren) complex as synthesized would be expected to bind oxygen in its vacant sixth coordination site.

The tetren ligand is a liquid which is soluble in water and so the synthesis of the zeolite encapsulated complex could take place in an aqueous slurry of CoY and tetren. This should greatly increase the mobility of the ligand when compared to a solid state synthesis. This increased mobility should in turn result in larger amounts of the complex being formed.

The formation of the oxygen adducts of Co(tetren) is of
special interest because it is an extremely strong binder of oxygen. In solution it very readily binds oxygen and this results in the formation of the \( \mu \)-peroxo dimer. The formation constant for \( \text{Co}_2(\text{tetren})_2\text{O}_2 \) is \( 10^{36.7} \) M\(^{-3}\) atm\(^{-1}\).\(^{13}\) It has been shown that the formation of a superoxo complex precedes the formation of the \( \mu \)-peroxo dimer and it is possible that zeolite encapsulation could prevent the formation of the dimer and allow for the preparation of the superoxo complex.\(^{24}\)

The supercage of zeolite Y is apparently not small enough to prevent the formation of the \( \mu \)-peroxo dimer. The UV-VIS and EXAFS spectra of the zeolite encapsulated complex are identical to the \( \mu \)-peroxo dimer in solution. In addition, the EPR shows no evidence for the formation of the superoxo complex. Apparently dimerization is occurring inside the zeolite Y supercages.

Zeolite A with its smaller cage structure does allow for the formation of a superoxo complex of Co(tetren). This is clearly seen from the EPR which is characteristic of cobalt superoxide complexes. Since the mononuclear complex Co(tetren)\(_2\)O\(_2\) can not be formed in solution the closest known complex is the zeolite encapsulated oxygen adduct of cobalt ethylenediamine.\(^{25}\) In some ways the formation of the oxygen adduct of Co(tetren) is simpler. As a bidentate ligand three ethylenediamines bound to cobalt completely coordinates it and leaves no vacant site for oxygen binding. It is believed that the complex which is the active oxygen binder is
correctly formulated as Co(en)$_2$ with the fifth site occupied by an ethylenediamine acting as a monodentate ligand or by a site in the zeolite interacting with the cobalt. This leaves a vacant sixth site for oxygen binding. This is somewhat more complicated than the case for Co(tetren) where the single ligand occupies five sites leaving the sixth open for oxygen binding. These differences aside it would be expected that the two complexes should behave similarly due to the fact that in both cases the result is that the cobalt is bound by five nitrogen atoms.

Howe and Lunsford synthesized the oxygen adducts of zeolite encapsulated cobalt ethylenediamine and examined the material with EPR$^{25}$ They observed two different types of superoxide being formed. One was interacting with the cobalt and could be assigned to [Co$^{III}$(en)$_2$O$_2$. The other superoxide was not interacting with the cobalt and its formation was favored by the presence of Co(en)$_3^{2+}$ and was believed to result from an electron transfer from the ethylenediamine ligand to O$_2$.

Similar to the observations by Howe and Lunsford and Schoonheydt and Pelgrims the EPR spectra in Figure 4.22 appears to be due to the superposition of signals from a mononuclear superoxo complex which shows hyperfine splitting due to interaction with cobalt and from an uncoordinated superoxide.$^{25,26}$ As seen by comparison of Figures 4.22 and 4.23 evacuation of the sample causes no change in the spectral
appearance. This gives an indication of the strength of the binding of the oxygen to the cobalt. Such a strong interaction between oxygen and the Co(tetren) complex is not unexpected considering the basicity of the tetren ligand.

Our measured value for $K_{obs}$ of $3 \times 10^{-3}$ torr$^{-1}$ for the zeolite encapsulated Co(tetren) complex is comparable to value ($3.3 \times 10^{-3}$ torr$^{-1}$) obtained for zeolite encapsulated Co(salen) complex reported by Herron. It is of interest to note that it is considerably smaller than the oxygen binding constant for the dinuclear complex, Co$_2$(tetren)$_2$O$_2$. This decrease in oxygen binding affinity may be partly due to the steric effects of zeolite encapsulation which makes oxygen binding less energetically favorable. For a similar reason the encapsulation of Co(salen) inside zeolite Y results in a tenfold reduction in its oxygen binding ability. The fact that in solution a peroxo complex is formed compared to the formation of a superoxo complex inside the zeolite must account for the rest of the difference between the two materials. Having the oxygen bound to two cobalt atoms significantly decreases the reversibility of the oxygen binding.

CONCLUSIONS

The synthesis of a zeolite encapsulated cobalt Schiff base complex is complicated by several factors, all of which
tend to limit the total amount of complex produced. The
difficulties are due to restricted mobility within the
zeolite. The ligand must diffuse into the zeolite in order
to encounter the cobalt ion which often must diffuse from a
sodalite cage to the supercage in order for the reaction to
occur. In addition, the axial base of choice must enter the
zeolite pore structure to bind to the complex and the extent
to which this occurs can be quite small. The major limitation
upon the synthesis of a reversible oxygen binder is the
limited amount of Co(J-en)(pyridine) which can be synthesized
inside the zeolite.

The difficulties associated with the complex formation
are largely avoided with the use of tetren as the ligand. The
formation of the \( \mu \)-peroxo dimer occurs in the zeolite Y
supercage as it does in solution, but encapsulation inside
zeolite A hinders dimer formation and results in superoxide
formation. Oxygen binding by the zeolite encapsulated
Co(tetren) superoxo complex is reversible when compared to the
solution peroxo complex.
REFERENCES


CHAPTER V

EFFECT OF THE ADDITION OF ORGANIC COSOLVENTS UPON ZEOLITE CRYSTALLIZATION

INTRODUCTION

Original efforts toward zeolite synthesis used relatively insoluble forms of silica and alumina in mildly alkaline solutions (pH 8-11) containing calcium, magnesium, and sodium cations at temperatures of 200-300°C. These attempts were modeled after natural geologic processes and produced small pore mordenite and analcime. The more commercially important large capacity zeolites were synthesized when more soluble forms of silica and alumina were mixed under highly alkaline conditions at 100°C. The highly reactive aluminosilicate gel was capable of transforming into zeolite crystals in a few hours. Variation of the relative amounts of silica, alumina, sodium oxide and water were critical in determining which zeolite was formed. Other important factors were the reaction temperature and whether the gel was stirred or aged. This work was done in 1949 and in the forty years since all new zeolite structures have been synthesized via "trial and error" methods. While this has resulted in the synthesis of over 150 zeolites, including synthetic analogs of naturally occurring...
minerals, it is time consuming and inefficient. Without an understanding of the crystallization mechanisms and the controlling factors of the process, progress will be through experimental phase chemistry. For this reason a greater understanding of the basic processes which occur during zeolite synthesis is desirable.

It has been pointed out that the chemistry of the reaction system is extremely complex for a variety of reasons. The usual synthetic method involves the formation of an intermediate aluminosilicate gel phase. The formation of this gel takes place rapidly upon mixing the silicate and aluminate sources and small perturbations at this stage can have consequences as to the nature of the final product. The commercially useful zeolites are metastable and there is also the possibility of a zeolite beginning to transform into a more stable form before the initial crystallization is complete. Sensitive nucleation phenomena can sometimes hinder the reproducibility of zeolite synthesis. To further illustrate the complexities of zeolite synthesis it can be noted that the following reactions can occur simultaneously during zeolite synthesis:

- precipitation of a gel phase
- dissolution of the gel
- nucleation of the zeolite(s)
- continued crystallization and crystal growth of the zeolite(s)
-dissolution of the initial metastable phase(s)
-nucleation of a more "stable" metastable phase or phases
-continued crystallization and crystal growth of the new crystalline phase(s) while the initial crystals are dissolving
-dissolution of the metastable phase(s)
-nucleation of the equilibrium phase(s)
-crystallization and crystal growth of the final crystalline phases

Most of the experimental work thus far has been rather empirical with zeolite synthesis being run under a variety of conditions with the results often tabulated in some sort of a phase diagram. This approach has thus far not resulted in the sort of deeper understanding necessary to allow willful synthesis of novel zeolite structures. However from this body of data one can find certain trends which may prove useful in understanding the zeolite crystallization process.\textsuperscript{5}

The number of possible variations in zeolite synthesis is quite large as in addition to the major factors of time, temperature and gross composition of the reaction mixture, factors such as aging or stirring of the gel, the order of mixing of the reactants and the nature of the source materials all play a role in determination of the final product.\textsuperscript{6} Again the process is so complicated with many interrelated factors at work that seemingly minor changes in the reaction
conditions can cause large effects in the product formation.

Certain choices have to be made as to what conditions are appropriate for synthesizing the types of zeolites which are of interest. In this study we are interested in the larger pore low silica content zeolites such as A, X and Y and will be using temperatures in the range 50-100°C as this has been shown to be both appropriate and convenient for our purposes. Time as a parameter is handled by periodically checking the progress of the crystallization via XRD. This way the reaction can proceed to whatever end it would normally achieve while yielding information on any possible intermediates in the process. The source of the raw materials and physical treatments such as gel aging are based upon accepted synthetic methods. Keeping all of these variables under control allowed us to examine the effect of varying the gross reaction composition, for instance the effect of the addition of cosolvents. It is useful at this time to summarize the literature regarding the effects seen when various changes in the reaction composition are made.

The silica/alumina ratio of the gel helps to determine the Si/Al ratio of the zeolite framework. Generally all the aluminum present will be incorporated into the framework with the excess silica left in solution. Adjusting the Si/Al ratio of the zeolite framework is not as simple as changing the composition of the reaction mixture. Lowering the amount of aluminum present in the reaction mixture may simply result in
less zeolite of a similar Si/Al ratio being produced. This is an unfortunate limitation as increasing the Si/Al ratio of a zeolite increases its acid resistance and thermal stability and the direct synthesis of a faujasite structure with higher Si/Al ratios could have profound industrial applications. Methods for increasing the Si/Al ratio for some zeolites have been developed and they include the addition of large organic cations to the reaction mixture. This approach has not been successfully transferred to a faujasite type structure and the direct synthesis of a high Si/Al ratio zeolite of this structure is still a much sought after goal.

The hydroxide ion plays a crucial role in zeolite crystallization. The hydroxide is capable of complexing the silicon or aluminum ion while still allowing them to react further to form the zeolite. The hydroxide can exert an effect upon which zeolite is formed by controlling the hydrolysis rates and the degree of polymerization when several possibilities are competing. In general an increase in the hydroxide concentration causes an increase in the rate of crystallization. Also as the hydroxide concentration increases the Si/Al ratio of the framework decreases.

The role of the inorganic cation in the zeolite crystallization process is open to some speculation. The cation, which acts as a counterion in the final zeolite structure often seems to be a dominant factor in determining which zeolite structure is obtained. Exactly how the cation
exerts its influence is not well understood. It is possible that the hydrated cation acts as a template or void filler and allows the zeolite to form. This is the accepted explanation for the observation that the presence of tetramethylammonium cations (TMA⁺) results in the formation of a high silica form of zeolite A to be formed.⁸ The larger cations take up more space and thereby limit the number of the corresponding aluminum atoms incorporated into the zeolite. The possibility that the water-cation interaction is a critical one is what made the addition of cosolvents an interesting idea. Perhaps the organic cosolvents will change this critical interaction and in turn effect the structure of the final product.

The work described here includes a study of the effect of the addition of a variety of organic cosolvents upon the crystallization of zeolites A, X, and Y. There have been reports of zeolite synthesis in either pure alcoholic solutions in which sodalite was the major product or in solvents such as hexanol, glycol, glycerol, sulfolane and pyridine.⁹-¹⁰ The interest is to contrast the products and the rate of formation between a purely aqueous system and one containing water and an organic cosolvent. Also results are described from a series of experiments to determine the possibility of direct synthesis of high silica content faujasite. This work focuses on the possibility of perturbing the reaction mixture after room temperature aging in such a
way to obtain a zeolite Y structure with higher silicon content.

EXPERIMENTAL

Materials. SiO₂ gel (Aldrich) or Ludox (Du Pont) and aluminum powder (40 mesh, Alfa) or sodium aluminate were used as the silicon and aluminum sources. Methyl sulfoxide (DMSO), acetonitrile, tetramethylammonium chloride (TMACl) and hexamethylphosphoramide (HMPA) were obtained from Aldrich and used as received. All experiments were carried out in Teflon bottles and synthesis was done in a thermostated water bath without stirring.

Instrumentation. Powder X-ray diffraction patterns were obtained with a Rigaku Geigerflex D/Max 2B diffractometer with a Ni filtered Cu K source. Elemental analysis (Si/Al ratios) was done with an energy dispersive X-ray fluorescence spectrometer (Kevex) using direct excitation. Zeolites, whose elemental analysis was known independently, were used to construct a calibration curve.

Synthesis of Zeolites A and X. For the Si/Al=1 trials, separate aqueous solutions of 0.3M Si and 0.3M Al were prepared in 1.72M NaOH, dissolved until the solutions were clear and then the appropriate volume per cent of cosolvent was added before the solutions were combined to form the gel.
The procedure was identical for other Si/Al ratios except that a solution of 0.6M Si was mixed with an aluminum solution of the appropriate concentration. The gel formed was put into a water bath thermostated to 80°C and the gel was periodically checked for crystal formation.

**Gel Addition Method of Synthesis.** In this method of zeolite synthesis, a gel of the desired composition was formed by mixing the appropriate basic solutions of silica and aluminum. After gel formation the material is filtered to remove excess water and any unreacted components. A portion of this gel was then added to a basic solution containing the organic cosolvent, if desired. This method eliminates any effects an organic cosolvent may exert upon the gel formation step.

**Gel Formation and Zeolite Synthesis in the Presence of Cosolvent.** Some experiments were performed in which the organic cosolvent was present throughout the entire process. Generally the hydroxide and aluminum or silicon source were dissolved in water and the cosolvent was added to either solution before combining to form a gel.

**Synthesis of Zeolite Y.** Zeolite Y was synthesized via literature methods. Gel formation was followed by forty eight hours of room temperature aging. Perturbations such as the addition of tetramethylammonium chloride, hydrochloric acid or silica from a hydroxide solution were performed after this aging step.
RESULTS

To determine if the addition of cosolvents to a zeolite synthesis mixture had any effect, experiments were performed where different quantities of water were substituted with a variety of cosolvents. Table 5.1 shows the effect of ethanol upon zeolite crystallization. The times given in all of the following tables represent the point at which crystals were first observed, not when crystallization was complete. These experiments were done by the gel addition method explained in the experimental section. Generally it is seen that the presence of EtOH speeds up the formation of the zeolite with the replacement of 10 mL of water with 10 mL of ethanol having a dramatic effect on the rate of formation of crystals. Also it is noted that at higher concentrations of ethanol more condensed zeolites (cancrinite, sodalite) are formed.

Table 5.2 shows that the addition of HMPA has an effect similar to ethanol, with an increase in rate and a tendency to form more condensed phases at higher percentages of HMPA. One complication with this system is that at the 50 and 75% levels there are two immiscible phases present. The bottom phase in the 50% HMPA system contains approximately one fourth the total volume and the gel is completely immersed in this phase.
Table 5.1
Effect of Ethanol Upon Zeolite Crystallization

<table>
<thead>
<tr>
<th>Ethanol</th>
<th>Si/Al of gel</th>
<th>1.33</th>
<th>1.48</th>
<th>4.28</th>
</tr>
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<tr>
<td>0%</td>
<td>No crystals</td>
<td>(24 hours)</td>
<td>No crystals</td>
<td>(24 hours)</td>
</tr>
<tr>
<td>10%</td>
<td>zeolite A,X</td>
<td>zeolite A</td>
<td>(poor)</td>
<td>(poor)</td>
</tr>
<tr>
<td></td>
<td>(7 hours)</td>
<td>(9 hours)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25%</td>
<td>zeolite X</td>
<td>zeolite X</td>
<td>(good)</td>
<td>(good)</td>
</tr>
<tr>
<td></td>
<td>(9 hours)</td>
<td>(12 hours)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50%</td>
<td>zeolite A,X</td>
<td>zeolite A,X</td>
<td>(poor)</td>
<td>cancrinite</td>
</tr>
<tr>
<td></td>
<td>cancrinite</td>
<td>cancrinite</td>
<td>(poor)</td>
<td>(9 hours)</td>
</tr>
<tr>
<td>75%</td>
<td>cancrinite</td>
<td>cancrinite</td>
<td>(fair)</td>
<td>(fair)</td>
</tr>
<tr>
<td></td>
<td>(9 hours)</td>
<td>(8 hours)</td>
<td></td>
<td></td>
</tr>
</tbody>
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Table 5.2

Effect of HMPA Upon Zeolite A Crystallization

<table>
<thead>
<tr>
<th>%HMPA</th>
<th>Product</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>25%</td>
<td>zeolite A</td>
<td>2 hours</td>
</tr>
<tr>
<td>50%</td>
<td>zeolite A</td>
<td>35 minutes</td>
</tr>
<tr>
<td>75%</td>
<td>sodalite</td>
<td>35 minutes</td>
</tr>
</tbody>
</table>

Table 5.3

Effect of DMSO Upon Zeolite A Crystallization

<table>
<thead>
<tr>
<th>% DMSO</th>
<th>Product</th>
<th>Time(hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>NaA</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>NaA</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>NaA</td>
<td>7</td>
</tr>
<tr>
<td>20</td>
<td>NaA</td>
<td>6</td>
</tr>
<tr>
<td>30</td>
<td>NaA(NaX,sodalite)</td>
<td>3</td>
</tr>
<tr>
<td>40</td>
<td>sodalite</td>
<td>4</td>
</tr>
<tr>
<td>50</td>
<td>sodalite</td>
<td>4</td>
</tr>
</tbody>
</table>
DMSO was also used as a cosolvent and the results from these trials are in Table 5.3. In these experiments, the gel was formed and the entire synthesis process was done in the presence of DMSO as described in the experimental section. Again a similar trend is observed when a portion of the water is replaced by a cosolvent.

A comparative study using a variety of cosolvents was performed and the results are given in Table 5.4. These were gel addition experiments and the number of moles of solvent were identical in each trial. The total volume of liquid added was constant so the amount of water varied for each cosolvent and the percent by volume of cosolvent is given in the table. Generally the trend is that as the percent volume of cosolvent increases the crystallization time decreases. Not listed in the table is a trial performed with CH₃CN. Acetonitrile slowed the formation of zeolites and at levels greater than 10%, no crystallization was seen. This exception will be accounted for later.

So it is seen that the substitution of cosolvents for water speeds up the formation of zeolite crystals and that greater amounts of cosolvent cause a greater increase in rate. For the 50% HMPA experiment it must again be noted that there are two phases present and that only the bottom phase contacts the gel. Analysis of this lower phase by titration shows that it is 5.5 M in OH⁻ and this may explain the increase in the rate.
Table 5.4

Comparison of Effect Upon Zeolite A Crystallization of Cosolvents Present in Equal Molar Quantities

<table>
<thead>
<tr>
<th>Solvent (vol%)</th>
<th>Product</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMPA (50)</td>
<td>zeolite A</td>
<td>45 minutes</td>
</tr>
<tr>
<td>DMSO (20)</td>
<td>zeolite A,X</td>
<td>5 hours</td>
</tr>
<tr>
<td>EtOH (16)</td>
<td>zeolite A,X</td>
<td>6 hours</td>
</tr>
<tr>
<td>MeOH (11)</td>
<td>zeolite A</td>
<td>7 hours</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>zeolite A</td>
<td>7 hours</td>
</tr>
</tbody>
</table>

Table 5.5

Effect of Hydroxide Concentration Upon Zeolite A Crystallization

<table>
<thead>
<tr>
<th>[NaOH]</th>
<th>Product</th>
<th>time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.72 M</td>
<td>zeolite A</td>
<td>7 hours</td>
</tr>
<tr>
<td>2.29 M</td>
<td>zeolite A</td>
<td>3 hours</td>
</tr>
<tr>
<td>3.44 M</td>
<td>zeolite A</td>
<td>1.5 hours</td>
</tr>
<tr>
<td>6.88 M</td>
<td>sodalite</td>
<td>30 minutes</td>
</tr>
</tbody>
</table>
Table 5.5 shows the effect of increasing the hydroxide concentration for zeolite synthesis in a strictly aqueous mixture. The effect is similar to that observed when increasing amounts of cosolvents are added. Increasing the hydroxide content speeds up the formation of the zeolites and higher levels promote the formation of more condensed phases. The HMPA is concentrating the hydroxide via the formation of two immiscible layers, one of which is rich in hydroxide, but it also appears that the cosolvents are capable of effectively concentrating the OH⁻ even when only one phase is present.

To further define the role of the cosolvent in affecting the concentration of hydroxide, a set of experiments were performed where the ratio of moles of hydroxide to volume of water was kept constant. In each of these trials a volume of cosolvent equal to 25% of the water present was added. The results for this series of experiments is tabulated in Table 5.6. The XRD patterns were checked hourly for crystal formation. The XRD patterns of the DMSO, HMPA and H₂O samples at three and four hours are shown in Figures 5.1 and 5.2.

A similar experiment was performed keeping the OH⁻ to water ratio constant and varying the amount of DMSO added. The XRD patterns of these crystals at three and four hours are shown in Figures 5.3 and 5.4.

To explore if the addition of cosolvents allows one to vary the composition of a zeolite synthesis mixture outside the range of the usual allowable values a series of
### Table 5.6

Effect of Cosolvent Addition Upon Zeolite A Crystallization with Constant [OH']/[H₂O]

<table>
<thead>
<tr>
<th>Cosolvent</th>
<th>Product</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O (1.72M)</td>
<td>zeolite A</td>
<td>3 hours</td>
</tr>
<tr>
<td>DMSO</td>
<td>zeolite A,X</td>
<td>3 hours</td>
</tr>
<tr>
<td>HMPA</td>
<td>zeolite A</td>
<td>3 hours</td>
</tr>
<tr>
<td>EtOH</td>
<td>zeolite A,X</td>
<td>3.5 hours</td>
</tr>
<tr>
<td>MeOH</td>
<td>zeolite A</td>
<td>3.75 hours</td>
</tr>
<tr>
<td>H₂O (1.38M)</td>
<td>zeolite A</td>
<td>4 hours</td>
</tr>
<tr>
<td>DMSO (20%)</td>
<td>zeolite A,X</td>
<td>3 hours</td>
</tr>
<tr>
<td>DMSO (40%)</td>
<td>zeolite A,X</td>
<td>3 hours</td>
</tr>
</tbody>
</table>

### Table 5.7

Effect of Varying Si/Al with DMSO as a Cosolvent

<table>
<thead>
<tr>
<th>Si/Al</th>
<th>Product</th>
<th>time(hrs)</th>
<th>Product</th>
<th>time(hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% DMSO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>NaA</td>
<td>8</td>
<td>NaA(NaX)</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>NaX</td>
<td>22</td>
<td>NaX(NaA)</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>NaX</td>
<td>22</td>
<td>NaX</td>
<td>11</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>-</td>
<td>NaX</td>
<td>14</td>
</tr>
<tr>
<td>12</td>
<td>-</td>
<td>-</td>
<td>NaX</td>
<td>14</td>
</tr>
<tr>
<td>16</td>
<td>-</td>
<td>-</td>
<td>NaX(chabazite)</td>
<td>16</td>
</tr>
<tr>
<td>24</td>
<td>-</td>
<td>-</td>
<td>chabazite</td>
<td></td>
</tr>
<tr>
<td>20% DMSO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>NaA(NaX)</td>
<td>4</td>
<td>NaX(NaA)</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>NaX</td>
<td>11</td>
<td>NaX</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>NaX(chabazite)</td>
<td>16</td>
<td>chabazite</td>
<td></td>
</tr>
</tbody>
</table>

### Table 5.8

Effect of [OH'] Concentration Upon Zeolite Formation with DMSO as a Cosolvent

<table>
<thead>
<tr>
<th>[NaOH]</th>
<th>Product</th>
<th>Time(hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5M</td>
<td>P</td>
<td>40</td>
</tr>
<tr>
<td>0.8M</td>
<td>NaX(P)</td>
<td>65</td>
</tr>
<tr>
<td>1.1M</td>
<td>P</td>
<td>41</td>
</tr>
<tr>
<td>1.4M</td>
<td>NaX(chabazite,P)</td>
<td>41</td>
</tr>
<tr>
<td>1.7M</td>
<td>NaX</td>
<td>14</td>
</tr>
</tbody>
</table>

Si/Al = 12 20% DMSO
Figure 5.1. XRD patterns of zeolite crystals after three hours.
Figure 5.2. XRD patterns of zeolite crystals after four hours.
Figure 5.3. XRD pattern after three hours heating.
Figure 5.4. XRD pattern after four hours heating.
experiments was done where the Si/Al ratio was increased by dropping the amount of Al present (Table 5.7). These experiments were done with a constant amount of DMSO, hydroxide and water with the only change being the amount of aluminum used. Blank experiments were also done in strictly aqueous solutions. No solid product was recovered at Si/Al ratios greater than eight for the strictly aqueous solution, while product was formed in the presence of 20% DMSO.

Table 5.8 summarizes the results of a series of experiments where the [OH'] is decreased in a system which contains 20% DMSO. The motivation of using lower hydroxide concentrations is that the Si/Al ratio is expected to increase as [OH'] decreases. A gradual trend in that direction is seen as the hydroxide is decreased, however formation of products other than zeolite X or Y interfere. Due to the formation of more than one zeolite, and also the presence of amorphous materials, X-ray fluorescence is not an acceptable technique for estimating the Si/Al ratio of the products. However the XRD patterns in the two theta region between 50° and 60° shows shifts in peak position as the Si/Al ratio changes. An estimate of the Si/Al ratio of the zeolite X or Y which is formed can be obtained by comparing the peak position in this material to that of authentic zeolite X and Y whose Si/Al ratios can be measured via XRF. Figure 5.5 shows the peaks in this region for NaY (Si/Al= 2.55), NaX (Si/Al= 1.32) and for samples in this series of experiments where [OH'] = 0.8
and 1.1 M.

In an effort to determine if zeolite Y with higher Si/Al ratios could be directly synthesized several sets of experiments were performed. Variations were made with the goal of increasing the Si/Al ratio of the final product. Perturbations such as the addition of excess silicon, lowering the hydroxide concentration by the addition of hydrochloric acid and the addition of TMA⁺ were made to the normal zeolite Y synthesis mixture.

Doubling the quantity of silicon which is mixed with the aluminum source essentially prevents zeolite formation. After 350 hours of heating no crystals had formed and it was desirable to explore possible means of increasing the silicon content of the reaction mixture without preventing zeolite formation. A typical gel for zeolite Y synthesis was allowed to age for two days before perturbations were applied. Also to encourage zeolite crystal formation, zeolite seeds whose preparation is described in the Experimental Section, were added to the reaction mixture. The addition of 120, 240, and 450 mmoles of excess SiO₂ dissolved in a sodium hydroxide solution did not prevent the formation of zeolite Y crystals. However the crystal quality decreased as more silicon was added. In addition, based upon the XRD pattern in the 2θ from 50 to 60° the Si/Al ratio of the final product was not significantly affected by this great excess of silicon.

Another factor which would be expected to cause an
increased Si/Al ratio is a lowered hydroxide ion concentration. A lowering of hydroxide concentration can have an effect just like the addition of silicon and slows down or prevents crystal formation. Concentrated hydrochloric was added to the zeolite gel after normal room temperature aging to reduce the hydroxide concentration. The amounts added were equivalent to 10 and 20% of the total hydroxide concentration. This perturbation seems to have very little effect as zeolite Y crystals formed and neither the time required for synthesis nor the crystal quality or Si/Al ratio was significantly affected.

The presence of large cations had allowed the synthesis of a high silicon content analog of zeolite A and it could possibly be expected to play a similar role in zeolite Y synthesis. This was tested by adding TMA+ after room temperature aging of the zeolite Y gel. The addition of TMACl in an amount equal to 10% of the Na+ content caused no change in the formation of zeolite Y. However the addition of TMACl in an amount equal to 20% of the Na+ resulted in the formation of mazzite (Figure 5.6).

**DISCUSSION**

The addition of organic cosolvents to zeolite synthesis mixtures has been seen to result in an increase of rate of formation, a tendency to form more condensed zeolites at higher levels and sometimes a tendency to favor the formation
Figure 5.5. Comparison of XRD pattern to determine Si/Al ratio of zeolite Y product.
Figure 5.6. XRD pattern of mazzite.
of competing products to form. Within the range of solvents studied, these observations seem to hold with only the exception of acetonitrile. This exception can be explained by the reactivity of acetonitrile in a basic media at the temperatures used in these experiments (80°C). Under these conditions acetonitrile forms the unstable amide, CH₃CONH₂ which decomposes to acetic acid and ammonia.¹² This was known to be occurring to some extent as the odor of ammonia was noted. This reaction would effect the pH of the reaction mixture and could explain the decrease in the rate of crystal formation in the presence of CH₃CN.

The addition of cosolvents to water will have a structure breaking or structure building effect upon the hydrogen bonding network present in liquid water.¹³ Using this criteria all solvents can be divided into two categories: solvents which can enhance the structure of water at certain levels and solvents which disrupt this structure when present in any amount. Monohydric alcohols, acetone, tetrahydrofuran and dioxan are examples of the first category as there is some enhancement of water structure at low levels of these organic cosolvents. Increasing the amount of these cosolvents eventually leads to the disruption of the solvent structure and the amount required to cause this change is dependent upon the particular cosolvent. Acetonitrile, dimethyl sulphoxide and hexamethylphosphoramide are classified as structure breakers. DMSO and HMPA are structure breakers because they
compete with water for hydrogen bonding. This phenomenon was introduced as a possible explanation for the increase in rate when only alcohols had been examined. An increase in the structure of water could have an effect upon the rate of formation on zeolite crystals. However since the effect is seen to be a general one with both structure building and breaking cosolvents speeding the formation of zeolite crystals it is felt that this explanation is no longer reasonable.

Raising the hydroxide concentration increases the rate of zeolite formation and also encourages the formation of more condensed phase zeolites. This can be seen in Table 5.5 for a purely aqueous system. This is also evident from 50% HMPA solutions which form a bottom phase which is rich in hydroxide. Contact with this phase greatly speeds up the formation of zeolite crystals. The formation of a second phase is an obvious example of how the addition of a cosolvent can bring about an increase in hydroxide concentration. The apparent increase in hydroxide concentration in a single phase system can be explained by the concept of selective solvation. Selective solvation is a term which is applied to ions when the composition of the solvent components in the neighborhood of the ions is different from the composition of the bulk solution.

In the experiments in which water has been replaced by the organic cosolvent, water is still the preferred solvent for the hydroxide anion, but now there is less water to go around so the effective concentration of the
Hydroxide is increased.

Hydroxide plays a crucial role in the formation of zeolites and its concentration is critical in determining both the product and the rate at which it is formed. The hydroxide functions as a structure director through control of the degree of polymerization of silicates in solution. It also modifies the nucleation time by influencing the transport of silicates from the solid phase to solution. Hydroxide is responsible for enhancing crystal growth by influencing transport between the solution phase and the growing crystal. Similarly it controls phase purity by influencing the rate of transport of silicate species from one crystalline phase to another. As a general rule as the hydroxide concentration increases, the aluminum content of the final zeolite increases and the time required for crystallization decreases.

If the addition of an organic cosolvent is effectively increasing the hydroxide concentration in the zeolite synthesis mixture as would be expected due to selective solvation, this explains the general trends which are being observed. Both the increase in rate and the tendency to form condensed phases is indicative of increased hydroxide concentration, but there may be other factors at work. The addition of an organic cosolvent may cause other changes between the mixed solvent system and the aqueous system which can not be explained strictly on this basis. If the addition of an organic cosolvent is simply resulting in an increase in
hydroxide concentration this effect should be able to be reproduced just by increasing the hydroxide concentration by decreasing the amount of water present. This was done in the experiment which is summarized in Table 5.6 and it can be seen that when the hydroxide to water ratio is kept constant the presence of DMSO and HMPA no longer dramatically speeds the formation of zeolite crystals as it did when water was replaced with the cosolvent. It is also seen that the addition of 20 mL of ethanol or methanol slows the formation of zeolites although not as much as the addition of 20 mL of water. So it appears that DMSO and HMPA are very ineffective in diluting hydroxide, the alcohols in this study dilute it to some extent although not as much as water itself does. It appears on the basis of this experiment that the major cause of the increase in the rate of zeolite crystallization observed upon the addition of an organic cosolvent is due to the increase in the effective hydroxide concentration due to selective solvation. Results in Table 5.6 which show that the addition of more DMSO has no effect upon the rate of formation of zeolite crystals reinforces the perception that DMSO is virtually totally ineffective in diluting the hydroxide anion and therefore the rate is not effected by the addition of this cosolvent.

Just looking at the times for the appearance of the first crystals may not tell the entire story concerning what effects the addition of cosolvents has. Other important charact-
eristics to consider are the amount of time to necessary to complete crystallization, the quality of the crystals formed, the amount of amorphous material remaining and if any other zeolite phases have been formed at the same time. Reference to Figures 5.1-5.4 does show some differences between the crystals formed in the different systems even after identical times. It is seen that in the HMPA system the crystals are of higher quality than for the other systems. This can be seen both from the peak intensity and also from the relative heights of the broad band due to amorphous scattering. Also it must be noted that DMSO and EtOH both encourage the formation of zeolite A and X under conditions where all the other solvents produce just zeolite A. Thus it appears that the addition of cosolvents are causing effects other than the ones which can be attributed to increased hydroxide concentration.

In addition to effects due to selective solvation and any possible templating effects due to interaction with the cations present, the addition of an organic additive can have other effects upon the zeolite synthesis process. The organic additive may be interacting with the system chemically or physically and altering the character of the gel. Such interactions can cause changes in the pH of the system, alter the gelling process by changing the solubility of various species, change the transport of material between the liquid and solid phase or affect the time of crystallization. Iler
has pointed out a couple of mechanisms by which an organic additive can affect the gel chemistry.\textsuperscript{15} The formation of silica-organic complexes will increase the solubility of the silica in solution which will affect the silica content of the solid phase as well. In contrast the adsorption of an organic onto the surface of colloidal silica will tend to retard its solubility. These types of subtle interactions could be coming into play when organic cosolvents are present in the zeolite synthesis mixture and could be causing the differences in products formed as slight changes in the conditions can result in a different product being formed.

Thus far the direct synthesis of a material with a zeolite Y structure and a Si/Al ratio greater than three has not been accomplished. High silica content zeolite Y can be obtained via secondary synthesis dealumination procedures. These procedures include steaming, treatment of the zeolite with acids such as EDTA or a reaction with SiCl\textsubscript{4}.\textsuperscript{16,17,18,19} Direct synthesis of a silica rich zeolite Y would not only avoid the expense of the extra dealumination step, but also the material would have no extra framework aluminum atoms.

Zeolite Y is a metastable structure under the conditions in which it is synthesized. If left in the reaction solution too long after the formation of crystals zeolite P will begin to form. For similar reasons the reaction conditions for the formation of zeolite Y can not be varied too greatly as another zeolite may form or zeolite crystallization may be
prevented altogether. This was seen when the amount of silica in the zeolite synthesis mixture was doubled and no zeolite crystals were formed. Such severe perturbations at the early stage of gel formation have profound implications as to when and if a zeolite structure will form. For these reasons the gel was allowed to age before variations from the normal reaction mixture were tried.

The ultimate goal is to synthesize a final product with a high silicon content and the means toward that goal is to increase the silicon content of the intermediate gel. Increasing the amount of silicon in the original reaction mixture may force more of it to be included in the gel. However because while all of the aluminum tends to go into the gel phase, excess silicon content stays in solution so the ability to increase the silicon content of the gel or the final product in this manner is limited. Indeed it was observed that the addition of the excess silicon after the aging step had no significant effect upon the Si/Al ratio of the final product.

Decreasing the amount of hydroxide ion in the reaction mixture will increase the degree of gel polymerization which has been observed to result in an increase in the final silicon content of the zeolite. The addition of concentrated acid after the gel aging step showed no effect upon the process or products of the zeolite formation. This, along with the results from the silicon addition experiment, seem
to indicate that perturbations after the aging process exert very little control over the composition of the final product.

This is also seen in the addition of an amount of TMACl equal to 10% of the sodium cation content. Again this treatment seemed to show very little effect upon the formation of zeolite Y. This is what made the changes due to the addition of TMACl in an amount equal to 20% of the sodium cation content so surprising. The presence of the TMA⁺ in this amount caused the formation of a totally different zeolite structure, mazzite. The addition of TMA⁺ to a reaction mixture expected to form zeolite Y has been known to result in the formation of mazzite. As seen in Table 5.9 the amount of TMA⁺ necessary to form mazzite is considerably higher when the TMA⁺ is added after the aging step.

Table 5.9

Effect of Addition of TMA⁺ to Zeolite Y Reaction Mixture²⁰

<table>
<thead>
<tr>
<th>Zeolite Formed</th>
<th>Na⁺/SiO₂</th>
<th>TMA⁺/SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y²¹</td>
<td>0.8</td>
<td>0</td>
</tr>
<tr>
<td>mazzite²²,²³</td>
<td>0.8</td>
<td>0.04</td>
</tr>
<tr>
<td>mazzite²¹</td>
<td>0.6</td>
<td>0.14</td>
</tr>
<tr>
<td>Y*</td>
<td>0.8</td>
<td>0.08</td>
</tr>
<tr>
<td>mazzite*</td>
<td>0.8</td>
<td>0.16</td>
</tr>
</tbody>
</table>

*This work. TMA⁺ added after 48 hours aging.
All these results seem to indicate that perturbations applied to the zeolite Y synthesis after the aging step generally have little effect upon the composition of the product. The exception to this general trend is in the addition of sufficient TMA\(^+\) to cause the formation of mazzite. This seems to indicate that the species present after the aging step are common building blocks for both zeolite Y and mazzite. The presence of the TMA\(^+\) is favoring the formation of the 14-hedreral cages which are representative of mazzite. The building blocks which the mazzite and faujasite structures have in common are the simple four membered aluminosilicate rings. Other building blocks specific to zeolite Y are also probably present because it was observed that a considerable amount of TMA\(^+\) was necessary to bring about the formation of mazzite, and so a considerable perturbation is needed to allow the formation of mazzite to compete with the formation of zeolite Y. Furthermore the addition of zeolite Y seeds cause for the formation of zeolite Y even under the conditons when mazzite formed in the absence of seeds. The presence of the TMA\(^+\) favors the formation of mazzite while the addition of seeds allows zeolite Y to form. Thus it is seen that the reaction composition is near the frontier between zeolite Y and mazzite crystallization and small changes in the reaction conditions can result in the formation of either phase.
CONCLUSIONS

The addition of organic cosolvents to a zeolite synthesis reaction mixture has been shown to result in an increase in the rate of zeolite formation and at higher cosolvent levels more condensed zeolite products are formed. This is due to an increase in the effective concentration of hydroxide which is a result of the selective solvation of the hydroxide ion. The rate of crystallization could be reproduced by simply increasing the hydroxide concentration. There were other differences such as mixtures of products which also seem to be due to the presence of the organic cosolvent and these results are not easily explained. The current hypothesis is that the organic cosolvent is exerting an effect upon the critical nucleation process.

When the synthesis of zeolite Y is altered in ways which would be expected to result in a higher Si/Al ratio crystallization is often prevented from occurring. Thus lowering the initial hydroxide concentration or increasing the silicon content of the reaction mixture is not a feasible means of synthesizing a high silica zeolite Y. Perturbations to the system after the aging step allowed zeolite formation, but the composition of the final products was not affected except in the case of the addition of TMA⁺ in sufficient quantities to cause the formation of mazzite.
REFERENCES


APPENDIX A

DETERMINATION OF METAL CONTENT OF ZEOLITES VIA XRF

X-ray fluorescence (XRF) is a convenient means of determining the metal content of zeolites. It is a rapid, nondestructive method which requires a minimum amount of sample preparation. The majority of the effort expended goes toward making up a set of suitable standards. For zeolites this entails ion exchanging a known amount of metal into the weighed amount of zeolite. If the exchange levels are low it can be assumed that all the metal goes from solution into zeolite. At higher levels or as a check of this assumption UV-VIS spectrophotometry can be used to quantitate the metal salt solution concentration before and after ion exchange.

Using these standards a calibration curve is produced plotting the ratio of the intensities of the metal and silicon peak versus weight percent of the metal. The silicon content of the zeolite is used essentially as an internal standard. Sample calibration curves for the determination of manganese, cobalt and ion loading levels are given in Figures A1, A2, and A3.
Figure A1. XRF calibration curve for the determination of iron in zeolite matrix. Standards prepared by ion exchanging with FeCl$_3$·6H$_2$O solution. Excitation using a Ge target at 20 kV and 2.0 mA for 100 seconds.
Figure A2. XRF calibration curve for the determination of manganese in zeolite matrix. Standards prepared by ion exchange with MnCl$_2$·4H$_2$O solutions. Direct excitation at 13 kV and 0.01 mA for 100 seconds was used.
Figure A3. XRF calibration curve for the determination of cobalt in zeolite matrix. Standards prepared by ion exchanging with Co(acetate)$_2$·4H$_2$O. Direct excitation at 11 kV and 0.01 mA for 100 seconds was used.
REFERENCES


237


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