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Synthetic, mechanistic and structural chemistry of zeolitic and intercalation materials

Twu, Jen, Ph.D.
The Ohio State University, 1990
SYNTHETIC, MECHANISTIC AND STRUCTURAL CHEMISTRY
OF ZEOLITIC AND INTERCALATION MATERIALS

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

By

Jen Twu, B. S., M. S.

*****

The Ohio State University

1990

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Advisor
Department of Chemistry
To the Memory of
Gui Fun Fon Twu
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CHAPTER I

INTRODUCTION TO INTERCALATION AND ZEOLITIC MATERIALS

Introduction

Intercalation compounds are defined as materials which are formed by reversible insertion of guest species into a host matrix which preserves its structure during the reaction. These exhibit a wide range of compositions, structures, chemical and physical properties, and a wide range of applications such as in technologies involving battery, shape-selective catalysts and ionic conductors\textsuperscript{1-4}. Recently, there has been considerable interest in intercalation compounds due to following reasons: (i) systematic variations of chemical compositions and structures can be achieved by changing the compositions of both host matrix and guest species. For example, by varying the silicon/alumina ratio in synthesis, different type of zeolites can be generated. (ii) intercalation reactions provide a widely variable method for the low temperature preparations of new metastable materials which are not accessible by other techniques. For example, pillars can be intercalated into a clay matrix at low temperature and then subjected to a high temperature treatment to generate fine-dispersed catalysts. (iii) studies on the formation
process and on structural aspects yield new insight into the mechanisms of the solid state processes as well as on ordering states and dynamics of guest species. Since these type of materials offer controllable synthesis conditions, fundamental and complicated processes can be investigated in a systematic way.

Depending on the structure of the host matrix, shown in Fig. 1.1, intercalation materials can be divided into several categories:

(i) 3-dimensional compounds: zeolites and pyrochlores are examples of such systems. A zeolite's framework is composed of interconnecting \( \text{SiO}_4 \) and \( \text{AlO}_4 \) tetrahedra along with exchangeable cations. They have been widely used as supports for catalysts containing highly dispersed metals to
provide product selectivity and poly-functional activity.\textsuperscript{2,3}

Among the important commercial applications, hydrocracking and isomerization are processes using metal-loaded zeolites as catalysts. (ii) 2-dimensional compounds: clays, alkali oxometalates, and graphite\textsuperscript{1,10,19} are members of this class. These materials exhibit a planar array of neighboring vacant sites between the layers. The flexible distance between the layers can accommodate different solvents and ions. By controlling the ordering and loading of the intercalated solvents and ions, they can be used as catalysts, optical devices and ionic conductors. (iii) 1-dimensional compounds: such as manganese dioxide\textsuperscript{16}. These materials consist of matrix units that form a chain structure and offer tunnel-like inner space. However, due to the weak interaction between these chains which generate severe structural defects, the applications of these materials have been limited.

Zeolite

(I) Structure of zeolite

(A) Fundamental building blocks: zeolites can be regarded as aluminosilicate polymers that are obtained by the building of a three dimensional network of Al\textsubscript{2}O\textsubscript{4} and SiO\textsubscript{4} tetrahedra linked by sharing of oxygen atoms\textsuperscript{7,8,9} and containing exchangeable cations inside the framework. The
framework contains pores, channels, and cages, or interconnected voids. The cations are mobile and may occupy various exchange sites depending on their radius, charge, or degree of hydration. This past decade has seen great advances in zeolite structural research. This has been brought about by significant improvement of existing techniques and the advent of new methods including $^{27}$Al and $^{29}$Si magic angle NMR and X-ray Rietveld refinement using high-resolution powder diffractometer data. The structures of a zeolitic framework can be viewed in various ways. A pictorial approach is to discuss the linking of building blocks as can be done to relate the structures of sodalite, faujasite, and A, X, and Y zeolite or to describe the structure of the synthetic ZSM-5 zeolite and mordenite.

(B) Structures of sodalite, faujasite, and A, X, and Y Zeolite: In these zeolites, the silica and alumina tetrahedra are linked together to form a cubic-octahedron, as shown in Fig. 1.2. This cubic-octahedron is also called the sodalite unit since it is the basis for the structure of sodalite. It can be seen from Fig. 1.2a that a sodalite unit is built from six- and four-membered rings. Sodalite is obtained by directly connecting such cubic-octahedrons through sharing of the four-membered rings (Fig. 1.2b). If the
Fig. 1.2. Structures of (a) the sodalite cage, (b) sodalite, (c) A zeolite (d) faujasite.
sodalite units are linked together by oxygen bridges between the four-membered rings, one obtains the framework shown in Fig. 1.2c which corresponds to type A zeolite. A third possibility consists of connecting the sodalite units by oxygen bridges between the six-membered rings. This leads to the structure of faujasite, as shown in Fig. 1.2d. The X and Y zeolites are topologically similar to faujasite. These three materials differ chemically by their Si/Al ratios, which are 1-1.5, 2.3, and 1.5-3.0 for X zeolite, faujasite, and Y zeolite, respectively. It can be seen from Fig. 1.2c and d that the stacking of the sodalite cages leads to larger cavities (supercages), which are connected by apertures of variable sizes. These cavities and pores constitute the internal surface of these zeolites.

(C) Structures of ZSM-5 and mordenite: The framework of ZSM-5 involves a new type of building block (Fig. 1.3a). These units can be linked together, leading to chains (Fig. 1.3b). The latter in turn can be combined to form sheets (Fig. 1.3c), which can generate the ZSM-5 framework when they are connected, leading to the formation of four- and six-membered rings. ZSM-5 then shows a unique pore structure that consists of two intersecting channel systems: one straight and the other has ten-membered elliptical ring openings (ca. 5.5 Å in diameter). Mordenite is built from chains of tetrahedra cross-linked by oxygen
Fig. 1.3. Structure of (a) ZSM-5 building block (b) linear chain (c) combination of linear chain (d) framework diagram of ZSM-5 (e) framework diagram of mordenite.
Figure 1.3
bridges. Each Al or Si tetrahedron is, in addition, part of a five-membered ring. The chains are then interconnected to obtain mordenite structure (Fig. 1.3e). The mordenite pore structure consists of elliptical and non-interconnected channels parallel to the c axis of the orthorhombic structure. Their openings are limited by twelve-membered rings (6.7-7Å).

(II) Synthesis of zeolites

The diverse structures of a zeolite framework have offered an unique challenge for the synthesis of new zeolites. Currently, 60 different topologies have been identified in natural and synthetical zeolites. It has been widely recognized that only a small fraction of zeolites have been synthesized from the possible compositions and structures. Three variables have major influence on the zeolite's structure during crystallization: the gross composition of the reaction mixtures, temperature, and time. Although each variable contributes to a specific aspect of crystallization, the interactions between these elements have been complicated and are also critical in the crystallization. A list of individual factors contributing to the zeolite's structure is provided in Table 1.1. Attempts to make better zeolitic catalysts have resulted in a family of diversified zeolites and the evolution of
Table 1.1 Factors Influence Zeolite Structures

I. Gross Composition
   A. Si/Al : framework composition
   B. Si/H_{2}O : crystallization mechanism
   C. Si/OH' : silicate species, OH'
   D. Inorganic cations: structure, cation distribution
   E. Organic cations: framework aluminum content

II. History dependent factors
   A. Aging
   B. Stirring
   C. Nature of mixing
   D. Order of mixing

III. Temperature

IV. Time
zeolitic composition and structure in the past forty years. Major recent developments and efforts in the synthesis of zeolites can be divided into several categories: (i) Increase of the Si/Al ratio of faujastic zeolite from 3.5 to a few hundreds. (ii) Incorporation of new atoms: isomorphous substitution of new atoms into the zeolite framework to replace Si or Al atom have generated new zeolites contains Ga, B, Fe, Ti, Co, Mg and Mn. (iii) Development of new framework structures which include the larger pore structure of the 18-membered-ring from VPI-5 and different secondary building units such as 3-member and seven-membered-rings from ZSM-18. The unique structure of ZSM-18 and the critical feature of the templating agent, shown in Fig.4, certainly will bring more efforts in both synthesis and structure-determination in this area. (iv) Use of the zeolitic framework to generate novel optical and electronic materials. Because of the appropriate sizes, periodicity and uniformity of their inner space, zeolites could be ideal supports to control the quantum size of the substrate such as CdS and hence offer new optical and electronic activities.

Clay

(I) Natural clay

Natural clays are layered aluminasilicates made up of
Fig. 1.4. ZSM-18 (a) templating agent (b) secondary building units and templating agent (c) framework structure.
Fig. 1.5 Schematic representation of clay framework.
Figure 1.5
tetrahedral and octahedral silicates, alumina and isomorphously substituted metals \(^{19,20}\). These octahedral and tetrahedral units are combined by sharing the oxygen atoms. Depending on their compositions, these layered sheets can have either negative or positive charges which are balanced by exchangeable counterions. Natural clays have a wide occurrence in nature, they exhibit interesting properties such as fine-grained particles and easy dispersion in water.

(II) Synthetic clay

Acid-modified smectites were first identified in the 1940's as petroleum-cracking catalysts \(^{17}\). These modified clays were used extensively as commercial catalysts until the 1960's when they were replaced by more thermally stable and selective zeolite catalysts. Interlamellar reactions in ordinary metal ion exchange clays at high temperatures (200°C) are difficult due to collapse of the clay framework. This limitation can be overcome by the intercalation of thermally stable, robust cations which act as molecular props or pillars, keeping the silicate layers separated in the absence of a swelling solvent. By using new pillars and clay-frameworks, these materials exhibit features such as: (i) larger spacings between the clay sheets, (ii) higher thermal and steam stability, (iii) and novel catalytic
species between the pillars\textsuperscript{21}.

Due to their potential to have as a catalytic material, efforts and developments committed to these materials can be divided into three categories: (i) New chemical understanding of clays. The ordering within the tetrahedral layer of Si and Al follows the general rules of the Al avoidance characteristic of zeolites proposed by Lowenstein. This implies that cations, including pillaring cations, are likely to be evenly spaced within the interlayer spacing. The molecular sieve sorption properties of pillar-clay indicate zeolite-like behavior with a sharp cut-off in molecular size separations which supports the original assumption that pillared-clay can be regarded as a molecular sieve having evenly spaced pillars propping open the layers\textsuperscript{21}. Exploration of the pillar-clay interactions has shown that different chemical cross-linking can happen between the pillar and tetrahedral layers in a biedellite montmorillonite, and it does not occur in hectorite\textsuperscript{22}. (ii) New sheet structure: Most successful pillaring has been carried out on smectite type clays. A new type of material which uses rectorite for pillaring gives this pillared material an enhanced stability which shows superior activity in catalytic reactions.\textsuperscript{22,23} (iii) New pillaring: The original pillar-clay compositions were based on a family of pillaring species, such as $\text{Si}_8\text{O}_{12}(\text{OH})_8$, $[\text{Al}_{11}\text{M}_2\text{O}_4(\text{OH})_{26}]^{7+}$ and
[Zr₄(OH)₆(H₂O)₁₆Clₓ]⁺⁺⁺⁺ that resulted in a wide spectrum of quite different PILC products. By this unique arrangement, these pillars act as a reservoir for creating catalytic metal clusters in the interlayer, leading to novel and enhanced reactivities²³,²⁴.

Raman spectroscopy

Observation of the Raman effects were first reported in 1928 by Raman in the study of light-scattering of molecules²⁵,²⁶. Raman scattering is generated by an inelastic collision of an incident photon with a molecule. In contrast to fluorescence and phosphorescence, the Raman effect does not require the incident light be coincident with the absorption band. However, by choosing an appropriate wavelength, different effects can be observed, shown in Fig. 1.6. The schematic of the Raman spectrometer used in this thesis is shown in Fig. 1.7.

Since Raman effects depend on the polarizability of the molecule induced by the electric field of the incident light, the vibrational selection rules are determined entirely by symmetry considerations. The discrimination between alternate models of differing molecular geometries, which might originate from surface interaction, protonation, dimerization, fragmentation and polymerization, can be realized when the vibrational modes and bands are analyzed.
Fig. 1.6. Scheme of Raman Scattering Process.
Figure 1.6
Fig. 1.7. Block diagram of Raman Spectrometer.
Figure 1.7
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<th>V-O-V*</th>
<th>V=O/V atoms</th>
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<tr>
<td>$V_{10}O_{28}^{-6}$</td>
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* : cm$^{-1}$
+ : coordination number
This is shown for vanadium compounds in Table 1.2.\textsuperscript{27} Raman spectroscopy is a powerful technique for the characterization of several complicated systems. For instance, the multiple chemical states that can simultaneously be present in the supported metal oxide phases have been a source of confusion and ambiguity\textsuperscript{28}. They have hampered progress in the understanding of supported metal oxide catalysts because of the lack of suitable characterization techniques that can discriminate between different states. In the past few years, characterization studies of supported metal oxides have shown that the different chemical states in the supported oxides can be distinguished by the use of Raman spectroscopy since each state has a different geometry. In addition, it has been demonstrated that cross sections of Raman scattering differ significantly between the supports, substrates and their complexes. This unique feature has made Raman spectroscopy more informative than IR which suffers severe problem due to the strong extinction coefficients of these species. To date, the supported metal oxide such as molybdenum oxide\textsuperscript{29} and vanadium oxide\textsuperscript{28} have been studied by Raman spectroscopy. On the other hand, there is considerable interest devoted to the study of the amorphous intermediates in the synthesis of materials\textsuperscript{30,31}. The lack of understanding of the molecular structures has
been the major obstacle in designing new materials and in improving the desired properties for better materials. Having the advantage of probing both the short range order and offering a good sensitivity for the long range order of a chemical system, Raman spectroscopy offers a unique advantage and presents a complementary, and sometimes indispensable picture of these chemical systems as compared with other techniques such as XRD, MAS-NMR.

Conclusion

Although the level of understanding of the synthetic chemistry and its relationship to the resulting structural features of both zeolites and clays has advanced substantially over the period of forty years, the ability to execute molecular architecture and delineate the details of structures and dynamics has not been established completely over the same period\textsuperscript{32,33}. The synthesis of new zeolites and clays is now focusing on the innovative alteration of the chemistry of the synthesized systems, rather than having the ability to design the chemistry to form a desired structure. For instance, hydrothermal synthesis of high Si/Al ratio faujasites has not been realized after forty years of intense efforts, and a lack of understanding of gel chemistry has made the manipulation of metal oxides and hydroxides in highly alkaline conditions difficult. Hence,
only limited structures and compositions of zeolites are generated and their applications are restricted to a few reactions. On the other hand, the structures for both clays and their pillars are difficult to determine especially in the amorphous states and in situ catalysts. This thesis covers both zeolites and layered materials. In the first part, vanadate and molybdate ions are pillared into a layered framework which is composed of LiAl₂(OH)₆⁺ and Mg₂Al(OH)₆⁺; and their ion exchange reactions, interlayer reactions, and solid state reactions are studied. The second part deals with the mechanisms of synthesis and framework structures of zeolites X, Y and mordenite. By varying synthetic conditions and adopting a combination of complimentary techniques and conducting in-situ characterizations, a clear molecular picture of these two systems has been established.
References


CHAPTER II
STRUCTURE AND REACTIVITY OF OXOVANADATE ANIONS IN LAYERED LITHIUM ALUMINATE MATERIALS

Introduction

Supported metal oxide catalysts have found wide application in industrial processes.\(^1\) For instance, vanadium oxides are used for selective oxidation of hydrocarbons to manufacture butadiene, maleic anhydride, acrolein, acetaldehyde, acetic acid, methanol, formaldehyde, and phthalic anhydride.\(^2\) Considerable interest exists in understanding the correlation between the structure of the metal oxide and its reactivity, as well as the role of the support.\(^3\) Novel methods for generating metal oxide layers on supports in order to maximize the distribution and interaction with reactants is an area of active research, since it plays a critical factor in determining the performance of the catalyst.\(^6\)\(^8\)

The role of specific vanadate species in well defined coordination geometries has been proposed to be responsible for catalytic performance on different supports.\(^9\)\(^11\) These materials are typically synthesized by impregnation of aqueous vanadate solution into supports, followed by
Dutta et al have recently reported studies of a layered lithium aluminate hydroxide material which exhibits selective uptake of specific anions by the process of ion-exchange from a complex equilibrium of ions in solution. In this study, we focus on the ion-exchange of vanadate ions. These ions exhibit a complex equilibria in solution, depending on both the pH and concentration of vanadium. For a 0.1M aqueous vanadate solution, these equilibria can be roughly summarized as:

Decavanadate (pH 1-3) \( \rightleftharpoons \) Metavanadate (pH 4-6) \( \rightleftharpoons \) Pyrovanadate (pH 8-11) \( \rightleftharpoons \) Vanadate (pH > 12)

\[ \text{(V}_{10}\text{O}_{26}(\text{OH})_{2}^{\cdot 4}, \text{V}_{10}\text{O}_{27}(\text{OH})_{\cdot 5}, \text{V}_{10}\text{O}_{28}^{\cdot 6}) \rightleftharpoons \text{(VO(OH)}_{3}, \text{VO}_{2}(\text{OH})_{\cdot 1}, \text{V}_{3}\text{O}_{9}^{\cdot 3}, \text{V}_{4}\text{O}_{12}^{\cdot 4}) \rightleftharpoons \text{(VO}_{3}(\text{OH})_{\cdot 2}, \text{HV}_{2}\text{O}_{7}^{\cdot 3}, \text{V}_{2}\text{O}_{7}^{\cdot 6}) \rightleftharpoons \text{VO}_{4}^{\cdot 3} \]

These layered lithium aluminate material represented by the formula \([\text{LiAl}_{2}(\text{OH})_{6}]^{\cdot} \cdot \text{X}^{-}\) can be pictured as sheets of lithium and aluminum atom octahedrally surrounded by hydroxyl groups. These sheets, which form the framework are positively charged and need to be neutralized by the anions, \(\text{X}^{-}\). The anions position themselves between the sheets and can be readily ion-exchanged. These materials
resemble the more commonly studied hydrotalcites, whose anion exchange behavior has been well investigated. A recent communication by Pinnavaia and coworkers reported on the exchange of $V_{10}O_{28}^{6-}$ into a transition metal hydrotalcite and the photoxidation of isopropylalcohol using this material as a catalyst. Dredzon has also reported the ion-exchange of $V_{10}O_{28}^{6-}$ into hydrotalcite via an organic acid exchanged material.

We report here the ion-exchange of vanadate ions into $LiAl_2(OH)_6^-$ over a wide pH range. Combination of spectroscopy and diffraction measurements provide information about the ion-exchange process and the orientation of ions in the interlayers. Thermal treatment promotes the reaction between the vanadate ions inside the lithium aluminate layers and provides materials that exhibit selective catalytic properties towards the oxidation of $o$-xylene. This study indicates the feasibility of generating novel materials by ion-exchange of polyoxometallic anions into layered compounds.

Experimental Section

Analytical reagent grade chemicals were used for all preparations described in this work. Preparation of clay is adapted from the method by Serna et al. 0.05 mole of Al was dissolved in 100ml of 2M NaOH solution. 0.25M of LiCl
was dissolved in this solution and the mixture heated for 48 hours at 90°C. The product was washed with water followed by 0.1M NaCl. Care was taken to exclude CO₂ during the synthesis. Vanadate solutions were prepared by dissolving NaVO₃ in water and the pH-value was adjusted by mixing with NaOH or HCl solution. Ion-exchange of the clay was carried out with 0.1M vanadate solution for 3 to 24 hours at room temperature. During the ion-exchange, the pH-values of solutions were monitored, and adjusted, if necessary. The samples were washed with deionized water and air dried prior to the spectroscopic experiment. Heat activations of these material was done under ambient conditions in an oven from Technical Products Corporation. Powder X-ray diffraction was obtained with a Rigaku Geigerflex D/Max 2B diffractometer using Cu Kα radiation. The vanadium content of the clay was determined by X-ray fluorescence with a Kevex 0700 spectrometer. Intensity of V Kα radiation was measured by excitation with a Fe secondary target. Excitation for the Raman spectrum was done with 10-50 mw of 457.9nm radiation from a Spectra Physics Argon ion laser or 647.1nm radiation from a Coherent Krypton ion laser. The scattered light was collected and dispersed through a Spex 1403 double monochromator and detected with a GaAs PMT with photon counting. A Shimadzu UV-265 spectrophotometer with a diffuse-reflectance attachment was used to obtain the
electronic spectrum. BET/surface area measurements were conducted on a Micromeritics Pulse Chemisorb 2900 instrument using N₂. The catalytic performance of the samples for the oxidation of o-xylene was studied in a glass reactor composed of 1g of clay and 5g of glass beads. The reaction was carried out at 350°C. Air at a velocity of 25 ml/min was passed through an o-xylene generator immersed in a temperature-controlled water bath. The products were trapped by condensation with cold water and were analyzed by a Varian 920 gas chromatograph, using standards to estimate the retention times.

Results and Discussion

Ion-exchange of Oxovanadate Anions: The ion-exchange process involving the replacement of interlayer chloride ions in [LiAl₂(OH)₆]⁺Cl⁻ by vanadate ions from a 0.1M aqueous solution of sodium vanadate was investigated over the pH range of 2 to 14.

At pH's exceeding 13, it was not possible to ion-exchange vanadates into the lithium aluminate, since the hydroxide anions selectively replace the interlayer chloride ions.

Ion-exchange between pH 8-11 resulted in the formation of a vanadate exchanged material, whose powder X-ray diffraction pattern and Raman spectrum are shown in Figures
Figure 2.1. Powder X-ray diffraction pattern of (a) [LiAl₂(OH)₆]Cl and (b) [LiAl₂(OH)₆]Cl exchanged with 0.1M vanadate solution at pH - 10 (c) Raman spectrum of the vanadate exchanged material. Excitation - 457.9 nm.
Figure 2.1
Figure 2.2  Raman spectrum of material obtained after exchange of \([\text{LiAl}_2(\text{OH})_6]\text{Cl}\) with 0.1M vanadate solution at pH - 5. Excitation - 457.9 nm.
Figure 2.2
2.1b and 2.1c, respectively. Figure 2.1a is the diffraction pattern for the starting lithium aluminate chloride. Comparison of Figures 2.1a and 2.1b clearly indicate that the gallery height increases from 3 Å ($d_{001} = 7.8$ Å) to 6 Å ($d_{001} = 10.8$ Å) as the chloride ions are replaced by the vanadate ions. No residual reflections corresponding to the chloride ions in the interlayer are evident after ion-exchange, indicating complete exchange. This is also supported by the X-ray fluorescence measurements, which indicate a vanadium loading of 19 weight percent. The Raman spectrum in Figure 2.1c is characterized by bands at 350, 483, 605, 837 and 878 cm$^{-1}$. The band at 605 cm$^{-1}$ has been assigned to the Al-O stretching motion of the framework,$^{12}$ whereas the rest of the bands arise from the vanadate species.

Ion-exchange between pH 5 and 6 also leads to complete exchange of vanadate species for chloride ions. Figure 2.2 shows the Raman spectrum of the ion-exchanged material at this pH. The X-ray diffraction of this material is identical to that shown in Figure 1b, with a gallery height of 6 Å, but the Raman spectrum is quite distinct. The major Raman bands are observed at 358, 520, 606, 877 and 944 cm$^{-1}$. The band at 877 cm$^{-1}$ is similar to that observed upon ion-exchange at pH 8-11, whereas the other bands are indicative of the presence of new vanadate species. Initial ion-
exchange at this pH usually results in the appearance of Raman bands at 330 and 977 cm\(^{-1}\), which disappear upon washing, indicating that the species responsible for this band are adsorbed on the surface.

Upon lowering the pH of the ion-exchanging solution to 3-4, the exchange of vanadates still occur, but as shown in the X-ray diffraction pattern in Figure 2.3, reflections due to interlayer chloride are present, indicating incomplete exchange. In order to obtain the exchanging solutions at these lower pH's, acidification of these solutions were carried out with HCl. Thus, under these conditions, vanadate ions compete with chloride ions for ion-exchange. The gallery height is 6 Å, and Raman bands are observed at 326, 353, 521, 605, 835, 946 and 982 cm\(^{-1}\). The bands at 326 and 982 cm\(^{-1}\) are not removed by extensive washing, as observed in the pH range between 5-6. Exchange at a pH lower than 3 led to progressive destruction of the lithium aluminate material, as evidenced by the appearance of a broad band in the diffraction pattern at 20-25 Å.

Griffiths and co-workers have reported on the Raman spectra of vanadate ions in solution as a function of pH.\(^{23,24}\) The most prominent Raman band of these species occur in the 800-1000 cm\(^{-1}\) region due to the stretching motion of the V-O functionality. Several trends are manifested by this band. Its frequency increases as the number of terminal oxygen
Figure 2.3. (a) Powder X-ray diffraction pattern and (b) Raman spectrum of \([\text{LiAl}_2\text{(OH)}_6]\text{Cl}\) exchanged with 0.1M vanadate solution at pH - 3. Excitation - 457.9 nm.
Figure 2.3

(b)

Wavenumber

400 600 800 1000

(a)

2θ (degree)

10.00 20.00 30.00
atoms decrease. For example, the frequency of the V-O stretch for tetrahedrally coordinated vanadium with four, three, two and one terminal oxygen atoms occur at 827, 877, 945 and 1030 cm\(^{-1}\), respectively. Increasing polymerization along with branching at the vanadium atom to form oxovanadate species should therefore lead to an increase in the V-O stretching frequency in the Raman spectrum. Such effects have been reported for molybdates and silicates and can be understood as arising from increased bond order of the terminal metal-oxygen atoms as polymerization at the metal center proceeds. Another general feature in the vibrational spectra of metal oxoanions is the increase in frequency of the terminal metal-oxygen stretch as the other oxygen atoms around the metal center are protonated.

The Raman spectrum of the vanadate exchanged material at pH 10 (Figure 2.1c) is best assigned to the V\(_2\)O\(_7^\cdot\)\(^4\) ion, which in solution exhibits bands at 351, 503, 810, 850 and 877 cm\(^{-1}\) due to VO\(_3\), VO(V), VO(V), VO(V) and VO(V) motions, respectively. The presence of VO\(_4^\cdot\)\(^3\), HV\(_2\)O\(_7^\cdot\)\(^3\), and (VO\(_3\))\(_n\)\(^\cdot\)\(^x\)(n>3) can be definitely excluded due to the lack of the corresponding prominent Raman bands at 340, 820, 915 and 945 cm\(^{-1}\). However, HVO\(_4^\cdot\), which is characterized by Raman bands at 351, 545 and 877 cm\(^{-1}\) cannot be considered to be absent in the interlayer, based on the Raman data alone. The weakness of the Raman band at 545 cm\(^{-1}\) makes it difficult
to distinguish between HVO$_4$$^{2-}$ from V$_2$O$_7$$^-$.

The major components in the ion-exchanging solution at pH 10 and 0.1M concentration of vanadium are V$_2$O$_7$$^-$, HV$_2$O$_7$$^3$ and HVO$_4$$^{2-}$ and are present in an equilibrium molar ratio of 6:3:1. We have noted in an earlier study, that ions with higher charge densities are preferentially ion-exchanged into [LiAl$_2$(OH)$_6$]$^+$, e.g. for the phosphate and sulfate series, the exchange selectivity followed the order PO$_4$$^{3-}$ > HPO$_4$$^{2-}$ > H$_2$PO$_4$$^-$$^1$ and SO$_4$$^{2-}$ > HSO$_4$$^-$$^1$. The present observation that V$_2$O$_7$$^-$ is preferentially exchanged over HV$_2$O$_7$$^3$ is in agreement with the previous studies. The much lower concentration of HVO$_4$$^{2-}$ in the exchanging solution as compared to V$_2$O$_7$$^-$ ion would also favor the ion-exchange of the latter species. Based on these factors, we conclude that V$_2$O$_7$$^-$ is the predominant species in the interlayers of [LiAl$_2$(OH)$_6$]$^+$ for this range in pH. Information about the orientation of the V$_2$O$_7$$^-$ anion can be derived from the gallery height of 6 Å. This ion is formed by sharing of two VO$_4$ tetrahedra as in VO$_3$-O-VO$_3$.

The two distinct arrangements are:
From the single crystal data on Mg$_2$V$_2$O$_7$\(^{25}\), we estimate that the dimension of the V$_2$O$_7$$^-$$^4$ ion corresponding to arrangements A and B are 7.8 Å and 5.0 Å, respectively. The van der Waals radii of the oxygen atoms have been taken into account. Based on the observed gallery height of 6 Å, arrangement B appears to be more likely. Also, it is to be noted that different orientations of the anion are possible in arrangement B, involving rotation around the V-O-V plane.

For an ordered arrangement of the lithium and aluminum atoms in the octahedral sheet\(^{14}\), the surface area around each unit positive charge is 25Å\(^2\). In the arrangements A and B, the ion is distributed over areas approximating 25Å\(^2\) and 40Å\(^2\), respectively. The energetics of the ion-exchange process favor the more charge delocalized distribution as in B, indicating that the energy required to spread the layers further apart as in arrangement A is not compensated for in the vertical orientation. In order to account for the gallery height of 6 Å for arrangement B, a layer of water molecules sandwiching the V$_2$O$_7$$^-$$^4$ is required. The spaces between the vanadate ions is also filled with water molecules. This system bears a resemblance to hydrated salt forms of alpha-zirconium phosphates.\(^{26}\)

Upon exchange between pH 5-6, the Raman features due to V$_2$O$_7$$^-$$^4$ including the band at 877 cm\(^{-1}\) appears weakly in the spectrum (Figure 2.2). The set of prominent Raman bands at
360, 520 and 944 cm\(^{-1}\) is assigned to \(V_{4}O_{12}^{4-}\), which in solution exhibits prominent bands at 360 and 945 cm\(^{-1}\).\(^{23,24}\) The Raman bands at 330 and 980 cm\(^{-1}\) which are removed upon washing are characteristic of a \(V_{10}O_{28}^{6-}\) species.\(^{23,24}\) Therefore, within this pH range, \(V_{4}O_{12}^{4-}\) is the predominant species exchanged into \([LiAl_{2}(OH)_{6}]^{+}\), with a minor amount of \(V_{2}O_{7}^{4-}\). The similarity in gallery height between the \(V_{2}O_{7}^{4-}\) and \(V_{4}O_{12}^{4-}\) exchanged material of 6Å results from the fact that the smallest dimension of these two units is similar. In this geometrical arrangement for \(V_{4}O_{12}^{4-}\), unit negative charge is distributed over a larger area as compared to the \(V_{2}O_{7}^{4-}\) anion. At the lowest pH (3-4), the major species in the interlayers is still \(V_{4}O_{12}^{4-}\) ions, along with minor amount of \(V_{10}O_{28}^{6-}\). No Raman bands due to \(V_{2}O_{7}^{4-}\) are observed. The presence of \(V_{10}O_{28}^{6-}\) is indicated by the Raman bands at 320 and 980 cm\(^{-1}\), which cannot be removed upon washing. The gallery height in this case is also of the order of 6 Å, as observed in the previous samples. In contrast to this study, Pinnavaia and coworkers have found that \(V_{10}O_{28}^{6-}\) can be completely ion-exchanged into hydrotalcites containing zinc-aluminum, zinc-chromium and nickel-aluminum in the framework, with a gallery height of 7.1Å.\(^{20c}\) Dredzon has also noted complete exchange of \(V_{10}O_{28}^{6-}\) into a magnesium-aluminum hydrotalcite via pre-exchange of organic ions.\(^{22}\) Since \(V_{10}O_{28}^{6-}\) is only a minor component in the lithium
aluminate at pH 3-4, only reflections corresponding to the major species $V_4O_{12}^-\cdot$ are observed in the diffraction patterns. Attempts to increase the loading of $V_{10}O_{28}^-\cdot$ versus $V_4O_{12}^-\cdot$ by adjusting the concentration and pH were unsuccessful. The major difference between the lithium aluminate and the transition metal hydrotalcite is in the layer surface area per unit charge: 25 and 16.5 Å$^2$, respectively. The more concentrated charge density in the transition metal hydrotalcite may favor the more compact $V_{10}O_{28}^-\cdot$ ion. This is also in agreement with the observation of Pinnavaia and coworkers$^{20c}$ that ion-exchange of $V_4O_{12}^-\cdot$ ion into the transition metal hydrotalcite leads to a gallery height of 4.7 Å as compared to the 6 Å observed in this study. The smaller spacing can be attributed to the stronger electrostatic interaction due to the higher charge density in the transition metal hydrotalcite.

In summary, this study indicates that the vanadate ions exchanged into the lithium aluminate are a function of the pH of the exchanging solution. $V_2O_7^-\cdot$ is selectively ion exchanged between pH 8-11. At pH 5-8, $V_4O_{12}^-\cdot$ is the major species along with minor quantities of $V_2O_7^-\cdot$. For the most acidic solutions, (pH 3-5), $V_4O_{12}^-\cdot$ is still the major species along with $V_{10}O_{28}^-\cdot$ ions.

Thermal Treatment of LiAl$_2$(OH)$_6$ - $V_2O_7$: It is well
recognized that in order to generate catalytically active materials from hydrotalcites, thermal decomposition of the support is necessary.\textsuperscript{33-35} The fate of the vanadate ion, $V_2O_7^{4-}$ exchanged at pH 10, and its interaction with the support was investigated as a function of temperature. Figure 2.4 shows the powder diffraction pattern at different temperatures as the sample is heated from ambient to 450°C. There is a gradual decrease in the gallery height as the sample is heated. The layer structure begins to disappear at temperatures beyond 300°C. At temperatures over 450°C, a new phase is observed in the diffraction patterns. The gallery height upon heating the sample at 80, 200, 300°C are 3.4, 2.3 and 1.8 Å, respectively. The starting material had a gallery height of 6 Å. Rehydration of the heated samples resulted in a change of the gallery heights to 6, 2.4 and 1.8 Å for the 80, 200, 300°C samples, respectively. The sample heated to 80°C upon hydration regenerates the diffraction pattern of the starting material. In the thermal decomposition of hydrotalcites with anions such as carbonates, reversibility has been reported even after heating samples to temperatures of 500°C. The new crystalline phase formed by heating to temperatures exceeding 450°C is characterized by reflections at 2 theta = 18.7, 20.8, 28.2, 32.4, 37.5, 45.8, 58.8 and 66.4°.

In order to understand the structural changes that
Figure 2.4. X-ray diffraction pattern obtained after thermal treatment of a [LiAl₂(OH)₆]Cl-V₂O₇ sample. (a) Room temperature (b) 80°C, 2 hours (c) 200°C, 5 hours (d) 300°C, 1 hour (e) 300°C, 3 hours (f) 450°C, 24 hours.
Figure 2.4
Figure 2.5. Raman spectra of samples obtained after thermal treatment of [LiAl₂(OH)₆] - V₂O₅. (a) Room temperature (b) 80°C, 24 hours (c) 200°C, 3 hours (d) 300°C, 6 hours (e) 400°C, 6 hours (f) 450°C, 24 hours.
Figure 2.5
occur upon thermal treatment, diffuse reflectance and Raman spectroscopy were also carried out on the thermally treated samples. The electronic spectra of the material heated to 200 and 400°C exhibit bands at 270 and 320 nm, respectively. These are representative of charge transfer transitions \( \pi(t_2) \rightarrow d(e) \) and \( \pi(t_1) \rightarrow d(e) \) arising from tetrahedral vanadates.\(^{27,28}\)

The Raman spectra of the thermally treated LiAl\(_2\)(OH)\(_6\)-V\(_2\)O\(_7\) material as a function of temperature are shown in Figure 2.5. Upon heating to 80°C, a decrease in intensity of the bands at 350, 483 and 877 cm\(^{-1}\) due to V\(_2\)O\(_7\)^{4-} is observed, along with growth of bands at 338, 363, 514 and 942 cm\(^{-1}\). For samples heated to 200°C, broadening of the prominent bands at 877 and 945 cm\(^{-1}\) is observed. Upon further heating (300°C), these bands approach each other, and finally merge at 906 cm\(^{-1}\) for samples heated to 400°C. The band at 350 cm\(^{-1}\) progressively loses intensity as a function of heating. Beyond 450°C, the intensity of the band at 906 cm\(^{-1}\) decreases along with the growth of sharp Raman peaks at 791, 818, and 832 cm\(^{-1}\) and a broad band at 945 cm\(^{-1}\).

The new peaks that appear upon heating to 80°C can readily be assigned to V\(_4\)O\(_{12}\)^{4-} ion (Figure 2.5b).\(^{23,24}\) Therefore, initial heating promotes the dimerization reaction
$2\text{V}_2\text{O}_7^{4-} + 2\text{H}_2\text{O} \rightarrow \text{V}_4\text{O}_{12}^{4-} + 4\text{OH}^-$. 

As shown in Figure 2.4b, this reaction brings about a decrease of gallery height by 2.4 Å, possibly due to the loss of the interlayer water used up in the reaction. However, this process is reversible and rehydration generates the starting LiAl$_2$(OH)$_6$-V$_2$O$_7$ material. This is a novel example of reversible interlayer dimerization. This reaction reaches a steady state after 4-6 hours of heating at 80-120°C, after which the relative intensities of the Raman bands due to V$_2$O$_7^{4-}$ (877 cm$^{-1}$) and V$_4$O$_{12}^{4-}$ (945 cm$^{-1}$) do not change. The incomplete conversion could be due to the exhaustion of the interlayer water molecule necessary for the reaction.

The dimerization leads to vanadium atoms with two terminal oxygen atoms. Upon heating to temperatures of 200°C and above, further polymerization involving the formation of more condensed vanadate species can be excluded, since the Raman spectrum shows no evidence of bands in the range of ~1000 cm$^{-1}$ due to vanadium atoms bonded to one terminal oxygen atom. Instead, the VO$_2$(s) stretch decreases in frequency from 945 to 906 cm$^{-1}$, whereas the VO$_3$(s) stretch increases from 877 to 906 cm$^{-1}$. The layer
structure is evident until heat treatments of 300°C, with progressively decreasing gallery heights. This also supports the conclusion from the Raman data that condensation around the vanadium atom is not occurring, for it would necessitate increased spacings. We propose that at these temperatures, hydroxide mediated polymerization and depolymerization reaction do occur, leading to oligomeric chains of VO₄ tetrahedra linked by oxygen atoms. The vanadium atom, on the average, contains two terminal oxygen atoms, leading to a VO₂ stretch at 906 cm⁻¹. Such species resemble the metavanadates: (VO₃)ₓ⁻, whose most prominent Raman band occurs between 925-940 cm⁻¹. The hydroxide ions necessary for creating the metavanadate species in the lithium aluminate are produced in the above discussed dimerization reaction and progressive dehydroxylation of the lithium aluminate framework. The bands at 270 and 320 nm in the diffuse reflectance spectra are also supportive of VO₄ units.

At temperatures in excess of 450°C, both the Raman spectrum and X-ray diffraction indicate the creation of new vanadate species. In the Raman spectrum (Figure 2.5f), sharp peaks at 791, 818, and 832 cm⁻¹, along with a broad band at 945 cm⁻¹ are observed. The set of sharp peaks is characteristic of the discrete VO₄⁻³ anions, whereas the broad peak is in the range for metavanadates. The
diffraction data (Figure 2.4f) indicate sharp peaks at 2 theta = 37.5, 45.8 and 66.4 degrees, which are readily assigned to gamma-Al$_2$O$_3$. The broader peaks at 2 theta = 18.7, 20.8, 28.2, 32.4 and 58.8 degrees are indicative of Li$_3$VO$_4$ and LiVO$_3$, in agreement with the Raman spectrum. These results suggest that at temperatures of 450°C, the lithium aluminate framework is being destroyed, with formation of lithium oxide and alumina, analogous to the thermal decomposition of hydrotalcites. The basic Li$_2$O reacts with the vanadates to form Li$_3$VO$_4$ and LiVO$_3$.

It is of considerable interest to contrast this scheme with the extensive studies done on the thermal decomposition of oxo-vanadates on other supports, including Al$_2$O$_3$, SiO$_2$, TiO$_2$, MgO and CeO$_2$. Raman spectroscopy has been used in these studies and allows for a direct comparison with the present work. The initial Raman spectrum obtained upon impregnation of vanadates onto supports depends on the pH of the solution. Samples prepared by impregnation of pH ~ 10 on Al$_2$O$_3$ exhibit a broad band at 940 cm$^{-1}$ (estimated halfwidth ~ 75 cm$^{-1}$). The width of this peak is a reflection of the different vanadate species (all with VO$_2$ terminal groups) that are adsorbed on the surface. In comparison, the lithium aluminate at pH ~ 10 selectively adsorbs the V$_2$O$_7$$^-$ ion. Calcination of the alumina supported vanadates in air at 450°C leaves the 940
band relatively unperturbed along with an increase in intensity around 800 cm⁻¹. Since no well defined Raman peaks are observed, it is difficult to postulate the presence of discrete species. The increased intensity at ~800 cm⁻¹ has been assigned to polymeric tetrahedral vanadate species.³⁶ If these samples are calcined in dry O₂, a sharper peak at 1026 cm⁻¹ is observed,³⁷ which has been assigned to vanadium with single terminal oxygen atoms and/or neighboring vacancy sites.³⁹ No effect was found on the Raman spectrum for the LiAl₂(OH)₆-V₂O₇ sample for calcination in dry or ambient conditions. Thus, the initial adsorption of vanadates onto other supports and subsequent polymerization is different for the lithium aluminate support. Another difference between the impregnated supports and this study is that even at 19 wt% V loadings on [LiAl₂(OH)₆]⁺, no evidence for the formation of crystalline V₂O₅ was noted, indicating a very well dispersed system. This is not surprising, since the lithium aluminate layers isolate the oxovanadate ions.

Oxidation Reaction: Oxovanadate ions on supports have been extensively studied as catalysts for the oxidation reaction of hydrocarbons.¹,² As discussed above, the lithium aluminate material provides a unique support for incorporation of well dispersed vanadate ions. The reactivity of the O-(-VO₂-)nO layer in the interlayers of the
lithium aluminate generated by thermal decomposition of LiAl₂(OH)₆-V₂O₇ at 350-450°C was examined for the oxidation of O-xylene. In order to provide access to the vanadium sites in the interlayers, it is necessary to partially destroy the framework. This, as has been shown above, is brought about by thermal decomposition. The surface area provides a sensitive measure of the accessibility to the internal sites of the system. Reichle and coworkers have shown that the surface area of hydrotalcites exhibit an increase as water molecules generated by dehydroxylation force their way out of the layers, thereby generating a porous support. The onset of higher surface area depends on the material and temperature, as shown recently for a series of hydrotalcites. The surface area for LiAl₂(OH)₆-V₂O₇ heated to 400°C is ~15m²/g. The reaction product upon xylene oxidation was collected by condensation at room temperature and found to be primarily o-tolualdehyde along with unreacted o-xylene. The ratio of o-tolualdehyde to o-xylene as determined by gas chromatography was 1:6, indicating about 15% conversion. Since there was no analysis for the volatile gases, (CO, CO₂), an exact mass balance cannot be made. However, this preliminary study of reactivity shows that vanadium generated primarily in the tetrahedral form selectively promotes the oxidation of one of the methyl groups. A more detailed analysis of the products along with
comparison with other supports is in progress. The LiAl₂(OH)₆-Cl thermally decomposed under conditions described above for making the vanadate catalyst exhibit no reactivity in the oxidation of o-xylene, indicating the important role of the vanadium center.

Conclusions

The major conclusions of the three areas examined in this study are:

(a) Ion-exchange of vanadate ions into LiAl₂(OH)₆⁻ from an aqueous solution is influenced by pH. At pH 8-11, V₂O₇⁴⁻ is selectively ion-exchanged, whereas as the pH is dropped, V₄O₁₂⁻⁴ is the major interlayer species, along with minor amounts of V₂O₇⁻⁴ (pH 5-6) and V₁₀O₂₆⁻⁶ (pH 3-4).

(b) Thermal treatment of LiAl₂(OH)₆-V₂O₇ was carried out to temperatures of 500°C. The layer structure is maintained until temperatures of 300°C, as evidenced from the diffraction patterns. However, only samples heated to ~ 100°C will revert back to the original starting material upon rehydration. At these temperatures, V₂O₇⁻⁴ dimerizes in the interlayers to form V₄O₁₂⁻⁴. Beyond 300°C, polymeric O-(VO₂)_n-O species are
formed. At 450°C, the lithium aluminate structure is completely destroyed, leading to formation of Li₃VO₄, LiVO₃ and Al₂O₃.

(c) Material formed upon heat treatment of LiAl₂(OH)₆⁺ to 300-400°C exhibits catalytic activity for the selective oxidation of o-xylene to o-tolualdehyde.
References


1984, 85, 260.


Chapter III

DECAVANADATE ION-PILLARED HYDROTALCITE: SPECTROSCOPIC STUDIES OF THE THERMAL DECOMPOSITION PROCESS

Introduction

Layered materials that are characterized by structures held together by strong covalent bonds in the 'xy' plane but considerably weaker bonds in the 'z' direction include materials such as graphite, silicic acids, zirconium phosphates, smectites and hydrotalcite minerals\(^1\)\(^-\)\(^5\). The weakness of bonding in the 'z' direction can be readily exploited to introduce atoms, molecules and ions into the interlayer space, thereby generating a diverse group of materials with applications in technologies involving batteries, catalysts and ionic conductors\(^6\)\(^-\)\(^8\).

Of particular interest to this paper are the materials resembling the minerals belonging to the pyroaurite-sjogrenite type, represented by the general formula \([M_{1-\chi}M^{\text{III}}_{\chi}(OH)_2] A_{\delta/n} \cdot zH_2O\), where \(M^{\text{II}} = \text{Mg, Zn, Fe, Co, Ni, Cu, and } M^{\text{III}} = \text{Al, Cr, Fe}^{9}\). As an example, the structure of the mineral hydrotalcite, \(\text{Mg}_2\text{Al(OH)}_6\text{Cl}\), can be thought of as derived from brucite \((\text{Mg(OH)}_2)\), in which the \(\text{Mg}^{2+}\) cations are octahedrally surrounded by edge-sharing \(-\text{OH}\) groups in a
layer. The layers are stacked upon each other. Replacement of a certain fraction of the divalent cations by trivalent cations, such as Al$^{3+}$, leads to a positively charged metal hydroxide layer, necessitating the presence of anions such as Cl$^-$ in the interlayer space$^{10}$. A large variety of ions can be introduced into these materials$^{11-17}$. These systems are therefore complementary to the more commonly occurring cationic clays, in which cations such as Na$^+$, K$^+$ in the interlayers neutralize the negatively charged alumino-silicate sheets. Considerable work has been done in order to generate novel catalytic materials by pillaring the aluminosilicate layers in smectite type cationic clays with polyhydroxo aluminum and zirconium cations$^{18-20}$. The unique catalytic properties of these materials stem from the novel acidic sites, thermal stability and large internal surface area.

Pinnavaia and co-workers have recently shown that it is possible to introduce polyoxometalate ions as pillars into layered metal hydroxides$^{21}$. The decavanadate ion (V$_{10}$O$_{28}$$^{2-}$) was exchanged into the layers of Zn$_2$Al(OH)$_6^+$, Zn$_2$Cr(OH)$_6^+$ and Ni$_3$Al(OH)$_6^+$. Drezdzon has also reported the exchange of V$_{10}$O$_{28}$$^{2-}$ and Mo$_7$O$_{24}$$^{6-}$ into Mg$_2$Al(OH)$_6^+$ via an intermediate terephthalate derivative$^{22}$. Complex Keggin ion structures have also been introduced into the Zn$_2$Al(OH)$_6^+$ material$^{23}$. Drezdzon, based on thermal analysis data, concluded that the heptamolybdate
and decavanadate pillared hydrotalcites are stable above 500°C. We have recently reported on the ion-exchange of vanadates into the layered hydroxide LiAl_2(OH)_6. Over the pH range of 3-11, the predominant species ion-exchanged into the lithium aluminate were V_2O_7^- and V_4O_12^-.

Thermal treatment of LiAl_2(OH)_6-1/4 V_2O_7 was examined and it was found that the V_2O_7^- dimerizes to V_4O_12^- around 100°C. The interlayer polymerization proceeds till temperatures of 350°C, with formation of polymeric metavanadates in the interlayer. At higher temperatures, degradation of the framework occurs, with ultimate formation of Li_3VO_4 and LiVO_3.

Like their counterparts of pillared smectite clays, interest in these polyoxometalate-hydrotalcite materials also stems from their potential use as catalytic materials. A patent in 1984 refers to their use for exhaust-gas and hydrocarbon conversion catalysts. Thermal decomposition of various layered hydroxides has led to catalysts active for aldol condensation, olefin isomerization, β-propiolactone polymerization and methanol synthesis via water gas shift reaction. Photo-oxidation of isopropyl alcohol and selective oxidation of xylene to tolualdehyde has been reported for the polyvanadate-hydrotalcite systems, similar to the materials discussed in this paper.

In this chapter, we focus on the V_{10}O_{28} - Mg_2Al(OH)_6
system, synthesized by procedures similar to that described by Drezdzon. We have followed the interlayer chemistry upon thermal decomposition of this system by x-ray diffraction, Raman spectroscopy, and x-ray absorption near edge spectroscopy (XANES). These data are subsequently correlated to provide a consistent model.

The relevance of the structural studies described in this paper to catalytic applications of these materials arises from several factors. It is obviously of importance to establish the exact nature of the intercalating anion and its interaction with the layered hydroxide framework, especially under conditions typical of catalytic reactions. This paper shows that Raman spectroscopy provides a powerful probe for examining the structure of the interlayer species and their reactivity upon thermal treatment.

Experimental Section

Analytical reagent grade chemicals from Aldrich were used for preparation of all the samples described in this work. Preparation of the decavanadate pillared hydrotalcite was adapted from the procedure described by Drezdzon. To a solution of 14g of terephthalic acid, 30g of NaOH in 200 ml of H₂O was added a solution of 40g of Mg(NO₃)₂ H₂O, 30g of Al(NO₃)₃ 9H₂O and 125 ml of H₂O. This mixture was heated at 90°C for 24 hours, separated by centrifugation and
thoroughly washed. The exchange of the terephthalate with vanadate was carried out with a solution of 20g of NaVO₃ in 100 ml of H₂O adjusted to a pH of 4.5 with 2 M HNO₃. Thermal treatment of the decavanadate-hydrotalcite samples was carried out in an oven manufactured by Technical Products Corporation.

Powder x-ray diffraction patterns were obtained with a Rigaku Geigerflex D/Max 2B using nickel filtered CuKα radiation. Raman spectra were recorded with excitation from a Spectra Physics Argon Ion Laser (Model 170) and the scattered light was collected and dispersed with a Spex 1403 double monochromator and detected by a C 31034 GaAs photomultiplier tube. Typical power at the sample was between 10-20 mW. The slit widths were 6 cm⁻¹ and scan times of 1-3 s/cm⁻¹ were used. XANES measurements in the fluorescence mode were carried out at the National Synchrotron Light Source, Brookhaven National Laboratory (Beam line X-9A), with an electron energy of 2.5 GeV and ring currents between 100 and 200 mA. Data were collected at the V K-edge (5465 eV). A Si(111) crystal monochromator was used for selecting the appropriate wavelength.

Results

The decavanadate ion was exchanged into the Mg₂Al(OH)₆⁺ material by replacing the terephthalate ion using an aqueous
Figure 3.1 Powder x-ray diffraction patterns of (a) terephthalate - Mg₂Al(OH)₆ and (b) V₁₀O₂₈ - Mg₂Al(OH)₆ at room temperature and heated to (c) 100°C and (d) 160°C (12 hours at each temperature).
Figure 3.1
Figure 3.2 Raman spectra of (a) $V_{10}O_{28}^{6-}$ ions in solution (b) $V_{10}O_{28} - Mg_2Al(OH)_6$ at room temperature and heated to (c) 100°C, (d) 160°C (12 hours at each temperature). Excitation - 457.9 nm.
Figure 3.4
vanadate solution at pH 4.5, as described in the literature\textsuperscript{22}. Figures 3.1a and 3.1b show the powder pattern for the phthalate-hydrotalcite sample and upon ion-exchange by vanadate. The (001) reflections are marked on the figure, and are in agreement with previous studies\textsuperscript{21,22}. The basal spacing ($d_{001}$) corresponding to these reflections is 11.9 Å, and leads to a gallery height of 7.1Å, indicating a $V_{10}O_{28}^6$ orientation with the $C_2$ axis parallel to the layers. The Raman spectrum of this vanadate exchanged material is shown in Figure 3.2b and is compared to $V_{10}O_{28}^6$ in solution (Figure 3.2a). Though the S/N of the spectrum for the hydrotalcite is poorer than that of solution, it is quite clear that all the characteristic peaks of the decavanadate ion at 320, 454, 534, 595, 834, 975 and 998 cm$^{-1}$ are clearly observed in the hydrotalcite samples\textsuperscript{29}. No other Raman bands characteristic of $V_2O_7^{4-}$ or $V_4O_{12}^{12-}$ are observed\textsuperscript{29}. Therefore, the Raman spectrum provides an unambiguous description of the intercalated species.

The powder pattern and Raman spectrum of the $V_{10}O_{28} - Mg_2Al(OH)_6$ sample after heating to 100°C for 12 hours are shown in Figures 3.1c and 3.2c, respectively. There are no significant changes in these data over the room temperature spectra, indicating that the decavanadate ion as well as the framework remains intact. For a sample heated to 160°C, changes are apparent in the XRD and Raman spectrum (Figures
Figure 3.3  Powder x-ray diffraction patterns of $V_{10}O_{28} - Mg_2Al(OH)_6$ heated to (a) 220°C (b) 280°C, (c) 350°C and (d) 450°C. (12 hours at each temperature)
Figure 3.3
Figure 3.4  Raman spectra of $\text{V}_{10}\text{O}_{28} - \text{Mg}_2\text{Al(OH)}_6$ heated to (a) 220°C, (b) 280°C (c) 350°C and (d) 450°C. (12 hours at each temperature). Excitation = 457.9nm
Figure 3.4
These include a new reflection at 4.76Å, and the appearance of a broad band centered at 880 cm⁻¹. The characteristic Raman bands of the decavanadate are still present, as are the XRD reflections characteristic of the decavanadate-hydrotalcite complex. However, it is clear that the decavanadate species is beginning to transform into other vanadate species at temperatures over 100°C. This becomes obvious upon examining the diffraction pattern and Raman spectrum of the sample heated to 220°C (Figures 3.3a and 3.4a). Though the x-ray diffraction is still characteristic of a layered compound with three (001) reflections, the peaks characteristic of the decavanadate-hydrotalcite complex have all disappeared. The gallery height has decreased to 4.6Å (d₀₀₁ = 9.4Å). There is only slight intensity in the Raman spectrum at ~1000 cm⁻¹, which is characteristic of the V-O stretch of the non-bonded oxygen atom of the V_{10}O_{28}^{6-} ion. The prominent Raman bands occur at 870 cm⁻¹, with shoulders at 800 and 960 cm⁻¹. Monomeric and dimeric vanadate ions exhibit prominent Raman bands in the region 800-900 cm⁻¹ (29). For example, the strongest bands in the spectrum of VO₄³⁻, HVO₄²⁻, V₂O₇⁴⁻ and HV₂O₇³⁻ occur at 827, 877, 880, and 877 cm⁻¹, respectively. Cyclic metavanadate structures (VO₅)ₙ²⁻ (where n=3,4) exhibit strong bands around 950 cm⁻¹. These bands are all assigned to symmetric stretching motions of the VO₃ and VO₂ groups.
Clearly, the decavanadate ion is losing its integrity and transforming to simpler vanadate ions at temperatures beyond 160°C. Samples heated to 280°C still exhibit a layered structure (Figure 3.3b), but prominent reflections are also present at d=3.0, 2.57Å. In the Raman spectrum, the peak at 950 cm\(^{-1}\) emerges as the strongest peak, with shoulders at 870 and 750 cm\(^{-1}\) (Figure 3.4b). We propose that the interlayer chemistry occurring between 160-280°C can best be described as the depolymerization of the decavanadate ion:

\[
\text{V}_{10}\text{O}_{28}^- + 3\text{H}_2\text{O} \longrightarrow 3\text{V}_3\text{O}_9^3^- + \text{HVO}_4^2^- + 5\text{H}^+ \quad (1)
\]

The kinetics of this reaction have been reported to be slow at room temperature\(^{30}\). However, as we discuss later, the high charge densities of the layer and the anion as well as elevated temperatures can promote this reaction. The Raman bands at 950 and 870 cm\(^{-1}\) observed at 280°C are characteristic of \(\text{V}_3\text{O}_9^3^-\) and \(\text{HVO}_4^2^-\), respectively\(^{29}\). The considerable intensity in the region around 800 cm\(^{-1}\) could be due to \(\text{VO}_4^3^-\) (827 cm\(^{-1}\), \(\nu \text{VO}_2\)), formed by deprotonation of \(\text{HVO}_4^2^-\). The interlayer distance of ~4.6Å corresponds well to the width of the \(\text{V}_3\text{O}_9^3^-\) ion (~5Å). Upon heating to 350°C, the Raman spectrum sharpens up with no contribution below 800 cm\(^{-1}\) and the peak is observed at ~920 cm\(^{-1}\) (Figure 3.4c). The diffraction pattern still shows the layer structure,
along with the d=3.00 and 2.57Å reflections (Figure 3.3c). The samples activated at 450°C show a Raman spectrum very similar to that of the 350°C sample, except that the two peaks at 884 and 938 cm\(^{-1}\) can now be clearly discerned (Figure 3.4d). However, the diffraction pattern indicates that the layer structure is no longer intact and only a large angle reflection at 2.47Å is observed (Figure 3.3d). The vanadate species, at least as evidenced from the Raman spectrum, does not change between 350 and 450°C though the layer structure of the framework collapses in this temperature range. We assign the Raman bands at 884 and 938 cm\(^{-1}\) to a chain-like polymeric metavanadate species \((-O-VO_2-O-VO_2)_n\), based on reported studies of metavanadates in solution and the solid state\(^3\). For example, KVO\(_3\) in solution exhibits bands at 945 and 860 cm\(^{-1}\) and in the solid state at 940 and 910 cm\(^{-1}\).\(^2\) These vibrations arise from stretching motions of the VO\(_2^+\) unit. The reaction of the vanadate species occurring between 220 and 450°C can best be described as:

\[
 n(V_3O_9)^{-3} \quad \rightarrow \quad 3n (VO_3)^{-1} \quad (2)
\]

Upon heating the decavanadate-hydrotalcite sample to 550°C, sharp Raman bands appear at 825, 860, 905 and 955 cm\(^{-1}\) on the broad metavanadate peak (Figure 3.5c). With increase in
Figure 3.5 Powder x-ray diffraction (a,b) and Raman spectra of $V_{10}O_{28} - Mg_2Al(OH)_6$ (c,d) heated to 550°C and 650°C, respectively. (12 hours at each temperature).
Figure 3.5
temperature to 650°C, the metavanadate peak altogether disappears and only the sharp bands remain (Figure 3.5d). The powder diffraction patterns of these samples are shown in Figures 3.5a and 3.5b. The Raman spectra are characteristic of alpha-Mg$_2$V$_2$O$_7$ (950, 905 cm$^{-1}$) and Mg$_3$(VO$_4$)$_2$ (863, 828 cm$^{-1}$)$^{32}$. The x-ray diffraction peaks at 550°C are characteristic of a spinel structure (MgAl$_2$O$_4$, 2.52, 2.02 and 1.43Å$^{13}$ whereas at 650°C, reflections are characteristic of Mg$_3$(VO$_4$)$_2$ (3.28, 3.02, 2.55 and 2.49Å$^{34}$). The reflections due to beta-Mg$_2$V$_2$O$_7$ are not observed. As seen from the Raman spectrum, they form the minor component. Therefore, between the temperature ranges of 450-650°C, reaction between the vanadate species and the collapsed framework species are occurring. Previous studies of the thermal decomposition of the Mg$_2$Al(OH)$_6$ framework has shown that poorly crystalline MgO is formed at temperatures in excess of 500°C$^{27}$. In the presence of metavanadate, reactions schematically represented as

$$\text{MgO} + (\text{VO}_3)^n^- \rightarrow \text{Mg}_2\text{V}_2\text{O}_7 + \text{Mg}_3(\text{VO}_4)_2$$  \hspace{1cm} (3)

can proceed readily. Only the alpha-form of Mg$_2$V$_2$O$_7$ is observed, since temperatures in excess of 700°C are required to form the beta- and gamma- forms$^{30}$.

Further characterization of this system was done by
examining the vanadium XANES data for the thermally treated decavanadate-hydrotalcite samples and model systems. The x-ray absorption near-edge structure (XANES) within ~100 eV of the threshold absorption has been shown to have considerable structural information\textsuperscript{35-38}. Figure 3.6a-d shows the normalized V K-edge XANES spectra of the decavanadate-hydrotalcite samples heated to 100°, 200°, 350° and 450°C, respectively. The characteristic features of the V XANES spectrum include a pre-edge absorption (~ 0 eV) assigned to a 1s \(\rightarrow\) 3d transition. Vanadium pentoxide was used as the standard to define the origin of the pre-edge absorption peak. This dipole forbidden transition typically derives intensity by the mixing of the 3d orbitals with 4p metal and 2p ligand orbitals. This mixing is promoted by the lowering of symmetry around the vanadium atom from strictly octahedral to distorted octahedral and tetrahedral structures, respectively\textsuperscript{35}. It is clear from figure 6 that the intensity of this peak increases as the decavanadate-hydrotalcite sample is heated from 100 to 450°C, and can be correlated with the change in V geometry from distorted octahedron (\(V_{10}O_{28}^-\)) to tetrahedral structures ((VO\(_3\))\(_n^+\)) upon thermal decomposition, in agreement with the Raman studies. The small change in the peak position (0.6 eV) of this band upon thermal treatment is indicative of the retention of the +5 oxidation state during the thermal treatment. The
prominent band above the absorption edge is due to the 1s \rightarrow 4p transition and is part of the continuum, where features due to multiple scattering resonances that are sensitive to coordination geometry and interatomic distances are also observed. We have compared the edge profile for the samples at 350 and 450°C treatment with a variety of model vanadium oxide systems that have been published and find the best correlations with tetrahedral vanadate, as in NH₄VO₃ and vanadinite (Pb₅(VO₄)₃Cl)³⁵. These results are consistent with the previously discussed Raman spectra of these systems.

Discussion

From the thermal decomposition data (XRD, Raman, XANES) presented above, we can distinguish between three temperatures ranges. At temperatures below 350°C, the metal hydroxide framework remains more or less intact, but the intercalated decavanadate ion reacts with interlayer water molecules to form metavanadates. This is similar to our observations in Chapter II for the LiAl₂(OH)₆ - V₂O₇ system, in which the V₂O₇⁴⁻ was found to polymerize to metavanadates¹⁷. In both these instances, it is clear that even though the framework structure remains intact till 350°C, interlayer chemistry involving the vanadate species is beginning at temperatures as low as 100°C. This is
Figure 3.6 Vanadium K-edge XANES spectra of $V_{10}O_{28} - Mg_2Al(OH)_6$ heated to (a) 100°C, (b) 220°C, (c) 350°C and (d) 450°C.
somewhat unique to the layered metal hydroxide supports. Previous studies on alumina supports prepared by impregnation of vanadate solutions have shown that both the tetrahedral V$_2$O$_7^{2-}$ and octahedral V$_{10}$O$_{28}^{2-}$ species maintain their structural integrity until calcination temperatures of 450°C$^{39,40}$. The question then arises as to what is the cause of the thermal instability of the decavanadate ion in the hydrotalcite. The driving force for the decavanadate decomposition in the hydrotalcite can be rationalized on the basis of the high charge density of the framework and the intercalated anion. There is some controversy about the exact value of the charge density for Mg$_2$Al(OH)$_6^+$ type compounds in the literature$^{12,21,23}$. Values of 16.6 and 25 Å$^2$ per unit positive charge on the layer have been reported. For an ordered arrangement of cations in a hexagonal cell, we calculate a value of 25 Å$^2$ per charge$^{13}$. For the decavanadate anion, we estimate from the crystallographic data that a unit negative charge is distributed over an area of 15Å$^2$. Thus, in the case of the decavanadate-pillared hydrotalcite, the charge density in the interlayers is more localized than the metal hydroxide layer. The presence of high dielectric constant water molecules helps stabilize the electrostatic interactions. Thermogravimetric analysis of hydrotalcites has shown that water loss from the interlayers begins at 100° C and continues until 300° C$^{10,27}$. We propose
that this water loss brings about the chemical changes associated with the decavanadate ion. With increasing water loss from the interlayers, the decavanadate ion due to its high charge density promotes the polarization and hydrolysis of the remaining water molecules, resulting in formation of OH⁻ and H⁺ ions. The hydroxide ions are responsible for the decomposition of the decavanadate ion into lower charge density cyclic metavanadate species.

At temperatures between 350 and 450°C, the layer structure collapses but without any significant chemical reaction between the vanadate and the framework species. Thermal analysis studies of a series of hydrotalcites with varying metal ion composition have shown that dehydroxylation begins at temperatures greater than 350°C (27,28,42). In some cases, the layer structure can also be restored by rehydration, even after treatment at temperatures as high as 450°C27.

It has been recognized that at temperatures of 500°C and beyond, the framework atoms begin to form metal oxides27. In this study, we find that magnesium oxide then reacts with the metavanadate species to form specific magnesium vanadates, namely, alpha-Mg₂V₂O₇ and Mg₃(VO₄)₂.

Conclusion: The most important conclusion of this chapter is that the interlayer space in the hydrotalcite
provides a reactive environment for the polyoxometalates, even upon gentle thermal treatment. Therefore, in preparation of pillared catalytic materials using this approach, consideration needs to be given to the fact that the polyoxometalate ion may lose its structural integrity, even though the layered structure may remain intact. This study has also shown that Raman spectroscopy and XANES can provide structural information about the various intercalated and product species.
References


CHAPTER IV
SPECTROSCOPIC STUDIES OF INTERCALATION AND STRUCTURES OF MOLYBDATE IONS IN LAYERED MATERIALS

Introduction

Layered materials can intercalate various molecular species between the layers. This ability has made these materials an important candidate for creating new types of molecular architecture, since both the host matrix and guest species can be manipulated\textsuperscript{1,2}. In addition, many of these layered materials have charges on their framework. The electrostatic forces induce localized interactions within the structure and provide micro-structural control making it possible to generate well-dispersed materials\textsuperscript{2,3}. Layered double hydroxides represent an important class of layered materials. These materials consist of positively charged brucite-like layers separated by intercalated anions, and their compositions could be exemplified by $[\text{M}^{II}_{1-x}\text{M}^{III}_{x}(\text{OH})_2][\text{A}^-]^n_{\gamma/n}\text{yH}_2\text{O}$, where $\text{M}^{II}$ and $\text{M}^{III}$ represent divalent and trivalent metal ions occupied octahedral positions in the hydroxide layers and $\text{A}^-^n$ is the intercalated anion\textsuperscript{2}. In the past decade, several different molecular species have been intercalated into these materials, such as carbonate and
phosphate, and their structure and applications have been studied\textsuperscript{3,4}. More recently, polyoxometalate ions\textsuperscript{5} have been intercalated and due to the catalytic applications and the large numbers of structures that can be generated, they have attracted a lot of attention. For instances, Keggin ions\textsuperscript{6}, vanadate\textsuperscript{7} and molybdate ions\textsuperscript{8,9} have been reported. Supported molybdate catalysts are used in several applications such as metathesis, oxidation and hydrogenation of hydrocarbons and more recently hydrodesulfurization and hydrodenitrogenation of petroleum products. A wide range of spectroscopic techniques such as \textsuperscript{95}Mo NMR\textsuperscript{10}, XPS and EXAFS\textsuperscript{11} are applied for characterizing their structures in order to establish a correlation between their catalytic performance and structures. Raman spectroscopy has been used extensively in the past decade for characterizing species in solution, supported surface species and solid state materials involving molybdate species. For instances, Al\textsubscript{2}O\textsubscript{3}\textsuperscript{12,13}, TiO\textsubscript{2}\textsuperscript{14} and SiO\textsubscript{2}\textsuperscript{11}-supported molybdate catalysts have been studied. These studies indicate that supported molybdates can be divided into specific structure groups: three dimensional crystal, monomeric tetrahedral, and polymeric octahedral species. The prevalence of these structures depend on the concentration, impregnation condition, calcination and dispersion. On the other hand, more recently, supports such as MgO and SnO\textsubscript{2}\textsuperscript{10}, NiO- and CoO-promoted supported molybdate\textsuperscript{15}, and a bismuth
molybdate complex\textsuperscript{16} have been studied as catalysts and their vibrational spectra measured. Examination of these previous studies yields two conclusions. The supports play a critical role in the molybdate's surface structure, and hence their catalytic performance. The second conclusion indicates that Raman spectroscopy is a powerful technique for characterizing molybdate species because it can distinguish molybdate species of different geometries generated on various supports. We have studied the interlayer reactions, ion exchange and solid state reactions of vanadate ions intercalated into LiAl and MgAl framework. The framework interlayer offered a unique and reactive environment thereby generating which novel reactions such as dimerization, polymerization, fragmentation, and solid state reaction between the framework layer and intercalated vanadate ions\textsuperscript{17,18}. In this chapter, molybdate and heptamolybdate ions are intercalated into layered materials, LiAl\textsubscript{2}(OH)\textsubscript{6}\textsuperscript{1+} and Mg\textsubscript{2}Al(OH)\textsubscript{6}\textsuperscript{1+}, and their ion exchange reactions, interlayer reactions and solid state reaction, with the support are investigated by XRD and Raman spectroscopy.

Experimental Section

Analytical reagent grade chemicals were used for all preparations described in this work. Preparation of clay is adapted from the method by Serna et al.\textsuperscript{17} 0.05 mole of Al was
dissolved in 100ml of 2M NaOH solution. 0.25M of LiCl was dissolved in this solution and the mixture heated for 48 hours at 90°C. The products were washed with water followed by 0.1M NaCl. Care was taken to exclude CO₂ during the synthesis. Ion-exchange of the clay was carried out with saturated MoO₄⁻² solution prepared by mixing Na₂MoO₄·H₂O with water and then mixed with clay for 24 to 48 hours at room temperature. Preparation of the decavanadate pillared hydrotalcite was adapted from the procedure described by Drezdzon. To a solution of 14g of terephthalic and, 30g of NaOH and 200 ml of H₂O was added a solution of 40g of Mg(NO₃)₂·H₂O, 30g of Al(NO₃)₃·9H₂O, and 125 ml of H₂O. This mixture was heated at 90°C for 24 hours, separated by centrifugation and thoroughly washed. The exchange of the terephthalate with vanadate was carried out with a solution of 50g of Na₂MoO₄·H₂O in 100 ml of H₂O adjusted to a pH of 4.5 with 2 M HNO₃. Thermal treatment of the decavanadate-hydrotalcite samples were carried out in an oven manufactured by Technical Products Corporation. Powder x-ray diffraction patterns were obtained with a Rigaku Geigerflex D/Max 2B using nickel filtered CuKα radiation. Raman spectra were recorded with excitation from a Spectra Physics Argon Ion Laser (Model 170) and the scattered light was collected and dispersed with a Spex 1403 double monochromator and detected by a C 31034 GaAs photomultiplier tube. Typical power at the
Results:

\[ \text{LiAl}_2(\text{OH})_6\text{MoO}_4 \] : The XRD patterns of the wet \( \text{MoO}_4^{-2} \) ion exchanged samples at room temperature to 90° C, 400° C and 500° C are shown in Fig. 4.1. Fig. 4.1a, 4.1b and 1c have reflections \( 2\theta = 11.71, 20.22, 23.57 \) and \( 35.8 \) which are due to the starting material of \( \text{LiAl}_2(\text{OH})_6\cdot\text{Cl}^{-} \). Fig. 4.1a shows additional reflections \( 2\theta = 7.96 \) and 16.11 degrees, and these two reflection disappear upon drying at room temperature. These reflections are assigned to \((00l)\) \( l=1,2 \) and 3 for 4.1a, 4.1b and 4.1c, \( l=1 \) and 2 for 4.1a) reflections. The d-spacing is determined by the thickness of framework and sizes of the intercalated ions. The framework and chloride ion have been determined to be 4.8 Å and 2.8Å in size. The size of \( \text{MoO}_4^{-2} \) has been determined to be 6.2Å. Since the 7.96 degree reflection indicates the d-spacing is equal to 11.2Å and matches the combination of framework and \( \text{MoO}_4^{-2} \), it can be concluded that \( \text{MoO}_4^{-2} \) is being ion exchanged. When the temperature is raised to 400° C, no reflections are observed. This indicates that the layered feature of this material is destroyed. When the temperature is raised to 500° C, reflections due to \( \text{Al}_2\text{O}_3 \) \( 2\theta = 37.47, 45.3 \) and 65.9) and \( \text{Li}_2\text{MoO}_4 \) \( 2\theta = 18.5 \) are observed. The Raman spectra of
Fig. 4.1 Powder XRD patterns of (a) LiAl₂(OH)₆ Cl exchanged with saturated MoO₄⁻² solution and dried at (b) room temperature (c) 90°C 1 hour (d) 400°C 5 hours (e) 500°C 24 hours.
Figure 4.1
Fig. 4.2 Raman spectra of (a) 0.2M MoO$_4^{2-}$ solution (b) wet LiAl$_2$(OH)$_6$ 1/2 (MoO$_4$) and (c) dried in N$_2$ at room temperature.
Figure 4.2
Fig. 4.3 Raman spectra of LiAl$_2$(OH)$_6$ 1/2 (MoO$_4$) (a) dried at room temperature (b) dried at 90°C 1 hour (c) dried at 400°C 5 hours (d) dried at 500°C 24 hours.
these materials are shown in Fig. 4.2 and 4.3. Fig. 4.2a shows MoO$_4^{2-}$ species in solution (.2M and pH=10). The peaks at 898 and 850 cm$^{-1}$ are assigned to symmetric and antisymmetric stretching modes of Mo-O bond and 320 cm$^{-1}$ is assigned to Mo-O bending mode as pointed out by Griffith$^{24}$. Fig. 4.2a shows the Raman spectrum of the still wet product after ion exchange reaction of LiAl$_2$(OH)$_6$Cl with 10M MoO$_4^{2-}$ solution. Since this sample has been washed extensively before taking the spectrum, the possibility of surface adsorbed species can be excluded. Peaks at 898 cm$^{-1}$ are due to the Mo-O stretching of intercalated MoO$_4^{2-}$ and the peak at 600 cm$^{-1}$ is due to the Al-O$^{17}$ stretching of the framework. When the sample was dried in N$_2$ and kept in a closed cell to prevent any contact with the air during the Raman experiment, it shows the same spectrum obtained in wet form, shown in Fig. 4.2c. Fig. 4.3 shows Raman spectra of the samples being dried in air at room temperature, 90°C, 400°C and 500°C. When dried in air (Fig. 4.3a), new peaks at 918, 1047 and 1065 cm$^{-1}$, appear. These bands can be assigned to HMOO$_4^{-1}$, CO$_3^{2-}$ and HCO$_3^{-1}$ species. Upon being heated at 90°C for 1 hour, Fig. 4.3b, the peak at 918 cm$^{-1}$ disappears and the ratio between the carbonate and bicarbonate species also change slightly. When the temperature is increased to 400°C, both carbonate and framework peaks have disappeared which indicate a complete decarboxylation and delamination of the layered structure.
The diffuse peak around 900 cm\(^{-1}\) is due to the molybdate species having short range order since both Raman and XRD indicate that there is no long range crystallinity. When the temperature was raised to 500\(^\circ\)C, the Raman peaks became sharp and well resolved. The Raman results are in agreement with the XRD conclusion (that Al\(_2\)O\(_3\))\(^{26}\), which has much weaker Raman scattering is not observable in this study,) Li\(_2\)MoO\(_4\))\(^{27}\) is being generated.

\(\text{Mg}_2\text{Al-Mo}_7\text{O}_{24}\) : Ion exchange procedure of heptamolybdate ions into \(\text{Mg}_2\text{Al(OH)}_6\)\(^{2-}\) framework layer follows the method of Drezdzon\(^6\). The XRD spectra of the precursor, \(\text{Mg}_2\text{Al(OH)}_6\cdot\text{TA (TA=terephthalate anion), wet Mg}_2\text{Al(OH)}_6\cdot 1/3(\text{Mo}_7\text{O}_{24}\cdot 6^-)\) and samples after having been heated at different temperatures are shown in Fig. 4.4 Exchange of terephthalate-pillared hydrotalcite with \(\text{Mo}_7\text{O}_{24}\cdot 6^-\) ion produces a different XRD pattern that has reflections at \(2\theta = 7.60, 13.0, 16.06, 20.71\) and 29.00 degrees. These reflections have been assigned by Drezdzon to a d-spacing of 12.2Å and correspond to a \(\text{Mo}_7\text{O}_{24}\cdot 6^-\) orientation in which the \(C_2\) axis is parallel to the brucite layers\(^19\).

Raman spectra of aqueous heptamolybdate ion have been reported by Griffith\(^{24}\). Peaks at 950 and 898 cm\(^{-1}\) are assigned to symmetric and antisymmetric stretching modes of Mo-O bond, the peak at 860 cm\(^{-1}\) is due to Mo-O-Mo stretching
Fig. 4.4 Powder x-ray diffraction patterns of (a) terephthalate- Mg$_2$Al(OH)$_6$ and (b) wet Mo$_7$O$_{24}$ - Mg$_2$Al(OH)$_6$ and heated to (c) 100°C and (d) 220°C and (e) 320°C (f) 400°C (12 hours at each temperature).
Figure 4.4
Fig. 4.5  Raman spectra of (a) Mo$_7$O$_{24}$$^{6-}$ ions in solution (b) wet Mo$_7$O$_{24}$$^{6-}$ - Mg$_2$Al(OH)$_6$ and heated to (c) 200°C (d) 320°C (e) 400°C (12 hours at each temperature).
Figure 4.5
mode, and peaks at 360 and 220 cm\(^{-1}\) are assigned to Mo-O bending and Mo-O-Mo deformation modes. The intercalated species and aqueous species, shown in Figs. 4.5a and 4.5b, both show peaks at 220, 360, 898 and 950 cm\(^{-1}\) and therefore it can be concluded that intercalation of heptamolybdate ion is taking place. XRD patterns at room temperature for samples which had been heated to 100°C, 200°C, 330°C and 400°C are shown in Fig. 4.4c, 4.4d and 4.4e. For the sample heated to 100°C, the reflection at 2\(\theta\) = 7.6 degree has diminished compared with the wet sample, however, other reflections are still intact. When it is heated to 200°C, the reflections at 17.2 degree disappears. This may be due to a transformation of the heptamolybdate ion or due to disorder of the framework layer along the z-axis. Since the peaks at 14 and 22 degrees are still present the integrity of framework can be confirmed. At 320°C, Fig. 4.4e, all the features correspond to a layered structure have disappeared and hence the framework has collapsed completely.

Raman spectra at room temperature of Mg\(_2\)Al- Mo\(_7\)O\(_{24}\) are shown in Fig. 4.5 for samples heated at various temperatures. At 200°C, bands at 950 and 900 cm\(^{-1}\) are observed and these bands have the same position as in the wet samples. However, the bandwidth of the peaks for the 200°C sample have increased by a factor of 2 from 35 cm\(^{-1}\) to 70 cm\(^{-1}\). For samples at 300°C and 400°C, the spectra are very similar
Fig. 4.6 Raman spectra (a,b) and powder x-ray diffraction (c,d) of Mo₇O₂₄ - Mg₂Al(OH)₆ heated to 450°C and 700°C respectively (12 hours at each temperature)
Fig. 4.7. Phase diagram of molybdate ions in aqueous solution.
except a shift of 40 cm\(^{-1}\) to 910 cm\(^{-1}\) is observed. XRD and Raman spectra of samples after having been heated at 450°C and 700°C are shown in Fig. 4.6. The XRD patterns at both temperatures are identical and they are identified as MgAl\(_2\)O\(_4\)\(^{30}\) which has reflections \(\theta = 27.85, 36.62, 43.22\) and 63.32 degrees and MgMoO\(_4\) H\(_2\)O which has reflections \(\theta = 19.3\) and 26.3 and 26.95 degrees. Raman spectra of MgMoO\(_4\)\(^{31}\) have been reported which show peaks at 970, 959, and 912 cm\(^{-1}\) for Mo-O stretching and can be excluded. The Raman results agree with XRD and indicate that MgMoO\(_4\) is hydrated. This is due to the absorption of water during the cooling in air after heating at 450°C and 700°C.

Discussion

LiAl\(_2\)-MoO\(_4\): The distribution of molybdate ions in aqueous solution depends upon the concentrations of molybdate ions and the pH of the solution as indicated by the phase diagram shown in Fig. 4.7\(^{25}\). At 0.1M, molybdate and heptamolybdate ions are the dominant species. Their equilibria can be represented by the following equation:

\[
\text{Mo}_7\text{O}_{24}^{6-} + 8\text{OH}^- \rightleftharpoons 7\text{MoO}_4^{2-} + 4\text{H}_2\text{O}
\]

\(\text{pH}=6\) \hspace{1cm} \(\text{pH}=11\)

Ion exchange of MoO\(_4^{2-}\) ions into the LiAl\(_2\)(OH)\(_6\)^{+1}-framework
is limited to only a small percentage uptake of the molybdate ions even when a saturated, 10M, solution was used. Since it absorbs CO₂ from the air and the hydroxyl group has a similar size compared with Cl⁻⁻, it can be concluded that the Cl⁻⁻ spacing observed in the XRD pattern is partially due to hydroxide ions. Two mechanisms are attributable to the high concentration of interlayer hydroxide ions. First is the selective exchange of hydroxide ion. Although the concentration of MoO₄⁻² ion is about 10^6 higher, 10 M and 10⁻⁵ M each, it is still possible that OH⁻ ion is being exchanged into framework more favorably, since OH⁻⁻ ion has been demonstrated to have higher affinity for hydrotalcite compared with F⁻, Cl⁻, Br⁻, NO₃⁻ and I⁻.²²

Although the uptake of hydroxide ions with other dominant ions into the framework has been reported, due to the sizes and charges of molybdate and hydroxide ions, it is unlikely that the selective exchange is the only mechanism for the predominance of hydroxide and incomplete ion exchange of molybdate ions, since the hydroxide ion has been exchanged to a limited degree for several similar systems. Aqueous equilibrium of molybdate ions are dominated by monomeric and heptameric species and this are different from vanadate ions which have monomeric, dimeric, trimeric, tetrameric and decameric species.²³ Because of the high concentration of the hydroxide groups within the framework, the ion exchange of
the molybdate ions has been limited. The second mechanism is based on the interlayer reactions of MoO$_4^{2-}$ ion which, occupying the edge and preventing any further ion exchange, serves as a catalyst to deliver the hydroxide ion into framework layers. Because of the presence of OH$^-$ and HMoO$_4^-$ which is not stable in aqueous solution and shows in the room temperature dried sample only, the following interlayer reactions are proposed:

\[
\text{MoO}_4^{2-} \text{(edge)} + \text{H}_2\text{O} \rightarrow \text{HMoO}_4^- \text{(edge)} + \text{OH}^- \text{(edge)}
\]

\[
\text{OH}^- \text{(edge)} \text{ replace Cl}^- \text{(inside framework)}
\]

\[
\text{HMoO}_4^- \text{(edge)} + \text{OH}^- \text{(eq)} \rightarrow \text{MoO}_4^{2-} \text{(edge)} + \text{H}_2\text{O}
\]

On the other hand, the framework of LiAl$_2$(OH)$_6$ 1/2 MoO$_4^{2-}$ collapses at room temperature, as shown in Fig. 4.2. This behavior is completely different than carbonate, chloride, and vanadate intercalated materials$^{2,17,18}$. Their framework integrity is preserved even at 300°C, as can be observed in Fig. 4.2, since reflections at $2\Theta = 11.71, 23.59$ and $35.8$ are not affected. Because of their limited ability to ion exchange, it can be concluded that molybdate ions occupy the edge of the framework layers and block any further exchange. When the sample is dried at room temperature, the dehydration
causes these MoO$_4^{2-}$ ions to form polymeric species in the framework layers. However, since the molybdate ions do not form any species such as dimeric and trimeric ions, and heptamolybdate ions are not allowed equilibrium in at this pH range and concentration, the molybdate ions react with the framework upon dehydration and this results in the reaction between Li$^+$ and MoO$_4^{2-}$, to Li$_2$MoO$_4$ as observed in Fig. 4.1c, (2θ= 18.5 degree$^\circ$). These complexes migrate out of the framework layer and cause delamination of the framework in the area where molybdate ions have intercalated and other areas which do not have intercalated molybdate ions are not affected. This mechanism has not been reported before since none of the hydrotalcite materials have been shown to delaminate at such a gentle treatment. However, structural changes induced by a gentle drying treatment which causes the framework to lose its ability to conduct ion exchange reaction or lead to pore blockage were thought to be responsible$^{26}$. This pore blockage mechanism presents a similar interaction as compared with the molybdate ion. It is not clear yet why the MoO$_4^{2-}$ ion are selectively located along the edge since other ions with different sizes, charges and charge densities, such as$^{2,4,17}$ Cl$^-$, C$_6$H$_5$COO$^-$, Fe(CN)$_6^{3-}$, CO$_3^{2-}$, V$_2$O$_7^{4-}$ and V$_4$O$_12^{4-}$ have all been reported to be able to ion exchange into the LiAl$_2$(OH)$_6^{4-}$-framework layer completely. Kaszentan et al$^{20}$, compared the impregnation at different pH
values and concluded that the monomeric molybdate ion is easily washed away by aqueous solution compared with heptamolybdate ion generated at low pH values. This might explain the low ion exchange capability because ion exchange reaction may proceed initially via adsorption on the framework surface. Fig. 4.3a shows a peak at 918 cm⁻¹, which has also been identified as HMoO₄⁻ when being supported on Al₂O₃¹³,¹⁵. However, it has not been observed in aqueous solution and its limited stability could preclude its presence upon heating to 90°C. Two reports in the literature have observed a similar spectra to Figure 4.3a. Jeziorowski et al assigned the band at 918 cm⁻¹ to Mo=O stretching of distorted MoO₄²⁻ species bound to the heterogeneous support surface in varying local environments¹³. In contrast, a similar spectrum on Al₂O₃ obtained by heating at 100°C for 24 hours has been assigned to HMoO₄⁻¹ by Grimblot¹⁵. In this study, HMoO₄⁻¹ only shows transitional stability being supported on the LiAL₆(OH)₆⁺-layer. Since HMoO₄⁻¹ is generated simultaneously with HCO₃⁻¹, it can be concluded that the second interpretation is more reasonable and this also suggests that the basicity on HMoO₄⁻¹ is similar to HCO₃⁻¹. When the temperature is increased to 400°C both the carbonate and the framework peaks disappear which indicate the generation of an amorphous mixture of Al, Li and molybdate species. The solid state reactions can be summarized as
follows:

\[ 2 \text{LiAl}_2(\text{OH})_6 \frac{1}{2} (\text{MoO}_4) \rightarrow 2 \text{Al}_2\text{O}_3 + \text{Li}_2\text{MoO}_4 + 6 \text{H}_2\text{O} \]

\text{Mg}_2\text{Al-}\text{Mo}_7\text{O}_{24}: \text{Raman spectra of aqueous heptamolybdate ion and intercalated species are shown in Fig. 4.5a and 4.5b. The position and width of the 950 cm}^{-1} \text{ peak for aqueous and intercalated ions does not show any significant difference, which proves the existence of intercalated heptamolybdate ion. When being heated at 100°C and 200°C, Fig. 4.4c and 4.4d show only two strong reflections at } \theta = 15 \text{ and } 22 \text{ degrees and the reflection at } \theta = 7.6 \text{ degree has disappeared. Since no intermediate species exist between monomeric and heptameric ions in aqueous solution, the disappearance of heptamolybdate ion is an indication that a fragmentation reaction is being induced by the heating at 200°C. Further heating at 300°C and 400°C produce XRD patterns without any structural features and hence it can be concluded that delamination of the layered structure has generated amorphous material. Although the XRD pattern offers framework information, it does not allow any insight into the interlayer reaction. There have been many studies on the aqueous, supported and solid state molybdenum compounds in the past. Whether the bands are due to dimeric or heptameric species is still unclear because of the overlap of the peaks}
at 900 and 950 cm\(^{-1}\) and the fact that dimeric ions are not stable in aqueous solution. The Raman spectrum of the 200° C sample shown in Fig. 4.5c shows bands at 900 and 950 cm\(^{-1}\). In addition to that the bandwidth of the 200° C sample has increased by a factor of two, from 35 to 70 cm\(^{-1}\). This transition certainly is not brought about by the dehydration since it only removes a small percentage of the overall water\(^2\). Although dimeric species has long been known to be unstable in aqueous solution\(^{23}\), their presence on various supports have been proposed, and these supported dimeric molybdate ions have diffuse bands at 950 and 900 cm\(^{-1}\) and these features are in agreement with the results obtained here\(^{12,13}\). Between 200° C and 400° C, the dimeric bands do show about a 10 cm\(^{-1}\) shift and increase of band width. Both are due to the dehydration from the heating, no other structural change is observed. Pinnavia\(^{21}\) has reported the ion exchange and the thermal treatment of \([\text{Mo}_6\text{Cl}_{8}(\text{H}_2\text{O})_{6-n}(\text{OH})_n]^{(4-n)^+}\)-pillared-montmorillonite which transforms into \(\text{MoO}_3\) distributed nonuniformly on both the internal and external surface of the clay. The clay collapses at 300° C. In this study, no \(\text{MoO}_3\) peaks are observed which would show up at 1000 and 820 cm\(^{-1}\).\(^{13,15}\) On the other hand, supported \(\text{Mo}_7\text{O}_{24}^{6-}\) ions undergo similar reactions even supported on different supports when being heated. They generate both \(\text{MoO}_4^{2-}\) and \(\text{MoO}_3\) when heated at 400° C to 500° C\(^{12,13,15}\). This is different
compared to intercalated $\text{Mo}_7\text{O}_{24}^{6-}$ which transforms into dimeric species and then to $\text{MgMoO}_4\cdot\text{H}_2\text{O}$. The instability of heptamolybdate ion within the framework is in agreement with the results of decavanadate study. However, due to the lack of other intermediate species, dimeric molybdate ions cannot transform into other polymeric species like the vanadate ions. When the framework collapses at 400°C, the dimeric ions are transformed into $\text{MgMoO}_4\cdot\text{H}_2\text{O}$. These reactions can be summarized as follows:

\[
\text{at } 200^\circ\text{C} \quad 2 \text{Mo}_7\text{O}_{24}^{6-} + 2 \text{OH}^- \rightarrow 7 \text{Mo}_2\text{O}_7^{2-} + \text{H}_2\text{O}
\]

\[
\text{at } 450^\circ\text{C} \quad \text{Mg}_2\text{Al(OH)}_6\cdot\text{Mo}_2\text{O}_7 \rightarrow \text{MgO} + \text{MgAl}_2\text{O}_4
\]

\[
\text{MgO} + \text{Mo}_2\text{O}_7^{2-} \rightarrow \text{MgMoO}_4(\text{H}_2\text{O})
\]

For decavanadate ion which is stable on regular support, it is observed that at 160°C it decomposes into $\text{V}_3\text{O}_9^{4-}$ and $\text{HVo}_4^{2-}$ when intercalated in the MgAl-layers. Further heating promotes polymerization of the initial fragmentation products and generates polymeric vanadate species.

**Conclusion:**

Ion exchange, interlayer and solid state reactions of $\text{LiAl}_2(\text{OH})_6\cdot\frac{1}{2}(\text{MoO}_4)$ and $\text{Mg}_2\text{Al(OH)}_6\cdot\frac{1}{6}(\text{MoO}_7\text{O}_{24})$ have been studied by Raman spectroscopy and XRD. The limited uptake of
MoO$_4^{2-}$ ions by the LiAl$_2$(OH)$_6$-framework is due to the high concentration of OH$^-$ ions inside the framework. These OH$^-$ ions are transferred by the interlayer reactions of MoO$_4^{2-}$ which occupies the edge of the layered framework. Because of the strong affinity between Li$^+$ and MoO$_4^{2-}$ and lack of a polymeric molybdate intermediate between MoO$_4^{2-}$ and Mo$_7$O$_{24}^{6-}$, Li$_2$MoO$_4$ is formed at room temperature and causes the delamination of the LiAl$_2$(OH)$_6$-framework. Thermal treatment of LiAl$_2$(OH)$_6$ 1/2 (MoO$_4$) at 500°C generates Li$_2$MoO$_4$ and Al$_2$O$_3$. Mg$_2$Al(OH)$_6$ 1/6 (Mo$_7$O$_{24}$) undergoes interlayer reactions at 200°C and transformed into Mo$_2$O$_7^{2-}$ within the framework. Upon being heated at 400°C, the framework collapses and MoO$_4^{2-}$ is generated. From 450°C to 700°C, solid state reactions between the framework and MoO$_4^{2-}$ generate MgAl$_2$O$_4$ and MgMoO$_4$. By combining XRD and Raman spectroscopy, clear molecular pictures of the structures and dynamics of these materials are established.
References:


CHAPTER V
RAMAN SPECTROSCOPIC STUDIES OF THE SYNTHESIS OF
FAUJASITIC ZEOLITES: COMPARISON OF TWO SILICA SOURCES

Introduction

Faujasitic like zeolites, synthesized in the laboratory are denoted as zeolites X and Y and are distinguished by the Si/Al ratio of an otherwise identical framework. For frameworks of Si/Al with ratios between 1-1.5, the zeolite is called X and for values greater than 1.5, it is typically called zeolite Y. The distinction between these forms is partly historical and also stems from the fact that the typical synthesis procedures are quite distinct.\(^1,2\) Both these zeolites are commercially very useful, in ion-exchange processes and as catalysts in a wide variety of petroleum related processes.\(^3,4\)

In this chapter, we focus on a spectroscopic examination of the mechanism of synthesis of these two zeolites, starting with two of the most common commercial silica sources: Ludox and N-Brand. The goal here is to examine both the reactivity and the formation of intermediate species as the silicate species react with Al(OH)\(_4\). Dutta et al have pioneered the development of
Raman spectroscopy to examine zeolite crystallization process. In previous studies, we have separated the solid and liquid phases and examined them independently, typically after washing the solid phase. This was required because of the high background levels observed for the solid phase. However, in this study, due to improvement in the Raman technique, we were able to examine the gel phase directly during the crystallization process without any sample pretreatment. Examination of the gel phase provides simultaneously the spectrum from both the solid and solution phase, since the gel is composed of solution species trapped in the solid.

There have been many previous studies on formation of faujasitic zeolites, regarding the influence of silica source, nucleation kinetics and other crystallization parameters. A spectroscopic study emphasizing multinuclear NMR techniques has been used to examine the formation of zeolite Y. However, spectroscopic examination of the zeolitic growth process as a function of silica source has not been reported previously in the literature.

Experimental Section

Chemicals - Two types of silica sources were used in zeolite X and Y synthesis. The first one was Ludox LS manufactured by Dupont and contains 30.0% SiO₂ and 70% of
water. The second source was N-Brand (PQ Corporation) which contains 29.5% SiO₂, 8.8% Na₂O, and the balance water. Sodium aluminate and sodium hydroxide were purchased from Chem Service and Baker Chemical Co.

Zeolite X, Y synthesis - For zeolite X, a solution containing 40 g of NaAlO₂, 54g of NaOH and 755g of H₂O was added to 209 g of N-Brand solution. The two solutions were combined while stirring to form a homogeneous mixture. The resulting gel crystallized while in a steam bath at 95°C for 47 hrs. When using Ludox, 200 g of silica solution was used to replace the N-Brand solution.

For zeolite Y, a solution containing 5.82g of NaAlO₂, 180g of H₂O, and 37g of NaOH were added to 200g of Ludox. The two solutions were combined while stirring to form a homogeneous mixture. The resulting gel was aged at room temperature in a polypropylene jar for 24 hrs, then crystallized on a steam bath at 95°C for 50 hrs. When N-Brand was used, the water content and sodium hydroxide were adjusted so that the overall composition was the same as the Ludox preparation.

Several batches of reaction mixtures were prepared and at various times during the aging and crystallization process, samples were removed, and centrifuged at 1000 rpm for 20 to 30 mins to separate the solution phase. After centrifugation, the solid gels were used for Raman
The Raman Spectra were obtained with a Spex 1403 spectrometer controlled by a Spex Datamate computer. Excitation of all samples was done with the 457.9 nm radiation from a Spectra-Physics Ar-ion laser. The scattered light was detected with a RCA-C31034 GaAs PM tube. Slit widths of the monochromator were typically 6 cm⁻¹ and scanning rate varied between 1-3 seconds per wave number. Spectracalc was used to correct the background due to the Rayleigh scattering. Powder X-ray diffractions pattern were obtained with a Rigaku Geigerflex D/Max 2B diffractometer with a Ni-filtered CuKα source. Elemental analysis was done by X-ray fluorescence using a Kevex 0700 instrument.

Results

The experimental data on zeolite X and Y are treated in separate sections, followed by a comparison of these systems in the Discussion section. The Raman spectroscopic studies, in all instances, were carried out on the gel phase. This was typically obtained by centrifuging the reaction mixture, which results in separation of a solid and solution phase. The solid phase, referred to as the gel, also contains trapped solution species. Therefore, Raman spectroscopic examination of the gel, in principle, provides information
Figure 5.1. Raman spectra of the gel phase during zeolite X crystallization from Ludox. Spectra are of (a) Ludox solution and reaction mixture heated to 95°C for (b) 0 hour (c) 2.5 hours (d) 5.5 hours (e) 8 hours (f) 12 hours.
Figure 5.1
Figure 5.2. Raman spectra of the gel phase during zeolite X crystallization from N-Brand. Spectra are of (a) N-Brand solution and reaction mixture heated at 95°C for (b) 0 hour (c) 3 hours (d) 12 hours and (e) 14 hours.
Figure S.2
about both the solid and solution phases. The basis for distinguishing these phases in the Raman spectra arises from our earlier studies of silicate and aluminate solutions, and will be discussed, as appropriate.16,17

Zeolite X - A typical synthesis procedure for zeolite X involves rapid mixing of a silicate and aluminate source, both of which may contain alkali, followed by immediate heating at 95°C. In this study, two sources of silicon were examined: Ludox, a colloidal silica solution and N-Brand, a sodium silicate solution. In both these cases, a certain volume of the solution containing equivalent amount of silicon were added to identical solutions of sodium aluminate in NaOH. The initial composition for Ludox and N-Brand preparations was 0.243 \( \text{Al}_2\text{O}_3 \) 1 \( \text{SiO}_2 \) 0.91 \( \text{Na}_2\text{O} \) 49 \( \text{H}_2\text{O} \) and 0.243 \( \text{Al}_2\text{O}_3 \) 1 \( \text{SiO}_2 \) 1.20 \( \text{Na}_2\text{O} \) 49 \( \text{H}_2\text{O} \), respectively. The higher \( \text{Na}_2\text{O} \) concentration in the N-Brand preparation arises from the NaOH present in the sodium silicate solution.

Figures 5.1 and 5.2 show the Raman spectra of the gel obtained after various periods of heating the Ludox and N-Brand preparations, respectively. The initial spectrum of the Ludox solution (Figure 5.1a) is characterized by a broad band centered at 440 cm\(^{-1}\), a sharp shoulder at 485 cm\(^{-1}\) and bands at 793 and 978 cm\(^{-1}\). The first three bands are all characteristic of vitreous \( \text{SiO}_2 \),18 whereas the 978 cm\(^{-1}\) band
has been assigned to Si-OH stretching vibrations. These spectral bands are in agreement with the well-known structure of Ludox as consisting of particles of SiO₂ of diameter of 30 nm (30 wt %). The presence of the 978 cm⁻¹ band indicates that the surface of these particles are covered with -OH groups. The aluminate solution is characterized by a band at 620 cm⁻¹ due to Al-OH stretching of the Al(OH)₄⁻ ion. The spectral pattern obtained after mixing the Ludox with aluminate solution is shown in Figure 1b. The broad Raman band in the 400-500 cm⁻¹ region arising from the framework vibration of SiO₂ is still present. However, the Si-OH band at 978 cm⁻¹ has disappeared. The sharp band at 620 cm⁻¹ is due to unreacted Al(OH)₄⁻ trapped in the gel. The solid formed upon initial mixing of the Ludox and aluminate solution is then best described as SiO₂ spheres surrounded by an Al(OH)ₓ sheath. Elemental analysis of similar preparations in the literature have reported Si/Al ratios of ~30. The band at 1068 cm⁻¹ is due to CO₃²⁻ formed by the reaction of NaOH in the gel with ambient CO₂ during the recording of the Raman spectrum. This can be prevented by using an anaerobic cell, but with considerable loss in signal to noise from the already poorly scattering gel samples, and was therefore avoided. The reaction of the excess NaOH in the gel with CO₂ is not expected to influence the aluminosilicate species present. Figure 5.1c shows the
spectrum of the gel obtained after 2.5 hours of heating at 95°C. New bands at 496, 590, 777, 935 and 1004 cm⁻¹ are observed. Along with the shoulder at ~450 cm⁻¹, the bands at 590, 777, 935 and 1004 cm⁻¹ are all characteristic of monomeric and dimeric silicate ions, indicating that the Al coated SiO₂ particles formed upon initial mixing has dissolved, reacted with Al(OH)₃ to generate an aluminosilicate solid and released excess monomeric and dimeric silicate ions in solution.¹⁶ The band at 496 cm⁻¹ is representative of the solid phase and has been assigned previously to v₅ (T-O-T) vibrations characteristic of disordered four-membered aluminosilicate rings.⁵ Upon heating for 5.5 hours, the band at 505 cm⁻¹ becomes prominent, along with a band at 778 cm⁻¹ due to the monomeric silicate species. Further heating leaves the spectrum unchanged, except for an improvement in signal and the shift of the prominent band to 510 cm⁻¹, characteristic of that for zeolite X. Figure 5.3a,b shows the powder X-ray diffraction patterns obtained from the Ludox samples after 5.5 and 8 hours of heating. Zeolite crystals are only apparent after 8 hours of crystallization time. However, the Raman spectrum after 5.5 hours of heating clearly indicates the formation of the basic zeolite X framework (505 cm⁻¹ band). For powder diffraction patterns to appear, the zeolite
Figure 5.3. Powder X-ray diffraction patterns of Ludox composition heated to 95°C for (a) 5.5 hours (b) 8 hours and (c) N-Brand composition heated for 12 hours.
Figure 5.3

2-theta (degree)
crystals must reach an minimum size of ~ 200 Å. The Raman spectrum, on the other hand, provides localized information. Yet, the sensitivity of Raman spectroscopy is low with typical cross-sections of $10^{-32} \text{m}^2 \text{sr}^{-1}$, which implies that the number density or concentration of the Raman scattering species has to be high.\(^2\) Thus, we conclude that for the sample heated for 5.5 hours, a considerable fraction (1-5 wt%) of the aluminosilicate solid is made up of zeolite X nuclei.

Figure 5.2 shows the Raman spectra of gel at various stages during the synthesis of zeolite X using N-Brand as the source for silicon. As expected, the Raman spectrum of the N-Brand silicate solution (Figure 5.2a) is quite distinct from that of Ludox (Figure 5.1a). The spectrum is characterized by a strong band at 1040 cm\(^{-1}\) due to Si-O\(^-\) arising from polymeric silicate species. The band at 521 cm\(^{-1}\) in the Si-O-Si bending region is close in frequency to the ring breathing mode of trimeric cyclic silicate species (530 cm\(^{-1}\)).\(^16\) In addition, bands at 430, 600, 781 cm\(^{-1}\) are characteristic of monomeric and dimeric silicate species. The spectrum changes considerably upon reacting with aluminate as shown in figure 5.2b. In contrast to the Ludox system, no evidence for excess aluminate ion is observed, indicating immediate incorporation of Al(OH)\(_4\) into the aluminosilicate solid. The bands at 595, 780, 932 and 1021
can be assigned to monomeric and dimeric silicate species trapped in the gel. The broad band centered at 500 cm\(^{-1}\) is arising from the solid phase, and is indicative of four-membered aluminosilicate rings.\(^5\) Figures 5.2c-d show the Raman spectrum of the gel after heating for 3, 12 and 14 hours at 95°C. Diffraction patterns characteristic of zeolite X are observed after 12 hours of heating (Figure 5.3c). After 3 hours of heating, the Raman spectrum is best represented as an aluminosilicate solid composed of, random four-membered aluminosilicate solid (498 cm\(^{-1}\)) in contact with mostly monomeric silicate ions (450, 780, 927 cm\(^{-1}\)). The first evidence of zeolite X crystals in the Raman spectra appear after 12 hours of heating (505 cm\(^{-1}\)).

Comparison of the Ludox and N-Brand preparation for zeolite X indicate the following: (a) the initial reaction between the silicate and aluminate sources is different for N-Brand and Ludox, although upon heating for 2-3 hours they produce similar solid and solution state species; (b) the solution species are intimately mixed with the solid phase throughout the nucleation period and early stages of crystallization. This indicates that the solid phase is considerably porous and traps the solution species. With the formation of zeolite crystals, the retention of soluble species decreases. (c) Zeolite X is formed from the Ludox system at earlier times than from the N-Brand system even
though the latter system is considerably more basic. Also, the Raman spectrum shows the formation of zeolite X nuclei in the Ludox preparation well before XRD indicates its formation. In the case of N-Brand, these times are comparable.

Zeolite Y - The general synthetic procedure followed for zeolite Y was to mix the silicon and aluminum containing reactants, age the system for 24 hours, followed by crystallization at 95°C. The aging step appears to be an important part of this synthesis procedure. Similar to our studies on zeolite X, two preparations involving Ludox and N-Brand as silicon sources were examined. Zeolite Y was formed with Ludox as evidenced by both the Si/Al ratio (2.2) and diffraction pattern (zeolite X and Y are readily distinguished by examining the 2 theta region between 50-60°). However, the N-Brand preparation led to the formation of zeolite P. Considering that this difference could be arising from the excess NaOH in the N-Brand, the procedure was repeated with N-Brand with a composition identical to that for the Ludox system, by adjusting the NaOH concentration of the aluminate solution (final composition: 1.74 Na₂O 0.13 Al₂O₃ 3.53 SiO₂ 62 H₂O). In this case, too, zeolite P was formed. Below we have focused on why these two systems, with identical overall compositions and similar procedures result in the formation of different zeolitic
Figure 5.4. Raman spectra of the gel phase during zeolite Y crystallization from Ludox. Spectra are (a) Ludox, and reactant mixture aged at room temperature for (b) one hour (c) 6 hours (d) 12 hours and then heated to 95°C for (e) 3.5 hours (f) 13 hours and (g) 18 hours.
Figure 5.4
Figure 5.5. Raman spectra of the gel phase during zeolite P crystallization from N-Brand. Spectra are (a) N-Brand, and reactant mixture aged at room temperature for (b) 1.5 hours (c) 6 hours and heated at 95°C for (d) 5 hours (e) 9 hours (f) 12 hours (g) 14 hours and (h) 17 hours.
Figure 5.5 WAVENUMBER
Figure 5.4 a-d show the Raman spectra of the gel during the aging of the Ludox samples. Within an hour of aging, the bands characteristic of the Ludox (440, 490, 795 cm\(^{-1}\)) and the Si-OH groups (978 cm\(^{-1}\)) are lost. Instead, a broad band at 450 cm\(^{-1}\) due to the aluminosilicate solid with monomeric silicate ions (771 cm\(^{-1}\)) are observed. Six hours of aging promotes further solubilization of silicate species, with evidence of dimeric silicates (603 cm\(^{-1}\)) and Si-O\(^-\) (1039 cm\(^{-1}\)) from oligomeric silicates as well as the 450 cm\(^{-1}\) due to the aluminosilicate solid. The ring breathing modes of the oligomeric silicates at 433, 490 and 530 cm\(^{-1}\) are obvious in the 12-hour aged sample. No bands characteristic of the solid phase are evident. This spectral pattern dominates the spectrum till the appearance of zeolite Y crystals (503 cm\(^{-1}\)) after 18 hours of heating. The high concentration of silicon in this preparation results in a high concentration of silicate species in the gel that precludes the observation of the solid phase in the Raman spectrum after aging for 12 hours.

The Raman data for the N-Brand system identical in overall composition to the Ludox system but which results in zeolite P formation is shown in Figure 5.5. The presence of monomeric, dimeric and oligomeric silicate species (450, 600, 780 and 1038 cm\(^{-1}\)) are present at the initial stages of
aging (1-6 hours). A band at -500 cm⁻¹ due to the aluminosilicate solid is also apparent. Upon heating the aged samples, the spectral pattern of the gel is characterized by soluble silicate species and resembles the Ludox preparation. Zeolite P crystals are evident, both in the powder diffraction pattern and Raman spectrum (424, 490 cm⁻¹) after 14 hours of heating.

Similar to the zeolite X system, it is of interest to note that the trapped soluble silicate species in the gel are released as crystals begin to appear.

The spectral differences between Ludox and N-Brand preparations are only apparent in the first hours of the aging process. Beyond this time, the spectra are dominated by the solution species trapped in the gel. This is not surprising since the silicate concentration is very large. As discussed above for zeolite X, the initial reaction between the silicate and aluminate species is different in the case of Ludox and N-Brand. The question then arises is whether these differences translate into the formation of different microstructures for the aluminosilicate species in the solid.

Since the solution species are similar in the two systems during the crystallization process, the structure of the solid phase of the gel must be influencing the nucleation of the two different zeolites. A similar model
Figure 5.6. Powder X-ray diffraction patterns of zeolites synthesized from the N-Brand composition with added tetramethylammonium chloride (a) TMA⁺/Na⁺ = 1:2 (b) TMA⁺/Na⁺ = 3:2
Figure 5.6

2-theta (degree)
has been discussed in the literature, based on elemental analysis.\textsuperscript{16} Clearly, since the compositions are identical, the only difference in the structure of the solid phase can arise from the local ordering of the Si and Al atoms. The Raman spectroscopic studies indicate that the initial structure of the solid phase from which the nuclei ultimately evolve are different. However, it could be expected that given enough time, these structures should become similar and reach an equilibrium state through the depolymerization-polymerization process. Since the aging process provides a mechanism for restructuring the gel, the N-Brand and Ludox systems were aged for periods extending to 21 days. Zeolites Y and P were still formed from the Ludox and N-Brand system, except that zeolite Y crystallization took longer heating times. Extensive aging is therefore only very slowly restructuring the solid phase.

In another set of experiments, we tried to influence the structure of the solid phase, especially the position of the Al atoms by electrostatic factors. This was accomplished by the addition of tetramethylammonium (TMA\textsuperscript{+}) chloride to the N-Brand preparation. Figure 5.6 shows the powder diffraction patterns as a function of increasing TMA\textsuperscript{+}/Na\textsuperscript{+} ratio. The TMA\textsuperscript{+} does promote the formation of zeolite Y crystals from the N-Brand preparation to a certain degree. The quality of crystals were poor, even after
extended periods of heating. We propose that the bulky TMA favors a different siting for the Al atoms in the solid phase due to steric reasons, which lead to the nucleation of zeolite Y.

Discussion

The two interrelated aspects of this chapter include the influence of the silicon source at a fixed overall reactant composition on the formation of zeolites (Ludox and N-Brand in case of formation of Y and P) and the formation of different zeolites as a function of the concentration of a reactant (Ludox in the case of X and Y and N-Brand in the case of X and P).

The spectroscopic data indicate that the initial reaction between the silicate species and Al(OH)₄ depends on the nature of the silicon source, and is quite distinct for N-Brand and Ludox. A schematic diagram of this process as derived from the above spectroscopic data is shown below, Figures 5.7 and 5.8, for the two silicon sources:

Ludox

The following points are relevant in drawing up the above scheme: (a) The initial rapid dissolution of Ludox SiO₂ in the case of zeolite X synthesis proceeds by hydrolysis of SiOSi bonds by OH⁻ ions. The Si-OH linkages thus formed are
Fig 5.7 Mechanism of Ludox for zeolite Y.
Figure 5.7
capped off by reaction with Al(OH)$_4$ resulting in an aluminosilicate solid. This reaction proceeds until all the aluminate is consumed, and therefore depends on the Si/Al ratio of the starting composition.

(b) In the case of zeolite Y synthesis, an aging step is necessary. The Raman spectrum of Ludox resembles very closely that of vitreous silica, which contains networks of four, five six and higher membered rings.\textsuperscript{22} We propose that during the aging step, aluminum is incorporated into these silicate networks. The broad Raman band at ~450 cm$^{-1}$ in the six hour aged sample is assigned to such species. Support for Al incorporation into the SiO$_2$ network is also provided by the presence of excess monomeric and oligomeric silicates (771, 1039 cm$^{-1}$) in the six hour aged samples. These species react rapidly with soluble aluminates. Polak and Cichoki also report a significant drop in the soluble aluminolate species during aging of zeolite Y.\textsuperscript{14}

(c) Since the Raman spectrum of the gel at later stages during the zeolite Y synthesis are dominated by soluble silicate species, we are unable to obtain information about the structure of the solid phase. Since washing away the solution species alter the structure of the solid phase, this experiment was not attempted. In an earlier study of zeolite Y,\textsuperscript{7} in which the gel samples were washed to remove the soluble species, we noted that the solid phase in the
earlier stages of synthesis resembles nepheline glass, which is thought to be made up of six-membered aluminosilicate rings.\textsuperscript{23}

(d) The four membered aluminosilicate rings formed in the gel of zeolite X evolve to form nuclei and crystals. However, this spectroscopic study does not provide any information about the connectivity of these building blocks.

N-Brand

(a) N-Brand is a concentrated sodium silicate solution which contains a variety of silicate ions in dynamic equilibrium. \textsuperscript{29}Si NMR studies indicate the presence of cage-like polysilicate species along with typical monomeric, dimeric, trimeric and tetrameric species.\textsuperscript{24} Reaction with aluminate ions leads to rapid incorporation of the aluminum into the silicate framework resulting in the formation of aluminosilicate solids with four membered rings (\~{}500 cm\textsuperscript{-1} band). We have shown two of the many possible ways for reaction of Al with the silicate structure, resulting in four membered aluminosilicate solids. The Raman spectrum of N-Brand indicates, that, in addition to monomeric, dimeric and tetrameric silicate species, trimeric structures (\~{}520-530 cm\textsuperscript{-1}) are also prominent. This is in agreement with NMR studies, and forms the basis of our representation of
Fig. 5.8 Mechanism of N-brand for zeolite Y.
Figure 5.8 Mechanism for N-brand for zeolite Y.
N-Brand as trimeric-cage like species.

(b) Another route for formation of aluminosilicate solid arises from the reaction of monomeric silicate ions and $\text{Al(OH)}_4^-$. This is due to the fact that addition of siloxane linkages increases the overall acidity i.e. $\text{Si(OH)}_4 < \text{SiOSi(OH)}_2 < \text{SiO}_2\text{Si(OH)}_2 < \text{SiO}_3\text{SiOH}$ thus making $\text{Si(OH)}_4$ the most nucleophilic. As the monomeric silicate ions are consumed, the polymeric silicate ion equilibria will shift resulting in formation of simpler oligomers. The incorporation of aluminum is therefore very rapid, since it is a solution phase reaction, unlike that in Ludox. The Raman spectroscopy indicates that the solid phase formed by this reaction consists mostly of four membered aluminosilicate rings ($\sim 500 \text{ cm}^{-1}$).

(c) We have indicated two different intermediate building blocks for zeolites X and P, though Raman spectroscopy is incapable of distinguishing between them. The basis for this scheme is that with the increase in concentration of aluminate, zeolite X is formed. In order to lend credence to this hypothesis, a series of gel aging experiments using mixtures of Ludox- and N-Brand - containing gels were monitored by X-ray diffraction. These syntheses and the observed zeolitic phases are summarized in Table 5.1. Freshly prepared Ludox- and N-Brand containing gels (containing both aluminate and silicate species with
Scheme 5.1

Gismondine - type

Faujasite - type

\[ \text{o-Al} \]

\[ \rightarrow \ Y \]

\[ \rightarrow \ P \]

Scheme 5.2
composition 1.86 Na₂O 0.13 Al₂O₃ 3.53 SiO₂ 59 H₂O), as described in the Experimental Section were mixed after various aging times at room temperature. These aged gel mixtures were then heated at 95°C. As can be seen from Table 5.1 zeolite P dominates the product selectivity whenever N-Brand gel is present. However, zeolite Y is obtained under conditions which may shed some light on the underlying mechanism.

When 10 minutes aged Ludox-containing gels (LG) are mixed with similarly aged N-Brand-containing gels (NG) and heated, zeolite P is the only product. Only when freshly prepared Ludox-containing gels are mixed with N-brand-containing gels, which have been aged at various times prior to mixing, is zeolite Y observed. When one hour aged NG is mixed with LG and heated, zeolite P is crystallized. But a mixture of zeolites Y and P are obtained by heating a mixture of LG and a 3 1/2 hour aged N-Brand-containing gel. Furthermore, when the aging time for the NG is increased to 7 hours, then mixed with LG and heated, zeolite Y is the primary product obtained.

We propose that the reason zeolite P is formed with N-brand - with indications of P as early as 10 minutes after mixing - is that the undulating tetrameric Si-O chains which are the important building units of the gismodine structural type of P are immediately formed by reaction of aluminate
with the sodium silicate solution.

As the concentration of these tetrameric species is reduced via Al incorporation to yield P nuclei, another reaction path can also begin to influence the zeolitic phase selectivity as LG is added to this NG mixture. This pathway arises from the reaction of monomeric silicate species in NG which are stabilized by high pH, with Al(OH)$_3$ from the Ludox preparation to yield zeolite X nuclei. Under these conditions then, two types of nuclei are present. Lechert et al., have shown that under conditions in which zeolite X seeds are added to a reaction mixture that forms zeolite P, zeolite Y is the product.$^{25}$ The crystallization of zeolite Y via zeolite X nuclei as seeds is also well established.$^{26}$ As the Al is consumed and the Si/Al of the reacting species increases by incorporation of SiO$_2$ from the Ludox preparation, zeolite Y is formed. The observation that after 7 hours of aging zeolite Y is present is consistent with this model.

It is quite clear that the initial reactions between the Al(OH)$_3$ and the silicate species depends to a large degree on the source of silicon. The structures initially formed ultimately determine the zeolite formed. In an earlier paper, we had proposed that related zeolites evolve from similar yet unique building blocks$^9$ e.g. The motivation for this model grew from the fact that different
zeolites can readily be formed from similar reaction mixtures,\(^9\) as has been documented for zeolites X and P.\(^{27}\)

The stabilization of these units depends on (a) electrostatic factors e.g. minimization of repulsion between Al atoms, (b) initial local ordering of Si and Al atoms as the aluminosilicate gel is formed from different reactants, and (c) the size and charge of the neutralizing cation. For example, the formation of faujasitic zeolite (Si/Al=2) over P will be stabilized by structures shown in Fig. 5.10, since the Al-OH groups cannot condense with each other. This may explain how the addition of TMA\(^+\) to a N-Brand preparation helps nucleate faujasitic zeolites by promoting both the formation of six membered rings and the para arrangement of Al atoms due to steric effects resulting from the bulky cation.

Conclusion: This chapter has shown that the initial reaction between the aluminate and silicate sources depend on the nature of the reactants and can result in (a) formation of different aluminosilicate structures such as zeolite Y from Ludox and zeolite P from N-Brand for systems with identical composition and (b) influences the nucleation process as in the rapid formation of zeolite X nuclei in the case of Ludox as compared to N-Brand.
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CHAPTER VI
SPECTROSCOPIC EXAMINATION OF THE FORMATION
OF MORDENITE CRYSTALS

Introduction

Zeolites with the mordenite-type framework are important in various adsorption and catalytic applications. The crystal structure of mordenite has been examined by Meier, and consists of sheets of five and four membered aluminosilicate rings. The interconnection of these rings results in two parallel channels of twelve and eight membered rings having the dimensions 6.7 x 7.0 Å and 2.9 x 5.7 Å, respectively. These channels are interconnected via small side pockets of diameter of 2.9 Å.

The synthesis of mordenites has been recently reviewed by Bajpai. Various silicon and aluminum containing reactants, including natural sources have been used for the synthesis of mordenite type zeolite. The two important parameters are the SiO$_2$/Al$_2$O$_3$ ratio and the pH of the starting composition, as is typical of most zeolite synthesis. The SiO$_2$/Al$_2$O$_3$ ratio of mordenites usually range from 9 to 12. Higher ratios up to 20 can be obtained by carefully adjusting the Na$_2$O/SiO$_2$ ratio of the reactant.
mixture. Siliceous mordenite can also be synthesized in the presence of organics such as tetraethylammonium or diethylpiperidinium ions, with SiO₂/Al₂O₃ ratios reaching 40.  

Other materials that form competitively along with mordenite are analcime, phillipsite, ZSM-5 and quartz. Only a few studies have been reported on the mechanism of crystallization of mordenite. These were limited to the study of the kinetics of the synthesis process, and the influence of reactant composition on the SiO₂/Al₂O₃ ratio of the product. Bodart et al., have studied the liquid and solid precursors and intermediate species during mordenite synthesis by ²⁷Al and ²⁹Si NMR spectroscopy. They concluded that the formation of mordenite crystals proceeded through soluble aluminosilicate species obtained by dissolution of the amorphous phase.  

In this chapter, we report the first Raman spectroscopic study of the mordenite crystal growth process for an inorganic and organic preparation. Specifically, by using Raman spectroscopy and x-ray diffraction, we have focused on the following issues:

- the structure of the gel phase during nucleation, and its evolution into the zeolite;
- nature of interaction between the organic species and the gel framework during zeolite formation;
Experimental Section

For the inorganic preparation \textsuperscript{11}, a solution of sodium aluminate in NaOH was added to colloidal silica (Ludox AS 30 from DuPont), with extensive stirring. The gel composition was \(3 \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 13.1\text{SiO}_2 \cdot 22\text{H}_2\text{O}\) and the pH was measured to be \(\sim 11\). The mixture was heated in Teflon lined autoclaves to 190°C. Different batches of identical reaction mixtures were heated for various times as indicated in the text. Upon quenching the reaction, the mixture was centrifuged and the wet solid phase was directly examined by Raman spectroscopy and x-ray diffraction.

For the organic preparation \textsuperscript{11b}, an alkaline silicate solution (N-Brand from PQ Corporation) was added to a mixture of \(\text{Al}_2(\text{SO}_4)_3\), \(\text{H}_2\text{SO}_4\) and tetraethylammonium bromide (TEA\textsuperscript{+}Br\textsuperscript{−}). The resultant gel composition was \(7.38\text{Na}_2\text{O} \cdot 1\text{Al}_2\text{O}_3 \cdot 24.7\text{SiO}_2 \cdot 3.41\text{TEABr} \cdot 597\text{H}_2\text{O}\). The mixture was heated in Teflon lined autoclaves to 120°C. As in the inorganic preparation, a set of Teflon lined Parr bombs with identical reactant compositions were heated to various times, quenched and examined by spectroscopic methods.

The powder diffraction patterns were obtained using a
Rigaku Geigerflex D/Max 2B diffratometer with a nickel filtered CuKα source. The Raman spectra were obtained using radiation of 457.9 nm from an Argon-ion laser (Spectra Physics 171). Power at the sample was ~20mW. A Spex double monochromator (Spex 1403) was used to discriminate against scattered radiation. The Raman light was detected using a Ga-As PMT with photon counting. Typical slit widths were 6 cm⁻¹ and scanning times ranged from 1-3 seconds per wavenumber. The background from the Rayleigh scattering in the low-frequency Raman spectra was removed Spectracalc programs.

Results and Discussion

The results of the inorganic mordenite preparation are discussed first, followed by the organic mordenite and the vibrational band analysis of the framework.

Inorganic Preparation

In the inorganic preparation, Ludox colloidal SiO₂ was reacted with Al(OH)₄ at a pH of ~11. Figure 6.1 shows the room temperature Raman spectra of the gel phase obtained during the crystallization process at 190°C. Ludox is a colloidal suspension of SiO₂ particles of diameter of 30 nm. The Raman spectrum of this material shown in Figure 6.1a is characterized by bands at 440, 485 and 793 cm⁻¹ and is
Figure 6.1. Raman spectra of gels obtained during synthesis of mordenite from an inorganic preparation. (a) Ludox, (b) - (e) reaction mixture heated for 4, 12 and 20 hours, respectively.
Figure 6.1

WAVENUMBER
Figure 6.2 Raman spectra of gels obtained during synthesis of mordenite from an inorganic preparation. (a) 27 hour (b) 40 hour (c) 67 hour and (d) 72 hours.
Figure 6.2
typical of vitreous silica. In addition, there is a band at 978 cm\(^{-1}\) due to the Si-OH groups on the surface of the SiO\(_2\) particles. The spectrum of the gel formed upon immediate mixing of the reactants is shown in Figure 6.1b. A broad band centered at 450 cm\(^{-1}\) and arising from the SiO\(_2\) network is observed. Unreacted Al(OH)_4\(^{-}\) retained in the gel gives rise to the band at 620 cm\(^{-1}\). The band at 978 cm\(^{-1}\) due to the Si-OH groups of the SiO\(_2\) disappears upon interaction with aluminate, indicating that initial incorporation of aluminum occurs by reaction of surface Si-OH with Al(OH)_4\(^{-}\). The sharp band at 1060 cm\(^{-1}\) arises from the CO\(_3\)^{2-} ion. After the reaction mixture has been heated for 4 hours, the 620 cm\(^{-1}\) band due to Al(OH)_4\(^{-}\) is no longer observed, indicating that all the aluminum (as detected by Raman spectroscopy) has been incorporated into the aluminosilicate solid. Raman bands characteristic of soluble monomeric, dimeric and other oligomeric silicate species (450, 500, 530, 600, 780 cm\(^{-1}\)) are not observed. This is a reflection of the low pH of the reaction mixture. In a previous study of silicate solutions by Raman spectroscopy, we have shown that soluble silicate species are not detected in the Raman spectrum below a NaOH concentration of 0.1 M. The solubility of silica at pH ~11 corresponds to 0.05 M, whereas the typical detection limits for spontaneous Raman spectroscopy are in the 0.1 M
range. Therefore, the observed bands in Figure 6.1c at 495, 800, 895 and 1025 cm\(^{-1}\) are all characteristic of the solid part of the gel phase. This spectral pattern remains essentially unchanged until the synthesis has proceeded for 20 hours. At that time, broad bands appear at 402 and 465 cm\(^{-1}\), in addition to the 495 cm\(^{-1}\) and the 1030 cm\(^{-1}\) band. The broad bands at 402 and 465 cm\(^{-1}\) sharpen to 400 and 471 cm\(^{-1}\), upon 27 hours of heating (Figure 6.2a). The bands at 495, 900 and 1030 cm\(^{-1}\) are still observed at this time. After 40 hours of heating this initial set of bands disappears, and the bands at 400, 450, 471, 817, 1047 and 1160 cm\(^{-1}\) remain. All these bands become prominent with increasing times of crystallization. Figure 6.3a-c shows the x-ray diffraction pattern obtained from the gel phase after crystallization times of 4, 20 and 40 hours. The formation of zeolite crystals are only apparent after 27 hours of heating. Therefore, the first 20 hours defines the nucleation period. At the early stages of this period (4-12h) the Raman spectra of the gel is characterized by bands at 495, 800, 900 and 1030 cm\(^{-1}\). In earlier publications, we have discussed the assignments for the Raman spectra of amorphous aluminosilicate solids present during zeolite crystallization by comparison with published data for minerals \(^{17,18}\). The band at 495 cm\(^{-1}\) is characteristic of \(v_s\), (T-O-T) vibrations of four membered aluminosilicate rings
Figure 6.3. X-ray powder diffraction patterns of samples obtained from the inorganic mordenite preparation after (a) 4 hours (b) hours and (c) 40 hours of heating.
Figure 6.3
in solids, and was observed in the Raman spectra during the early stages of synthesis of zeolite A, X and P. The difference between these systems and the present mordenite synthesis is the lower pH, which should result in an increased degree of connectivity of the Si chains attached to the Al. Thus, we can schematically represent the amorphous aluminosilicate in the mordenite preparation, shown in Scheme 6.1. The bands at 900 and 1030 cm\(^{-1}\) arise from Si-O stretches of nonbonded oxygen atoms.

After 12 hours of heating, only minor changes are observed in the spectrum, such as a narrowing of the 495 cm\(^{-1}\) band by 10 cm\(^{-1}\). The most significant changes occur after 20 hours of heating, well before the appearance of crystals in the X-ray diffraction patterns (27 hours). These changes include the appearance of broad Raman bands at 402 and 465 cm\(^{-1}\), which upon further heating emerge as sharp bands characteristic of the mordenite framework. Clearly, we are observing an intermediate "mordenite-like" structure in the evolution from the four membered aluminosilicate gel to the crystal. The broadness of the 402 and 465 cm\(^{-1}\) peaks indicates that the structures responsible for these bands are considerably disordered even though on average, mordenite-like units are present. As discussed later, bands at 470 and 400 cm\(^{-1}\) are assigned to the (T-O-T) modes of the four and five membered rings, respectively. This would
Scheme 6.1

\[ a - Al \]

\[ (Si)_n \quad (Si)_n \quad n > 1 \]

490 cm\(^{-1}\) 470, 400 cm\(^{-1}\)

Scheme 6.2
indicate that the four membered rings initially present in the amorphous gel are undergoing changes in structure (495 to 470 cm\(^{-1}\)) as they accommodate the five membered rings (400 cm\(^{-1}\)) around them. For example, structural changes such as depicted in Scheme 6.2 could cause these spectroscopic changes.\(^{20}\)

The broadness of the peaks arises from the disordered environment around these building blocks, giving rise to a distribution of T-O-T angles. Also, since the sensitivity of spontaneous Raman spectroscopy is low, it is clear that a significant concentration of these units will have to exist to make it possible to observe the Raman bands. We propose that these "mordenite-like" building units are dispersed throughout the solid phase and the formation of crystals involves the proper orientation and connection between these units. This appears to be a rapid process since mordenite crystals are observed within another 7 hours of heating. It is also of interest that the Raman spectroscopy indicates that the initial gel consists of four membered aluminosilicate rings, which are ultimately incorporated into the crystal, as shown above. This is in agreement with the current understanding of the structure of mordenite, in which it is thought that the Al atoms are preferentially located in the four membered rings, with double occupancy of these rings being favored \(^{21-23}\). This
results in SiO₂/Al₂O₃ ratio similar to that observed of the mordenite framework to be ~10, for the preparation used in this study.

Organic Preparation

The synthesis of mordenite using organic reagents has been reported in the literature as a route to make materials with SiO₂/Al₂O₃ ratio approaching 40²⁶. We have examined the system formed by reacting Na silicate (N-Brand) with aluminum sulfate and TEABr at 120°C. The reaction proceeded for 192 hours and the gel phase examined periodically during the crystallization process.

Figures 6.4a-c and the corresponding inserts a'-c', show the Raman spectra of a solution of TEABr(0.1 M), crystalline TEABr, and a fully crystalline mordenite sample, respectively. The vibrations due to the aluminosilicate framework of mordenite are marked as 'M' on Figure 6.3c; the rest of the bands arise from the TEA+. There are slight differences in intensities and splitting patterns between the TEA+ in solution and crystals (380, 675, 3000 cm⁻¹ bands), presumably due to crystal packing effects. However, the spectrum of the trapped TEA+ in mordenite is almost identical to that in solution, indicating that perturbation of the quaternary ammonium by the mordenite framework is minimal. This mechanism is quite distinct from the
Figure 6.4. Raman spectra of (a) TEABr in solution (0.1 M) (b) mordenite crystals grown in the presence of TEABr. M corresponds to framework vibrations of mordenite. (a' - c') corresponding spectra in the 2800 - 3100 cm⁻¹ region.
Figure 6.4
tetrapropylammonium in ZSM-5, which undergoes a major change in conformation in order to be accommodated in the zig-zag channels of the zeolite. In the case of TEA⁺ in mordenite, the size of the cation (6.5 - 7.5 Å) would indicate that it is being held in the puckered 12-ring channels (6.7 x 7.0 Å). The -CH₃ end of the ethyl groups can protrude into the interconnecting channels of dimension 2.9 Å, which connect the parallel 12 and 8 membered channels. There appears to be enough room around the TEA⁺, and therefore the vibrational spectrum resembles that of free TEA⁺ during the zeolite synthesis and does not provide any information about the crystallization process, unlike that of ZSM-5.

Figures 6.5 and 6.6 show the Raman spectra of the gel during the zeolite crystallization process. The bands observed in the material upon initial mixing (Figure 6.5a) can all be assigned to the TEA⁺ cation (compare with Figure 6.4a) and the sulfate ion (980 cm⁻¹). No bands characteristic of aluminosilicate species are observed. Figure 5b shows the spectrum from the gel after 24 hours of heating at 192°C. Besides the clear indication that the sulfate ion is being excluded from the gel, new bands are also observed at 360, 390, 460, 490, 600, 780 and 1030 cm⁻¹ and are indicated on the figure. These bands could be arising from both solution and solid phases in the gel. The
Figure 6.5. Raman spectra of gels obtained during crystallization of mordenite from an organic preparation (a) 0 hour (b) 24 hour (c) 68 hour.
Figure 6.6. Raman spectra of gels obtained during crystallization of mordenite from an organic preparation (a) 144 hours (b) 168 hours and (c) 192 hours (6a'). Difference spectra of TEAOH and TEA-silicate solution.
Figure 6.6 WAVEHUMBER
insert in Figure 6.6 (a') shows a difference spectrum between a solution of TEA'OH' and TEA+ silicate ([Si]=1 M). The bands at 600, 780 and 1030 cm⁻¹ are characteristic of monomeric and dimeric silicate species. These same bands are appearing in the gel spectrum after 24 hours of heating and can be assigned to solubilized silicate species trapped in the gel. The remaining bands in the 300-600 cm⁻¹ region are assigned to the solid phase, and for the sake of clarity, have been replotted in Figure 6.7. The prominent band at 418 cm⁻¹ is due to the TEA+, which also has a weak band at 387 cm⁻¹ as seen for the 0-hour gel spectrum in Figure 6.7a. The mordenite crystals exhibit framework bands at 396, 445 and 467 cm⁻¹ as shown for the 192-hour sample in Figure 6.7g. Upon heating the reaction mixture for 24 hours (Figure 7b), bands characteristic of the mordenite framework appear at ~390 and ~470 cm⁻¹. There is also considerable intensity at ~490 cm⁻¹ due to disordered four membered aluminosilicate rings (as was observed in the inorganic synthesis). The Raman spectrum in the 300-600 cm⁻¹ region remains unchanged till 168 hours of heating, and only for the 192 hour sample, the band at ~490 cm⁻¹ due to disordered aluminosilicate rings are not observed. The XRD in Fig. 8 shows the presence of zeolite crystals only after 192 hours of heating.

What is most interesting about the spectra of the
Figure 6.7. Raman spectra in the 300 - 600 cm$^{-1}$ region for gels obtained at various times during the crystallization of mordenite from organic preparation. (a) through (g) correspond to crystallization times of 0, 24, 68, 96, 144, 168 and 192 hours, respectively.
Figure 6.8. X-ray diffraction patterns of gels obtained from mordenite in an organic preparation at (a) 168 and (b) 192 hours.
Figure 6.8
samples between the 24 and 168 hours treatment is the appearance of bands at 390 and 470 cm\(^{-1}\) characteristic of the framework of mordenite. Actual crystals, however, are only observed after 192 hours of heating. In the inorganic preparation, it was noted that zeolite crystals are formed subsequent to the appearance of the 'mordenite-like' units in the gel phase. This raises the question as to why in the organic preparation, do the mordenite crystals take so long to form, even though the building blocks are apparent after only 24 hours of heating. It is difficult to unambiguously answer this question based on this study. However, it is a general observation for many zeolite systems, that the synthesis of the higher Si/Al ratio material takes longer times as in ZK-4 compared to A, or zeolite Y compared to X and other systems 25. The SiO\(_2\)/Al\(_2\)O\(_3\) ratio in the organic mordenite preparation was found to be ~16. It will be important in these cases to preserve the nuclei of the particular zeolites long enough so that crystals can be formed. A role for the organic molecule could be to stabilize these nuclei over extended period of times. Stabilization could be promoted by the prevention of OH\(^-\) attack on the nuclei by means of an organic envelope created by the TEA ions associated with the structure. This organic cladding may also serve a role in promoting spatial ordering of these "mordenite-like" building units via organo-organo
interactions. Further experiments will be needed to confirm these hypotheses.

Mordenite Framework Vibrations

The vibrations of the mordenite aluminosilicate framework are similar for both the inorganic and organic preparation and are characterized by bands at 395, 445, 470, 817, 1047 and 1160 cm$^{-1}$. The vibrations above 1000 cm$^{-1}$ are characteristic of Si-O stretching modes, as observed in SiO$_2$.$^{12}$ In the frequency range of 300 - 600 cm$^{-1}$, we have established empirical correlations between the frequency of the Raman bands and the ring sizes and T-O-T angles.$^{19,25}$ According to this correlation, four membered rings exhibit bands in the 450 - 550 cm$^{-1}$ region and five membered rings in the 350 - 450 cm$^{-1}$ region. Based on this model, the band at 390 cm$^{-1}$ in the mordenite framework can be assigned to five membered rings and the prominent band at 470 cm$^{-1}$ to four membered rings. We have also examined a series of zeolites having four membered ring and found that as the average T-O-T angle increases the Raman band characteristic of the T-O-T bend decreases in frequency.$^{26}$ Based on this correlation the average T-O-T angle of the four membered rings of mordenite would correspond to larger angles as compared to typical zeolites such as zeolites A and faujasite.$^{26}$
Conclusion: We have established the following characteristics of mordenite synthesis and structure:

a) in the inorganic preparation, four membered aluminosilicate rings formed in the initial stages evolve to produce disordered mordenite - like building units consisting of five and four membered rings, which connect rapidly to form mordenite crystals;

b) in the organic preparation, mordenite - like structures are formed in the early stages of nucleation and remain so for extended periods of time before zeolite crystals appear;

c) the Raman spectrum of the aluminosilicate framework of mordenite shows bands characteristic of five and four membered rings.

Further studies are continuing on the differences in crystallite size, distribution of Al atoms across the crystal and their sining for the inorganic versus organic mordenite synthesis.
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