





THESIS

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THE INTERCALATION AND CONVERSION OF NIOBIUM, TANTALUM, AND MOLYBDENUM CLUSTER CATIONS TO INTER-LAYER OXIDES AS A NOVEL ROUTE TO PILLARED MONTMORILLONITES, AND MOLYBDENUM CLUSTER BINDING TO PROTON EXCHANGED ZEOLITE Y presented by

Steven Patrick Christiano

has been accepted towards fulfillment of the requirements for

Ph.D. degree in Chemistry

ofessor

J. PINNAVAIA THOMAS

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THE INTERCALATION AND CONVERSION OF NIOBIUM, TANTALUM, AND MOLYBDENUM CLUSTER CATIONS TO INTERLAYER OXIDES AS A NOVEL ROUTE TO PILLARED MONTMORILLONITES, AND MOLYBDENUM CLUSTER BINDING TO PROTON EXCHANGED ZEOLITE Y

By

1

Steven Patrick Christiano

An Abstract of a Dissertation

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

ABSTRACT

THE INTERCALATION AND CONVERSION OF NIOBIUM, TANTALUM, AND MOLYBDENUM CLUSTER CATIONS TO INTERLAYER OXIDES AS A NOVEL ROUTE TO PILLARED MONTMORILLONITES, AND MOLYBDENUM CLUSTER BINDING TO PROTON EXCHANGED ZEOLITE Y

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The research presented in this dissertation demonstrates that a novel method for synthesizing metal oxide pillared montmorillonites was developed. This synthesis utilizes intercalated metal cluster cations as pillar precursors; converting them to metal oxide props <u>in situ</u> by calcination under vacuum.

Intercalation of the mixed oxidation state cations $Nb_6Cl_{12}^{2+,3+}$ and $Ta_6Cl_{12}^{2+,3+}$ into Na^+ -montmorillonite was performed through aqueous ion exchange reactions. Ion exchange isotherms and sodium release measurements were made. Intercalates containing $Nb_6Cl_{12}^{2+,3+}$ (33 mmoles/100 g silicate) and $Ta_6Cl_{12}^{2+,3+}$ (23 mmoles/100 g silicate) were characterized by chemical analysis and ESR, UV-visible and infrared spectroscopy. X-ray diffraction indicated d_{001} spacings of 18.4±0.2 Å and 18.3±0.3 Å for these intercalates, respectively.

Calcination of the intercalates at 120-130°C (24 h)

and 240° (24 h) decomposed the metal clusters to interlayer M_2O_5 (M=Nb and Ta) deposits. A reaction scheme showing the hydrolysis and oxidation of the intercalated clusters is proposed. The niobium and tantalum oxide pillared clays formed possessed surface areas of 63 and 70 m²/g. The interlayer spacings of ~9.5 Å were maintained up to 400° and 350°, respectively.

A cationic molybdenum cluster, formed at pH 1.5 after the argenometric precipitation of the terminal chlorides of $(Mo_6Cl_8)Cl_4\cdot 2H_2O$, was intercalated into Na⁺-montmorillonite by ion exchange. A plot illustrating sodium release upon cluster binding is given. The intercalate containing 53.6 mmoles of $Mo_6Cl_8(OH)_{2.7}(OH_2)^{1.3+}_{3.3}$ per 100 g of silicate was characterized by chemical analysis and by UV-visible and infrared spectroscopy. X-ray diffraction indicated a d₀₀₁ spacing of 16.6 Å.

Calcination of this intercalate at 130° (24 h), 200° (24 h), and 280° (24 h) decomposed the cluster. A reaction scheme involving the hydrolysis and oxidation of the intercalated cluster is proposed. A biphasic system was formed containing collapsed smectite and MoO₂OH interlayered clay, which possessed an interlamellar separation of 3.4 Å and was stable to 300°.

The pH dependent binding of $Mo_6Cl_8(OH)_n(OH_2)_{(6-n)}^{(4-n)+}$ to H⁺-Y was investigated. Binding was strongly dependent of the exchange form of the zeolite. Approximately 3% Mo was bound while a high degree of zeolite crystallinity was maintained. A binding scheme which involves cluster protonation by zeolite H^+ ions is proposed. To Pat and Mary, Marsha and Lisa, my wonderful family. To my good friend Jack. Especially to Sue, who stood by me through the many evenings of writing. Without your love and support I could not have completed this work.

Mere words cannot express the love that I have for you.

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LIST OF ABBREVIATIONS

Abbreviation	Description
bipy	Bipyradine
DMF	N,N-Dimethylformamide
DMSO	Dimethylsulfoxide
DSC	Differential Scanning Calorimetry
ESCA	Electron Spectroscopy for Chemical Analysis
ESR	Electron Spin Resonance
ICP	Induction Coupled Plasma
phen	<u>o</u> -Phenathroline
Y	The aluminosilicate frame- work of a faujasitic zeo- lite; [(AlO ₂) _{53.97} , (SiO ₂) _{138.03}] ^{53.97} -

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I. INTRODUCTION

A. Foundations of Catalysis

Catalysis has grown to assume tremendous importance in the large scale production of chemicals and petrochemicals. Recently, the area has received heightened interest due to the ability of catalysts to increase the rate and selectivity of a reaction, which allows for lower operating temperatures and pressures. This holds considerable economic impact in view of our limited energy and feedstock resources.

In general, a catalyst is a substance which influences the rate of a chemical reaction, by affecting the kinetic barrier to reaction, but is not itself consumed in the process. Catalysts are described as being either homogeneous or heterogeneous based on their physical state of dispersion during reaction. Homogeneous catalysts are evenly dispersed, as gases or as compounds soluble in the reaction medium. Heterogeneous catalysts are solids under reaction conditions, with the chemical conversion of reactant molecules occurring at the solid/gas or solid/liquid interfacial surface of the catalyst. There are many important examples of industrial processes utilizing each type of catalyst.

There are several homogeneous catalytic processes of industrial significance. The Wacker process¹⁻³, for example, utilizes a soluble Pd/Cu catalytic system in the production of acetaldehyde by the oxidation of ethylene. The Oxo process⁴⁻⁶ makes use of a cobalt or rhodium carbonyl catalyst in the hydroformylation of an α -olefin containing n carbon atoms, to yield an aldehyde of (n+1) carbon atoms. The Monsanto process⁷ utilizes a methyl iodide promoted rhodium catalyst to produce acetic acid at 99% selectivity, through the carbonylation of methanol. The Oxirane process⁹ produces propylene oxide by using soluble molybdate compounds to catalyze the oxidation of propylene by organic peroxides.

The majority of commercial catalytic processes utilize heterogeneous catalysts, however. Some of these processes are operated on a vast scale. For example, the oxidation of sulfur dioxide to the trioxide is carried out over a silica supported vanadium oxide catalyst. This process allows for the production of greater than 80 billion pounds of sulfuric acid per year⁸. The synthesis of ammonia from hydrogen and nitrogen gases is carried out over a reduced, promoted iron catalyst at 450°C and high pressure^{11c}. Approximately 38 billion pounds of ammonia was produced by this process in 1981 worldwide⁸.

The petroleum industry relies very heavily upon heterogeneous catalysis to carry out complex hydrocarbon

conversions. Catalytic cracking¹⁰, hydrocracking¹¹, hydrodesulfurization (HDS)¹², and reforming¹³, are among the more important catalytic steps involved in the upgrading of crude oil to give high yields of lighter distillates and high octane gasoline blends. Approximately 5 million barrels of crude oil can be processed in the United States per day^{10a}.

There are many other catalytic processes used commercially today, but the examples above serve to illustrate the massive scale of operations. In addition, they illustrate the fundamental catalytic functionalities of reduction/oxidation, hydrogenation and acid/base catalysis.

The past 30 years has seen a great increase in catalytic research, much of which is devoted to the development of new catalytic processes. Fundamental to this effort is the search for new materials which would serve as catalysts or as catalyst supports¹⁴. The development and testing of new catalytic materials is essential to the future growth of catalysis.

B. Smectite Clay Minearls; Structure and Catalysis

Recently, work has refocused attention on layered silicates, especially the swelling philosilicates, known as smectite clays, as catalysts or catalyst support materials. The structure of the smectite clay mineral montmorillonite is illustrated schematically in Figure 1-1¹⁵.

·



Figure 1-1. The structure of the smectite clay mineral

montmorillonite.

The open circles represent oxide ions, the shaded circles are hydroxide ions, and the sinusoidally lined circles are water molecules coordinated to the interlayer cations, M^{2+} . Substitutions within the octahedral layer are indicated.

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Smectite clays are composed of negatively charged silicate layers which, in the natural form, are intercalated by alkali or alkaline earth cations. The silicate layers are structurally composed of four sheets of oxide or hydroxide anions. These anions construct two layers possessing tetrahedral coordination geometry with a layer of octahedral geometry condensed between them through shared oxide ions. Hydroxide ions complete the structure of the octahedral layer. These hydroxides are not shared between the layers, but reside at the bottom of hexagonal rings formed by tetrahedral units on the silicate interlayer surfaces. This clay structure is described as being a 2:1 layered structure based on the tetrahedral to octahedral layer ratio.

In montmorillonite, the tetrahedral sites are occupied mainly by silicon (IV) ions and the octahedral holes are two-thirds filled by aluminum, magnesium, or ferric ions. This clay is described as being dioctahedral due to the two-thirds fractional occupancy of the octahedral sites. Isomorphous substitutions within the layers, such as Mg^{2+} for Al³⁺ within the octahedral layer, or Al³⁺ for Si⁴⁺ within the tetrahedral layer, will impart a net negative charge on the lattice. This charge is balanced by the presence of interlayer cations.

Solvent molecules coordinated to the interlayer cations and adsorbed on the silicate interlayer surfaces will swell

the structure in a direction perpendicular to the plane of the layers. This solvent swelling will allow for the total exfoliation of Na⁺-montmorillonite in aqueous solution. The interlayer cations may be substituted with a wide variety of other cations utilizing ion exchange techniques¹⁶.

Historically, clays have found large scale use as heterogeneous catalysts in petroleum processing. Acid treated montmorillonites, and later halloysites and kaolinites, were used as petroleum cracking catalysts beginning in the 1930's¹⁷. Reduced nickel and iron supported on hydrofluoric acid treated montmorillonites were used as hydrocracking catalysts¹⁸ in England and Germany during this period. Acid treated clays have also been utilized as catalysts for polymerization^{19,20} and aromatic alkylation²¹.

More recently, Pinnavaia²² and coworkers have utilized the unique properties of solvent swelled layered silicates containing transition metal compounds as catalysts. These materials were shown to catalyze a variety of reactions such as the hydrogenation of alkenes²³, alkynes^{24,25}, and dienes²⁶, asymmetric hydrogenations²⁷, and the hydroformylation of α -olefins²⁸. In these reactions surface chemical equilibria and spacial restrictions within the clay interlayer played a major role in controlling reaction selectivity. Recently, hectorite intersalates containing

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metal chelate complexes have been shown to possess activity as triphase catalysts²⁹.

Thomas³⁰ and coworkers have reported a number of proton assisted reactions of organic molecules with transition metal exchange forms of smectites. The conversion of alkenes to dialkyl ethers³¹, dehydration of primary alcohols to produce dialkyl ethers³², the conversion of thiols to dialkyl sulfides³³, and reactions of primary amines to form secondary amines³⁴ have been reported. Other workers have also reported similar catalytic results utilizing transition metal exchanged smectites³⁵ and synthetic swelling clays¹⁸.

C. The Chemistry of Pillared Clays

Pillared clays are layered silicates which have been modified through the intercalation of robust cations. The large interlayer cations act as molecular props, which maintain separation of the silicate layers in the absence of swelling solvent. This creates a material possessing an extensive two-dimensional interlayer pore structure, as shown schematically in Figure 1-2. These materials possess large intracrystalline surface areas suitable for molecular adsorption and catalysis.

Early pillaring experiments by Barrer and coworkers³⁶ dealt with the intercalation of alkylammonium ions into montmorillonite. These bulky cations propped the silicate

E



Silicate Sheet

Metal Oxide Pillar

Figure 1-2. A schematic diagram of a metal oxide pillared

clay.

This edge-on view shows the presence of highly dispersed intercalated metal oxide which props the silicate sheets apart thus creating permanent interlayer pores. These pores may exist as an extensive 2-dimensional network.
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layers apart creating permanent interlayer separations of 4 to 4.5 Å and markedly improved the diffusive and sorbtive properties of the host silicate. The absence of appreciable hysteresis in the desorbtion of adsorbed O_2 , N_2 , Ar, and paraffins, indicated the ease of access to the interlayer in these compounds 37. Layer work by Shabtai³⁸, and independently by Mortland³⁹, utilized the intercalation of sterically ridged cations, such as 1,4diazabicyclo[2,2,2]octane (DABCO), or 1,4-diaminoadamantane to achieve interlayer spacings of approximately 5 Å. The intercalation of metal chelate cations, $M(Chel)_3^{2+}$ (where M equals Fe, Ni; Chel equals phen or bipy) by Loeppert et al.⁴⁰, produced pillared montmorillonites possessing interlayer spacings of about 8 Å. These materials are limited in their thermal stabilities (150-350°) due to the presence of organic components, however.

The most thermally stable, and thus, most promising pillared clay systems for catalytic applications, are those utilizing clusters or chains of inorganic oxides as molecular props. As shown by Endo, <u>et al</u>.⁴¹, clays interlayered with silica can be synthesized through the hydrolysis of intercalated tris(acetylacetonato)silicon (IV) cations. This pillared clay possesses excellent thermal stability (>500°), but the interlayer spacing was low (\sim 3.0 Å), corresponding to only one layer of siloxane polymer.

A more common preparative method for pillared clays utilizes the ion exchange of polynuclear metal hydroxy

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cations formed in aqueous solutions into sodium smectites. Calcination of the intercalates thus formed, yields the metal oxide pillared clays. Table 1-1 lists some of the inorganic pillaring species utilized to date, and some of the physical characteristics and thermal stabilities of the metal oxide pillared clays formed. The alumina pillared clay, for example, possesses an interlayer spacing of approximately 7-10 Å and stability to greater than 550°. This material possesses a surface area of between 500 and $200 \text{ m}^2/\text{g}$ depending on the loading of the pillaring ion. Variable loading has reportedly 45,46 been utilized to control the intrapillar distances in these materials. This variability allows for the controlled formation of pores possessing laterial dimensions averaging from 8-30 $Å^{46}$, which can be designed to suit a particular application.

Pillared clays, expecially the alumina and zirconia systems, have been tested for catalytic activity. For example, the alumina and zirconia pillared clays have been shown to possess the ability to crack middle weight petroleum fractions⁴⁴. Alumina pillared clays are also active toward the dealkylation of cumene and β -isonaph-thalene⁴⁵.

D. Research Objectives

Although the exchange reaction of smectite clays with polynuclear metal hydroxy cations is a promising route to

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Pillaring Species	Basal Spacing,	Max. Reported Temp. of Stability, oC	Surface Area, m ² /g	Refs.
[A1 ₁₃ 04(0H) ₂₄ (0H ₂) ₁₂] ⁷⁺	17	>550	500-200 ^b	44,42 46,47
[Zr4(0H)]4).mH20] ²⁺	18	500	300-400	43,44
[cr _x (0H), .mH ₂ 0](3x-y)+ ^a	16.8	>200°	280	48
(S10 ₂) _x	12.6	>500	220	Τη
[N1 _x (OH) _y .mH ₂ O] ^{(2x-y)+^a}	15	300	2	64
[B16(OH)16] ²⁺	16	>200°	80	50
^a The values x and y are u	unknown at this	time.		

^bSurface area is variable with dependence on pillar loading.

Table 1-1. Metal Oxide Pillared Clays.

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pillared clay synthesis, the process is quite dependent on the aqueous chemistry of the metal ion used to form the props. The aqueous chemistry of many transition metal ions is not amenable to this procedure due to the lack of formation of a sufficiently large cationic species.

An alternate route to pillared clay formation which circumvents this limitation is the use of metal cluster cations as pillar precursors. This unique approach would involve the electrostatic binding of metal cluster cations to the clay interlayer and their subsequent modification <u>in situ</u> to yield metal oxide pillars. This method could potentially provide better defined interlayer oxide props and, more importantly, would serve to move the pillaring process beyond the confines of aqueous metal ion chemistry. This would expand the number of transition metal oxide pillared clays available for study.

The objective of this study is to utilize metal cluster cations as precursors to metal oxide props in the formation of pillared clays. This major objective can be viewed as being comprised of four intermediate goals. (1) Develop an understanding of the novel metal cluster cation-smectite clay interaction, and to utilize this in the formation of metal cluster intercalate precursory materials. (2) Design and optimize a reaction scheme which will carry out the necessary <u>in situ</u> reaction of the metal cluster to yield an intercalated metal oxide.

(3) Characterize the physical and chemical properties of the pillared clays formed. (4) Investigate this approach in a general way, utilizing several metal cluster cations, in order to assess the general viability of this synthetic strategem.

E. The Chemistry of Metal Clusters

Molecules containing polyhedral groupings of three or more metal atoms possessing intermetallic bonding are defined 51 as metal cluster compounds. The metal cluster compounds, $(Nb_6Cl_8)Cl_2 \cdot 8H_2O$, $(Ta_6Cl_{12})Cl_2 \cdot 8H_2O$, and $(Mo_6 Cl_8)Cl_4 \cdot 2H_2O$, were chosen for this study because they contain cationic metal cluster cores. The structure of $M_6Cl_{12}^{n+}$, where M is Nb or Ta, is shown in Figure 1-3⁵². The dark circles represent the metal atoms, the open circles are the edge bridging halide atoms. X-ray crystallographic data⁵³ show an average metal-metal distance of approximately 2.9 Å for both the niobium and tantalum clusters. The metal-bridging chloride distance of 2.43 Å is approximately the same for both clusters, also. The metal cluster core, $M_6Cl_{12}^{n+}$ can adopt oxidation states of n=2,3,4, following reversible one electron oxidation steps. The niobium cluster core is less easily oxidized than the tantalum species, which can be oxidized to n=4by oxygen. The niobium core requires more rigorous oxidizing conditions, such as contact with chlorine gas, to



core.

M equals Nb or Ta, and n is 2, 3, or 4. The dark circles represent the metal atoms, the open circles are the edge-bridging chlorides. Each metal atom possesses an open terminal binding site.

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adopt the 4+ oxidation state $^{54}, 5^5$. The n=3 cation of $M_6 Cl_{12}^{n+}$ is paramagnetic, exhibiting a magnetic susceptability close to the spin only value expected for one electron⁵⁶. This unpaired electron resides in a nondegenerate molecular orbital, being equally distributed on the six metal atoms as shown by electron spin resonance (esr) spectroscopy of the niobium cluster⁵⁷.

Each metal atom possesses an open site through which it can be coordinated by a ligand in a terminal bonding position. A variety of ligands have been coordinated to the clusters yielding positive, neutral and anionic compounds^{53,58}. The instability of the metal clusters of niobium and tantalum toward hydrolysis to yield M_2O_5 is well established^{54,58,59} and makes these compounds excellent candidates for the <u>in situ</u> formation of metal oxide props for pillared clay formation.

The structure of the $Mo_6 Cl_8^{44}$ cluster core is shown in Figure 1-4⁵². This structure, originally established by Brosset⁶⁰, contains an octahedron of molybdenum atoms (dark circles) with intermetallic bonding, and an average Mo-Mo distance of 2.61 Å. The eight face bridging chlorides are represented by the open circles. The average Mo-Cl_{br} distance is 2.47 Å⁶¹. Each molybdenum is capable of bonding a ligand terminally. A variety of ligands⁶²⁻⁶⁶, including alkoxides⁶⁷ can be bound. This cluster can exhibit various oxidation states, however,

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Figure 1-4. The structure of $Mo_6Cl_8^{4+}$ metal cluster core.

The dark circles represent the metal atoms, the open circles are the face-bridging chloride ions. Each metal atom possesses an open terminal binding site. these are formed under rather pressing conditions. The oxidation of $(Mo_6Cl_8)Cl_4$ with chlorine gas can lead to the formation of $(Mo_6Cl_{12})Cl_3^{68}$. Reduction of the cluster can occur in the presence of excess phosphine to yield $Mo_6Cl_8Cl_3(P(Et)_3)_3^{66}$.

Detailed studies by Sheldon^{63,69-72} have shown that substitution of the bridging chlorides by hydroxide ions occurs by an S_N^2 mechanism, and can lead to the hydrolytic decomposition of the cluster structure. Potentially this type of cluster decomposition can be utilized within the interlayer region of montmorillonite to yield a molybdenum oxide pillared clay.

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II. EXPERIMENTAL

A. Materials

Niobium pentachloride was obtained from Alfa Chemical Co., and sublimed at 150°C <u>in vacuo</u> prior to use. Cadmium metal was used in the form of freshly prepared filings. Niobium metal (Alfa Chemical Co.) was used in the form of small shot. Tantalum pentachloride (Alfa Chemical Co.) was sublimed at 190° <u>in vacuo</u> prior to use. Aluminum metal was in the form of fine turnings. Molybdenum powder (100 mesh) was obtained from Climax Molybdenum Co. Molybdenum pentachloride was used as received from Alfa Chemical Co.

Natural Wyoming montmorillonite was received in a spray dried form from the Source Clay Minerals Repository, University of Missouri. The fraction containing particles less than 2μ was collected through sedimentation from aqueous suspension for 24 h. This procedure also served to remove carbonates and other impurities. The homoionic sodium exchanged form of the clay was prepared through treatment with 1.0 <u>M</u> NaCl solution. Excess sodium chloride was removed by successive washings with distilled water and centrifugation. The clay was dialysed against distilled water until free of chloride, and then lyopholized.

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Elemental analysis of the Na⁺-montmorillonite was performed using Inductively Coupled Plasma (ICP) emission analysis (<u>vide infra</u>). The unit cell composition was determined to be: Na_{0.50}[Al_{3.11}, $Mg_{0.50}$, $Fe_{0.40}$](Si_{7.91}, Al_{0.09})0₂₀(OH)₄.

Analysis of a homoionic Ni²⁺ exchanged form of the mineral indicated the cation exchange capacity (CEC) of a typical freeze dried montmorillonite sample to be 60.2 meq/ 100 g. The nickel content was measured gravimetrically by forming the dimethylglyoxime complex following digestion of the clay in boiling HCl/HNO₃.

Synthetic zeolite Y was obtained from Amoco Petroleum Research Corporation in a highly crystalline form. The unit cell formula was determined to be $Na_{53.97}$ [(AlO₂)_{53.97} (SiO₂)_{138.03}] by ICP analysis. The ammonium exchanged form of this zeolite was produced by ion exchanging twice with 1.0 <u>M</u> ammonium sulfate solutions for six hours at 70°⁷³. The NH⁺₄-Y was freed from excess salt by repeated washings with distilled water and centrifugation. The hydrogen exchange form of the zeolite was produced by heating the NH⁺₄-Y under flowing N₂ at 400° for 24 h, followed by 450° for 24 h or until wet litmus paper failed to detect NH₃ in the effluent stream.

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B. Synthesis

1. $(Nb_6C1_{12})C1_2 \cdot 8H_2O$

The niobium cluster salt was prepared following two different methods. The first method used was that described by Harned⁷⁴, which utilized the reduction of NbCl₅ with cadmium metal at 700°. The metal cluster salt thus produced was isolated from 10^{-4} <u>N</u> hydrochloric acid solution. This sample of cluster salt was found by quantitative ESR to contain an approximately 50/50 mixture of cluster molecules in the 3+ and 2+ oxidation states. <u>Anal</u>. Calcd. for (Nb₆Cl₁₂)Cl₂·8H₂O: Nb, 46.53; Cl, 41.43. <u>Found</u>: Nb, 46.71; Cl, 41.16. UV-visible; $\lambda_{max} = 905$, 405, 324, and 275 nm.

The second synthetic method used was that described by Koknat <u>et al</u>.⁷⁵. It utilized the conproportionation of NbCl₅ with niobium metal in the presence of NaCl at 850°. Dark green crystalline $(Nb_6Cl_{12})Cl_2 \cdot 2H_2O$ was quickly isolated from 10^{-4} M hydrochloric acid solution to limit air oxidation. In both cases, the electronic solution spectra matched the published spectral data for this cluster species. The product synthesized by the second method possessed absorbtion peaks as assigned⁷⁶ to the cluster ion in the 2+ oxidation state; $\lambda_{max} = 905$, 400, 324 and 275 nm. Quantitative ESR measurements on this salt indicated that approximately 10% of the cluster molecules were in the 3+ oxidation state.

2. <u>(Ta₆Cl₁₂)Cl₂·8H₂O</u>

The tantalum cluster salt was prepared in good yield by following the combined procedures of Kuhn and McCarley⁷⁷ and of Koknat <u>et al.⁷⁵</u>. A mixture of aluminum turnings and TaCl₅, the latter in slight excess, was placed in a pyrex tube which was then evacuated and sealed. The reduction of the tantalum pentachloride by the aluminum was carried out in a 400°/200° temperature gradient for 36 h. Dark green crystals of $(Ta_6Cl_{12})Cl_2 \cdot 8H_20$ were collected from 10^{-4} M hydrochloric acid solution under argon atmosphere. The electronic solution spectrum matches that described in the literature^{55,77} for the cluster ion in the 2+ oxidation state; $\lambda_{max} = 750$, 635, 472, 395, 327 and 282 nm.

3. (Mo₆Cl₈)Cl₄·2H₂O

The molybdenum cluster chloride was prepared by following the method of Nanelli and $\operatorname{Block}^{78}$. Molybdenum metal powder and MoCl₅ were placed in a quartz glass tube with a length of 125 cm. The pentachloride was sublimed at 650° in flowing N₂ over the molybdenum metal which was distributed along the length of the tube. The 650° zone was generated by a tube furnace that was 30 cm in length. This zone was moved the length of the quartz tube in the direction of nitrogen flow. The direction of sublimation was reversed four times. Bright yellow microcrystalline molybdenum

cluster was collected by extracting the crude product with 4 500 ml portions of 4<u>N</u> hydrochloric acid solution. The intracrystalline HCl was driven off by slowing heating the salt to 200° under vacuum. <u>Anal</u>. Calcd. for $(Mo_6Cl_8)Cl_4$. 2H₂O: Mo, 55.50; Cl, 41.02. <u>Found</u>: Mo, 55.39; Cl, 41.17. UV-visible: λ_{max} at 320 nm⁷⁹. IR: 340(br) cm^{-1 80}.

4. Hydrolysis of (Mo6Cl8)Cl4·2H20

An aqueous solution of $Mo_6Cl_8(OH)_n(OH_2)_{(6-n)}^{(4-n)+}$ was prepared from $(Mo_6Cl_8)Cl_4 \cdot 2H_2O$ by the use of a modification of a method of Cotton and Curtis⁶². A sample of $(Mo_6Cl_8)Cl_4$. $2H_{0}O$ (1.00 g, 9.64 x 10^{-4} moles) was dissolved by boiling in 944 ml of absolute methanol. The cooled solution was added dropwise to a solution containing 0.800 g (3.86 x 10^{-3} equivalents) of AgClO_µ dissolved in a mixture of 740 ml of reagent grade methanol and 55 ml of distilled water. The presence of approximately 7% water is a modification of the literature procedure and is necessary to avoid the precipitation of the molybdenum cluster. This precipitate has been reported to be $Ag_2[Mo_6Cl_{16}] \cdot nC_2H_5OH^{62,79}$. The combined solution was allowed to stir 30 min, after which, the AgCl precipitate was removed by centrifugation to yield a clear yellow solution.

The stock solution was stabilized against precipitation by dilution with 5L of distilled water and the subsequent removal of the methanol through evaporation utilizing a rotovap apparatus. The pH of the solution was adjusted to 10.0 by addition of either sodium or potassium hydroxide. The final solution was 1.7×10^{-4} <u>M</u> in molybdenum cluster. The solution was stored at 4° to retard degredative hy-drolysis.

5. $[M_{06}Cl_{8}(OH)_{n}(OH_{2})(6-n)](Cl_{4})(4-n)$

Portions of the molybdenum cluster stock solution described above were adjusted to pH 1.0 with 6 \underline{N} HClO $_{\underline{J}}.$ This reaction yielded precipitates which were quite variable in their color (ranging from bright yellow to brown) and quality. Variability in the quality of perchlorate precipitates of the metal cluster coordinated by organic ligands has been reported by Cotton and Curtis⁶². It must be noted that these workers found molybdenum cluster perchlorates to be quite explosive in the presence of organic ligands. The precipitates obtained from perchlorate solution were physically characterized. UV-vis; λ_{max} at 315 and 400 nm. The infrared spectrum of this precipitate contained absorbtion bands attributed to perchlorate ion (1075 $\rm cm^{-1}$) and metal cluster coordinated by water molecules and hydroxide ions (3040, 1410, 750, 510, and 340 cm^{-1}).

C. Metal Cluster Intercalation Reactions

1. Nb₆Cl^{2+,3+}-Montmorillonite

In a typical example, $36.9 \text{ mg} (3.08 \times 10^{-5} \text{ moles})$ of $(Nb_6Cl_{12})Cl_2 \cdot 8H_20$ was dissolved with heating and stirring in 100.0 ml of distilled water. After being cooled and filtered, the dark green solution had a pH of 4.5. To this rapidly stirring solution, a suspension of 100.0 mg of Na⁺-montmorillonite in 20.0 ml of water was added. After a reaction time of 6 h at room temperature, the resulting clay intercalate complex was washed with distilled water and centrifuged repeatedly to free the silicate from any excess cluster salt. The dark green product was then lyopholized. A cluster loading of 33 mmole/100 g of silicate was achieved. <u>Anal</u>. Calcd. for $(Nb_6Cl_{12})_{0.24}^{2+,3+}$, $Na_{0.06}^+[Al_{3.11}, Mg_{0.50}, Fe_{0.40}](Si_{7.91}, Al_{0.09})_{0.2}(OH)_4$: Nb, 13.84, Cl, 10.56; Na, 0.13. <u>Found</u>: Nb, 13.84; Cl, 10.65; Na, 0.13. UV-visible; λ_{max} at 895, 405 and 280 nm.

The determination of an ion exchange isotherm (<u>vide</u> <u>infra</u>) made it possible to obtain predictable loadings of the niobium cluster on the montmorillonite. The desired cluster equilibrium solution concentration and loading on the clay was achieved by controlling the ratio of moles of cluster to montmorillonite equivalents.

2. $\underline{\text{Ta}_6\text{Cl}_{12}^{2+,3+}-\text{Montmorillonite}}$

The exchange reactions of the tantalum cluster were carried out in essentially the same manner as those of its niobium analog. The tantalum cluster is susceptable to air oxidation under the exchange reaction conditions, therefore, all manipulations were carried out under argon atmosphere. For example, 41.6 mg (2.41 x 10^{-5} moles) of $(Ta_6Cl_{12})Cl_2 \cdot 8H_2O$ was dissolved in 100.0 ml of degassed distilled water. The resulting blue-green solution possessed a pH of 4.5. To this solution was added 50.0 mg of Na⁺-montmorillonite suspended in 34.0 ml of degassed distilled water. The resulting clay intercalate complex was successively washed with degassed distilled water and centrifuged to free the silicate from any excess cluster salt. The intercalated clay was then lyopholized. This dried material was quite oxygen sensitive as indicated by a rapid color change to red upon exposure to air. A loading of 23 mmole/100 g of silicate was thus achieved. <u>Anal</u>. Calcd. for (Ta₆Cl₁₂)^{2+,3+}, Na_{0.04}[Al_{3.11}, Mg_{0.50}, Fe_{0.40}](Si_{7.91}, Al_{0.09})0₂₀(OH)₄: Ta, 18.23; Cl, 7.14; Na, 0.10. Found: Ta, 18.23; Cl, 7.92; Na, 0.095. UVvisible; λ_{max} at 775, 652 and 355 nm.

3. $\underline{Mo_6Cl_8(OH)}_{2.7}$ (H₂O)^{1.3+}-Montmorillonite

Molybdenum cluster intercalation in montmorillonite was found to be dependent on the cation formation by the

cluster at low pH. For example, (150.0 mg, 9.03 x 10^{-5} exchange eq) of Na⁺-montmorillonite was suspended in 200.0 ml of distilled water. To this suspension was added 1.05 $x 10^{-4}$ moles of $[Mo_6Cl_8(OH)_n(H_2O)_{(6-n)}]^{(4-n)+}$ from stock solution. Distilled water was added to adjust the cluster solution concentration to 5×10^{-5} M or lower. The pH of this solution was adjusted to 1.5 by the dropwise addition of 0.1 \underline{N} HClO₄. This resulted in the formation of a bright yellow flocculated clay. Ultrasonic agitation (50 watts for 3 minutes) was used to assist the exchange reaction. The bright yellow intercalate was separated from the colorless supernatant by centrifugation. The intercalate was then repeatedly washed with distilled water and centrifuged until the wash water was pH 7.0. The product was collected and air dried on a glass slide. This procedure yielded a cluster loading of 53.6 mmole/100 g of clay. <u>Anal</u>. Calcd. for [Mo₆Cl₈(OH)_{2.7}(OH₂)_{3.3}]^{1.3+}_{0.39}-[A13.11, Mg0.50, Fe0.40] (Si7.91, A10.09)020(OH)4: Mo, 20.35; Cl, 10.03; Na, 0.00. Found: Mo, 20.35; Cl, 7.57; Na, 0.0065. UV-visible; λ_{max} at 330 and 405 nm.

D. Ion Exchange Isotherms

1. <u>M₆Cl²⁺, 3+/Na⁺-Montmorillonite Ion Exchange Isotherms</u>

The room temperature ion exchange reaction of $M_6Cl_{12}^{2+,3+}$ and homionic Na⁺-montmorillonite was measured in strictly analogous fashion for both niobium and tantalum clusters. Montmorillonite was allowed to equilibrate 18 h with solutions containing known initial concentrations of $(M_6Cl_{12})Cl_2$. These solutions contained initial quantities of 8H_O. cluster salt varying up to six moles per cation exchange equivalent of the clay. The metal cluster concentration in each centrifuged sample solution was determined spectrophotometrically using a Cary 17D Spectrophotometer. The absorbance peak measured at 405 and 395 nm for the niobium and tantalum clusters, respectively, was compared to a standard solution absorbtion curve. The amount of the metal cluster bound to the silicate was determined by the difference between the $(M_6Cl_{12})Cl_2 \cdot 8H_2O$ present initially, and the amount remaining in solution at equilibrium.

The quantity of sodium released by Na⁺-montmorillonite into solution upon reaction with $M_6 Cl_{12}^{2+,3+}$ was measured by atomic emission using a Jarrell-Ash spectrometer. Measurements were then taken at $\lambda_{max} = 5889.9$ Å. The quantity of sodium released from the montmorillonite was obtained from the total amount measured in each sample solution by correcting for sodium present in the cluster stock solution and in a montmorillonite blank.

2. Mo₆Cl₈(OH)_{2.7}(OH₂)^{1.3+}/Na⁺-Montmorillonite Ion Exchange Isotherm

The amount of sodium released upon molybdenum cluster binding at room temperature and pH 1.5 was determined on individual samples containing up to 1.5 moles of cluster per clay cation exchange equivalent. Samples were stirred and equilibrated 12 h in polypropylene vials, then centrifuged to remove the montmorillonite. Sodium concentrations were measured by atomic emission as described above. Corrections were applied to compensate for sodium content in the cluster stock solution, the perchloric acid and the clay blank. Error bars were calculated for each point using the standard deviations determined from the five atomic emission readings for each sample and the estimates of errors in volume readings.

E. Metal Oxide Pillared Montmorillonites

1. (Nb₂0₅)-Montmorillonite

Niobium oxide pillared montmorillonite was prepared from a clay intercalate containing 33 mmole $Nb_6Cl_{12}^{2+,3+}/100$ g of silicate. Heating the compound under dynamic vacuum at 130° for 24 h, limited the amount of interlayer water present, but the cluster integrity was maintained as evidenced by the Nb:Cl ratio of 1:1.96. <u>Anal</u>. Calcd. for $(Nb_6Cl_{12})_{0.14}^{2+,3+}$, $Na_{0.06}^+-[Al_{3.11}, Mg_{0.50}, Fe_{0.40}] - (Si_{7.91}, Al_{0.09})_{20}(OH)_4$: Nb, 8.72; Cl, 6.65. <u>Found</u>: Nb, 8.72; Cl, 6.51.

Heating the intercalate <u>in vacuo</u> at 240° for 24 h following the 130° treatment, promoted the hydrolytic

decomposition and oxidation of the cluster <u>in situ</u>. This procedure produced a niobium oxide pillared clay. <u>Anal</u>. Calcd. for $(Nb_2O_5)_{0.57}$, $H_{0.44}^+$, $Na_{0.06}^+$ -[Al_{3.11}, $Mg_{0.50}$, $Fe_{0.40}^{[Si_{7.91}]}$, $Al_{0.09}^{[O_20}(OH)_4$: Nb, l2.17; Cl, 0.00. Found: Nb, l2.17; Cl, 0.91.

2. <u>(Ta₂O₅)-Montmorillonite</u>

Montmorillonite pillared by tantalum oxide was prepared from an intercalate with 23 mmole $Ta_6Cl_{12}^{2+,3+}/100$ g of clay. The cluster remained intact following calcination under dynamic vacuum at 120° for 24 h, as evidenced by the 2.18:1 Cl to Ta ratio. <u>Anal</u>. Calcd. for $(Ta_6Cl_{12})_{0.16}^{2+,3+}$, $Na_{0.04}^{+}$ -[Al_{3.11}, Mg_{0.50}, Fe_{0.40}](Si_{7.91}, Al_{0.09})0₂₀(OH)₄: Ta, 17.90; Cl, 7.01. <u>Found</u>: Ta, 17.90; Cl, 7.66.

Heating the intercalate <u>in vacuo</u> for 24 h at 240° following the 130° treatment promoted the formation of interlayer tantalum oxide. <u>Anal</u>. Calcd. for $(Ta_2O_5)_{0.48}$, $H_{0.46}^{+}$, $Na_{0.04}^{+}$ -[Al_{3.11}, $Mg_{0.50}$, $Fe_{0.40}$](Si_{7.91}, Al_{0.09})O₂₀-(OH)₄: Ta, 18.35; Cl, 0.00. <u>Found</u>: Ta, 18.35; Cl, 0.46.

3. Molybdenum Oxide Interlayered Montmorillonite

The molybdenum oxide interlayered montmorillonite was prepared from an intercalate containing 53.6 mmoles of $Mo_6Cl_8(OH)_{2.7}(OH_2)^{1.3+}_{3.3}/100$ g of silicate. The preliminary heating under dynamic vacuum of 130° for 24 h followed by

24 h at 200°, was designed to limit the amount of interlayer water present. Calcination at 280° for 24 h yielded the molybdenum oxide interlayered montmorillonite. This material contained no detectable chloride as determined by the absence of an AgCl precipitate upon digesting the product in H_2SO_4 and adding alcoholic AgNO₃.

F. Molybdenum Cluster Binding to H⁺-Y Zeolite

Molybdenum cluster binding to synthetic fausasitic zeolite Y is dependent on both the pH of the solution and the cation exchange form of the zeolite. H^+-Y zeolite (1.00 g, 4.70 meq) was suspended in 1.27 L of distilled water with rapid stirring. To this suspension was added 340.3 ml (5.82 x 10^{-5} moles) of $Mo_6Cl_8(OH)_n(OH_2)_{(6-n)}$ $(ClO_4)_{(4-n)}$ stock solution. The pH of the solution was observed to drop from 7.2 to 5.6 during 30 minutes of rapid stirring of this mixture. The suspension was then heated to 70° and 1.61 L of 1 x 10^{-4} <u>N</u> HClO₄ solution was added over the course of 1 h to provide a final pH of 4.0. This mixture was stirred an additional 3 h. The light yellow solid was separated from the clear supernatant by centrifugation, and then washed repeatedly with distilled water. Anal. Calcd. for [Mo₆Cl₈(OH)₃(OH₂)₃]_{0.47}, H⁺_{53.50}-[(AlO₂)_{53.97}-(SiO₂)_{138.03}]: Mo, 2.27; Cl, 1.11. <u>Found</u>: Mo, 2.27; Cl, 0.51.

This material was heated to 200° for 2 h, under flowing

 N_2 as a preliminary drying step. This was followed by a calcination at 430°C for 5 h. The latter treatment resulted in the apparent decomposition of the cluster and a series of color changes from yellow to blue (\sim 340°) to white (\sim 400°). This white color is consistent with the presence of Mo(VI) oxide. <u>Anal</u>. Calcd. for (MoO₃)_{3.06}, $H_{53.97}^+$ -[(AlO₂)_{53.97} (SiO₂)_{138.03}]: Mo, 2.44; Cl, 0.00. Found: Mo, 2.44; Cl, 0.013.

G. Physical Methods

1. X-ray Diffraction

X-ray diffraction data were collected utilizing either a Phillips X-ray diffractometer or a Siemans Crystalloflex-4. Both instruments utilized Ni-filtered CuK_a radiation ($\lambda = 1.5405$ Å). Clay samples were generally in the form of thin films deposited on a glass slide by evaporation of an aqueous suspension at room temperature. Goiniometer measurements were collected from 2° to 30° as values of 20. The peak positions were converted to d spacings using the Bragg equation.

2. Electron Spin Resonance

Electron spin resonance spectra were obtained at room temperature using a Varian E-4 spectrometer. Samples were prepared as freeze dried powders or microcrystalline solids. A numerical double integration method⁸¹ was used to integrate the ESR spectrum for quantitative measurements. The intensity of the sample peak was calibrated against a $CuSO_4 \cdot 5H_2O$ reference using the method of Aasa and Vanguard⁸².

3. UV-visible Spectroscopy

Electronic spectra were recorded on a Cary 17D or a Cary 219 spectrophotometer. Solution spectra were measured versus solvent in matched 1 cm path length cells. Clay samples were prepared as mulls in Nujol and held between quartz plates, or dried on quartz slides and spread with Nujol.

4. Infrared Spectroscopy

Infrared spectra were measured in the range 4000-250 cm⁻¹ utilizing a Perkin-Elmer 457 spectrophotometer. Samples were prepared as potassium bromide pellets or were mulled in Nujol and suspended on cesium iodide or potassium bromide plates.

5. ESCA

Electron spectroscopy for chemical analysis (ESCA) measurements were furnished by Dr. Luis Matienzo of the

Martin-Marietta Corp. These measurements were made using a Physical Electronics Model 548 XPS with the aluminum $K_{\alpha l2}$ line as the exciting source and the carbon is line (284.6 eV) as a reference. The position of the Nb_{3d} 5/2 line observed from niobium intercalated montmorillonites was compared to those of Nb₂O₅, Nb metal and KNbO₃.

6. Surface Area Measurements

Nitrogen B.E.T. surface area measurements were performed using a Perkin-Elmer Model 212B sorbtometer with a thermal conductivity detector. Samples were activated at elevated temperatures under flowing argon or under vacuum. Nitrogen was adsorbed onto the sample at liquid nitrogen temperatures from He/N_2 flow mixtures of known composition. The volume of nitrogen adsorbed was determined by comparison of the area of the desorbtion peak to the area of a nitrogen peak obtained from calibration tubes of known volume. Surface areas were determined by a three point B.E.T. method.

7. Thermal Analysis

Thermal analysis was performed using a DuPont Model 990 thermal analyser operating in either the differential scanning calorimetry (DSC) or differential thermal analysis (DTA) mode. These analyses were carried out at a heating rate of 10°C/min. Al₂0₃ was used as a reference material.

8. Conductimetric Titration

Electrolytic solution conductivities were measured using a Beckman Model RC 16BZ conductivity bridge with a cell containing the 1 cm² bright platinum electrodes held approximately 1 cm apart. Solution conductivity was measured in arbitrary units of ohm⁻¹ multiplied by the total solution volume in milliliters to compensate for volume changes during titration. The titration was carried out with the addition of a 6.04×10^{-4} <u>M</u> methanolic solution of $(Mo_6Cl_8)Cl_4 \cdot 2H_2O$ to a 4.86×10^{-6} <u>N</u> AgBF₄ solution in methanol/water as described above for the $Mo_6Cl_8(OH)_n(H_2O)_{(6-n)}^{(4-n)+}$ stock solution synthesis (Section 3-4). An equilibration time of twenty minutes was allowed prior to each conductivity measurement. The data points were fit to lines using a least squares method.

9. Elemental Analyses

Inductively coupled plasma (ICP) emission analyses of Si, Al, Fe, Mg and Na was performed using a Jarrell-Ash Model 955 Autocomp spectrophotometer at the Michigan State University Agricultural Experimental Station. Samples were fused in lithium metaborate at 1000° and the melt was dissolved in 0.1 \underline{N} nitric acid. The analyses of five independent samples was averaged. A National Bureau of Standards clay sample was used as a calibration
standard. Analyses for Nb, Ta, Mo, and Cl were performed by Galbraith Laboratories, Inc., Knoxville, TN.

10. Electron Microprobe Analysis

Electron Microprobe analysis was performed using an Applied Research Laboratories ARL-SM microprobe in conjunction with a VG HB 501 scanning transmission microscope (STEM). Measurements were made at an X-ray takeoff angle of 52.5°. The zeolite sample was exchanged with molybdenum cluster in the usual manner and air dried. The sample was then embedded in epoxy resin and ultra-thin (700Å) sections were cut by Dr. K. K. Baker of the Michigan State University Pesticide Research Department. The sample was placed within the microscope at 10^{-8} torr for 12 h in order to limit the amount of intracrystalline water present in the zeolite. This procedure is reported 83 to help maintain the crystallinity of zeolite samples subjected to electron bombardment during microscopy. Molybdenum content was measured using the ${\rm MoL}_{\alpha}$ emission line, and chlorine content was determined using the ClK_{α} line. Quantitative molybdenum and chlorine analyses were made on two regions of a zeolite particle. The first region was apparently an interior portion of the zeolite which had been exposed by cleavage of the particle during sample preparation. The second region was an exterior portion of the particle. The relative strengths of the molybdenum

and chlorine signals recorded can be directly compared because the instrument settings and data acquisition times were identical. The micropore analyses were performed by Mr. V. Shull at the Michigan State University Physics Department.

III. THE PILLARING OF MONTMORILLONITE BY NIOBIUM AND TANTALUM OXIDE AGGREGATES THROUGH METAL CLUSTER INTERCALATION AND CONVERSION

A. <u>Metal Cluster Synthesis and Assignment of Oxidation</u> <u>States</u>

The niobium cluster salt was synthesized following two different literature procedures. The first procedure was described by Harned⁷⁴, and utilized the reduction of niobium pentachloride with cadmium metal at 700°C. This reaction can be written⁷⁵:

$$6NbCl_5 + 8Cd_{700^{\circ}} Cd_2(Nb_6Cl_{12})Cl_6 + 6CdCl_2.$$
 (3-1)

The crude cluster product was dissolved in water and the cadmium dications were precipitated as the sulfide by reaction with H_2S . The metal cluster salt, $(Nb_6Cl_{12})Cl_2$. $8H_2O$, was isolated as dark green crystals from hydrochloric acid solution. The UV-visible spectrum of this salt in aqueous solution contains absorbtion bands at λ_{max} equal to 905, 405, 324, and 275 nm, as shown in Figure 3-la. The position of these absorbtion maxima, especially the exact location of the peak around 400 nm, is indicative of the oxidation state of the cluster.



Figure 3-1. UV-visible absorbtion spectra of (a) $(Nb_6Cl_{12})-Cl_2\cdot 8H_2O$ in aqueous solution and (b) $Nb_6Cl_{12}^{2+,3+}-montmorillonite$.

Spectrum (a) is of the mixed 2+,3+ oxidation state cluster salt. Spectrum (b) is of the intercalate containing 33 mmoles of cluster/100 g of clay prepared as a Nujol mull suspended between quartz glass plates measured <u>versus</u> a mulled Na⁺-montmorillonite reference. Absorbance was measured in arbitrary units. Absorbtion maxima of the electronic spectra published for the niobium and tantalum salts in the non-anated form and in the 2+, 3+, and 4+ oxidation states are compiled in Table 3-1. There is considerable disagreement within the literature as to the exact locations of the absorbtion bands for the metal clusters in the lower oxidation states. The positions of the absorbtion maxima included in this table are taken from relatively recent and reliable sources.

The results of spectroscopic investigations indicate several important aspects of the electronic spectra of the niobium and tantalum clusters. The absorbtion bands at wavelengths longer than <u>ca</u>. 333 nm show only slight shifts upon replacement of the bridging chlorides with other halides. Therefore, these lower energy bands are assigned to electronic transitions between molecular orbitals derived mainly from metal atom d-orbitals within the cluster core. The position of these bands is strongly dependent on the oxidation state of the metal cluster. This is especially true of the bands at wavelengths longer than 600 nm in the absorbtion spectrum of the tantalum cluster.

The higher energy bands ($\lambda < 333$ nm) are shifted toward the red upon changing the bridging halides from chlorine to bromine^{54,86,87}. These absorbtion bands are therefore interpreted as being ligand to metal charge-transfer bands. Substitution of the terminal ligands results in only slight shifts in the absorbtion spectra of these clusters⁸⁶.

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Table 3-1.

Compound	Solvent	λ _{max} , nm	Ref.
(Nb ₆ c1 ₁₂)c1 ₂ .8H ₂ 0	Н ₂ О	901,606,480,396,320,274	84
(Nb ₆ c1 ₁₂)c1 ₂ .8H ₂ 0	Н ₂ 0	901,598,465,397,310,273	76
(Nb ₆ c1 ₁₂)c1 ₂ .8H ₂ 0	Н ₂ 0	877,588,473,400,311,272	85
[(c ₂ H ₅) ₄ N] ₃ (Nb ₆ c1 ₁₂)c1 ₆ ^a	с ₂ н5он	962,550,,426,,288	57
$[(c_{2}H_{5})_{4}N]_{2}(Nb_{6}cl_{12})cl_{6}$	с ₂ н ₅ он	935 , 571 ,, 453 , ,297	57
(Ta ₆ c1 ₁₂)c1 ₂ .8H ₂ 0	Н ₂ 0	760,640,,398,330	55
(Ta ₆ c1 ₁₂)c1 ₂ .8H ₂ 0	Η ₂ 0	755,637,470,398,329	77
(Ta ₆ c1 ₁₂)c1 ₃ ^b	Н ₂ 0	820,710,,405,338	55
(Ta ₆ c1 ₁₂)c14 ^b	Н ₂ О	740,405,345	55

 $^{\rm b}{\rm Oxidized}$ by addition of stoichiometric quantities of ${\rm Fe}^{3+}$. ^aAssumed to be non-anated in ethanol. No HCl added.

The spectrum of the $(Nb_6Cl_{12})Cl_2 \cdot 8H_2O$ synthesized by following Harned's method is shown in Figure 3-la, and possesses a sharp absorbtion band at 405 nm. Comparison of this peak position to the published data indicates that it lies between the analogous peak for the cluster in the 2+ oxidation state which is located at λ_{max} equal to 396 nm, and that for the cluster in the 3+ oxidation state located at 426 nm. This suggests that the niobium cluster salt is present as a mixture of oxidation states, with the average lying between 2+ and 3+.

Quantitative electron spin resonance (ESR) measurements were performed on the solid niobium cluster salt to ascertain the average oxidation state. The intensity of the resonance absorbtion peak was determined by using a numerical double integration method⁸¹. The integrated sample peak was compared to the resonance absorbtion peak of a crystalline $CuSO_4 \cdot 5H_2O$ reference using the method of Aasa and Vangard⁸² to determine the number of unpaired electrons present in the cluster salt.

The metal cluster core in the 3+ oxidation state contains one unpaired electron in a non-degenerate orbital. The metal cluster salts in the 2+ and 4+ oxidation states are diamagnetic^{56,88} and are not ESR active⁵⁷. It was determined that approximately 50% of the niobium cluster molecules were in the 3+ oxidation state in this sample of $(Nb_6Cl_{12})Cl_2 \cdot 8H_20$. The remainder of the sample was

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assumed to be in the 2+ oxidation state as indicated by the UV-visible spectral data. This mixture of oxidation states may have been the result of incomplete reduction during the synthesis of the salt, or may be attributed to air oxidation of the cluster during the isolation step. This cluster salt containing mixed oxidation states was used for the majority of the studies for niobium, and will be referred to as $Nb_6Cl_{12}^{2+,3+}$.

The second procedure used to synthesize the niobium cluster was described by Koknat <u>et al</u>.⁷⁵. This method utilized the conproportionation reaction between niobium pentachloride and niobium metal at 850° in the presence of sodium chloride. The stoichiometry of this reaction is shown in Equation (3-2):

$$14NbCl_{5} + 16Nb + 20NaCl + 5Na_{4}(Nb_{6}Cl_{12})Cl_{6}$$
 (3-2)

Crystalline $(Nb_6Cl_{12})Cl_2 \cdot ^{8H}_{2}O$ was isolated from the crude product containing the fully anated cluster by recrystallizing from hydrochloric acid solution. This step was performed quickly to limit air oxidation of the cluster. The UV-visible solution spectrum of this salt contains absorbtion bands at λ_{max} equal to 905, 400, 324, and 275 nm. Comparison of these peak positions to Table 3-1 indicates that the majority of the cluster molecules are in the 2+ oxidation state. Quantitative ESR measurements confirm that less than 10% of the cluster was present

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The tantalum cluster salt, $(Ta_6Cl_{12})Cl_2 \cdot 8H_2O$, was prepared by following the method of Kuhn and McCarley⁷⁷, which utilized the reduction of tantalum pentachloride with aluminum metal. The reaction stoichiometry is described by Equation (3-3).

$$18\text{TaCl}_{5} + 16\text{Al} \xrightarrow{400/200^{\circ}} 3(\text{Ta}_{6}^{\text{Cl}}_{12})\text{Cl}_{2} + 16\text{AlCl}_{3} \qquad (3-3)$$

This reaction was performed in a $400/200^{\circ}$ temperature gradient to promote the convective circulation of the volatile tantalum pentachloride. Dark green crystals of $(Ta_6Cl_{12})Cl_2\cdot 8H_20$ were isolated from hydrochloric acid solution. The UV-visible spectrum of this salt in a freshly prepared aqueous solution is illustrated in Figure 3-2a. This spectrum contains absorbtion bands at λ_{max} equal to 750, 635, 472, 395 and 327 nm. The appearance of the lower energy bands, especially the band at 635 nm, is important in the assignment of the oxidation state. Comparison of these absorbtion maxima to those published by Espenson and McCarley, shown in Table 3-1, indicates that the cluster salt is in the 2+ oxidation state.

The electronic absorbtion spectrum of the tantalum cluster salt after reaction with hydrogen peroxide in aqueous solution (pH 4.5) at room temperature is illustrated in Figure 3-2c. The presence of absorbtion maxima at 900,



Figure 3-2. UV-visible spectra of (a) (Ta₆Cl₁₂)Cl₂·8H₂O in aqueous solution, (b) Ta₆Cl₁₂^{2+,3+}-montmorillonite, and (c) (Ta₆Cl₁₂)Cl₂·8H₂O in aqueous solution after hydrogen peroxide oxidation to the 3+ oxidation state.

Spectrum (a) is of the cluster in the 2+ oxidation state. Spectrum (b) is of the intercalate containing 23 mmoles of cluster/100 g of clay prepared as a Nujol mull suspended between quartz glass plates measured <u>versus</u> a mulled Na⁺-montmorillonite reference sample. Absorbance was measured in arbitrary units. 715, 405 and 330 nm indicates that the cluster is in the 3+ oxidation state.

B. Intercalation of Niobium and Tantalum Cluster Cations Into Na⁺-Montmorillonite

The host silicate used for the metal cluster intercalation studies was a homoionic sodium exchange form of a naturally occurring montmorillonite from Wyoming. This smectite clay possesses the unit cell formula $Na_{0.50}^{-1}$ [Al_{3.11}, $Mg_{0.50}$, $Fe_{0.40}^{-1}$ [Si_{1.91}, $Al_{0.09}^{-1}$) O_{20}^{-1} (OH)₄, as determined by inductively coupled plasma (ICP) emission analysis.

The niobium and tantalum cluster salts dissolve in aqueous solution to yield chloride anions and solvated metal cluster cations. The $M_6Cl_{12}^{n+}$ cations will react with aqueous Na⁺-montmorillonite suspensions to form unique metal cluster-layered silicate intercalation compounds. The metal cluster cations bind to the smectite electrostatically, displacing the interlayer sodium ions through an ion exchange reaction. The ion exchange reaction is written schematically in Equation (3-4).

$$nNa^{+} + M_6Cl_{12}^{n+} + M_6Cl_{12}^{n+} + nNa^{+}$$
 (3-4)

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Preliminary experiments suggested that the ion exchange reactions of the metal cluster cations with Na^+ montmorillonite exhibited a somewhat anomolous behavior in comparison to the reactions of simple metal ions. This behavior necessitated a more detailed study of the ion exchange characteristics of these metal cluster cations. One method of characterizing the metal cluster-smectite interaction is through the measurement of an ion exchange isotherm. Figure 3-3 illustrates the isotherm measured for the ion exchange of $Nb_6Cl_{12}^{2+,3+}$ into Na^+ -montmorillonite. The isotherm is plotted as millimoles of $Nb_6Cl_{12}^{2+,3+}$ bound per 100 g of silicate relative to the metal cluster solution concentration at equilibrium with the clay. The initial portion of the curve shows a rather strong uptake of $Nb_6Cl_{12}^{2+,3+}$, indicating that this cation competes favorably with sodium for the ion exchange sites. At higher equilibrium solution concentrations, the cluster binding attains a maximum value of approximately 50±2 mmoles of $Nb_6Cl_{12}^{2+,3+}$ per 100 g of silicate. This loading is considerably higher than the level expected, which is indicated by the dashed line in the figure. The maximum binding anticipated was 24 mmole/100 g of clay, based on the average charge per cluster of 2.5+, and the cationexchange capacity (CEC) of the montmorillonite; 60 meq/ 100 g. The cluster binding clearly exceeds this maximum



Figure 3-3. The ion exchange isotherm of $Nb_6Cl_{12}^{2+,3+}$ into homoionic Na⁺-montmorillonite.

The dashed line indicates the level of cluster loading expected based on the average metal cluster oxidation state and the cation exchange capacity of the montmorillonite. The amount of cluster actually bound was measured spectrophotometrically. level anticipated.

The ion exchange isotherm measured for the tantalum cluster is qualitatively the same as that for the niobium analog. As evident in Figure 3-4, this isotherm features a very steep initial uptake of the cluster cation which indicates that initially the tantalum cluster is bound to the montmorillonite almost quantitatively. Apparently, the tantalum cluster interacts more favorably with the montmorillonite than the niobium cluster. The isotherm curve rapidly reaches a plateau at 50 mmoles of tantalum cluster bound per 100 g of silicate, above which no additional cluster uptake is observed. This loading is considerably higher than the level expected. The dashed line in Figure 3-4 illustrates the maximum loading anticipated for the cluster with an average charge of 2.7+. This value is determined by measuring the amount of sodium released upon cluster binding (vide infra).

Apparently, oxidation of the cluster salt in the solid state upon only brief exposures to air, and in solution during the exchange reaction despite attempts to avoid air exposure has led to the formation of a mixed oxidation state tantalum cluster. This mixed oxidation state cluster will be referred to as $Ta_6Cl_{12}^{2+,3+}$. The UV-visible spectrum of a tantalum cluster intercalate protected from oxygen exposure after lyophilization and mulled in Nujol, is illustrated in Figure 3-2b. This spectrum contains



Figure 3-4. The ion exchange isotherm of $Ta_6Cl_{12}^{2+,3+}$ into homoionic Na⁺-montmorillonite.

The dashed line indicates the level of cluster loading expected based on the average metal cluster charge of 2.7+ as determined by measuring sodium release during exchange, and the cation exchange capacity of the montmorillonite. The amount of metal cluster bound was determined spectrophotometrically. components of the solution spectra of the cluster salt in the 2+ and 3+ oxidation states. This indicates that the intercalated cluster possesses an average oxidation state somewhere between 2+ and 3+, and is consistent with the average oxidation state of 2.7+ assumed above.

In contrast to the reaction of the tantalum cluster, quantitative ESR measurements utilizing (Nb₆Cl₁₂)Cl₂. $8H_{2}O$ which contains approximately 10% of the molecules in the 3+ oxidation state, indicate that no significant oxidation of the niobium cluster occurs during ion exchange reactions in solution exposed to the air. The estimate of the number of unpaired electrons present in a lyophilized intercalate which had not been exposed to oxygen after drying was made. This value was used in conjunction with the number of cluster molecules present in the sample as determined by elemental analysis to show that no significant increase in the number of cluster molecules in the 3+ oxidation state had occurred. This result is supported by the UV-visible spectrum in Figure 3-lb. The spectrum of $Nb_6Cl_{12}^{2+,3+}$ -montmorillonite is directly comparable to the solution spectrum of that salt containing mixed oxidation The positions of the absorbtion maxima are unstates. changed following the intercalation reaction, therefore, no oxidation of the cluster cation has occurred.

To better elucidate the phenomena involved in these ion exchange reactions, the amount of sodium liberated from Na⁺-montmorillonite was measured as a function of

metal cluster loading. Figure 3-5 illustrates the plot of milliequivalents of Na⁺ released per 100 g of montmorillonite <u>versus</u> millimoles of $Nb_6Cl_{12}^{2+,3+}$ bound per 100 g of silicate. The initial portion of this plot is linear, indicative of a simple ion exchange reaction. The slope of this line, 2.5 Na⁺ released/cluster bound, is consistent with the average cluster charge of 2.5+.

This linear relationship is retained until approximately two-thirds of the interlayer sodium is displaced. The decreasing scope beyond this point suggests a reduced charge per cluster. The curve eventually levels out upon release of one cation exchange equivalent of sodium at high metal cluster loadings. Interestingly, the niobium cluster continues to load onto the clay in the absence of exchangeable interlayer sodium.

The analogous plot showing sodium release upon binding of $Ta_6 Cl_{12}^{2+,3+}$ is shown in Figure 3-6. The initial section of the plot is assumed to be linear, in direct analogy to the niobium results. This line was drawn using a least squares fit to the first four points, with quadruple weighting on the zero point. This approach was necessary because the point at 4 mmole $Ta_6 Cl_{12}^{2+,3+}$ bound/100 g of montmorillonite appears to show considerable error. The slope of this line is 2.7 Na⁺ released per $Ta_6 Cl_{12}^{2+,3+}$ bound. This value for the average oxidation state of the tantalum cluster is consistent with the UV-visible data as discussed above.



Figure 3-5. Milliequivalents of sodium released from homoionic Na⁺-montmorillonite relative to millimoles of Nb₆Cl $_{12}^{2+,3+}$ bound. The initial linear relationship is indicative of an ion exchange reaction, with the slope of this line indicating the liberation of 2.5 Na⁺ ions per cluster molecule bound.



Figure 3-6. Milliequivalents of sodium released from homoionic Na⁺-montmorillonite relative to millimoles of $Ta_6Cl_{12}^{2+,3+}$ bound.

The initial portion of this plot was assumed to be linear, and was fit to the first four points by a least squares method, with multiple weighting to the zero point. The slope of this line indicates the release of 2.7 Na⁺ ions per cluster bound. The tantalum cluster continues to bind to the montmorillonite beyond the point where all of the interlayer sodium has been replaced. Under conditions where the clay has been fully saturated with the metal cluster cations, approximately 50 mmoles of $M_6 Cl_{12}^{2+,3+}$ are bound per 100 g of silicate. This loading is nearly the maximum value calculated for the binding of a close-packed monolayer of hydrated metal cluster cations within the clay interlayer. The diameter of a hydrated cluster molecule is estimated to be 12.6 Å from the anhydrous cluster diameter of 9.8 Å calculated from x-ray crystallographic data^{53,55,89,90}. At this maximum loading the average cluster charge is calculated to be 1.3+, assuming the interlayer cluster molecules simply balance the charge on the silicate layers.

Two reactions are proposed which could effectively reduce the cluster charge to this level: hydrolysis, Equation (3-5), and anation with the chloride counter ions in solution, Equation (3-6).

Hydrolysis occurs when a water molecule which is terminally coordinated to the cluster, releases a proton to

solution, to produce a bound hydroxide ion. Hydrolysis is evident upon dissolution of $(M_6Cl_{12})Cl_2 \cdot 8H_2O$ in water, whereupon the pH of the solution falls. The anation reaction scheme, Equation (3-6), proposes that a chloride ion from solution displaces a coordinated water molecule and binds to the cluster in a terminal position.

The positions of the equilibria as defined above, appear to be a function of the cluster loading within montmorillonite. As cluster loading increases above the level of the simple ion exchange regime, these equilibria shift to the right, allowing for the binding of additional cluster ions. Presumably, the binding of larger numbers of lower charged cluster cations is favored by the montmorillonite. This would better satisfy the rather diffuse negative charge originating from the octahedral clay layer. It is possible that neutral $M_6Cl_{12}(X)_n$ species could form, however, electrostatic binding to the silicate would not be possible. The formation of $[M_6Cl_{12}(X)_6]^{(6-n)-}$ ions by the complete anation of the cluster is a well known procedure^{53,55}.

The use of the ion exchange isotherms and the plots of sodium release upon cluster binding makes it possible to obtain predictable and reproducible loadings of the metal cluster on the montmorillonite. These plots indicate that a loading of 33 mmoles of $Nb_6Cl_{12}^{2+,3+}$ or 23 mmoles of $Ta_6Cl_{12}^{2+,3+}$ per 100 g of montmorillonite should

result in the release of approximately one cation-exchange equivalent of sodium from the clay. Loadings below this level result in the formation of interstratified materials as shown by x-ray powder diffraction. Higher loadings simply result in the clogging of the clay interlayer with large amounts of metal cluster cations of reduced charge. Therefore the cluster loadings enumerated above were used for all physical characterization and pillaring studies.

Elemental analyses confirms that greater than 90% of the interlayer sodium has been replaced through ion exchange by $M_{6}Cl_{12}^{2+,3+}$ ions. The anhydrous unit cell formula for montmorillonite loaded with 33 mmoles of $Nb_6Cl_{12}^{2+,3+}$ per 100 g was established to be $[(Nb_6Cl_{12})^{2+,3+}(X)_{0.67}]_{0.24}^{1.8+}$, Na⁺_{0.06}-[A1_{3.11}, Mg_{0.50}, Fe_{0.40}](Si_{7.91}, A1_{0.09})0₂₀(OH)₄, where X equals OH or Cl. The average cluster charge of 1.8+ can be calculated from this formula based on 0.50 exchange equivalents per unit cell. The anhydrous unit cell formula for montmorillonite loaded with 23 mmoles of $Ta_6Cl_{12}^{2+,3+}$ per 100 g was established to be $[(Ta_6Cl_{12})^{2+,3+}]$ $(X)_{v}_{0.17}^{2.7+}$, Na⁺_{0.04}-[Al_{3.11}, Mg_{0.50}, Fe_{0.40}](Si_{7.91}, Al_{0.09})- $O_{20}(OH)_4$, where $0 \le y \le 0.3$. The average cluster charge of 2.7+ can be calculated from this formula. The maximum oxidation state of 3+ for the cluster can be designated based on the UV-visible spectral data of the intercalates.

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C. <u>Physical Characterization of $M_6Cl_{12}^{2+,3+}$ -Montmorillonites</u>

X-ray diffraction studies on oriented film samples of $M_6Cl_{12}^{2+,3+}$ -montmorillonites indicate a mean basal spacing of 18.4±0.2 Å and 18.4±0.4 Å for niobium and tantalum cluster intercalates respectively. The observed spacing is near the value expected from the combined thickness of the silicate sheet (9.6 Å) and the diameter of the an-hydrous intercalated cluster ion, 9.8 Å as determined from x-ray crystallographic data^{53,88,89}. The basal spacing is slightly less than the value calculated from the simple addition of the two components, suggesting that the cluster cation partly fits into the hexagonal holes on the basal surfaces of montmorillonite.

The diffraction pattern for a $Nb_6Cl_{12}^{2+,3+}$ -montmorillonite, with a loading of 33 mmole/100 g of clay is illustrated in Figure 3-7. The x-ray diffraction pattern for a $Ta_6Cl_{12}^{2+,3+}$ -montmorillonite with a loading of 23 mmole/100 g of clay, is shown in Figure 3-8. The observation of at least 6 orders of 002 diffraction is typical of these materials and indicates a regular ordering of the interlayer. Presumably, the degree of hydration and positioning of the cluster cations is quite uniform throughout the clay interlayer. The basal spacing and interlayer ordering appear to be independent of cluster loading above the levels of these samples. Higher cluster loadings cause no increase in the basal spacing, thus only a single

The x-ray diffraction pattern of $Nb_6Cl_{12}^{2+,3+}$ -montmorillonite con-Figure 3-7.

taining 33 mmoles of cluster/100 g of clay.

The sample was in the form of a thin film supported on a glass slide. The mean basal spacing of 18.4±0.2 Å was calculated using the higher order diffractions.





The x-ray diffraction pattern of $Ta_6Cl_{12}^{2+,3+}$ -montmorillonite con-Figure 3-8.

taining 23 mmoles of cluster/100 g of clay.

The sample was in the form of a thin film supported on a glass slide. The mean basal spacing of 18.4 ± 0.4 Å was calculated utilizing the higher order diffraction spacings.





-0 -U, Ľ f S W 0 С с с a 1 n f

layer of $M_6Cl_{12}^{2+,3+}$ ions occupy the clay interlayer. For comparison, a Na⁺-montmorillonite possesses a spacing of 12.5 Å with only two or three orders of diffraction evident under analogous conditions.

Both metal cluster intercalates retain approximately 10% of their CEC in the sodium form at the cluster loadings used. The sodium montmorillonite is randomly interstratified with the cluster exchange form and only makes a slight contribution to the x-ray diffraction pattern as a whole. This contribution is manifested as a decrease in the depth and symmetry of the valley between the 001 and 002 diffraction peaks relative to that of montmorillonite containing cluster loadings of 50 mmoles/100 g of silicate.

Infrared spectra of the $M_6Cl_{12}^{2+,3+}$ -montmorillonites consist essentially of the spectrum of the metal cluster chloride superposed on that of the silicate. Figures 3-9 and 3-10 illustrate the relevant IR spectra in the region 1000-250 cm⁻¹. The very sharp band at 330 cm⁻¹ for the niobium cluster (Figure 3-9a) is also observed for the $Nb_6Cl_{12}^{2+,3+}$ -montmorillonite. The broad band at 340-310 cm⁻¹ for the tantalum cluster (Figure 3-10a) is similarly observed in the $Ta_6Cl_{12}^{2+,3+}$ intercalate (Figure 3-10c). These infrared bands at 330 cm⁻¹ and 340-310 cm⁻¹ are assigned to the M-Cl_{br} wagging vibrational mode of the cluster core^{57,91}. These bands roughly coincide with one of the absorbtion peaks attributed to carbonate impurities present in the clay sample⁹².



Figure 3-9. Infrared spectra of (a) (Nb₆Cl₁₂)Cl₂·8H₂O, (b) Na⁺-montmorillonite, (c) Nb₆Cl₁₂^{2+,3+}- montmorillonite, and (d) Nb₆Cl₁₂^{2+,3+}-mont- morillonite treated at 130° (24 h) and 240° (24 h) <u>in vacuo</u>.

> Spectra (c) and (d) are of intercalates containing 33 mmoles of cluster/100 g of clay. All samples were prepared as KBr disks.



morillonite after thermal treatment at 120° (24 h) and 240° (24h) in vacuo.

Spectra (c) and (d) are of intercalates con-taining 23 mmoles of cluster/100 g of clay. All samples were prepared as KBr disks.

The UV-visible spectra of the $M_6 Cl_{12}^{2+,3+}$ -montmorillonites are shown with the solution spectra of the respective cluster salts in Figures 3-1 (p. 38), and 3-2 (p. 44). These have already been discussed with respect to the oxidation states of the intercalated metal clusters. The spectra in Figure 3-1 are virtually identical indicating that the niobium cluster is unchanged upon intercalation. The spectrum shown in Figure 3-2b demonstrates that the intact tantalum has been intercalated, although some shifting of the average oxidation state has occurred.

The ESR spectrum of $Nb_6Cl_{12}^{3+}$ -montmorillonite consists of a single broad (ΔH is equal to 600 G) resonance at g equal to 1.95 as illustrated in Figure 3-11. Line broadening due to anisotropic interactions within the solid state, cause the hyperfine splittings expected from equal interaction of the unpaired electron in the $Nb_6Cl_{12}^{3+}$ with the six niobium nuclei (I = 9/2) to be unresolved. This spectrum is quite similar to that reported for polycrystalline $[(C_2H_5)_4N]_3(Nb_6Cl_{12})Cl_6^{57}$. Figure 3-12 shows the room temperature ESR spectrum of $Ta_6Cl_{12}^{3+}$ -montmorillonite formed upon partial oxidation of the metal cluster intercalate. This ESR signal at g equal to 1.92 is sufficiently line broadened to obscure the hyperfine splitting expected from electron interactions with six equivalent tantalum nuclei (I = 7/2). This spectrum is quite similar to that recently reported for a phosphine derivative of the $cluster^{58a}$.


Figure 3-11. The ESR spectrum of $Nb_6Cl_{12}^{3+}$ -montmorillonite.

This spectrum consists of a single broad resonance ($\Delta H \sim 600$ G) at g equal to 1.95. The spectrum of the DPPH reference is shown. The sample was in the form of a freeze-dried powder packed into a quartz glass tube. The spectrum was taken at room temperature.





The spectrum consists of a single broad resonance at g equal to 1.92. The spectrum of the DPPH reference is shown. The sample was in the form of a freeze-dried powder which was exposed to the air for several hours and then packed into a quartz glass tube. The spectrum was taken at room temperature. The air oxidation of the intercalated metal cluster cations is promoted by the high acidity in the interlayers of dried clay samples. Color changes for the intercalated tantalum cluster are suggestive of oxidation to a 4+ cluster within hours of oxygen exposure in a dried form. Absorbtion bands in the UV-visible spectrum of an air oxidized sample appear at λ_{max} equal to 750, 505, 425 and 353 nm. The presence of the broad band at 750 nm and the sharper band at 425 nm supports the assignment of the 4+ oxidation state to the interlayer tantalum cluster in comparison to the literature values listed on Table 3-1.

Air oxidation of the intercalated niobium cluster to the 3+ oxidation state requires days to occur. A sample of $Nb_6Cl_{12}^{2+}$ -montmorillonite was prepared which contained less than 10% of the cluster molecules in the 3+ oxidation state as shown by quantitative ESR measurements. After 3 days of exposure to the air ESR measurements indicate that approximately 30% of the clusters have been oxidized.

The hydrolysis reaction with interlamellar water maintains the interlayer charge balance during air oxidation of the intercalated metal cluster. Significantly, the air oxidized clusters remain intercalated and maintain the high interlayer spacings. A sample of $Ta_6Cl_{12}^{4+}$ -montmorillonite formed upon complete air oxidation of the intercalated cluster possessed a basal spacing of 17.9 Å after approximately 6 months of exposure to air.

D. <u>The Pillaring of Montmorillonite by Niobium and Tantalum</u> Oxide Aggregates

The essential step in the pillaring process is the formation of a dispersion of metal oxide which is distributed uniformly throughout the silicate interlayer so as to form a propping system of high structural integrity. Previously, this has been accomplished through the calcination of polynuclear hydroxy cations formed in aqueous solution and placed within the clay interlayers through ion exchange. The present work makes use of an alternative approach in which metal cluster cations function as pillar precursors. This function requires the metal clusters to decompose in situ to produce interlayer metal oxide props.

The well established $^{54}, 5^{8}, 5^{9}$ hydrolytic instability of the M₆Clⁿ⁺₁₂ cluster ions suggests that the refractory M₂O₅ oxides may be formed through decomposition of the metal cluster. The investigation of the niobium cluster hydrolysis by Allen and Sheldon^{58c} led these workers to propose the formation of a µ-hydroxo species, $[Nb_6Cl_{(12-n)}-(OH)_n]Cl_2 \cdot mH_2O$ as a precipitate from alkaline solution. A more in depth study of the hydrolysis and decomposition of niobium and tantalum bromide clusters was carried out by Sc hafer and Brnicevic⁵⁹. To explain the sudden decrease in pH during base titration, and the apparent cluster decompOsition, they proposed the reaction:

$$[M_6Br_8(OH)_4](OH)_6^{4-} + 5H_2O \rightarrow 3M_2O_5 + 4H^+ + 8Br^- + 8H_2.$$
(3-7)

The cluster containing both bridging and terminal hydroxides undergoes hydrolytic decomposition and simultaneous oxidation of the metals to yield the pentoxides with production of hydrogen gas. For this type of reaction to be applicable to the pillaring of smectite clays, however, the metal oxides formed must remain within the clay interlayers. Any anionic species formed during reaction would be repelled by the negatively charged silicates, and thus be expelled from the interlamellar region. Therefore, intermediates leading to the pillaring oxides must be either cationic or neutral. This requirement can be met through the use of carefully controlled reaction conditions.

Differential scanning calorimetry (DSC) was utilized to observe the thermal transitions of the $M_6Cl_{12}^{2+,3+}$ -montmorillonites and thus delineate the interlayer reactions of the metal cluster. Figures 3-13a and 3-14a illustrate the calorimograms of the niobium and tantalum cluster salts, respectively. The strongly endothermic transitions observed at approximately 200° are associated with the loss of water molecules coordinated to the metal clusters and water within the crystallographic lattice. This assignment is consistent with the results reported by Schafer⁹³. Mass spectroscopy in high vacuum has demonstrated the loss of HCl from these metal clusters in the



Figure 3-13. The differential scanning calorimograms of
 (a) (Nb₆Cl₁₂)Cl₂·8H₂O, (b) Na⁺-montmoril lonite, and (c) Nb₆Cl₁₂^{2+,3+}-montmorillonite
 containing 33 mmoles of cluster/l00 g of
 silicate.

These thermograms were measured in the DSC mode, however the ordinate is measured in arbitrary thermal units.



Figure 3-14. The differential scanning calorimograms of (a) $(Ta_6Cl_{12})Cl_2 \cdot 8H_2O$, (b) Na⁺-montmorillonite, and (c) $Ta_6Cl_{12}^{2+,3+}$ -montmorillonite containing 23 mmoles of cluster/100 g of clay.

> Thermogram (d) is a typical baseline measured with empty pans at sample and reference positions. The thermograms were measured in the DSC mode however, the ordinate is measured in arbitrary thermal units.

temperature range $200-260^{94}$. The low intensity endothermic peaks in the calorimograms 3-13a and 3-14a are probably associated with loss of additional HCl and crystallographic transitions associated with the cluster decomposition. Infrared spectroscopy indicates that these clusters are no longer intact following heating up to 500° inside the thermal analyzer. The 330 cm⁻¹ and 340-310 cm⁻¹ infrared absorbtion bands typical of the M-Cl_{br} vibrational modes are absent.

Figures 3-13b and 3-14b illustrate the calorimogram typical for a Na⁺-montmorillonite. The broad endotherm at approximately 120° is associated with the loss of water adsorbed on the silicate¹⁵. Figures 3-13c and 3-14c illustrate the calorimograms of the $M_6Cl_{12}^{2+,3+}$ -montmorillonites. The broad dehydration endotherms of the montmorillonite and the metal cluster are clearly evident. At about 260° weak endotherms are discernable in both figures which are probably associated with the hydrolytic degredation of the intercalated metal clusters.

A combination of these DSC results and experimental observations led to the establishment of a calcination sequence which provides the necessary conditions for the formation of interlayer metal oxide props. Thermal treatment of the $M_6Cl_{12}^{2+,3+}$ -montmorillonites at 120-130° under dynamic vacuum for 24 h was designed to limit the amount of interlayer water present while retaining the integrity of the intercalated metal cluster ion. This is an essential

step in the pillaring process, otherwise, the $M_6Cl_{12}^{2+,3+}$ montmorillonites quickly collapse at only moderately elevated temperatures (200°). Further calcination of the pretreated intercalate <u>in vacuo</u> at 240° for 24 h, promotes the decomposition of the cluster within the clay interlayer and the successful formation of metal oxide pillars.

Typical experimental results for $M_6Cl_{12}^{2+,3+}$ -montmorillonites following the various calcination steps are correlated in Table 3-2. The observation of a color change after 24 h at 240° suggests that a decomposition of the metal cluster has occurred. This conclusion is corroborated by spectroscopic changes in these materials. Loss of the infrared absorbtion bands associated with the intact metal clusters is evident in Figures 3-9d and 3-lod. The UV-visible spectra of these calcined materials, illustrated in Figures 3-15b and 3-16b, consist merely of a broad tailing into the UV. These spectra are in marked contrast to those of the $M_6Cl_{12}^{2+,3+}$ -montmorillonites also illustrated in these figures. Also, the ESR signals attributed to intercalated $M_6Cl_{12}^{3+}$ ions are no longer observed in these materials after calcination.

The chlorine to metal ratio determined by elemental analysis is included in Table 3-2, as an indication of the integrity of the metal cluster. The ratio is close to the theoretical value of 2.0 following the thermal treatment at 130°, but is reduced by an order of magnitude after Calcination at 240° under vacuum. The intercalated metal

Table 3-2. Some Physical Characteristics of Thermally Treated Niobium and Tantalum Interlayered Montmorillonites.

Α.	Niobium	Interlayered	Montmorillonite	(33	mmoles	of
	Nb6C12+	³⁺ /100 g of	Silicate).			

Temp., °C ^a	Time, h	Color	Cl/Nb	a ₀₀₁ , Å
25		Green	2.02	18.4±0.2
130	24	Khaki	1.96	19.3±0.6
240	24	Grey	0.20	19.2±0.4
325 ^b	6	Grey		18.7±0.6
400 ^b	8	Grey		18.4,10.0
450 ^b	24	Cream		10

B. Tantalum Interlayered Montmorillonite (23 mmoles $Ta_6Cl_{12}^{2+,3+}/100$ g of Silicate).

Temp., °C ^a	Time, h	Color	Cl/Ta	d ₀₀₁ , Å
25		Blue-Green	2.22	18.3±0.3
120	24	Blue-green	2.18	18.9±0.3
240	24	Grey	0.13	19.1±0.5
350 ^b	5	Grey		19.1±0.4
400 ^b	4	Grey		9.7

^aAll calcinations were performed under dynamic vacuum.

^bThese samples were calcined at 120-130° for 24 h followed by 240° for 24 h prior to treatment at these temperatures.



Figure 3-15. UV-visible spectra of (a) Nb₆Cl^{2+,3+}-montmorillonite, (b) Nb₆Cl^{2+,3+}-montmorillonite after thermal treatment at 130° (24 h) and 240° (24 h) <u>in vacuo</u>, and (c) Na⁺-montmorillonite.

Spectra (a) and (b) are of intercalates containing 33 mmoles of cluster/100 g of clay. These spectra were measured versus a Na⁺-montmorillonite reference. Samples were mulled in Nujol and suspended between quartz glass plates. Absorbance was measured in arbitrary units.



Figure 3-16. UV-visible spectra of (a) $Ta_6Cl_{12}^{2+,3+}$ -montmorillonite and (b) $Ta_6Cl_{12}^{2+,3+}$ -montmorillonite after treatment at 120° (24 h) and 240° (24 h) <u>in vacuo</u>.

Both intercalates contained 23 mmoles of cluster/100 g of clay. Samples were mulled in Nujol and suspended between quartz glass plates. Spectra were measured against a mulled Na⁺-montmorillonite reference sample. Absorbance was measured in arbitrary units. clusters have decomposed at 240°. The HCl given off during this decomposition can be detected if the 240° calcination is performed under flowing nitrogen gas. Wet litmus paper placed in the effluent gas stream rapidly turns red indicating the presence of HCl.

The degredation of the cluster at 240° probably occurs through the hydrolytic displacement of bridging chlorides similar to the reaction occurring in solution. A reaction scheme analogous to Equation (3-7) can be written:

$$\frac{M_{6}Cl_{12}^{2+} + 15H_{2}O}{vacuum} \xrightarrow{240^{\circ}} \frac{3M_{2}O_{5} + 2H^{+}}{2H^{+}} + 12HCl_{(g)} + \frac{8H_{2}(g)}{(g)},$$
(3-8)

wherein the horizontal lines represent the silicate layers. At elevated temperature, water molecules terminally coordinated to the cluster cation and physisorbed on the silicate interlayer surfaces will react with the intercalated $M_6Cl_{12}^{n+}$ ion. This results in the displacement of the bridging chlorides by hydroxide ions, presumably by an S_{N^2} mechanism and the liberation of HCl. Eventually hydroxide substitution promotes the oxidative degradation of the cluster structure to yield the interlayer metal oxide and H_2 gas. Protons formed during the reaction remain within the montmorillonite to balance the Charge, either as discrete interlayer cations, or as interlayer hydroxides formed upon H⁺ penetration into the crystalline lattice of the clay.

Strict stoichiometric control over the number of waters participating in the reaction is impossible due to the nature of the silicate, but sufficient water is apparently available for complete reaction of the cluster to occur. It is only when a relatively large excess of interlayer water is present that the reaction leads to collapse of the pillaring system at low temperatures.

Elemental analysis of a montmorillonite loaded with 33 mmoles of Nb₆Cl₁₂^{2+,3+} per 100 g of clay which has been calcined <u>in vacuo</u> at 130° for 24 h and 240° for 24 h corresponds to the unit cell formula $(Nb_2O_5)_{0.57}$, H⁺_{0.44}, $Na_{0.06}^+$ -[Al_{3.11}, Mg_{0.50}, Fe_{0.40}](Si_{7.91}, Al_{0.09})O₂₀(OH)₄. Analysis of a Ta₆Cl₁₂^{2+,3+}-montmorillonite containing 23 mmoles of cluster per 100 g of clay treated following the same calcination sequence indicates the anhydrous unit cell formula $(Ta_2O_5)_{0.48}$, H⁺_{0.46}, Na⁺_{0.04}-[Al_{3.11}, Mg_{0.50}, Fe_{0.40}]-(Si_{7.91}, Al_{0.09})O₂₀(OH)₄. The interlayer metal oxide has been formulated as M_{2O5} but may exist in an aggregate containing six metal atoms (<u>vide infra</u>). These analyses indicate that essentially the original amounts of metal remain on the clay and are not volatilized off during the thermal treatment.

Table 3-2 also lists the mean x-ray diffraction basal spacings of the niobium and tantalum interlayered montmorillonites following treatment at various temperatures.

These average spacings and the standard deviations on the values are calculated using d_{nn1} values derived from the higher 001 diffractions present. The mean basal spacing remains essentially constant, within experimental uncertainty, up to 325° and 350° for niobium and tantalum interlayered clays, respectively. This is quite remarkable in light of the drastic structural changes which must occur in the metal cluster species during the degredative hydrolysis and oxidation reactions. These large basal spacings indicate that an interlayer spacing of approximately 9.5 Å is maintained due to the presence of intercalated M_2O_5 molecular props. An interlayer expansion of this magnitude is consistent with the presence of a multinuclear pillar containing three or four planes of oxide anions. For comparison, at 225° a Na⁺-montmorillonite will possess a basal spacing of approximately 10 Å, indicative of a collapsed interlayer.

Representative x-ray diffraction patterns of tantalum intercalated montmorillonites are shown in Figure 3-17. One important and consistent feature of these patterns is that the 002 diffraction is more intense than the 001. This is characteristic of the $M_6Cl_{12}^{n+}$ -montmorillonites with the intensity difference being more pronounced in the tantalum cluster intercalates. The large basal spacings are confirmed using the 003 and 005 reflections, which indicate that the tantalum oxide pillared clay is still intact at 350°, despite the lack of an observable 001

Figure 3-17. Representative x-ray diffractograms of thermally treated $Ta_6Cl_{12}^{2+,3+}$ -montmoril-

lonites.

These samples were (a) air dried at room temperature, (b) heated 120° (24 h) and 240° (24 h) under dynamic vacuum, (c) treated as in (b) and heated 350° (5 h) in vacuo, and (d) treated as in (b) and heated 400° (4 h) in vacuo. All samples contained 23 mmoles of cluster/100 g of clay. Samples were in the form of thin films deposited on glass slides.



Figure 3-17

diffraction peak. There is no evidence to suggest stability of the pillared clay beyond 350° , however. The diffraction peaks observed in Figures 3-17d, and similarly, in 3-18d, are attributable to the Na⁺-montmorillonite present as an $\sim 10\%$ impurity in both metal cluster intercalates. These peaks may also contain H⁺-montmorillonite, formed according to Equation 3-8, which has collapsed in sufficiently ordered multilayer domains to cause a coinciding x-ray diffraction pattern.

Figure 3-18 shows the x-ray diffraction patterns for niobium interlayered montmorillonites. Four orders of diffraction are evident following calcination at 240°, but after six hours at 325°, the high interlayer spacing is retained but only two orders of diffraction are evident. After eight hours at 400° the niobium oxide pillared structure begins to break down creating a biphasic system containing collapsed clay with externally deposited Nb205, and montmorillonite which remains pillared. Longer treatment times and higher temperatures bring about the disorder and collapse of the pillaring system through the fragmentation and migration of the interlamellar metal oxide. X-ray diffraction patterns assigned 95 to bulk Nb_2O_5 have been observed (arrows) from a sample of $Nb_6Cl_{12}^{2+,3+}$ -montmorillonite treated to 450° in vacuo and carefully handled with exclusion of oxygen. This is consistent with the suggested formation of interlayer $\mathrm{M}_{2}\mathrm{O}_{5},$ and demonstrates that the niobium oxide possesses

Figure 3-18. Representative x-ray diffractograms of thermally treated $Nb_6Cl_{12}^{2+,3+}$ -montmorillonites. These samples were $Nb_6Cl_{12}^{2+,3+}$ -montmorillonite containing 33 mmoles of cluster/ l00 g of clay (a) heated at 130° (24 h) and 240° (24 h) under dynamic vacuum, (b treated as in (a) and heated at 320° (6 f

These samples were Nb₆Cl₁₂^(+,5)-montmorillonite containing 33 mmoles of cluster/ l00 g of clay (a) heated at 130° (24 h) and 240° (24 h) under dynamic vacuum, (b) treated as in (a) and heated at 320° (6 h) in vacuo, (c) treated as in (a) and heated at 400° (8 h) under vacuum, and (d) treated as in (a) and heated at 450° (24 h) under vacuum with exclusion of oxygen during the sample handling and x-ray diffraction. Arrows in (c) and (d) designate points of ingrowth of diffraction peaks attributed to Nb₂O₅. All samples were prepared as thin films deposited on glass slides.



Figure 3-18

sufficient mobility at these temperatures to form a separate crystalline phase.

ESCA measurements⁹⁶ of $Nb_6Cl_{12}^{2+,3+}$ -montmorillonites before and after calcination at 240° are consistent with the formation of an oxidized niobium species. The $Nb_{3d_{5/2}}$ binding energy was measured versus several known niobium samples, and showed a 1.7 eV increase in binding energy to 208.2 eV, indicating that an increase in the oxidation state of niobium had taken place during calcination. Definite assignment of an oxidation number to Nb is not possible based solely on this data, however.

Despite the major changes in the cluster structure at 240° , multiple orders of 00l diffraction are still evident in the x-ray patterns of both the niobium and tantalum interlayered systems. This well-ordered interlayer suggests that a fairly uniform distribution of metal species is retained throughout the hydrolysis and oxidation reactions of the cluster.

Metal oxide moieties of molecular dimensions may be formed, representing a very high state of dispersion. The stoichiometry of Equation (3-8) suggests the formation of a M_6O_{15} species. This M_6O_{15} would probably be structurally similar to the hexanuclear niobate or tantalate $M_6O_{19}^{8-}$ anions formed in solution⁹⁷. The metal atoms of the proposed M_6O_{15} species would be arranged in an octahedron containing a central oxide anion which coordinates to all the metal atoms. The remaining fourteen oxide ions would

adopt terminal and face bridging positions to complete the octahedral coordination of each metal atom. These interlayer oxide species could possibly migrate short distances to form more condensed islands or chains of M_2O_5 , however.

Nitrogen BET surface area data for niobium and tantalum interlayered montmorillonites are listed in Table 3-3. The numbers in parenthesis are surface areas calculated per gram of silicate, compensating for the large mass of the interlayer metals present. These values can be directly compared to the total interlayer surface area available in montmorillonite; approximately 750 m²/g.

Both the niobium and tantalum oxide pillared clays possess available surface areas significantly below those expected based on their retention of high interlayer spacings. The M_6O_{15} moiety, which is assumed to be the pillaring species, can be estimated to be approximately spherical and 9.4 to 9.6 Å in diameter based on measurements of models. Calculations suggest that only about 40% of the silicate surface areas should be occupied by M_2O_5 at the metal cluster loadings used. Thus, surface areas of 250 m^2/g and 230 m^2/g for niobium and tantalum interlayered montmorillonites, respectively, can be calculated. As shown in Table 3-3, the actual surface areas for these interlayered montmorillonites, as measured by using a nitrogen BET method, are approximately one-quarter as large as expected. Apparently, adsorbent molecules are

Table 3-3. Surface Areas of Niobium and Tantalum Oxide Pillared Clays.

A. Niobium In cluster/10	. Niobium Interlayered Montmorillonite (33 mmoles of cluster/100 g of clay).					
Temp., °C	Time, h	Surface Area, m ² /g ^a				
130	24	58(68) ^b				
240	24	64(78) ^b				
325	6	63(77) ^b				
B. Tantalum Interlayered Montmorillonite (23 mmoles of cluster/100 g of clay).						
240	24	32(40) ^b				
350	5	70(88) ^b				

^aSurface area per gram of intercalated material.

^bValues in parenthesis are surface areas calculated per gram of silicate exclusive of intercalated $M_6Cl_{12}^{2+,3+}$ or M_2O .

unable to penetrate very deeply into the silicate interlayer due to the formation of narrow pores (~ 5 Å) and to blockages of the pore openings. These blockages may be due to migrations of metal oxide fragments. The surface areas measured per gram of silicate are somewhat higher than the 15 m²/g measured for a freeze dried Na⁺-montmorillonite sample totally collapsed at 225°. By comparison, the niobium and tantalum pillared clays may contain some interlayer pore openings available for adsorbtion. This is supported by the observation of hysteresis peaks in the nitrogen desorbtion curve measured at low p/p₀.

E. Conclusions and Recommendations

The $M_6Cl_{12}^{2+,3+}$ metal cluster cations bind to Na⁺montmorillonite through ion exchange for interlayer sodium ions to form metal cluster-montmorillonite intercalate compounds. This ion exchange reaction is complicated by cluster oxidation and by hydrolysis and anation reactions. The latter two reactions reduce the average charge carried by the cluster and allow for significantly higher $M_6Cl_{12}^{2+,3+}$ loadings on the layered silicate than was originally anticipated. The level of understanding of the $M_6Cl_{12}^{2+,3+}$ montmorillonite intercalation reaction that was gained by this study, was sufficient to allow for the successful application of these intercalates as precursors for pillared clay formation. The intercalated metal cluster cation serves as a pillar precursor, undergoing degredative hydrolysis and oxidation <u>in situ</u> to yield M_2O_5 props. These metal oxide pillared clays are formed through calcination <u>in vacuo</u> are are stable to 400° and 350° for niobium and tantalum interlayered montmorillonites, respectively.

Future work in this area should be concerned with increasing the surface areas of these materials. This would allow for greater adsorbtion of reactant molecules within the interlayer pore structure, and thus, increase the general utility of these pillared clays as sorbents and catalyst supports. One possible approach would utilize smectite clays, either natural or synthetic, with lower cation exchange capacities as the host silicate. A lower CEC would necessitate lower metal cluster loadings to achieve homoionic replacement of the interlayer sodium ions. This study was performed using a montmorillonite possessing a relatively low CEC, perhaps only a small reduction in layer charge is necessary. The use of a clay possessing a charge which has been significantly reduced by penetration of Li⁺ ions into the lattice may not be applicable for pillaring reactions however. This type treated clay failed to exhibit any ability to be pillared by zirconyl polynuclear cations⁴³.

The formation of the mixed metal cluster salts $[(C_2H_4)_4N]_x[(Ta_{(6-y)},Mo_yCl_{12})Cl_6]$, where x is equal to 2

or 3 and y is equal to 1 or 2, has recently been reported by Meyer and McCarley⁹⁸. It is quite conceivable that the mixed metal cluster cationic core contained in these compounds could be intercalated into smectite clays and oxidized <u>in situ</u>. This would produce mixed metal oxides containing molybdenum, which might prove to be quite interesting catalytically.

One important limitation to the application of metal oxide pillared clays in catalysis is their hydrothermal instability. The collapse of the pillared structure in the presence of steam appears to be characteristic of metal oxide pillared clays in general, and is especially true in the case of niobium and tantalum oxide montmorillonites. This places severe limitations on the types of catalytic reactions or regeneration steps these materials may be subjected to.

IV. THE INTERLAYERING OF MONTMORILLONITE WITH MOLYBDENUM OXIDES BY THE INTERCALATION AND CONVERSION OF MOLYBDENUM CLUSTER CATIONS

A. <u>Intercalation of Molybdenum Cluster Cations into Na⁺-</u> <u>Montmorillonite</u>

To test the general utility of the technique of utilizing intercalated metal cluster cations as metal oxide pillar precursors in the formation of pillared clays, a brief study was undertaken using a molybdenum chloride cluster. This investigation was performed by using the procedure developed previously for the niobium and tantalum cluster reaction as a general guideline.

The formation of a thermally stable molybdenum oxide pillared clay would be highly interesting from the standpoint of catalysis. This pillared clay would contain a catalytically active metal oxide in a highly dispersed state within the unique environment of the clay interlayer. Thus, the metal oxide could serve a dual role as both a structural component of the intercalate and as a catalytically active agent. Molybdenum species are active catalysts for a variety of reactions including oxidation⁹⁹, ammonoxidation^{99,100}, and hydrodesulfurization (HDS)¹².

The molybdenum cluster chloride, $(Mo_6Cl_8)Cl_4 \cdot 2H_2O$ used in this study was prepared in good yield by following the procedure of Nanelli and $Block^{67}$. The synthesis utilizes the conproportionation reaction between molybdenum pentachloride and molybdenum metal powder according to Equation (4-1). The chloride was sublimed over the metal

2.4MoCl₅ + 3.6Mo
$$\xrightarrow{650^{\circ}}$$
 (Mo₆Cl₈)Cl₄ (4-1)

$$(H_30^+)_2(M_{06}Cl_8)Cl_6 \cdot 6H_2O \xrightarrow{200^{\circ}}_{vacuum} (M_{06}Cl_8)Cl_4 \cdot 2H_2O \quad (4-2)$$

+2HCl + 6H₂O

at 650°C under flowing nitrogen. The metal cluster is isolated from hydrochloric acid solution and heated to 200° under vacuum to yield the dihydrate salt according to Equation (4-2).

Initial attempts to intercalate the cluster into montmorillonite were thwarted by the limited solubility of the $(Mo_6Cl_8)Cl_4\cdot 2H_2O$ in aqueous solution. The cluster is rather soluble in absolute methanol, but binding of the cluster to Na⁺-montmorillonite is limited in this solvent. Apparently, insufficient swelling of the smectite clay in methanol (d₀₀₁ is 18.4 Å) and also, the low extent of ionization of this salt to yield a cationic metal cluster core and free chloride anions severely hampers the ion exchange and intercalation reaction. The bonding of the terminal anionic ligands is important to the stabilization of the cluster due to the inability of the Mo_6Cl_8 cluster core to tolerate a buildup of high positive charge. The replacement of a maximum of two terminal halide ions in the presence of a large excess of strongly donating ligands (DMSO, DMF) is indicative of the importance of terminal anion binding⁷⁹.

The lability of four of the twelve halides in the MoX_{2} salts was recognized as early as 1919^{101} due to their replacement by hydroxide ions. Isotopic studies by Sheldon⁶³ utilizing chlorine-36 indicated that exchange of the terminal halides occurs rapidly but that exchange of the bridging halides takes place immeasurably slowly. Several workers have utilized argenometric precipitation to remove the labile terminal halides. This procedure is utilized in the preparation of mixed halogen species⁶⁵, or for replacement by neutral ligands^{62,79}. This latter process would yield compounds of the type Mo₆Cl₈L₆ A₄, where A is ClO_4^- , or $[MO_6Cl_8L_2]A_4$, where A is $CH_3SO_3^-$ and L is DMSO or DMF. This procedure was only marginally successful, however. Many other ligands used in these studies tended to yield products of poor quality. In addition, the reaction is sensitive to the counterion present with silver. Nitrate ion reportedly⁷⁹ causes precipitation and decomposition of the molybdenum cluster.

It should be noted that the perchlorate salts of the cluster coordinated with pyridine, pyridine-N-oxide, and DMF are violently explosive, with the shock sensitivity diminishing upon removal of the organic ligands⁶².

Work in this laboratory led to an improvement of the reaction technique and indicated that the slow addition of a solution of the molybdenum cluster chloride in absolute methanol to an alcoholic solution of silver perchlorate or tetrafluoroborate containing small amounts of water ($\sqrt{7}$ %) results in the precipitation of AgCl and the formation of $[Mo_6Cl_8(OH)_n(H_2O)_{(6-n)}]^{(4-n)+}$ ions in solution. The presence of water is necessary to avoid the precipitation of the cluster with silver as $Ag_2[Mo_6Cl_8]Cl_6$. nROH which occurs in absolute methanol^{62,79}. The water molecules bind to the cluster terminally and help to increase its solubility in solution. Some dissociation of water probably occurs to reduce the net cluster charge (vide infra).

The reaction of silver ion with the terminal halides of the metal cluster can be monitored by utilizing solution electrical conductivity measurements. A conductimetric titration was performed with $AgBF_4$ as the silver source. Conductivity was measured in arbitrary units with compensation made for volume changes during titration by multiplying the measured conductivity (ohm⁻¹) by the total volume of the solution in milliliters.

As shown in Figure 4-1, solution electrical conductivity is plotted relative to the moles of cluster added per equivalent of silver. The plot consists of two linear sections with the titration end point at approximately 0.24 moles of $(Mo_6Cl_8)Cl_4\cdot 2H_2O$ per Ag⁺ equivalent. This value is within experimental error of the end point expected (0.25 moles of cluster/Ag⁺ equivalent) from the 1:4 stoichiometry of the proposed reaction:

$$4Ag^{+} + (Mo_6C1_8)C1_4 \cdot 2H_2O \xrightarrow{CH_3OH/H_2O} 4AgC1_{(s)} +$$

$$[Mo_6Cl_8(OH)_n(H_2O)_{(6-n)}]^{(4-n)+} + nH^+ .$$
 (4-3)

The terminal chlorides are precipitated by silver and replaced by water molecules in terminal coordination. These terminally-coordinated water molecules can hydrolyze to form a bound hydroxide ion and a proton which is released into solution.

The negative slope of the first portion of the plot indicates a net decrease in the electrical conductivity of the AgBF₄ solution as reaction proceeds. This is consistent with the replacement of four moles of Ag⁺ by one mole of $[(Mo_6Cl_8(OH)_n(H_2O)_{(6-n)}]^{(4-n)+}$ and n protons.

Electrolytic solution conductivity can be described by Equation (4-4).





(Mo₆Cl₈)Cl₄·2H₂O.

The AgBF₄ concentration was 6.93×10^{-5} N in methanol containing 7% water. The 6.04×10^{-4} M cluster salt solution in absolute methanol was added to the silver salt. Conductivity was measured in arbitrary units of ohm-1 mL.

$$\Lambda = \alpha F(u_{\perp} + u_{\perp}) \tag{4-4}$$

The equivalent conductance, Λ , is a function of the fractional ionization of the salt, α , the Faraday constant, F, and the ionic mobilities of each ion, u^{102} . The decrease in conductivity during the titration can be attributed to the low degree of ionization and low mobility of the products formed. The molybdenum cluster salt would be expected to possess low ionic mobility due to its large size.

In methanol solution, the protons formed would possess approximately the same specific conductivity as the Ag⁺ ions. The observed decrease in conductivity indicates that the number of protons formed, n, is less than four. The AgCl precipitate does not contribute to the conductivity due to its low solubility in the solvent used.

The addition of $(Mo_6Cl_8)Cl_4 \cdot 2H_2O$ beyond the end point results in a very slight rise in conductivity and is indicative of a small degree of cluster ionization to yield $[(Mo_6Cl_8)(H_2O)_3Cl_3]^+$ and chloride anion in solution. This observation is consistent with the very low extent of binding of $(Mo_6Cl_8)Cl_4 \cdot 2H_2O$ to Na⁺-montmorillonite which occurs in methanol solution.

The reaction described in Equation (4-3) is equally valid if the counterion to silver is perchlorate. $AgClO_4$ was utilized for all additional studies. The $[Mo_6Cl_8-(OH)_n(H_2O)_{(6-n)}]^{(4-n)+}$ species formed in methanol is readily soluble in aqueous solution, therefore, the stock solutions of this species were diluted with water and the major portion of the methanol was removed by rotary evaporation. Removal of the methanol eliminates the negative effects this solvent has on the metal cluster intercalation reaction into montmorillonite and reduces the chance of forming explosive molybdenum cluster perchlorate precipitates containing methanol.

In aqueous solution the molybdenum cluster possesses measurable acid/base properties. Sheldon⁶⁹ has published an acid titration curve of the $Mo_6Cl_8(OH)_6^{2-}$ ion formed at high pH. This curve demonstrates that this molybdenum cluster species reacts with two equivalents of acid and is precipitated at a pH of approximately 8.5. This precipitate is thought to be $Mo_6Cl_8(OH)_4 \cdot xH_2O^{69,103}$. The cluster solution concentration used for this experiment was not specified, however.

The acid/base properties of the molybdenum cluster can be utilized for its intercalation into Na⁺-montmorillonite. The reaction occurs during the dropwise addition of 0.1 <u>N</u> HClO₄ to a montmorillonite suspension which is 5×10^{-5} <u>M</u> or lower in $[Mo_6Cl_8(OH)_n(H_2O)_{(6-n)}]^{(4-n)+}$. The cluster stock solutions were adjusted to a pH of 10.0 during their synthesis to enhance their cold storage stability. Consequently, the intercalation reaction mixture containing Na⁺-montmorillonite and cluster stock solution possessed an initial pH of approximately 8.0.

The low cluster solution concentration is necessary to avoid the formation of $Mo_6Cl_8(OH)_4 \cdot xH_2O$ precipitates upon acid addition. Apparently, the tetrahydroxo species has a limited solubility in solution which was not reported by Sheldon. The slow addition of $HClO_4$ to achieve a final pH of 1.5, leads to further cluster protonation to form cationic $Mo_6Cl_8(OH)_3(H_2O)_3^+$ species in solution. This cation will then undergo ion exchange for sodium on the montmorillonite present in suspension. The rate of acid addition must be slow enough so that the rate of cluster protonation is roughly balanced by the rate of cluster intercalation. The use of a sufficiently slow rate of acid addition will minimize the formation of $[Mo_6Cl_8(OH)_n (H_2O)_{(6-n)}](ClO_4)_{(4-n)}$ precipitates (where $0 \le n \le 3$) which bind to the external surfaces of the montmorillonite.

The details of the molybdenum cluster intercalation were examined by measuring the number of equivalents of sodium liberated from homoionic Na⁺-montmorillonite relative to the number of moles of $[Mo_6Cl_8(OH)_n(H_2O)_{(6-n)}]^{(4-n)+}$ added. These data are plotted in Figure 4-2. This plot contains an initial section which indicates a linear release of sodium as cluster is added, indicative of an ion exchange reaction. The slope of this section, 1.05 Na⁺ released/cluster added, is consistent with the quantitative uptake by ion exchange of a cationic cluster ion as illustrated in Equations (4-5) and (4-6).




$$Mo_{6}Cl_{8}(OH)_{n}(H_{2}O)_{(6-n)}^{(4-n)+} + (n-3)H^{+} \stackrel{*}{\leftarrow} Mo_{6}Cl_{8}(OH)_{3}(H_{2}O)_{3}^{+}$$

pH = 10 pH = 1.5 (4-5)

$$Mo_{6}Cl_{8}(OH)_{3}(H_{2}O)_{3}^{+} + \underbrace{Na^{+}}_{Na^{+}} \underbrace{PH \ 1.5}_{Mo_{6}Cl_{8}(OH)_{3}(H_{2}O)_{3}^{+} + Na^{+}}_{(4-6)}$$

The horizontal lines represent the silicate sheets of montmorillonite. Essentially quantitative uptake of the cluster by the clay is observed through the range of this experiment, and up to 180 mmole/100 g silicate loading. Apparently the initial uptake of cluster is predominantly by ion exchange, but at higher cluster loadings both cationic and neutral species are bound. The binding of neutral $[Mo_6Cl_8(OH)_n(H_2O)_{(6-n)}](ClO_4)_{(4-n)}$ as ion pairs or in small crystalline aggregates occurs through hydrogen binding or physical adsorbtion to the external surfaces of the clay. This external binding becomes more prevalent as the fraction of ion exchange sites on the montmorillonite occupied by electrostatically bound cluster increases. The externally deposited clusters are easily removed by distilled water washings at pH 7, however. The infrared spectrum of the molybdenum cluster intercalated montmorillonite after several washings with distilled water, illustrated in Figure 4-4b (p.101), is free from bands assigned to the ClO_4^- ion indicating that any ion pairs originally present have been removed.

The elemental analysis of a molybdenum cluster intercalated montmorillonite prepared by the addition and quantitative uptake of 70 mmoles of cluster/100 g of clay indicated that greater than 99% of the interlayer sodium ions have been replaced. This analysis also showed that of the 70 mmoles of cluster originally bound per 100 g of silicate 53.6 mmoles remained electrostatically bound to the montmorillonite. Thus 16.4 mmoles of cluster/100 g of montmorillonite were freed from the clay during multiple distilled water washings.

The chemical analysis of the intercalate containing 53.6 mmoles of cluster/100 g of clay corresponds to the average unit cell formula $[Mo_6Cl_8(OH)_{2.7}(H_2O)_{3.3}]_{0.39}^{1.3+}$ - $[Al_{3.11}, Mg_{0.50}, Fe_{0.40}](Si_{7.91}, Al_{0.09})O_{20}(OH)_4$. The average charge per cluster can be calculated to be 1.3+ based on this formula. This correlates reasonably well with the charge of 1.05+ as determined by the sodium release measurements. A charge of greater than 1.0 suggests that double protonation to produce the dication $Mo_6Cl_8(OH)_2(H_2O)_4^{2+}$ occurs in some fraction of the clusters.

The difference between the average charge per cluster calculated by using the sodium release data (1.05+) and by using the analytical results (1.3+) is significant and suggests the occurrence of a surface equilibrium. Equation (4-7) shows the reaction of two intercalated monocations

$$\frac{2MO_{6}Cl_{8}(OH)_{3}(H_{2}O)_{3}^{+}}{(H_{2}O)_{3}^{+}} \ddagger \frac{MO_{6}Cl_{8}(OH)_{2}(H_{2}O)_{4}^{2+}}{(H_{2}O)_{4}^{2+}} + MO_{6}Cl_{8}(OH)_{4}(H_{2}O)_{2}$$

$$(4-7)$$

by proton transfer to produce an intercalated dicationic cluster and a neutral cluster in solution. The horizontal lines represent the silicate layers of montmorillonite. The position of this equilibrium shifts to the right (as written above) during the washings with distilled water.

B. <u>Physical Characterization of Mo₆Cl₈(OH)_{2.7}(H₂O)_{3.3}^{1.3+}-Montmorillonite</u>

The x-ray diffraction pattern of montmorillonite intercalated with 53.6 mmoles of molybdenum cluster/100 g of silicate is shown in Figure 4-3. The basal spacing of 16.6 Å is large enough to accommodate the thickness of the silicate sheet (9.6 Å) plus the height of the molybdenum cluster, (7.2 Å), as calculated from single crystal xray diffractometry^{60,104}, provided that this cluster cation partly fits into the hexagonal cavities present on the basal surfaces of montmorillonite. The keying of cations into these cavities is a fairly well known phenomenon. It has been observed for partly dehydrated interlayer alkali metal cations¹⁶ and is proposed to occur with intercalated alkyl ammonium ions as well^{36,37}.





The observation of three orders of OOL x-ray diffraction for the $Mo_6Cl_8(OH)_{2.7}(H_2O)_{3.3}^{1.3+}$ -montmorillonite indicates that only limited order exists within the clay interlayer. This would suggest that a somewhat uneven distribution or variable hydration of the molybdenum cluster occurs within the sample.

The intercalate can be characterized by its infrared spectrum in the region 1900-250 cm⁻¹ with respect to the molybdenum cluster precipitated from $HClO_4$ solution at pH 1.0. The spectrum of this precipitate, formulated as $[Mo_6Cl_8(OH)_n(H_2O)_{(6-n)}](ClO_4)_{(4-n)}$, is shown in Figure 4-4a. This spectrum contains bands attributed to the cluster cation and its coordinated water at 290-330, 785, and 1620 cm⁻¹ as assigned in detail below. The absorbtion band centered at 1050 cm⁻¹ is due to the vibrational modes of $ClO_{\mu}^{-62,106a}$.

The infrared spectrum of $Mo_6Cl_8(OH)_{2.7}(H_2O)_{3.3}^{1.3+}$ -montmorillonite is illustrated in Figure 4-4b. The absorbtion band at 290-330 cm⁻¹ is assigned ^{65,105} to the Mo-Cl stretching vibration of the bridging chlorides in the cluster core. The bands at 785 and 1620 cm⁻¹ are attributed ¹⁰⁶, respectively, to the rocking and the wagging modes of water molecules present in the sample, some of which are coordinated to the cluster core. The (Al,Si)-O deformation bands of the montmorillonite are present at 465 and 520 cm⁻¹. The intense band at 1025 cm⁻¹ is assigned ⁹² to the (Al,Si)-O



Figure 4-4. The infrared spectra of (a) $[Mo_6Cl_8(OH)_n - (H_2O)_{(6-n)}](ClO_4)_{(4-n)}$ precipitate, (b) $Mo_6Cl_8 - (OH)_{2.7}(H_2O)_{3.3}^{1.3+}$ -montmorillonite, and (c) $Mo_6Cl_8(OH)_{2.7}(H_2O)_{3.3}^{1.3+}$ -montmorillonite after thermolysis at 130° (24 h), 200° (24 h), and 280° (24 h) under dynamic vacuum. In sample (a), $0 \le n \le 3$. Samples (b) and (c) contained 53.6 mmoles of cluster/100 g of clay. All samples were prepared as KBr disks. stretching vibrations of the montrmorillonite⁹². The medium intensity band at 1430 cm⁻¹ is attributed to the C-H bending modes of methanol¹⁰⁷ impurity present in the sample, probably adsorbed on the montmorillonite interlayers. One interesting feature of this spectrum is the band at 1700-1670 cm⁻¹. Presumably this is a portion of the H₂O wagging vibrational manifold which is shifted 65 cm⁻¹ toward higher energy through interaction with intercalated molybdenum clusters.

The UV-visible spectrum of $Mo_6Cl_8(OH)_{2.7}(H_2O)_{3.3}^{1.3+}$ montmorillonite in a Nujol mull is shown in Figure 4-5a. It contains absorbtion bands at 320 and 405 nm attributable to the presence of the metal cluster. The shoulder at 220 nm is due to the montmorillonite. The spectrum of the precipitated $[Mo_6Cl_8(OH)_n(H_2O)_{(6-n)}](ClO_4)_{(4-n)}$ mulled in Nujol is shown in Figure 4-5b. The spectrum of (Mo_6Cl_8) - $Cl_4 \cdot 2H_2O$ in methanol solution is illustrated in Figure 4-5c. This spectrum contains an intense ($\epsilon \approx 4000$) absorbtion band centered at 330 nm which is attributed^{79,108} to ligand-tometal charge transfer from the bridging chlorides.

The spectra in Figure 4-5 are very similar to that of $Mo_6Cl_8(OH)_6^{2-}$ formed in 0.01 <u>N</u> NaOH solution (λ_{max} at 300, 330 nm) as reported by Sheldon⁶³, with the exception that both bands are shifted considerably toward the red. This red shift can be interpreted by using the molecular orbital diagram for the M₆X₈ cluster calculated by Cotton and Haas¹⁰⁹. Protonation of the intercalated cluster increases



Figure 4-5. Transmission UV-visible spectra of (a) Mo_6Cl_8 -(OH)_{2.7}(H₂O)^{1.3+}-montmorillonite, (b) [Mo₆Cl₈-(OH)_n(H₂O)_(6-n)](ClO₄)_(4-n) precipitate, and (c) (Mo₆Cl₈)Cl₄·2H₂O.

Sample (a) was prepared as a Nujol mull of the intercalate containing 53.6 mmoles of cluster/ 100 g of clay suspended between quartz glass plates. Spectrum (a) was measured versus mulled Na⁺-montmorillonite as a reference. Sample (b) was prepared by evaporation of suspension of the precipitate on a quartz glass plate. Sample (c) was a solution in methanol. Absorbance was measured in arbitrary units. the positive charge residing on each metal atom. The increase in positive charge contracts the metal atomic orbitals which decreases the overall cluster bonding. The diminished intermetallic bonding decreases the energy of the antibonding molecular orbitals of the cluster bringing them closer in energy to the atomic orbitals of the chloride ligands. Therefore the ligand-to-metal charge transfer energy is lowered resulting in the red shifting of the UV-visible absorbtion bands.

C. <u>The Interlayering of Montmorillonite with Oxides of</u> Molybdenum

The work described above establishes that molybdenum cluster cations can be intercalated into montmorillonite. The real interest in this material lies in its use as a precursor to a molybdenum oxide pillared clay, however. This application requires the <u>in situ</u> conversion of the cluster chloride to molybdenum oxide aggregates. A reaction scheme to carry out this conversion was designed to utilize <u>in vacuo</u> calcinations similar to the niobium and tantalum oxide pillaring process described in Chapter IV.

Early experimental results indicated that amodification of the preliminary drying step as used for niobium and tantalum cluster was necessary, however. The initial thermolysis at 130° for 24 h was supplemented by an additional 24 h at 200°. This time period at the higher temperature was designed to more thoroughly eliminate the excess amounts of interlayer water present in the samples. The decomposition of the cluster is promoted by calcination of the intercalate at 280° for 24 h <u>in vacuo</u>. This decomposition is accompanied by a change in the sample color from brilliant yellow to tan or light blue. If this calcination is performed under flowing nitrogen an acidic reaction product, presumably hydrochloric acid, is detectable by wet litmus paper placed in the effluent gas stream. In addition, no detectable (AgNO₃) chloride was present in a sample of Mo₆Cl₈(OH)_{2.7}(H₂O)^{1.3+}-mont-morillonite which had been calcined <u>in vacuo</u> at 280° and then digested in H₂SO₄.

The molybdenum cluster is clearly decomposing during the final thermolysis step. The infrared spectrum of the molybdenum cluster intercalate shown in Figure 4-4c lacks the broad band at 290-330 cm⁻¹ attributed to the metal cluster core. The appearance of a band at 900 cm⁻¹ is attributed¹¹⁰ to the Mo=0 stretching frequency of molybdenum oxides formed upon cluster decomposition.

The appearance of a blue tint in some samples is accompanied by the presence of an extremely broad absorbtion band centered at approximately 730 nm in the UVvisible spectrum. The observation of this absorbtion band indicates¹¹² that an isopoly molybdate known as a molybdenum blue has been formed. These blue oxides

contain molybdenum atoms possessing an average oxidation state between 5.2 and 6.0^{52} . Generally these compounds are anionic and as such, their formation is accompanied by collapse of the clay interlayer (d₀₀₁ equals 9.8 Å). The formation of the blue color seems to indicate that the sample was not thoroughly dried in the preliminary thermolysis steps.

The formation of a tan color upon calcination is indicative of a sufficient reduction of the interlayer water prior to the calcination and generally accompanies the formation of interlayer oxide formation. Unless specified otherwise the remainder of this discussion section refers to samples that were tan in color after calcination at 200°.

The x-ray diffraction pattern of a sample treated at 280° following the optimized thermolysis sequence is shown in Figure 4-6. The diffraction pattern shows that this material possesses a range of d₀₀₁ spacings from 9.8 Å up to 13.2 Å. This diffraction pattern may be the result of interstratification, in which a variable interlayer spacing is produced by a non-uniform distribution of interlayer molybdenum oxide aggregates. Alternatively, this diffraction pattern indicates the formation of a biphasic system consisting of collapsed montmorillonite with an interlayer spacing of 9.8 Å, and a molybdenum oxide interlayered clay possessing a basal spacing of 13.2 Å.



This second interpretation is more consistent with the observation of the broad peaks present at 5.0 Å and 3.2 Å, which are the (002) and (003) reflections of the collapsed clay. The weak reflection present at 6.6 Å is attributed to the (002) reflection of the expanded phase clay.

The expanded phase is interlayered with molybdenum oxides which prop the silicate sheets apart with an interlayer spacing of 3.6 Å. This separation indicates that the interlayer molybdenum oxide, presumably MoO_2OH , is aggregated in the form of sheet or chains slightly greater in thickness than a sheet of oxide anions. The identification of the interlayer species as a Mo(V) oxide, which is brown, is consistent with both the tan color of the expanded phase clays produced and with the cluster hydrolysis products proposed by Sheldon (vide infra). In addition, the series of color changes from bright yellow to tan to blue observed upon calcination of some pretreated molybdenum cluster intercalates at 280° strongly suggests an increasing extent of molybdenum oxidation along the series. This places the upper boundry for the oxidation state of molybdenum in the tan samples at approximately 5.2+, prior to the formation of the blue oxides.

The formation of metal oxide from the metal cluster chloride within the clay interlayer can be examined in comparison to studies in aqueous solution. The reactions of the molybdenum halide clusters in alkaline solution have been studied extensively by J. C. Sheldon^{71,72,113}.

He established that the hydroxide was capable of displacing the bridging chlorides, eventually leading to a decomposition of the cluster structure and the simultaneous production of hydrogen gas. It was determined⁷¹ that the replacement of the bridging halides follows kinetics first order in hydroxide concentration and first order in metal cluster solution concentration. Thus, the replacement of these chlorides was proposed to occur through reaction with hydroxide ions by an $S_{\rm N2}$ mechanism. The partial hydrolysis of the cluster as it occurs in alkaline solution can be written:

$$[Mo_{6}Cl_{8}](OH)_{6}^{2-} + nOH^{-} \rightarrow [Mo_{6}Cl_{(8-n)}(OH)_{n}]OH_{6}^{2-} + nCl^{-},$$
(4-8)

where n is equal to 1, 2, or 3. Studies on the kinetics of the decomposition of the molybdenum bromide cluster in alkaline solution were performed in the presence of H_2O_2 . The peroxide served to eliminate the apparently autocatalytic cluster hydrolysis term in the rate equation. Kinetics studies indicated⁷² that the hydrolysis of the chloromolybdenum cluster is autocatalytic at elevated (70-90°) temperatures. The products of this reaction were identified^{63,69} as hydrogen gas and Mo(V) oxide.

At elevated temperatures under dynamic vacuum, the intercalated cluster undergoes an in situ hydrolytic

degradation and oxidation to yield interlayer molybdenum oxide. The degradative hydrolysis occurs through reaction with water molecules and hydroxide ions coordinated to the cluster and with water adsorbed on the silicate interlamellar surfaces. The preliminary drying steps at 130° and 200° will limit the amount of adsorbed water present, but provides no accurate stoichiometric control over this reaction. In analogy to Equation (4-8) above, the interlayer reaction occurs through the displacement of the $\mu_{3}\text{-}$ chlorides by hydroxide ions to form face-bridging hydroxides. Interlayer water molecules would participate in the reaction following deprotonation. The chloride displacement would occur in a step wise manner until the metal cluster structure is sufficiently destabilized to promote its oxidative decomposition to the metal oxide and the simultaneous reduction of protons to yield hydrogen gas. The reaction is summarized in Equation (4-9), in which the area between the horizontal lines represents the clay interlayer region.

Mo ₆ Cl ₈ (OH) _{2.7} (H ₂ O) _{3.3} ^{1.3+}	+	12H ₂ 0	280° vacuum	6мо0 ₂ 0н	+	1.3H ⁺
				+ 8нсі		
				+ 9 ^H 2		
						(4-9)

The formation of a pillared clay from the molybdenum cluster intercalate by this reaction demands that the cluster decomposition yield interlayer metal oxide aggregates. This process is rather sensitive to the presence of amounts of water in excess of the stoichiometry of Equation (4-9) due to the tendency of molybdenum oxides to form anions which migrate from the clay interlayer. In comparison, this appears to be somewhat more problematic for the molybdenum oxides than for the niobium and tantalum interlayer oxide species.

The best molybdenum oxide interlayered clay produced to date, contained a mixed phase system. Presumably, the formation of this biphasic system was due to some variation in water content within the sample which promoted collapse of those interlayers which were hydrated to a greater extent. The formation of and migration by anionic metal oxide species is an important mode of collapse during the conversion of a metal cluster intercalate to a metal oxide pillared clay.

Collapse of the molybdenum oxide interlayered montmorillonite can occur even under the anhydrous interlayer conditions existing after 24 h at 280° <u>in vacuo</u>. The molybdenum oxide interlayered clay collapses at the relatively moderate temperature of 300° , with the oxide migrating from the interlayer to the outer surfaces of the clay.

There is a general relationship between the bulk properties of an anhydrous metal oxide and its ability

to pillar a smectite clay at elevated temperatures. This relationship can be illustrated by comparing the melting point of a metal oxide¹²⁸ to the maximum temperature of stability for a clay interlayered with that oxide reported in the literature (see Table 1-1 (p.7)). Figure 4-7 illustrates the linear relationship that exists. A least squares fit to these data produces the line shown which possesses a correlation coefficient of 0.75. This is a remarkably good fit for data gathered from many different sources and authors utilizing various techniques.

The empirical relationship illustrated by this plot strongly suggests that the maximum temperature of stability of a pillared clay is related to the bulk characteristics of the pillaring metal oxide. This relationship with the melting point of the metal oxide further suggests that the mode of collapse of the props may be fundamentally similar to the process of melting of the bulk oxide although occurring at substantially lower temperatures than the actual melting point. The decomposition of the metal oxide pillars probably involves the fragmentation of the props into smaller mobile moieties which easily migrate from the clay interlayer to deposit on the edge surfaces of the clay layers.





A correlation The line was drawn as a least squares fit of the data. coefficient of 0.75 was calculated for this fit.

oxide.

D. Conclusions and Recommendations

The molybdenum chloride cluster $(Mo_6Cl_8)Cl_4 \cdot 2H_2O$ can be utilized as a pillar precursor for the formation of an expanded phase montmorillonite containing molybdenum oxide aggregates. Modification of the metal cluster salt to the hydrated perchlorate form can be accomplished by removal of the terminally bound chloride anions through argenometric precipitation. Intercalation of the hydrated metal cluster into montmorillonite occurs by ion exchange for interlayer sodium ions under acidic conditions. These intercalated clusters undergo in situ hydrolytic decomposition and oxidation upon calcination at 280° under vacuum. The proposed reaction produces a molybdenum oxide interlayered material possessing an interlayer spacing of up to 3.6 Å due to the presence of a layer of molybdenum oxide. This interlayered material is stable only to the relatively moderate temperature of 300°, however. The success, albeit somewhat limited, of the synthesis of a molybdenum oxide interlayered clay through the reaction of a metal cluster intercalated montmorillonite demonstrates the general nature of this reaction and adds credence to the results described for niobium and tantalum in Chapter III.

A review of the maximum thermal stabilities of the metal oxide pillared clays described in the literature, in conjunction with the collapse temperatures for the

niobium, tantalum, and molybdenum oxide interlayered montmorillonites lead to the discovery of an interesting relationship between the melting point of a given metal oxide and the maximum temperature of stability for the pillared clay containing that oxide. It is strongly recommended that additional data points be gathered and added to Figure 4-7. With further refinements, this type of approach could lead to estimates of maximum thermal stability expected for pillared clays prior to their synthesis.

V. MOLYBDENUM CLUSTER BINDING TO H⁺-Y ZEOLITE

A. Introduction

A relatively brief investigation of the binding of the molybdenum cluster to a hydrogen exchange form of the synthetic faujasitic zeolite Y was performed. The objective of this study was to utilize the ion exchange chemistry of the molybdenum cluster developed for montmorillonite, as a method of binding the compound to zeolites. Ion exchange could potentially place the molybdenum cluster within the intracrystalline voids of these aluminosilicates. Calcination of this exchanged zeolite could potentially create a catalyst containing a well-defined molybdenum oxide species within the intracrystalline channels of a zeolite. The rigid zeolite structure might serve to support and stabilize the molybdenum oxide species without imposing structural requirements on them as is the case within pillared clays.

Zeolites are crystalline, hydrated aluminosilicates of Group I or II elements in their natural forms. These tectosilicates consist of a three-dimensional framework of $(Al,Si)O_4$ tetrahedra linked together by the sharing of all oxygens. This framework contains channels or

interconnected voids within the crystal, which are occupied by cations and water molecules. The cations are present to balance the charge on the lattice originating from substitutions of Al^{3+} for Si^{4+} ions. These intracrystalline cations are ion exchangeable to some degree, depending on the zeolite framework and the cations in question. The intrachannel or "zeolitic" water can be reversibly adsorbed. However, high vacuum ($\sim 10^{-6}$ torr) and elevated temperatures ($\sim 350^{\circ}$ C) are generally necessary to totally dehydrate the crystal.

There are 34 naturally occurring zeolites and about 100 synthetic types. The synthetic zeolite Y possesses a crystalline framework similar to the structure of faujasite, with a silica-to-alumina ratio of 1.5 to 3.0. The structure of faujasite, illustrated in Figure 5-1, consists of (A1,Si)O₄ tetrahedra assembled into truncated octahedra known as β -cages. These cages are linked together through their hexagonal sides to form prisms of double-6-rings. A void approximately 13 Å in diameter, known as the supercage, is created within the assembly. Access to the supercage is available through a 12-ring opening, shown in the foreground in Figure 5-1, which is 7.4 Å in diameter as determined crystallographically. Molecules as large as $(C_{4}H_{9})_{3}N$, which has a kinetic diameter of 8.1 Å, are permitted through this opening¹¹⁴.



Figure 5-1. A schematic diagram of the structure of

faujasite.

The verticies indicate the location of $(Al,Si)O_4$ tetrahedra, the midpoints of the lines indicate the positions of shared oxygens. The truncated octahedra, known as β -cages, are linked together through double-6-ring prisms. A large cavity, known as the supercage, is thus formed. The supercage is visible in this diagram through the 7.4 Å, 12-ring pore open-ing in the foreground. Diagram taken from Reference 11b, p. 168.

Recently, there has been a great deal of interest in placing transition metals, in highly dispersed forms¹¹⁵. and as aggregates or clusters¹¹⁶, within the pore structure of zeolites. It has been suggested¹¹⁷ that intracrystalline metallic species would possess exceptional catalytic activity. This activity would be as a result of the high state of dispersion and the formation of unique metal assembleges made possible through interaction with the zeolite matrix. The zeolite framework may also impart a size selectivity to a catalytic reaction based on the relative rates of diffusion of product or reactant molecules through the crystal, or by limiting the size of the transition state complex of the reaction. The juxtapositioning of acidic sites on the aluminosilicate and the intracrystalline metallic catalytic sites may also impart an important bifunctionality to the catalyst. Rabo et al.¹¹⁸ and Weisz¹¹⁹ were among the first to demonstrate that reduced transition metal loaded zeolites possessed great promise as catalysts in petroleum refining. For example, after hydrogen reduction at 450°, 0.5 wt % Pt dispersed within a Ca-Y zeolite exhibits high stability to sulfur poisoning in its use as a reforming catalyst¹¹⁷. This catalyst actively demonstrates the size selectivity and bifunctionality expected of an active metal dispersed within a zeolite.

Recently, much work has dealt with the formation of metal clusters or metal aggregates within the zeolite intracrystalline channels¹²⁰. The formation of metal clusters

and bimetallic species such as Ru-Cu and Ru-Ni indicates that controlled metallic aggregation can yield extremely high dispersions of metals and alloys supported on zeolites¹²⁰. The maintenance of high dispersion is a function of the preliminary treatment^{116a}. It is extremely difficult, however, to ascertain the exact location of the metal aggregates; whether they are deposited on the external zeolite surfaces or within the intracrystalline voids.

Metals and metal clusters can be deposited within zeolites by adsorbtion of the vapor of organometallic or volatile inorganic compounds. The metal carbonyls of Mo^{121} , Fe^{122} , Re, Ru^{123}, Ni, Cr, W, and Mn^{117} and the metal cluster carbonyls $Fe_2(CO)_9$, $Fe_3(CO)_{12}^{122}$ and $Re_2(CO)_{10}$, $Ru_3(CO)_{12}^{123}$ have been adsorbed within zeolites by vapor deposition. The carbonyl ligands are easily removed by thermal decomposition to yield active metal species.

Recent work by Lundsford¹²⁴ has utilized the vapor adsorbtion of MoOCl₄, followed by the decomposition of the chloride at 400°, to place molybdenum oxides within H^+-Y and ultrastable Y zeolites. These materials were shown to be active for the selective oxidation of cyclohexene to the epoxide within a slurry reactor. Similarly, work by Wilhelm¹²⁵, has utilized the vapor deposition of volatile molybdenum oxychlorides, formed by reaction of MoO₃ with anhydrous HCl, or of MoO₂ with Cl₂, to place 3 to 10 wt % molybdenum loadings on mordenite zeolites. These molybdenum containing zeolites are viewed in contrast to commercially available catalysts which are prepared by coextrusion or impregnation techniques that deposit the metal exclusively on the external surfaces of the zeolite.

The ion exchange of molybdenum compounds into zeolites could potentially produce a more even metal distribution, and thus, higher catalytic activity, than the vaporization techniques mentioned above. There are, however, few cationic forms of molybdenum available for ion exchange, and these are formed only in strongly acidic environments, well beyond the acid stability of large pore zeolites. Therefore, previous attempts at ion exchange of molybdenum compounds into zeolites have produced poorly crystalline, low surface area products¹²⁵.

B. Binding of the Molybdenum Cluster by H⁺-Y Zeolite

It has been demonstrated in Chapter IV, that the molybdenum cluster exhibits the ability to ion exchange into Na⁺-montmorillonites at low pH. The molybdenum intercalate thus formed, also possessed the desired ability to undergo the thermochemical transformation to yield interlayer molybdenum oxide. It is possible to envisage a similar kind of pH dependent ion exchange into the pores of a Y type zeolite, and the subsequent decomposition of the cluster to yield molybdenum oxide trapped

within the supercages.

The ion exchange of the protonated molybdenum cluster into Na⁺-Y, in direct analogy to the reaction with Na⁺montmorillonite is not possible due to the acidic conditions (pH 1.5) of that reaction. Faujasitic zeolites possess only limited acid stability, suffering dealumination and loss of crystallinity at a pH of 3.0 (HClO₄; 24 h) or lower. Therefore, a modified approach was used.

The reaction of $Mo_6Cl_8(OH)_n(H_2O)_{(6-n)}^{(4-n)+}$ from a stock solution with the hydrogen exchange form of zeolite Y utilized the zeolite as a source of acid. This reaction was performed at 70°, with a dropwise (1.5 mL/min) addition of 0.1 <u>N</u> HClO₄ to adjust the solution pH to 4.0. At this pH and temperature little loss of zeolite crystallinity was observed (vide infra).

Approximately 70% of the molybdenum cluster present in solution was bound to the zeolite, producing a molybdenum loading of 2.27 wt% as shown by chemical analysis. In contrast, a Na⁺-Y bound only about 12% of the molybdenum cluster, to produce a loading of 0.39 wt % molybdenum, under identical conditions. Little, if any molybdenum was noticeably bound to Al_2O_3 or SiO₂ samples under similar conditions. No chemical analyses were performed on these samples, however.

Comparison of the chemical analyses for H^+-Y and Na^+-Y indicates that the binding of molybdenum is

strongly dependent on the cation exchange form of the zeolite used. This suggests that the molybdenum cluster is not simply physically adsorbed on the zeolite under reaction conditions. The strong binding of the cluster to the H⁺-Y zeolite is probably a result of the acid/base chemistry of $Mo_6Cl_8(OH)_4(OH_2)_2$ present in solution at pH 4.0. The protonation of the cluster in contact with the zeolite will result in the electrostatic binding reaction as shown in Equation (5-1),

$$M_{0_{6}Cl_{8}(OH)_{4}(H_{2}O)_{2} + H^{+}} \xrightarrow{A_{1}} M_{0_{6}Cl_{8}(OH)_{3}(H_{2}O)_{3}^{+}} \xrightarrow{A_{1}} (5-1)^{+}$$

s

1

where the serpentine lines represent the zeolite aluminosilicate framework. The protons in a hydrogen form of the zeolite would be present either as exchangeable cations bound electrostatically near the aluminum sites or as hydroxyl groups on silica tetrahedra adjacent to the aluminum ions¹²⁶. The former case would predominate in the hydrated zeolite.

The binding of the molybdenum cluster to H^+-Y presumably involves protonation and interpenetration of the metal cluster into the zeolite. The molybdenum cluster could then occupy the large pores and supercages only, being too large to enter other cation binding sites. The molybdenum cluster can be viewed as a cubic assembly of chloride ions that is 7.2 Å on a side and 8.6 Å on the facial diagonal. The penetration of this large species through the 7.4 Å, 12-ring pore opening would prove to be a difficult step. Experimental observations indicate that the reaction of the molybdenum cluster with H^+-Y at 70° yields a product that is more homogeneous in appearance than the product of reaction at room temperature, all other factors being equal. This would be consistent with an ion exchange reaction of a large cation which requires high momentum in order to overcome the barrier to penetration that the tight fit of the pore opening presents.

Assuming that intracrystalline penetration and ion exchange has occurred, the cluster cation would be limited to occupancy of the supercage and the large pores. Similar restrictions are found for other cations. For example, the exchange of $(C_{2}H_{5})_{3}NH^{+}$, which has a diameter of approximately 6.9 Å, into a Na⁺-Y is limited to replacement of only 26% of the sodium ions¹¹⁴. The alkyl ammonium cation is too large to pass through the 2.2 Å pore openings into the β -cage, and thus cannot replace the cations in these positions. In addition, the ion exchange is limited by the volume of the cation (168 Å³) and the volume available in the supercage, approximately 6700 Å³ ¹¹⁴. Similarly, the maximum loading of the molybdenum cluster would be severely limited by its diameter and volume of occupancy (370 Å³).

Several experiments were performed to test the possibility of carrying out a cluster decomposition to the oxide within the zeolite. The quantity of water within a zeolite after drying under ambient conditions is far greater than that within a clay intercalate. Therefore, it was more practical to carry this water away from the zeolite under flowing nitrogen or oxygen at 200° for 2 h, rather than under vacuum. The subsequent calcination of the sample at 430° for 5 h under either gas results in its color change from yellow to blue ($\sim340^{\circ}$) to white, suggesting that the cluster structure has decomposed completely to produce MoO_3 . The appearance of the blue coloration at the intermediate temperature suggests that the metal cluster has undergone an hydrolysis and oxidation reaction to yield a molybdenum isopoly blue compound, similar to that described in Chapter IV. This probably indicates that the molybdenum oxide has migrated to the external surfaces of the zeolite. Chemical analysis of this material indicates that only traces of chloride remain following this treatment, indicating that the cluster has decomposed. The molybdenum is present in essentially the original quantities as indicated by the anhydrous unit cell formula $(MoO_3)_{3.06}$, $H_{53.97}^+$ -[(AlO₂)_{53.97}, $(SiO_2)_{138.03}$]. The presence of the full amount of molybdenum indicates that little is volatilized off the zeolite in the form of oxides or oxychlorides during reaction at 430°.

C. <u>Physical Characterization of $[Mo_6Cl_8(OH)_3(OH_2)_3(OH_2)_3]_{0.47}^+$ </u> <u> $H_{53,50}^-Y$ Zeolite</u>

The reaction at pH 4.0 and 70° between H^+-Y and $Mo_6Cl_8(OH)_4(OH_2)_2$ in a ratio of 0.67 moles of cluster per zeolite unit cell produced a light yellow solid. This stoichiometry was used because it would result in a loading of 5.0 wt % Mo_6Cl_8 , assuming quantitative uptake by the zeolite. Elemental analysis corresponded to an anhydrous unit cell formula of $[Mo_6Cl_8(OH)_3(OH_2)_3]_{0.47}^+$, $H_{53.50}^+[(AlO_2)_{53.97}, (SiO_2)_{138.03}]$. This, of course, is a bulk analysis and tells nothing about the actual interrelationship between the molybdenum cluster and the silicate.

As stated above, one of the major difficulties in placing molybdenum within zeolites by ion exchange is the loss of crystallinity and surface area by the tectosilicate under acidic conditions. The zeolite Y used in this study maintained excellent crystallinity down to a pH of 4.0 (HClO₄) as judged by x-ray diffraction peak intensities. Excellent zeolite crystallinity is also maintained in the presence of the molybdenum cluster at pH 4.0. Figure 5-2 shows the x-ray diffractograms of freshly prepared H⁺-Y, $[Mo_6Cl_8(OH)_3(OH_2)_3]_{0.47}^{+}$, $H_{53.50}^{+}$ - $[(AlO_2)_{53.97}$, $(SiO_2)_{138.03}]$ air dried, and after a predrying step at 200° (2 h) and calcination at 430° (5 h) under flowing oxygen. In each case the x-ray diffraction pattern contains narrow lines of high intensity. The assignment of Miller crystallographic

Y is equal to $[(Al0_2)_{53.97}, (Si0_2)_{138.03}]^{53.97}$. Samples were prepared as dry powders which were packed into aluminum planchens. $(H_2O)_3]_{0.47}^+$, $H_{53.50}^+$ Y air dried, and (c) $[Mo_6C1_8(OH)_3(H_2O)_3]_{0.47}^+$, $H_{53.50}^+$ Y after calcination at 430°C for 5 h under flowing oxygen. X-ray powder diffraction patterns of (a) $H^{+}-Y$, (b) $[Mo_6C1_8(OH)_3-$ Figure 5-2.



indicies is based on assignments by $\operatorname{Breck}^{114}$, and are identical for each sample as shown in Table 5-1. Zeolite crystallinity can be judged by the relative intensities of the (331), (440), (533), (642) and (751) diffraction peaks¹²⁶. These are changed very little during the reaction with the molybdenum cluster, and the subsequent oxidation of the material at 430°. Of interest, is the increase of the intensity of the (200) and (311) diffraction peaks relative to the (331) peak in the H⁺-Y following reaction with molybdenum cluster. This increase may simply be a result of rehydration of the zeolite lattice during the exchange reaction. The (220) and (311) diffractions of hydrated Na⁺-Y are of intensities similar to those of the [Mo₆Cl₈(OH)₃(OH₂)₃]⁺_{0.47}, H⁺_{53.50}-Y.

The presence of exchange cations of different sizes will shift the unit cell dimensions of the zeolite slightly. For example, a hydrated zeolite Y possessing a SiO_2/AlO_2 ratio of 2.43 will exhibit a unit cell dimension varying from 24.85 to 24.61 Å as the exchange cation is varied in size from tetramethylammonium ion to the H⁺ ion¹¹⁴.

Even though the H^+-Y zeolite is loaded with approximately 0.47 molybdenum clusters per unit cell, there is no change in the unit cell parameters detectable within the accuracy of the Siemens x-ray diffractometer used for these measurements. The lack of a change in unit cell dimensions does not support the theory of ion exchange of these clusters into the zeolite, but may simply indicate

Table 5-1. X-ray Powder Diffraction Data and Miller Indices for Na^+-Y^b , H^+-Y , and Molybdenum Cluster, H^+-Y .

Hyo	drated	н	[Ma	о _б ст8(он)3 н +	(OH ₂) ₃] _{0.47}
	· - ·			···53•	50
<u>hkl</u>	<u>d(Å)</u>	hkl	<u>d(Å)</u>	hkl	<u>d(Å)</u>
111	14.29	111	14.24	111	14.24
220	8.75	220	8.75	220	8.71
311	7.46	311	7.43	311	7.49
333	4.76	333	4.74	333	4.74
440	4.38	440	4.35	44O	4.35
620	3.91	620	3.90	620	3.88
533	3.775	533	3.77	533	3.74
711	3.466	711	3.45	711	3.45
642	3.308	642	3.30	642	3.28
731	3.222	731	3.22	731	
733	3.024	733	3.02	733	3.00
822	2.917	822		822	2.89
751	2.858	751	2.86	751	2.84
840	2.767	840	2.76	840	
911	2.717	911		911	
664	2.638	664	2.63	664	2.63
a = Si/	24.73 Å Al = 2.00	a = 24 Si/Al	.74 Å = 2.56	a = 24 Si/Al	.74 Å = 2.56

^bData taken from Reference 114, p. 369.

Table 5-1 (cont'd).

[Mo ₆ Cl ₈ (OH) ₃ (OH ₂ Calcined 5h at	2)3 []] 0.47, H ⁺ 53.50 ^{-Y} 430°C Under 0 ₂	
hkl	<u>a(Å)</u>	
111	14.02	
220	8.58	
311	7.37	
331	5.60	
333	4.69	
440	4.33	
620	3.86	
533	3.74	
711	3.42	
642	3.26	
731		
733	3.00	
822	2.88	
751	2.82	
840	2.74	
911	2.67	
664	2.60	
844	2.56	

a = 24.40 Å Si/Al = 2.56
that there is ample volume within the supercage to contain the metal cluster ion plus the rest of the hydrated exchangeable protons at the cluster loadings used.

Infrared spectroscopy may also be used to investigate the crystallinity of the zeolite. Work by Flanigen¹²⁷ has assigned vibrational bands to the structural components of the zeolites. Vibrational modes internal to the (Al,Si)O₄ tetrahedra are observed at 1250-950, 750-650 and 500-420 cm⁻¹, assigned to the asymmetric and symmetric stretching and (Al,Si)-O bending modes, respectively. The structure sensitive bands associated with the crystallinity of the zeolite are attributed to the vibrational modes external to the tetrahedra. Infrared bands attributed to vibrational modes of double ring prisms, pore openings, and the symmetric and asymmetric stretching of the intracrystalline channels of the zeolite are observed at 650-500, 420-300, 820-750 and 1050-1150 cm⁻¹, respectively.

Figure 5-3 shows the infrared spectra from 1400 to 250 cm^{-1} for H⁺-Y, $[Mo_6Cl_8(OH)_3(OH_2)_3]_{0.47}^{+}$, H⁺_{53.50}-Y, and $[Mo_6Cl_8(OH)_3(OH_2)_3]_{0.47}^{+}$, H⁺_{53.50}-Y after calcination at 430° under oxygen for 5 h. Only very slight differences between these spectra are noticeable. The bands assigned to the external lattice modes of the zeolite are strongly present in all three samples, therefore, the observation of high crystallinity in these samples by x-ray diffraction is corroborated by infrared spectroscopy. The



Figure 5-3. Infrared spectra of (a) H^+-Y , (b) $[Mo_6Cl_8-(OH)_3(H_2O)_3]_{0.47}^+$, $H_{53.50}^+Y$, and (c) $[Mo_6Cl_8-(OH)_3(H_2O)_3]_{0.47}^+$, $H_{53.50}^+Y$ after calcination

at 430°C for 5 h under flowing oxygen.

The scale along the top of the diagram indicates the regions assigned to the vibrational modes internal to the $(Al,Si)O_{4}$ tetrahedra(I), and to the structure sensitive vibrations which are external to the tetrahedra (E). The small arrows indicate the peaks which indicate the high degree of crystallinity in these samples. The band at 900 cm⁻¹ in (c) is assigned to the Mo=O stretching vibration of molybdenum oxide. broad Mo-Cl vibrational band of the molybdenum cluster $(340-290 \text{ cm}^{-1})^{65,105}$ is not observed in Figure 5-3b. This weak band is obscured by the strong absorbtions of the zeolite matrix. After calcination the appearance of the peak at 900 cm⁻¹ indicates the presence of molybdenum oxide. This band is assigned to the Mo=O stretching vibration^{110,124}.

The observation of perturbations of the external vibrational modes of the zeolite could be indicative of the presence of intracrystalline molybdenum cluster. Conclusions based on this type of observation must be made carefully, utilizing data gathered from a spectrophotometer of much higher resolving power than was used for this study, however.

Nitrogen B.E.T. surface area measurements were carried out on samples of H^+-Y and $[Mo_6Cl_8(OH)_3(OH_2)_3]_{0.47}^+$, $H_{53.50}^+-Y$. Both samples possessed surface areas of approximately 410 m²/g. The retention of full surface area during the exchange of the cluster is consistent with the high crystallinity of the sample. This measurement also indicates that the cluster is not clogging the pore openings of the zeolite as might be expected from a precipitation onto the external surfaces of the aluminosilicate crystallites.

UV-visible spectrophotometry was performed using a sample of $[Mo_6Cl_8(OH)_3(OH_2)_3]_{0.47}$, $H_{53.50}^+$ mulled in Nujol and supported on quartz glass plates. The spectrum was taken

with a Na⁺-Y mulled in a similar manner in the reference beam. The spectrum contained merely a broad tailing into the UV associated with the zeolite. No bands attributable to the molybdenum cluster were observed in the spectrum.

Electron microprobe analysis was performed on two regions of a particle that was crystalline in appearance under the magnification of the electron microscope. This particle had apparently been cleaved by ultramicrotoming the sample which was embedded in epoxy resin. This analysis yielded the plots shown in Figure 5-4. Region 1 (5-4b) was on the surface of the particle, and contained substantial amounts of molybdenum and chlorine as indicated by the number of counts in these regions. Region 2 (5-4a) was on a cleaved section of the particle which should have been representative of the internal portions of the zeolite crystal. These analysis were carried out using identical instrumental settings and acquisition times.

The analysis plotted in Figure 5-4a suggests that significant amounts of molybdenum and chlorine are present within the zeolite. This microprobe analysis indicates that a generally even distribution of the cluster is present and is strong evidence supporting the protonation and ion exchange of the molybdenum cluster into the pores of the zeolite as the method of cluster binding. Much care must be taken in the interpretation of these results and corroboration should be sought.

Figure 5-4. Electron microprobe analysis of [Mo₆Cl₈-

 $(OH)_3(OH_2)_3]_{0.47}^+$, $H_{53.50}^+$ embedded in epoxy resin and cleaved by an ultramicrotome.

The spot analysis on region 2 which was a cleaved portion of the particle is shown in (a). The spot analysis of an exterior portion of the particle (region 1) is shown in (b). Instrumental settings and acquisition times were identical for both measurements.





D. Conclusions and Recommendations

Several aspects of this study indicate that further research should be carried out to investigate the molybdenum cluster binding to H^+-Y zeolite. The binding of rather substantial amounts of the cluster to zeolite appears to be strongly dependent on the ion exchange form of the zeolite. Thus, the strong reaction of the cluster appears to be a function of the acidity of the intracrystalline regions of the zeolite. It can be estimated that the interior of hydrated protonic zeolites is approximately equivalent to $4.0 \text{ M} \text{ acid}^{114}$. This strongly suggests the possibility of an ion exchange reaction based on pH, as is the case for the exchange reaction of Mo₆Cl₈(OH)_n(OH₂)($^{(4-n)+}_{(6-n)}$ into montmorillonite.

In comparison to other methods, this ion exchange technique has several distinct advantages. This work has been shown that loading of molybdenum onto the zeolite can be accomplished with the retention of excellent crystallinity. The binding of a cluster species to the zeolites allows for the formation of well defined metal species through the decomposition of the cluster structure. Although little corroborating evidence exists, the microprobe analysis suggests that the molybdenum cluster is located within the zeolite pore structure. If this is indeed correct, this would represent the first time a molybdenum species, especially a metal cluster species, has been ion exchanged

into a crystalline zeolite. Clearly this claim should be verified by additional studies, and corroborating evidence.

The calcination of $[Mo_6Cl_8(OH)_3(OH_2)_3]_{0.47}^+$, $H_{53.50}^+$ Y results in the formation of molybdenum oxide supported on the zeolite, as shown by infrared spectroscopy. The observation of a light blue color during calcination suggests¹¹² the formation of molybdenum blue compounds prior to formation of the trioxide. It is most likely that the anionic isopoly blue compounds would have migrated from the pores of the zeolite. The presence of intracrystalline water would most certainly contribute to this process and should be limited by a preliminary treatment and reaction under high vacuum (10^{-6} torr). Experiments with reduction of Pt²⁺-exchanged Y zeolites indicates that the size of the platinum metal aggregates formed after reduction at 300° is a function of pretreatment temperature at 10^{-6} torr. This is apparently due to the presence of intracrystalline water which promotes platinum metal migration¹¹⁹.

It is recommended that future work on this project be persued. The initial goal should be to more firmly establish the ion exchange behavior of the molybdenum cluster into the H^+-Y zeolite. The ability of the cluster to decompose to molybdenum oxides upon calcination is quite well established, however, this reaction must occur within the zeolite framework to make full use of the properties of the zeolite during catalytic application.

Many avenues of catalytic research would be opened if this <u>in situ</u> reaction was established. Reactions such as size selective oxidation, hydrocracking studies, isomerizations or alkylations may be possible. These first generation catalysts could be readily modified by promoters which could be exchanged into the zeolite prior to the molybdenum cluster exchange. REFERENCES

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REFERENCES

- J. Schmidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Ruttiger, and H. Kojer, <u>Angew. Chem.</u>, <u>1959</u>, <u>71</u>, 176.
- 2. G. W. Parshall, J. Molec. Catal., <u>1978</u>, 4, 243.
- 3. G. Szonyi, Advan. Chem. Ser., 1968, 70, 53.
- D. Evans, J. A. Osborn, and G. Wilkinson, <u>J. Chem.</u> <u>Soc. (A)</u>, <u>1968</u>, 3133.
- 5. C. W. Bird, Chem. Rev., <u>1962</u>, <u>62</u>, 283.
- A. J. Chack and R. F. Harrod, <u>Adv. Organometallic</u> <u>Chem.</u>, <u>1968</u>, <u>6</u>, 119.
- 7. F. E. Paulik and J. F. Roth, U.S. Patent 3,769,329 (1973).
- 8. M. Heylin, C. E. News, 1982, 60 (24), 31.
- 9. J. L. Russell, U.S. Patent 3,418,340 (1968).
- 10. (a) B. C. Gates, J. R. Katzer, and G. C. A. Schuit, "Chemistry of Catalytic Processes", McGraw-Hill, Inc., New York (1979), pp. 1.

(b) P. B. Venuto and E. T. Habib, <u>Catal. Rev.</u>, <u>1978</u>, 18, 1.

11. (a) L. F. Hatch, Hydrocarbon Proc., <u>1969</u>, <u>48</u>, 77.

(b) C. N. Satterfield, "Heterogeneous Catalysis in Practice", McGraw-Hill, Inc., New York (1980), pp. 258.

(c) C. L. Thomas, "Catalytic Processes and Proven Catalysts", Academic Press, Inc., New York (1970), pp. 146.

12. (a) A. P. Kreuding, <u>AIChe Symp. Serv.</u>, <u>1972</u>, 72, 138.
(b) S. C. Shuman and H. Shalit, <u>Catal. Rev.</u>, <u>1970</u>, 4, 245.

- 12. (c) G. S. A. Schuit and B. C. Gates, <u>AIChe J.</u>, <u>1973</u>, <u>1973</u>, <u>19</u>, 417.
- 13. F. G. Ciapetta, R. M. Dobres, and D. N. Wallace, Catal. Rev., <u>1972</u>, <u>5</u>, 67.
- 14. J. J. Burton and R. L. Garten, "Advanced Materials in Catalysis", Academic Press, Inc., New York (1977), pp. 14.
- J. B. Dixon and S. B. Weed, "Minerals in Soil Environments", Soil Science Society of America, Madison, Wisconson (1977), pp. 294.
- 16. R. E. Grim, "Clay Minerology", 2nd Ed., McGraw-Hill, Inc., New York (1968), pp. 77-92.
- 17. (a) H. Herbst, Erdöl und Teer, <u>1926</u>, 2, 265 and 411.

(b) R. C. Hansford, <u>Advan. Catal.</u>, <u>1952</u>, <u>4</u>, 1.

(c) H. H. Vogue in "Catalysis", P. H. Emmett (Ed.), Reinhold, New York, 1958, 6, 407.

- H. E. Swift in "Advanced Materials in Catalysis", J. J. Burton and R. L. Garton (Eds.), Academic Press, Inc., New York (1977), pp. 209.
- 19. B. K. G. Theng, "The Chemistry of Clay-Organic Reactions", John Wiley and Sons, Inc., New York (1974), pp. 269.
- 20. R. C. Davidson, F. J. Ewing, and R. S. Shute, <u>Natl</u>. <u>Pet. News</u>, <u>1943</u>, 35, 318.
- 21. E. A. Zuech, U.S. Patent 3,849,507 (1974).
- 22. (a) T. A. Pinnavaia, <u>Science</u>, <u>1983</u>, <u>220</u>, 365.

(b) T. J. Pinnavaia, ACS Symp. Ser., <u>1982</u>, <u>192</u>, 241.

- 23. W. H. Quale and T. J. Pinnavaia, <u>Inorg. Chem.</u>, <u>1979</u>, <u>18</u>, 2840.
- 24. P. K. Welty and T. J. Pinnavaia, <u>J. Amer. Chem. Soc.</u>, <u>1975</u>, <u>27</u>, 3819.
- 25. T. J. Pinnavaia, R. Raythatha, J. G. S. Lee, L. J. Halloran and J. F. Hoffman, <u>J. Amer. Chem. Soc.</u>, <u>1979</u>, 101, 6891.
- 26. R. Raythatha and T. J. Pinnavaia, <u>J. Organomet. Chem</u>., <u>1981</u>, 218, 115.

- 28. F. Farzaneh and T. J. Pinnavaia, <u>Inorg. Chem.</u>, <u>1983</u>, <u>22</u>, 2216.
- 29. A. Kadkhodayan and T. J. Pinnavaia, <u>J. Molec. Cat.</u>, in press.
- J. M. Thomas, J. M. Adams, S. H. Graham, and D. T.
 B. Tennakoon, Adv. Chem. Ser., <u>1977</u>, <u>163</u>, 298.
- 31. J. M. Adams, J. A. Ballantine, S. H. Graham, R. J. Laub, J. H. Purnell, P. T. Reid, W. Y. M. Shaman and J. M. Thomas, <u>J. Catal.</u>, <u>1979</u>, <u>58</u>, 238.
- 32. J. A. Ballantine, M. Davies, H. Purnell, M. Rayanakorn, J. M. Thomas and K. J. Williams, <u>J. Chem. Soc. Chem.</u> <u>Commun., 1981</u>, 421.
- 33. J. A. Ballantine, R. P. Galvin, R. M. O'Neil, H. Purnell, M. Rayanakorn, and J. M. Thomas, <u>Ibid</u>, <u>1981</u>, 695.
- 34. J. A. Ballantine, H. Purnell, M. Rayanakorn, J. M. Thomas, and K. J. Williams, <u>Ibid</u>, <u>1981</u>, 9.
- 35. J. M. Adams, A. Bylina, and S. H. Graham, <u>J. Catal.</u>, <u>1982</u>, <u>75</u>, 1980.
- 36. R. M. Barrer, "Zeolites and Clay Minerals as Sorbents and Molecular Sieves", Academic Press, Inc., New York (1978), p. 407-483.
- 37. R. M. Barrer and D. M. Macleod, <u>Tran. Faraday Soc</u>., <u>1955</u>, <u>51</u>, 1290.
- 38. J. Shabtai, N. Frydman, and R. Lazar, <u>Proc. 6th Int</u>. <u>Congr. Catal.</u>, <u>B5</u>, <u>1</u> (1976).
- 39. M. M. Mortland and V. E. Berkheiser, <u>Clays Clay Miner</u>., <u>1976</u>, 24, 60.
- 40. R. H. Loeppert, M. M. Mortland, and T. J. Pinnavaia, <u>Ibid.</u>, <u>1979</u>, <u>27</u>, 201.
- 41. (a) T. Endo, M. M. Mortland, and T. J. Pinnavaia, <u>Ibid.</u>, <u>1980</u>, 28, 105.
 (b) T. Endo, M. M. Mortland, and T. J. Pinnavaia, <u>Ibid.</u>, <u>1981</u>, 29, 153.

(c) T. J. Pinnavaia, M. M. Mortland, and T. Endo, U.S. Patent 4,367,163 (1983).

- 42. G. W. Brindley and R. E. Semples, <u>Clay Miner.</u>, <u>1977</u>, <u>12</u>, 229.
- 43. S. Yamanaka and G. W. Brindley, <u>Clays Clay Miner.</u>, <u>1979</u>, <u>27</u>, 119.
- 44. R. J. Lussier, J. S. Magee, and D. E. W. Vaughan, Preprints, 7th Canadian Symp. on Catalysis, Vol. 1, <u>30th Canadian Engineering Conf.</u>, Edmonton, Alberta, Oct. 19-22, 1980, p. 88-95.
- 45. J. Shabtai, R. Lazar, and A. G. Oblad, "New Horizons in Catalysis", <u>1981</u>, <u>7</u>, 828.
- 46. J. Shabtai, U.S. Patent 4,238,364 (1980).
- 47. N. Lahave and U. Shani, <u>Clays Clay Miner</u>., <u>1978</u>, 26, 116.
- 48. G. W. Brindley and S. Yamanaka, <u>Amer. Miner.</u>, <u>1979</u>, <u>64</u>, 830.
- 49. S. Yamanaka and G. Yamashita, <u>Clays Clay Miner.</u>, <u>1978</u>, 26, 21.
- 50. S. Yamanaka, G. Yamashita and M. Hattori, <u>Ibid.</u>, <u>1980</u>, <u>28</u>, 281.
- 51. (a) F. A. Cotton, <u>Quart. Rev. Chem. Soc</u>., <u>1966</u>, 20, 389.
 - (b) R. B. King, <u>Progress Inorg. Chem.</u>, <u>1972</u>, <u>15</u>, 287
 - (c) H. Vahrenkamp, <u>Struct. Bond.</u>, <u>1977</u>, <u>32</u>, 1.
- 52. L. Pauling, "Nature of the Chemical Bond", 4rd. Ed., Cornell University Press (1960), pp. 440.
- 53. C. B. Thaxon and R. A. Jacobson, <u>Inorg. Chem.</u>, <u>1971</u>, <u>10</u>, 1460.
- 54. B. G. Hughes, J. L. Meyer, P. B. Fleming and R. E. McCarley, <u>Ibid.</u>, <u>1970</u>, 2, 1343.
- 55. J. H. Espenson and R. E. McCarley, <u>J. Amer. Chem. Soc.</u>, <u>1966</u>, <u>88</u>, 1063.
- 56. J. G. Converse and A. J. Thomson, <u>J. Chem. Soc.</u> <u>Dalton</u>, <u>1972</u>, 2350.
- 57. R. A. Mackay and R. F. Schneider, <u>Inorg. Chem.</u>, <u>1967</u>, <u>6</u>, 549.

- 58. (a) D. D. Klendworth and R. A. Walton, <u>Ibid.</u>, <u>1981</u>, 20, 1151.
 (b) R. A. Field and D. L. Kepert, <u>J. Less Common Met.</u>, <u>1967</u>, 13, 378.
 (c) R. J. Allen and J. C. Sheldon, <u>Aust, J. Chem.</u>, <u>1965</u>, 18, 277.
- 59. N. Brnicevic and H. Schafer, <u>Z. Allg. Chem., 1978</u>, 441, 219.
- 60. (a) C. Brossett, <u>Arkiv, Kemi. Min. Geoc.</u>, <u>1946</u>, 20A, No. 7.
 - (b) C. Brossett, Ibid., <u>1947</u>, <u>22A</u>, No. 11.
- 61. R. D. Hogue and R. E. McCarley, <u>Inorg. Chem.</u>, <u>1970</u>, 2, 1354.
- 62. F. A. Cotton and N. F. Curtis, Ibid., <u>1965</u>, <u>4</u>, 241.
- 63. J. C. Sheldon, <u>Nature</u>, <u>1959</u>, <u>184</u>, 1210.
- 64. W. M. Carmichael and D. A. Edwards, <u>J. Inorg. Nucl.</u> <u>Chem.</u>, <u>1967</u>, 22, 1535.
- 65. F. A. Cotton, R. M. Wing, and R. A. Zimmerman, <u>Inorg</u>. <u>Chem.</u>, <u>1967</u>, <u>6</u>, 11.
- 66. A. D. Hamer, T. J. Smith, and R. A. Walton, <u>Ibid.</u>, <u>1976</u>, <u>15</u>, 1014.
- 67. P. Nannelli and B. P. Block, Ibid., <u>1968</u>, 7, 2423.
- 68. D. L. Kepert, R. E. Marshall, and D. Taylor, <u>J. Chem</u>. <u>Soc. Dalton</u>, <u>1974</u>, 506.
- 69. J. C. Sheldon, J. Chem. Soc., <u>1960</u>, 1007.
- 70. J. C. Sheldon, Ibid., <u>1960</u>, 3106.
- 71. J. C. Sheldon, Ibid., <u>1963</u>, 4183.
- 72. J. C. Sheldon, Ibid., <u>1964</u>, 1287.
- 73. P. E. Dai and J. H. Lundsford, <u>J. Catal.</u>, <u>1980</u>, <u>64</u>, 173.
- 74. H. S. Harned, C. Pauling, and R. B. Corey, <u>J. Amer.</u> <u>Chem. Soc.</u>, <u>1960</u>, 82, 4815.

- 75. F. W. Koknat, J. A. Parsons, and A. Vongvushrintra, Inorg. Chem., <u>1974</u>, <u>13</u>, 1699.
- 76. B. Spreckelmeyer, <u>Z. Anorg. Allg. Chem.</u>, <u>1969</u>, <u>365</u>, 225.
- 77. P. J. Kuhn and R. E. McCarley, <u>Inorg. Chem.</u>, <u>1965</u>, <u>4</u>, 1482.
- 78. P. Nannelli and B. P. Block, <u>Inorg. Syn</u>., <u>1976</u>, <u>VII</u>, 170.
- 79. J. E. Fergusson, B. H. Robinson, and C. J. Wilkins, J. Chem. Soc. (A), <u>1967</u>, 486.
- 80. D. Hartley and M. J. Ware, <u>J. Chem. Soc. Chem. Commun.</u>, <u>1967</u>, 912.
- 81. P. B. Ayscough, "Electron Spin Resonance in Chemistry," Meuthan and Co., London (1965), Appendix Five.
- 82. R. Aasa and T. Vanngard, J. Mag. Res., <u>1975</u>, <u>19</u>, 308.
- 83. (a) J. Klinowski, J. M. Thomas, M. Audier and S. Vasudevan, <u>J. Chem. Soc. Chem. Commun.</u>, <u>1981</u>, 570.
 (b) L. A. Bursill, J. M. Thomas, and K. J. Rao, <u>Nature</u>, <u>1981</u>, 289, 157.
- 84. R. F. Schneider and R. A. Mackay, <u>J. Chem. Phys.</u>, <u>1968</u>, <u>48</u>, 843.
- 85. P. B. Fleming, L. A. Mueller, and R. E. McCarley, Inorg. Chem., <u>1967</u>, <u>6</u>, 1.
- 86. D. J. Robbins and A. J. Thomson, <u>J. Chem. Soc. Dalton</u>, <u>1972</u>, 2350.
- 87. P. B. Fleming and R. E. McCarley, <u>Inorg. Chem.</u>, <u>1970</u>, 2, 1347.
- 88. J. G. Converse and R. E. McCarley, <u>Ibid.</u>, <u>1970</u>, 2, 1361.
- 89. (a) A. Simon, H. G. Schnering, H. Wohrle, and H. Schafer, <u>Z. Anorg. Allg. Chem.</u>, <u>1965</u>, <u>33</u>9, 155.

(b) A. Simon, H. G. Schnering, and H. Schafer, <u>Ibid.</u>, <u>1968</u>, <u>361</u>, 235.

(c) F. W. Koknat and R. E. McCarley, <u>Inorg. Chem.</u>, <u>1972</u>, <u>11</u>, 1812.

- 90. P. A. Vaughan, J. H. Sturdivant, and L. Pauling, <u>J</u>. <u>Amer. Chem. Soc.</u>, <u>1950</u>, <u>72</u>, 5477.
- 91. P. B. Fleming, J. L. Meyer, W. K. Grinstaff, and R. E. McCarley, <u>Inorg. Chem.</u>, <u>1970</u>, <u>9</u>, 1764.
- 92. (a) H. Van Olphen and J. J. Fripiat, "Data Handbook for Clay Minerals and Other Non-Metallic Minerals", Pergammon Press, New York (1979), pp. 39.

(b) J. A. Gadsden, "Infrared Spectra of Minerals and Related Inorganic Compounds", Butterworths, London (1975), pp. 62.

- 93. H. Schafer, B. Plautz, and H. Plautz, <u>Z. Anorg. Allg.</u> <u>Chem.</u>, <u>1976</u>, 420, 1.
- 94. B. Spreckelmeyer, C. Brendel, M. Dartman, and H. Schafer, Ibid., <u>1971</u>, <u>386</u>, 15.
- 95. R. B. Hahn, J. Amer. Chem. Soc., <u>1951</u>, <u>73</u>, 5091.
- 96. S. A. Best and R. A. Walton, <u>Inorg. Chem.</u>, <u>1979</u>, <u>18</u>, 484.
- 97. (a) W. H. Nelson and R. S. Tobias, <u>Inorg. Chem.</u>, <u>1963</u>, 2, 985.
 (b) W. H. Nelson and R. S. Tobias, <u>Can. J. Chem.</u>, <u>1964</u>, 42, 731.
- 98. J. L. Meyer and R. E. McCarley, <u>Inorg. Chem.</u>, <u>1978</u>, <u>17</u>, 1867.
- 99. (a) N. N. Nag, T. Fransen, and P. Mars, <u>J. Catal.</u>, <u>1981</u>, <u>68</u>, 77.
 - (b) M. Akimoto and E. Echigoya, Ibid., <u>1973</u>, <u>31</u>, 278.

(c) H. Pines, "The Chemistry of Catalytic Hydrocarbon Conversions", Academic Press, New York (1981), Chapter 5.

- 100. K. Aykan, J. Catal., <u>1968</u>, <u>12</u>, 281.
- 101. R. Rosenheim, H. P. Kuhn, <u>Z. Anorg. Allg. Chem.</u>, <u>1910</u>, 66, 1.
- 102. D. P. Shoemaker, C. W. Garland, and J. I. Steinfeld, "Experiments in Physical Chemistry," McGraw-Hill, New York (1974), pp. 253.

- 103. R. M. Lindner, K. Haller, and S. L. Helwig, <u>Z. Anorg</u>. Chem., <u>1923</u>, 130, 209.
- 104. L. J. Guggenberger and A. W. Sleight, <u>Inorg. Chem.</u>, <u>1969</u>, 8, 2041.
- 105. D. Hartley and M. J. Ware, J. Chem. Soc. Chem. Commun. 1967, 912.
- 106. (a) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", John Wiley and Sons, 3rd Ed., New York (1978), pp. 227.

(b) I. Nakagawa and T. Shimanuchi, <u>Spectrochim</u>. <u>Acta, 1964</u>, 20, 429.

- 107. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric Identification of Organic Compounds", 3rd Ed., New York (1974), p. 208.
- 108. R. A. Plane and J. P. Hunt, <u>J. Amer. Chem. Soc.</u>, <u>1957</u>, <u>7</u>2, 3343.
- 109. F. A. Cotton and T. E. Haas, <u>Inorg. Chem.</u>, <u>1964</u>, <u>3</u>, 10.
- 110. P. C. H. Mitchell and F. Trifiro, <u>J. Chem. Soc. A.</u>, <u>1970</u>, 3183.
- 111. T. J. R. Weakley, <u>Struct. Bond.</u>, <u>1974</u>, <u>18</u>, 131.
- 112. (a) H. So and M. T. Pope, <u>Inorg. Chem.</u>, <u>1972</u>, <u>11</u>, 1441.

(b) J. J. Altenau, M. T. Pope, R. A. Prados, and H. So, <u>Inorg. Chem.</u>, <u>1975</u>, <u>14</u>, 418.

- 113. J. C. Sheldon, Chem. Indust., March 11, <u>1961</u>, 323.
- 114. D. W. Breck, "Zeolite Molecular Sieves; Structure, Chemistry, and Use", John Wiley and Sons, New York (1974), pp. 287.
- 115. (a) M. Boudart and R. A. Della Betta, in "Catalysis", J. W. Hightower (Ed.), North Holland, Amsterdam (1973), pp. 1329.

(b) T. E. Whyte, Jr., and R. A. Della Betta, <u>Catal</u>. <u>Rev.-Sci. Eng.</u>, <u>1982</u>, 24, 567.

116. (a) D. J. Elliot and J. H. Lundsford, <u>J. Catal.</u>, <u>1979</u>, <u>57</u>, 11.

- 116. (b) P. Gallezot, G. Coudurier, M. Primet, and B. Imelik, <u>ACS Symp. Ser</u>., <u>1977</u>, 40, 144.
- 117. M. Minachev and Y. Isakov, "Zeolite Chemistry and Catalysis", J. A. Rabo (Ed.), Am. Chem. Soc., Washington, D.C. (1976), pp. 552.
- 118. (a) J. A. Rabo, P. E. Pickert, D. N. Stamires, and J. E. Boyle, Actes Deuxieme Congr. Internat. Catalyse, Paris, <u>1961</u>, 2, 382.
 (b) J. A. Rabo, P. E. Pickert, R. L. Mays, <u>Ind.</u> Eng. Chem., <u>1961</u>, <u>53</u>, 733.
- 119. (a) P. B. Weisz, V. J. Frilette, R. M. Maatman, and E. B. Mower, <u>J. Catal</u>., <u>1962</u>, <u>1</u>, 307.

(b) P. B. Weisz, V. J. Frilette, <u>J. Phys. Chem.</u>, <u>1960</u>, <u>64</u>, 382.

120. (a) P. Gallezot, A. Alarcon-Diaz, J. A. Dalmon, A. J. Renouprez, and B. Imelik, <u>J. Catal.</u>, <u>1975</u>, <u>39</u>, 334.

> (b) P. Gallezot and B. Imelik, "Zeolite Chemistry and Catalysis", J. A. Rabo (Ed.), Am. Chem. Soc., Washington, D.C. (1976), pp. 66.

- 121. S. W. Bukata, C. A. Castor, and R. M. Milton, U.S. Patent 3,013, 988 (1966).
- 122. D. Ballivet-Tkchenko and G. Coudurier, <u>Inorg. Chem.</u>, <u>1979</u>, 18, 558.
- 123. B. Imlik, C. Naccache, Y. Bentaarit, J. C. VeDrine, G. Coudrier and A. Praciad, "Catalysis by Zeolites", Elsevier, New York (1980).
- 124. P. E. Dai and J. H. Lundsford, <u>J. Catal.</u>, <u>1980</u>, <u>64</u>, 173 and 184.
- 125. F. C. Wilhelm, "Preparation and Characterization of Mo-Containing Zeolite Catalysis", Climax Molybdenum Co., Report L-287-51, 1977.
- 126. A. P. Bolton and M. A. Lanewala, <u>J. Catal.</u>, <u>1970</u>, 18, 154.
- 127. (a) E. M. Flanigen, "Zeolite Chemistry and Catalysis", J. A. Rabo (Ed.), Amer. Chem. Soc., Washington, D.C. (1976), pp. 80.

- 127. (b) E. M. Flanigen, H. Khatami, and H. A. Szymanski, Advan. Chem. Ser., <u>1971</u>, 101, 201.
- 128. J. A. Dean (Ed.), "Lang's Handbook of Chemistry", 12th Ed., McGraw-Hill, New York, 1979.