

Intercalation in Montmorillonite of Molybdenum Cations Containing the Mo_6Cl_8 Cluster Core

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Molybdenum cations containing the Mo_6Cl_8 cluster core have been intercalated in montmorillonite. Cluster ions of the type $[\text{Mo}_6\text{Cl}_8(\text{H}_2\text{O})_{6-n}(\text{OH})_n]^{(4-n)+}$ were formed by argentometric titration of $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ to remove the four terminally bonded chlorines. At $\text{pH} = 1.5$ the clusters occupy the gallery region between the silicate layers of montmorillonite by displacement of Na^+ . The relationship between Na^+ released and cluster bound indicates the cluster intercalates mainly as monovalent cations ($n = 3$), along with some divalent cations ($n = 2$). As the cluster loading approaches the cation exchange capacity of the clay, the gallery acidity decreases and additional cluster binds as neutral molecules with $n = 4$. Thus the maximum cluster loading (80 mmoles/100 g) exceeds the value expected on the basis of ion exchange alone (60 mmoles/100 g). The gallery height of 7.3 Å for the new intercalate is compatible with the C_4 axis of the Mo_6Cl_8 core being oriented perpendicular to the silicate layers. Thermolysis of the intercalated clusters at 240°C results in the oxidation of the intercalated clusters to molybdenum oxide. Cluster decomposition is accompanied by the collapse of some galleries, while others remain propped open by 3.9 Å. The latter value corresponds to two layers of oxygen in the galleries. Thus the oxide is nonuniformly distributed on both the internal and external surfaces of the clay. Complete gallery collapse is observed at 300°C. © 1986 Academic Press, Inc.

Introduction

We have recently demonstrated that cationic metal cluster complexes of the type $M_6\text{Cl}_8^{n+}$ ($M = \text{Nb}, \text{Ta}; n = 2,3$) can be intercalated in montmorillonite and related smectite clays by ion exchange for interlayer sodium (1). Moreover, the intercalated clusters could be oxidized by water to small metal oxide aggregates which function as 10-Å pillars within the clay galleries. The results suggested that metal cluster complexes might provide a versatile route to new families of pillared clays (2).

In the present work we have extended the concept of utilizing halogenated metal cluster complexes as pillar precursors. The complexes of interest here are $[\text{Mo}_6\text{Cl}_8(\text{H}_2\text{O})_{6-n}(\text{OH})_n]^{(4-n)+}$ species derived from $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ as the source of the metal cluster core. Our main objectives were to elucidate the mode of binding of the cluster cations to montmorillonite and to examine their *in situ* oxidation to small molybdena aggregates.

Experimental

Materials. Na^+ -montmorillonite was obtained in a spray-dried form from the

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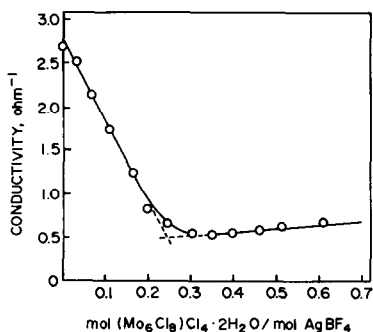


FIG. 1. Conductometric titration of $6.9 \times 10^{-5} M$ AgBF_4 in 93 : 7 (v/v) methanol–water solution with $6.0 \times 10^{-4} M$ $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ in absolute methanol.

Source Clay Repository, University of Missouri. A 1.0 wt% suspension of the clay in water was allowed to sediment 24 hr to remove carbonate and other dense impurities. The suspended clay fraction was collected by centrifugation and resuspended in 1.0 N NaCl to ensure complete exchange to the sodium form. The clay was then washed free of excess salt and lyophilized. The average of five independent chemical analyses for Na^+ , Al^{3+} , Fe^{3+} , Mg^{2+} and Si^{4+} corresponded to the anhydrous unit cell composition $\text{Na}_{0.50}[\text{Al}_{3.11}\text{Mg}_{0.50}\text{Fe}_{0.40}](\text{Si}_{7.91}\text{Al}_{0.09})\text{O}_{20}(\text{OH})_4$. Analysis of the Ni^{2+} exchange form indicated the cation exchange capacity to be 60.2 meq/100 g of air-dried clay. $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ was prepared by the reduction of MoCl_5 with Mo according to the procedure described by Nanelli and Block (3).

Hydrolysis of $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$. The four terminal chloride atoms in $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ were removed by the reaction with Ag^+ using a modification of the method of Cotton and Curtis (4). As shown in Fig. 1, the conductometric titration of AgBF_4 with $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ in methanol/water indicated the reaction to be stoichiometric. In a typical preparative reaction 1.00 g (9.64×10^{-4} mole) of $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 940 ml of boiling reagent grade absolute methanol.

The clear yellow solution was cooled and added dropwise to a stirred solution containing 0.800 g (3.86×10^{-3}) of AgClO_4 dissolved in 795 ml of 93 vol% methanol. The presence of some water was necessary to avoid precipitation of the cluster. The reaction mixture was protected from the light and stirred 30 min. The white AgCl precipitate was removed by centrifugation and the clear yellow supernatant was diluted with 5 liters of distilled water. The volume of solution was then reduced to about 1.0 liter on a rotary evaporator to decrease the concentration of methanol. The stock solution was stored for extended periods by adjusting the solution pH to 10.5 with NaOH to form the $\text{Mo}_6\text{Cl}_8(\text{OH})_6^{2-}$ anion and refrigerating at 4°C .

$[\text{Mo}_6\text{Cl}_8(\text{H}_2\text{O})_{6-n}(\text{OH})_n]^{(4-n)+}$ -montmorillonite. Binding of the hydrolyzed molybdenum cluster to Na^+ -montmorillonite was accomplished in acidic solution. In a typical preparative experiment, 150.0 mg (9.03×10^{-2} meq) of Na^+ -montmorillonite was suspended with stirring in 200 ml of distilled water. To this suspension was added 10.5×10^{-2} mmole of cluster cation from the stock solution described above. Distilled water was added to adjust the cluster solution concentration to $5 \times 10^{-5} M$ and the pH was adjusted to 1.5 by the dropwise addition of 0.1 N HClO_4 . The bright yellow flocculated clay was agitated ultrasonically for 3 min, separated from the clear supernatant solution by centrifugation, washed with distilled water until the wash supernatant was at pH 7.0, and lyophilized.

Molybdena pillared montmorillonite. The molybdenum oxide interlayered montmorillonite was prepared from a metal cluster intercalate containing 53.6 mmole of cluster/100 g of clay. Preliminary thermal treatment at 130 and 200°C for 24 hr at each temperature under vacuum was carried out to limit the amount of water present in the sample. This is an essential step in the reaction sequence. Further thermal treatment

of the intercalate at 280°C *in vacuo* produced the molybdenum oxide interlayered montmorillonite. Chemical analysis of the product indicates that no detectable amount of chloride was present.

Physical methods. X-Ray diffraction patterns were recorded on a Siemens X-ray diffractometer by using nickel-filtered $\text{CuK}\alpha$ radiation. Samples were prepared as thin oriented films supported on glass slides. UV-VIS spectra were obtained on a Cary 17D spectrophotometer. Samples were prepared either as solutions or as Nujol mulls supported on quartz glass plates. The spectra of mulled clay samples were recorded with a similarly prepared Na^+ -montmorillonite in the reference beam. IR spectra were measured on samples prepared in the form of KBr pellets by using a Perkin-Elmer 457 spectrophotometer.

Conductometric titration. The conductometric titration of AgBF_4 with $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ was carried out by using a Beckman Model RC 16BZ conductivity bridge with a cell containing 1-cm² bright platinum electrodes held approximately 1 cm apart. The solution conductivity was multiplied by the total solution volume in milliliters to compensate for volume changes during titration. An equilibration time of 20 min was allowed prior to each conductivity measurement.

Elemental analyses. Inductively coupled plasma emission analyses were performed using a Jarrell-Ash Model 955 Autocomp spectrophotometer. Clay samples were fused in lithium metaborate at 1000°C and the melt was dissolved in 0.1 N nitric acid. A National Bureau of Standards clay sample (98a) was used as a calibration standard. Analyses for Mo and Cl were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results

The molybdenum cluster in $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ consists of an octahedral Mo_6 core

with eight face-bridging chlorine atoms and four chlorines and two water molecules bonded to one metal atom in the cluster. $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ exhibits insufficient solubility in aqueous solutions to allow for the efficient ion exchange reaction with montmorillonite. Although the stability is greater in absolute methanol, the cluster shows little ability to bind to Na^+ -montmorillonite in this solvent. Presumably, the degree of ionization of the terminal chlorines on the cluster is low in methanol.

The removal of the four terminal halide ligands in $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ to produce a cation cluster core is readily accomplished by reaction with Ag^+ . This reaction is best carried out by adding a solution of $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ in absolute methanol to the BF_4^- or ClO_4^- salt of Ag^+ dissolved in a methanol solution containing 7 vol% distilled water (cf. Fig. 1). The presence of the H_2O improves the stability of the cluster by avoiding the precipitation of $\text{Ag}_2[\text{Mo}_6\text{Cl}_8]\text{Cl}_6 \cdot n\text{MeOH}$ during the reaction (4, 5). Upon the removal of the four terminal chlorides the cluster is sparingly soluble in water. Therefore, the cluster solution was diluted with water, and the methanol concentration was lowered by use of a rotary evaporator.

The binding of the cluster cations to Na^+ -montmorillonite is strongly pH dependent, the degree of binding increasing with decreasing pH. Quantitative studies of cluster binding were performed at a pH of 1.5 (HClO_4) and at cluster solution concentrations below $1.5 \times 10^{-5} M$. The low concentration of the cluster was necessary to avoid cluster precipitation upon acidification. Ultrasonification of the reaction mixture helped to produce intercalated products that were more uniform in appearance and possessed better layer stacking order as shown by X-ray diffraction.

The binding of the molybdenum cluster cation to montmorillonite was examined by measuring the equivalents of sodium liberated vs the number of moles of cluster

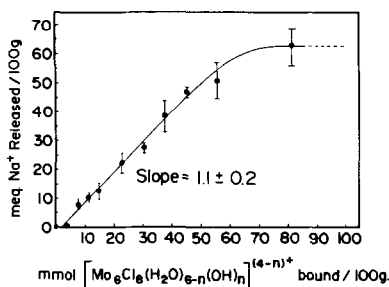


FIG. 2. Release of Na^+ upon binding of $[\text{Mo}_6\text{Cl}_8(\text{H}_2\text{O})_{6-n}(\text{OH})_n]^{(4-n)+}$ to montmorillonite at $\text{pH} = 1.5$.

added to solution at a pH of 1.5. This relationship is shown in Fig. 2. The uptake of the cluster by the clay is essentially quantitative over the range 0–80 mmoles of cluster. The sodium release plot shows an initial linear portion with a slope of 1.1 ± 0.2 of Na^+ /mole cluster. This result is indicative of the initial uptake of mainly monovalent and some divalent clusters of the type $[\text{Mo}_6\text{Cl}_8(\text{H}_2\text{O})_{6-n}(\text{OH})_n]^{(4-n)+}$ with $n = 2, 3$. At cluster loadings beyond approximately 80% of the cation exchange capacity of the clay (i.e., 60 $\text{mg Na}^+ / 100 \text{ g}$), the slope of the Na^+ release plot begins to decrease. The binding of the cluster up to the limit of 80 mmoles/100 g of clay is then observed.

Although the uptake of the cluster is essentially quantitative at $\text{pH} 1.5$, some of the molybdenum can be washed free at $\text{pH} 7.0$. Chemical analysis indicates that montmorillonite that had quantitatively taken up 70 mmole cluster/100 g of clay retains only 54 mmoles of cluster/100 g after repeated washes at $\text{pH} 7.0$. This product was used for all further experiments. The chemical analysis also indicates that greater than 99% of the gallery sodium ions are displaced by the reaction with the cluster and that 0.39 mole of cluster are bound per unit cell. This loading corresponds to an average charge of +1.3 per cluster cation.

The X-ray diffraction pattern of mont-

morillonite containing 54 mmoles of cluster per 100 g of clay is shown in Fig. 3. The pattern exhibits 001 and 003 diffraction peaks which indicate a basal spacing of about 16.6 Å. A weak 002 peak, somewhat obscured by the 001 reflection, is skewed toward lower spacings. This asymmetry indicates that not all galleries are uniformly occupied by the cluster, although sufficient interlayer ordering exists to allow three orders of 001 reflection.

The IR spectrum of the intercalate is shown in Fig. 4, along with the spectra for Na^+ -montmorillonite, and the intercalate after thermal treatment. The absorption due to the Mo—Cl stretching vibrations (6, 7) is visible for the intercalate near 320 cm^{-1} , indicating that the intact cluster is present in the intercalate. No bands associated with ClO_4^- are observed, indicating the absence of cationic cluster perchlorate precipitated onto the clay surfaces.

The UV-VIS spectrum of $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ in methanolic solution, together with the spectrum for a Nujol mull sample of the clay-intercalated cluster, are shown in Fig. 5. The cluster absorption shows a bathochromic shift upon displacement of the terminal chlorides. The intercalated cluster has a maximum absorbance at approximately 410 nm, which correlates with the hexahydroxo cluster as shown by Sheldon (8).

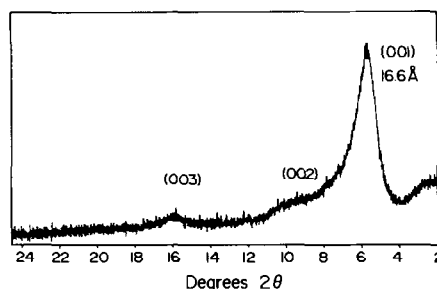


FIG. 3. X-Ray diffraction pattern (001 reflection) for an oriented film sample of $[\text{Mo}_6\text{Cl}_8(\text{H}_2\text{O})_{6-n}(\text{OH})_n]^{(4-n)+}$ montmorillonite. The loading is 54 mmoles of cluster per 100 g of clay.

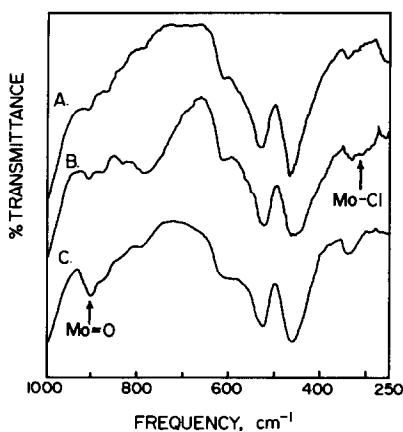


FIG. 4. Infrared spectra (1000–250 cm^{-1}) for (A) Na^+ -montmorillonite, (B) $[\text{Mo}_6\text{Cl}_8(\text{H}_2\text{O})_{6-n}(\text{OH})_n]^{4-n+}$ -montmorillonite, and (C) the clay-intercalated cluster after thermolysis at 280°C.

In an attempt to convert the cluster cation to polyoxometal aggregates, the *in situ* thermolysis of the intercalated molybdenum cluster was performed in a manner analogous to that developed for the thermolysis of related niobium and tantalum cluster intercalates (1). A thermal sequence of 130°C (24 hr) and 200°C (24 hr) was used to limit the amount of intercalated water, and a final step at 280° (24 hr) was used to promote the decomposition of the cluster. A color change from bright yellow to tan is normally observed at the latter temperature. However, some samples showed a color change to blue ($\lambda_{\text{max}} = 730 \text{ nm}$) indicating the formation of molybdenum blue. In the latter case the galleries are collapsed with $d_{001} = 10 \text{ \AA}$. The formation of the blue products appeared to be related to inadequate predrying steps. Only the tan products were studied further.

The IR spectrum of the thermolysis product shown in Fig. 4C clearly indicates the appearance of a band near 900 cm^{-1} attributable to $\text{Mo}=\text{O}$ stretching (9). Also the $\text{Mo}-\text{Cl}$ stretching band (6, 7) near 320 cm^{-1} characteristic of the halogenated cluster (Fig. 4B) is lost on thermolysis. The X-

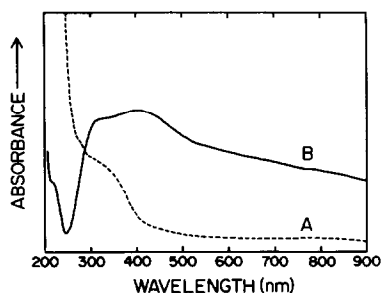


FIG. 5. UV-VIS spectra for (A) $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ in absolute methanol and (B) $[\text{Mo}_6\text{Cl}_8(\text{H}_2\text{O})_{6-n}(\text{OH})_n]^{4-n+}$ -montmorillonite as a Nujol mull suspended between quartz glass plates.

ray diffraction of the thermolysis product is shown in Fig. 6. The presence of two phases with basal spacings of 9.8 and 13.2 Å is indicated. The former phase is indicative of the nearly complete breakdown of the cluster and the collapse of the host layers to within van der Waals contact. Calcination of the thermally treated intercalate at 300°C (5 hr) results in the formation of a single, collapsed phase with a basal spacing of 9.8 Å .

Discussion

The terminal chlorines in $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ are not easily displaced by water or methanol, but they can be removed by stoichiometric argentometric titration according to

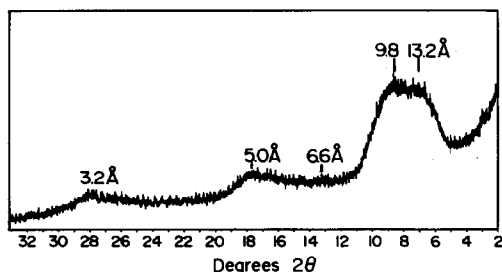
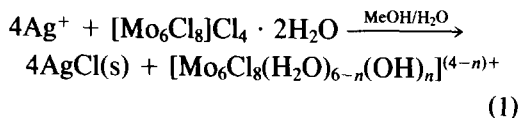


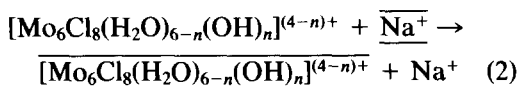
FIG. 6. X-Ray diffraction pattern ($\text{CuK}\alpha$) of an oriented $[\text{Mo}_6\text{Cl}_8(\text{H}_2\text{O})_{6-n}(\text{OH})_n]^{4-n+}$ -montmorillonite film after thermolysis at 280°C.



For instance, Cotton and Curtis have prepared shock sensitive $[\text{Mo}_6\text{Cl}_8\text{L}_6][\text{ClO}_4]_4$ salts and $[\text{Mo}_6\text{Cl}_8\text{L}_6][\text{CH}_3\text{SO}_3]_4$ salts by removing terminal chlorides through precipitation with Ag^+ . Also, $\text{Mo}_6\text{Cl}_8\text{Br}_4 \cdot 2\text{H}_2\text{O}$ has been prepared via a similar route (5). The addition of a methanolic solution of $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ to Ag^+ salts of ClO_4^- or BF_4^- typically result in the formation of yellow precipitates of $\text{Ag}_2[\text{Mo}_6\text{Cl}_8]\text{Cl}_6 \cdot n\text{MeOH}$. Our results indicate that the addition of 7% H_2O (v/v) to the methanolic silver solution eliminates this precipitation problem. Presumably, the H_2O occupies the terminal sites and partly dissociates to H^+ and bound hydroxide.

The removal of the terminal chlorine atoms leads to measurable acid/base chemistry for the cluster cation. Sheldon (10) studied the acid titration of the alkaline species $[\text{Mo}_6\text{Cl}_8(\text{OH})_6]^{2-}$ and determined a pH curve in the presence of Cl^- which finally ended with the formation of a $[\text{Mo}_6\text{Cl}_8](\text{OH})_4 \cdot n\text{H}_2\text{O}$ precipitate near neutral pH. It is our experience that the metal cluster is sufficiently soluble in water at acid pH to utilize the acid/base reaction of the terminally bound water molecules and promote the formation of a soluble cationic molybdenum cluster which can ion exchange for Na^+ in montmorillonite.

The initial slope of the Na^+ release vs cluster bound curve shown in Fig. 2 is consistent with the interaction of mainly monovalent ($n = 3$) and some divalent ($n = 2$) cluster ions in the galleries of montmorillonite. The reaction is described in Eq. (2), where the horizontal lines identify the intercalated species:



At low cluster concentrations the predominant binding reaction between the clay and the cluster is through ion exchange. At higher ratios of cluster to clay equivalents, the cluster continues to bind to a limit of approximately 80 meq/100 g, even though all Na^+ ions have been displaced from the galleries. This behavior is apparently the result of binding of the neutral cluster as the tetrahydroxo $\text{Mo}_6\text{Cl}_8(\text{OH})_4(\text{H}_2\text{O})_2$ species. Binding of the neutral cluster could occur through hydrogen bonding to the clay sheets or through physical adsorption. We have previously attributed similar bonding behavior at high loadings in the case of $[\text{Nb}_6\text{Cl}_{12}(\text{H}_2\text{O})_6]^{2+/3+}$ to a decrease in gallery acidity (increased complex hydrolysis) with increasing loading.

At a pH of 1.5 and a loading of 70 mmoles of cluster/100 g of clay, essentially all of the Na^+ initially present in the galleries has been displaced. However, the cluster loading can be reduced from 70 to 54 mmoles/100 g by washing with water. This further suggests that the cluster bound in excess of the cation exchange capacity (approximately 50 meq/100 g), most likely is present as neutral $\text{Mo}_6\text{Cl}_8(\text{OH})_4(\text{H}_2\text{O})_2$ aggregates. This explanation is favored over the alternative possibility of cluster-perchlorate ion pairing in the galleries, because the infrared data do not support the presence of perchlorate.

The X-ray results for the cluster-intercalated phase are indicative of a d_{001} spacing of 16.6 Å or a gallery height of 7.3 Å. This latter value is compatible with the presence of two layers of chlorine, the C_4 axis of the Mo_6Cl_8 core being oriented perpendicular to the silicate layers. The terminal OH or H_2O groups colinear with C_4 are smaller than the space-filling chlorine atoms and are presumably partially keyed into the hexagonal cavities of the layers. A schematic illustration of the intercalated complex is shown in Fig. 7.

The thermolysis results show that the in-

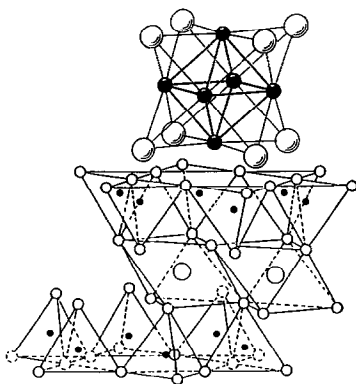


FIG. 7. Schematic illustration of the orientation of $[\text{Mo}_6\text{Cl}_8(\text{H}_2\text{O})_{6-n}(\text{OH})_n]^{4-n+}$ cations in the galleries of montmorillonite. The terminal H_2O and OH ligands on the molybdenum atoms are omitted for clarity.

tercalated clusters undergo reaction at 240°C with the loss of chloride and the destruction of the Mo_6 cluster core. The cluster decomposition is accompanied by the collapse of some clay galleries ($d_{001} = 9.8 \text{ \AA}$), but others remain propped open by approximately 3.9 \AA (cf. Fig. 6). The 3.9-\AA gallery height for the intercalated phase is consistent with the presence of two layers of oxygen. The loss of chloride and the appearance of the 900-cm^{-1} band in the IR spectrum of the decomposition product attributable to a $\text{Mo}=\text{O}$ stretching vibration (cf. Fig. 4) are strongly suggestive of the formation of a molybdenum oxide. However, this oxide is most likely distributed both within the galleries of the pillared phase and on the external surface of the collapsed phase. Previous solution studies by Sheldon (10) have shown that the bromo and chloro molybdenum clusters undergo stepwise substitution of face-bridging halides during the initial stages of alkaline hydrolysis. Continued substitution beyond four face-bridging halides resulted in the decomposition of the cluster by redox reaction with water to produce a molybdenum(V) oxide, water, and H_2 gas. We presume that an analogous redox reaction

operates in converting the intercalated chlorocluster to molybdenum oxide.

Heating the molybdena pillared phase to 300°C results in the collapse of all galleries. In contrast, niobia and tantalum pillared clays prepared by an analogous metal cluster route (1) are stable to 400°C . The thermal instability of the molybdenum analog may limit the catalytic utility of this pillared phase. However, it may be possible to stabilize the pillared products by utilizing clay hosts which are capable of coupling to the gallery oxide aggregates by reaction with aluminum or silicon centers in the tetrahedral sheet. For instance, recent MAS-NMR studies (14, 15) of alumina pillared clays indicate that the layers of montmorillonite retain their constitution at elevated temperature (350°C). That is, the interaction between the oxide aggregates and the layers involve either van der Waals interactions or, more likely, dative bond formation between the siloxane oxygens of the layers and coordinatively unsaturated metal ion sites on the oxide aggregate. On the other hand, related 2:1 layered silicate clays such as beidellite or fluorohectorite react with the gallery oxide by structure rearrangement of the silicate layers. The latter crosslinked pillared clays tend to be more stable than those formed with montmorillonite. Future studies will address the possibility of chemically crosslinking the clay layers with molybdena, niobia, and tantalum aggregates.

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