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Raman Spectroscopic Studies of Intercalated Molybdate Ions in Layered Metal Hydroxides

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X-ray diffraction and Raman spectroscopy have been used to investigate the chemistry of MoO_4^{2-} and $Mo_7O_{24}^{6-}$ ion-exchanged into the interlayers of layered metal hydroxide compounds. In the case of $LiAl_2(OH)_6 \cdot {}^1/_2MoO_4$, exposure of the sample to air leads to destruction of the layered structure as manifested by the diffraction pattern. Raman spectroscopy indicates that this occurs due to hydrolysis of the MoO_4^{2-} followed by reaction of OH^- with CO_2. It is proposed that this process occurs due to charge imbalance between the framework and the intercalated ions. For $Mg_2Al(OH)_6 \cdot {}^1/_6Mo_7O_{24}$, the heptamolybdate ion was found to survive treatments up to 400 °C, although the layer structure is lost at temperatures of 300 °C. The drastic differences between the thermal behavior of molybdates and an earlier reported study of vanadates on magnesium aluminate arise from the distinct hydrolysis chemistry of these two systems.

Introduction

The intercalation of atomic, ionic, and molecular species in layered materials is of considerable interest in solid-state chemistry.[1] In particular, if the layer is charged, then the size, location, and reactivity of the intercalated ions can be influenced by the charge density of the framework. Examples of such phenomena are known in aluminosilicate clays as in pillared montmorillonites[2] and zirconium hydrogen phosphates.[3] The class of materials discussed in this paper are layered double metal hydroxides, resembling the naturally occurring hydrotalcites.[4] These can be represented by the formula $[M^{II}_{1-x}M^{III}_x(OH)_2][A^{n-}]_{x/n} \cdot yH_2O$, where M^{II} and M^{III} represent metal ions such as Ca^{2+}, Mg^{2+}, Zn^{2+} and Al^{3+}, Cr^{3+}, Fe^{3+}, respectively.[5] Structurally, these compounds can be pictured as positively charged layers of $M(OH)_6$ edge-sharing octaredra, with the interlayer space being occupied by neutralizing A^{n-} anions and water. These anions can be readily ion exchanged, and that is the basis for describing these materials as anionic clays. A structurally related material is $LiAl_2(OH)_6^+ \cdot A^-$.[6]

Considerable less research has been done on these materials as compared to the complementary but ubiquitous cationic clays. Yet from studies of ion exchange of various inorganic and organic ions, much is known about the properties of these materials.[7-10] Of interest to this study is the intercalation of poly(oxometalate) ions in hydrotalcites.[11-13] Our previous publications in this area have dealt with ion exchange, alignment, and reactivity of intercalated species.[14-17] The latter subject is the focus of this study. In our examination of intercalated vanadate ions, we found that the interlayer space offered a reactive environment upon thermal treatment, leading to polymerization of simple vanadate species. However, at a high enough temperature (>400 °C), reaction between the intercalated species and the framework metal oxide was observed.[16,17] The motivation for this research has been the development of new routes for metal oxide supported catalytic materials.

In this paper, we focus on molybdate ions. These species are present in solutions used as impregnating agents for the synthesis of molybdate supported catalysts on Al_2O_3, SiO_2, TiO_2, MgO, and SnO_2 for a variety of applications.[18-22] In comparison to our previous studies on vanadates, the aqueous chemistry of molybdates is quite distinct, since the number of oligomeric species is considerably reduced.[23] In this study, the fate of the molybdate ions in the layered metal hydroxides is followed by Raman spectroscopy along with diffraction measurements.

Experimental Section

Analytical reagent grade chemicals were used for all preparations described in this work. Preparation of $LiAl_2(OH)_6 \cdot Cl$ was adapted from the method by Serna et al.[6] Al (0.05 mol) was dissolved in 100 mL of 2 M NaOH solution, 0.25 M of LiCl was dissolved in this solution, and the mixture was heated for 48 h at 90 °C. The products were washed with water followed by 0.1 M NaCl. Care was taken to exclude CO_2 during the synthesis. Ion exchange of the metal hydroxide was carried out with saturated MoO_4^{2-} solution prepared by dissolving Na_2MoO_4 with water. Preparation of the heptamolybdate pillared hydrotalcite was adapted from the procedure described by Drezdzon.[12] To a solution of 14 g of terephthalic and 30 g of NaOH in 200 mL of H_2O was added a solution of 40 g of $Mg(NO_3)_2 \cdot H_2O$ and 30 g of $Al(NO_3)_3 \cdot 9H_2O$ in 125 mL of H_2O. This mixture was heated at 90 °C for 24 h, separated by centrifugation, and thoroughly washed. The exchange of the terephthalate with heptamolybdate was carried out with a solution of 50 g of $Na_2MoO_4 \cdot H_2O$ in 100 mL of H_2O adjusted to a pH of 4.5 with 2 M HNO_3. Thermal treatment of the samples were carried out in an oven manufactured by Technical Products Corp. All measurements on the thermally treated samples were carried out at ambient temper-

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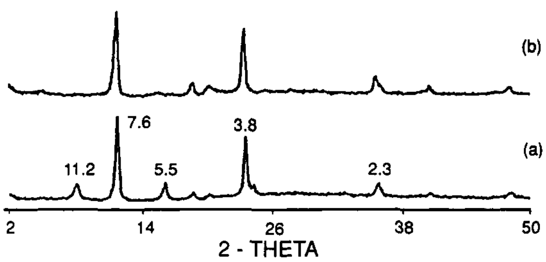

Figure 1. Powder X-ray diffraction patterns of (a) $LiAl_2(OH)_6Cl$ exchanged with saturated MoO_4^{2-} solution and dried at (b) room temperature. Numbers marked on the figures are in angstroms.

ature. Powder X-ray diffraction patterns were obtained with a Rigaku Geigerflex D/Max 2B using nickel-filtered Cu Kα radiation. Raman spectra were recorded with excitation (457.9 nm) from a Spectra Physics argon ion laser (Model 170), and the scattered light was collected and dispersed with a Spex 1403 double monochromator and detected by a C 31034 GaAs photomultiplier tube. Typical power at the sample was between 10 and 20 mW. The slit widths were 6 cm^{-1}, and scan times of 1–3 s/cm^{-1} were used. Analysis for Mo content was carried out with X-ray fluorescence using the instrument Kevex 0700. Since the synthesis for hydrotalcites followed closely the published procedures, elemental composition of these materials were assumed to be similar to those reported in the literature.[6,12]

Results and Discussion

The aqueous chemistry of molybdate ions has been thoroughly examined.[23] The distribution of ions depends on the concentration and pH. In basic solutions (pH > 7) MoO_4^{2-} is the primary species at concentration of 0.1 M and condenses to form heptamolybdate ($Mo_7O_{24}^{6-}$) ion in the pH range 4–6.[23] These two molybdate ions form the focus of this study. The ion exchange and reactions of these ions upon thermal treatment in the interlayers of layered metal hydroxides are examined. The behavior of MoO_4^{2-} in $LiAl_2(OH)_6^+$ and $Mo_7O_{24}^{6-}$ in $Mg_2Al(OH)_6^+$ has been studied. Much of our previous work has involved the $LiAl_2(OH)_6^+$ system and was the basis for choice in this study.[14-16] The magnesium aluminate system was included because it was not possible to exchange $Mo_7O_{24}^{6-}$ into $LiAl_2(OH)_6^+$, in agreement with our previous observation about the inability to ion exchange $V_{10}O_{28}^{6-}$ in $LiAl_2(OH)_6^+$.[16]

(a) $LiAl_2(OH)_6^+\cdot{}^1/_2MoO_4$ System. Unlike our previous experience with nitrates, sulfates, phosphates, and vanadates, it was not possible to find conditions under which MoO_4^{2-} would replace the Cl^- in the entire sample of $LiAl_2(OH)_6\cdot Cl$.[14-17] Figure 1a shows the X-ray powder diffraction pattern of the molybdate-exchanged sample. The reflections at 7.6, 3.8, and 2.3 Å are due to the initial starting material, whereas peaks at 11.2, 5.5, and 3.71 Å arise from the molybdate-exchanged material. The comparison of the intensities of the (001) reflection (e.g., 11.2 and 7.6 Å) are misleading as an estimate of the molybdate exchange, since the X-ray fluorescence data show that the Cl^- has decreased in intensity by 90% after the molybdate exchange. To completely ion-exchange out the Cl^-, the concentration and pH of the molybdate solution were varied from 0.5 to 2 and 9 to 12 M, respectively, but this fraction remained unreactive. It is unclear why this is so. The morphology of these crystals are not well defined. Scanning electron micrographs show particles of dimensions of several microns, with some of the crystals as hexagonal platelets. Molybdates are known to form complexes with hydroxo complexes.[24] A possibility is that MoO_4^{2-} may bind to edge hydroxy groups, blocking off access to the interlayers.

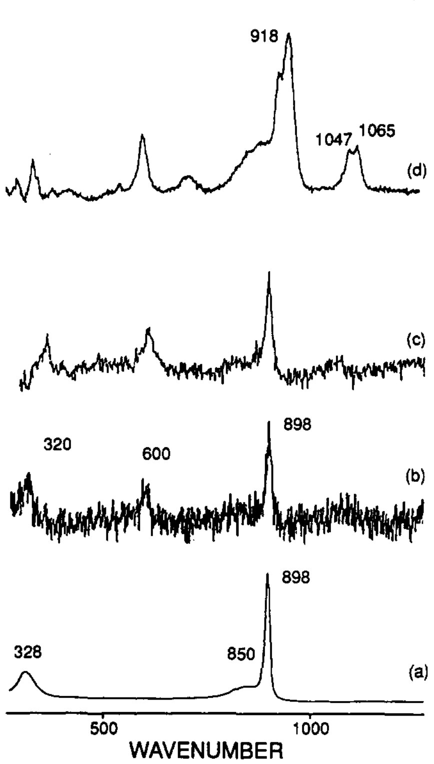

Figure 2. Raman spectra of (a) 0.2 M MoO_4^{2-} solution, (b) wet $LiAl_2(OH)_6\cdot{}^1/_2(MoO_4)$ and (c) dried in N_2 at room temperature, and (d) dried in air at room temperature.

The basal spacing corresponding to the 7.96° (001) reflection is 11.2 Å. Considering that the –OH groups extending into the layer contribute 4.8 Å, a spacing of 6.4 Å for the molybdate species is estimated. On the basis of the Mo–O distance of 1.77 Å for tetrahedral molybdates,[25] we estimate from a purely geometrical method that the distance between the oxygen atoms of MoO_4^{2-} is 5.2 Å along the C_3 axis and 4.8 Å along the C_2 axis (considering the van der Waals radius of O atom to be 1.4 Å). Thus, both these arrangements are possible in the interlayers. In other hydrotalcite type materials, the arrangement of tetrahedral ions such as SO_4^{2-} was proposed to be with the C_3 axis perpendicular to the layers, with water molecules in the interlayers.[26] Since only a fractional number of the divalent ions are required to balance the high charge density of the cationic layer, it is not unusual for these materials to have water molecules in the interlayers.[26]

Figure 1b shows the diffraction pattern of an air dried $LiAl_2(OH)_6\cdot{}^1/_2MoO_4$ sample, in which the characteristic reflections of the MoO_4^{2-}-exchanged material are lost. However, if the samples are dried in a N_2 atmosphere, these reflections are preserved. Raman spectroscopy of these samples provides a better picture of the chemical changes that occur upon air drying. Figure 2a is the Raman spectrum of Na_2MoO_4 (0.2 M, pH 10) and is characterized by bands at 328, 850, and 898 cm^{-1} which are assigned to bending, asymmetric, and symmetric stretches of the MoO_4 unit.[27] Figures 2b and 2c are those of a wet and N_2-dried sample of $LiAl_2(OH)_6\cdot{}^1/_2MoO_4$, which as expected resemble the spectrum of MoO_4^{2-} in solution.

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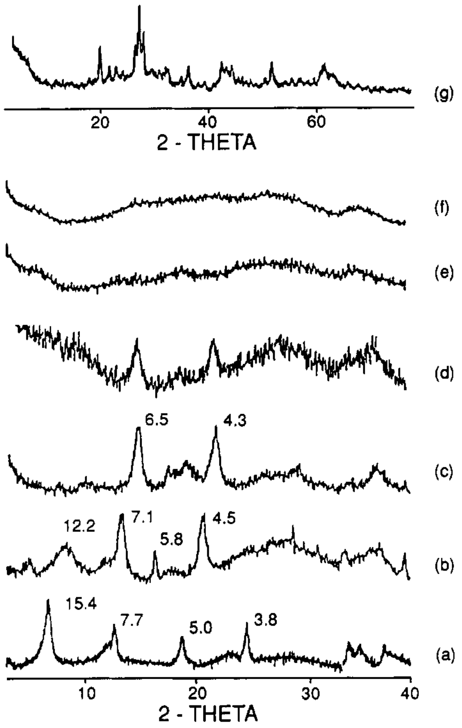

Figure 3. Powder X-ray diffraction patterns of (a) terephthalate–$Mg_2Al(OH)_6$ and (b) wet Mo_7O_{24}–$Mg_2Al(OH)_6$ and heated to (c) 100 °C, (d) 220 °C, (e) 320 °C, (f) 400 °C, and (g) 450 °C (12 h at each temperature). Numbers marked on the figure are in angstroms.

The ~600-cm^{-1} band arises from the $LiAl_2(OH)_6^+$ framework.[16] Figure 2d is the spectrum obtained upon air drying. Several new bands are observed at 918, 1047, and 1065 cm^{-1}. The latter two bands are characteristic of carbonate species,[28] whereas the band at 918 cm^{-1} is readily assigned to $HMoO_4^-$ species.[27] Thus, in the presence of CO_2 the following interlayer reactions are occurring:

$$MoO_4^{2-} + H_2O \rightleftarrows HMoO_4^- + OH^-$$

$$OH^- + CO_2 \rightarrow HCO_3^-$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-}$$

The hydrolysis of the MoO_4^{2-} ion, which is not favored in solution, is being driven by the reaction of OH^- with CO_2. This overall reaction leads to destruction of the lithium aluminate layers, which is indeed surprising concerning the mild nature of the treatment. Typically, temperatures in excess of 300 °C are required to bring about loss of diffraction peaks. A possible reason for this collapse could be the mismatch between charge densities of the layers and the interlayer anions. The framework positive charge density is 25 Å^2/unit charge,[7] whereas for MoO_4^{2-} this charge is distributed over ~33 Å^2 (2 units of charge). This is not a problem as long as the area per unit charge in the interlayer is less than that of the framework. Upon hydrolysis, the neutralizing ions are HCO_3^- and $HMoO_4^-$ and their collective size (>50 Å^2) leads to an imbalance in neutralizing the framework charge, thus leading to destabilization of the framework. If the monomeric molybdates could condense to form oligomeric species, as in the case of vanadates, then this destruction would be avoided.[16]

$Mg_2Al(OH)_6 \cdot {}^1/_6Mo_7O_{24}$ System. This material was prepared following the procedure by Drezdzon,[12] using the intermediate telephthalic ion-exchanged form followed by reaction with a molybdate solution at pH ~4.5. Figure 3a,b shows the X-ray diffraction patterns for the terephthalate- and molybdate-exchanged sample and agrees well with the published data. The basal spacing occupied by the molybdate species corresponds to 12.2 Å and is accounted for by the heptamolybdate ($Mo_7O_{24}^{6-}$) ion aligned such that the C_2 axis is parallel to the layers.[12] Comparison of the Raman spectra of $Mo_7O_{24}^{6-}$ ion in solution (Figure 4a) with the molybdate–$Mg_2Al(OH)_6$ sample (Figure 4b) indeed provides confirmation that the intercalated species is the $Mo_7O_{24}^{6-}$ ion. The bands at 898 and 950 cm^{-1} are assigned to asymmetric Mo–O–Mo and symmetric stretches of Mo–O (terminal) bonds.[26] The band at 360 cm^{-1} is due to a Mo=O bending mode. The layer structure survives upon heating treatment to 200 °C (Figures 3c,d) and remains amorphous in the 300–450 °C range, beyond which a well-defined crystalline material is formed (Figure 3g).

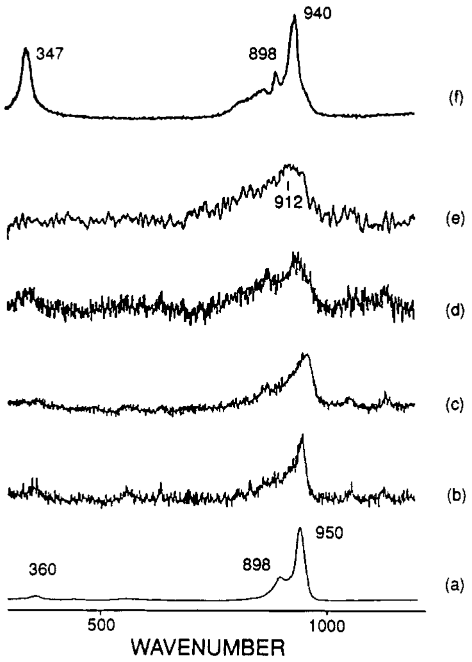

Figure 4. Raman spectra of (a) $Mo_7O_{24}^{6-}$ ions in solution (b) wet $Mo_7O_{24}^{6-}$–$Mg_2Al(OH)_6$ and heated to (c) 200 °C, (d) 320 °C, (e) 400 °C, and (f) 450 °C (12 h at each temperature). The spectra were recorded at ambient temperatures.

The prominent reflections in the diffraction pattern indicate the formation of $MgAl_2O_4$ (4.54, 2.45, 2.06, 1.43 Å), $MgMo_2O_7$ (4.54, 4.19, 3.73, 3.36, 3.30, 3.19, 2.74, 2.13 Å), and $MgMoO_4$ (3.96, 3.73, 3.36, 2.45, 1.73 Å). Drezdzon has indicated that $MgAl_2O_4$ and $MgMoO_4$ are formed at temperatures in excess of 580 °C.[12] The assignment of the pattern to $MgMoO_4$ is somewhat ambiguous, since these are sensitive to hydration effects.

Raman spectra of the heat-treated samples are shown in Figure 4c–f. The samples heated to 200 °C bears a strong resemblance to the initial $Mo_7O_{24}^{6-}$ species, except for a slight broadening. The frequency of the Mo–O stretching mode shifts from 950 to 920 cm^{-1} upon heating to 320 °C. The diffraction data suggest that the sample has lost its crystallinity at this point. The sample remains amorphous upon heating to 400 °C, and the Mo–O stretching mode shifts to 912 cm^{-1} and appears broadened. The spectral pattern indicates that the $Mo_7O_{24}^{6-}$ ion maintains its integrity until temperatures of 400 °C, the slight red shifts in the 300–400 °C region is probably due to a change in the local environment rather than a chemical change. This behavior is quite distinct from that of

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$V_{10}O_{28}^{6-}$, in which the decavanadate ion depolymerized to form oligomeric vanadate species at temperatures lower than 200 °C.[17] In the molybdate system, the lack of stable intermediates between the heptamolybdate and monomeric molybdates leads to the thermal stability of the ionic species. Drezdzon has also noted the stability of the heptamolybdate ion in magnesium aluminates based on thermal analysis data[12] but overestimated the stability to temperatures in excess of 500 °C. It is clear from the Raman spectrum showing in Figure 4f that samples heated to 450 °C result in reaction of the heptamolybdate ion with the magnesium aluminate framework. Raman bands at 347, 840, 860, 898, and 940 cm^{-1} characteristic of well-defined species are observed. On the basis of the reported Raman spectra of K_2MoO_4, $Na_2Mo_2O_7$, $(NH_4)_2Mo_2O_7$, and $MgMoO_4$,[29-32] these bands can be assigned to $MgMoO_4$ (940, 860, 840, 347 cm^{-1}) and $MgMo_2O_7$ (898 cm^{-1} $\nu_s(MoO_2)$), in agreement with the diffraction studies.

In conclusion, this study has shown two interesting aspects about the interlayer chemistry of molybdate ions in double metal hydroxides:

(a) The inability of MoO_4^{2-} to condense into oligomeric forms results in the destruction of the layer structure of $LiAl_2(OH)_6^+$ upon reaction of OH^- (hydrolyzed product of MoO_4^{2-}) with CO_2.

(b) $Mo_7O_{24}^{6-}$-intercalated $Mg_2Al(OH)_6^+$ can exist up to temperatures of 200 °C. At higher temperatures, the layer structure collapses, but the integrity of the $Mo_7O_{24}^{6-}$ is maintained until 400 °C.

Registry No. Al, 7429-90-5; LiCl, 7447-41-8; NaOH, 1310-73-2; $Mg(NO_3)_2$, 10377-60-3; $Al(NO_3)_3$, 13473-90-0; Na_2MoO_4, 7631-95-0; $LiAl_2(OH)_6 \cdot Cl$, 68949-09-7; $LiAl_2(OH)_6 \cdot 1/2MoO_4$, 125615-48-7; $HMoO_4^-$, 14259-84-8; terephthalate-$Mg_2Al(OH)_6$, 117687-65-7; $Mg_2Al(OH)_6 \cdot 1/6Mo_7O_{24}$, 138721-91-2; $MgMoO_4$, 13767-03-8; $MgMo_2O_7$, 58478-77-6; terephthalic acid, 100-21-0.

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Photoconductor Fatigue. 4. Effect of *p*-(Diethylamino)benzaldehyde Diphenylhydrazone Derivatives on the Photooxidation of the Charge-Transport Layer of Organic Layered Photoconductors

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The photooxidation of the hole-transport molecule *p*-(diethylamino)benzaldehyde diphenylhydrazone (DEH) gives rise to residual surface charges during light decay which cannot be photodischarged fast enough for electrophotographic applications. The "electrical fatigue" is attributed to a photochemically induced unimolecular rearrangement of DEH to an indazole derivative. By appropriate substitution of the DEH derivative, the photocyclization reaction and therefore the associated electrical fatigue in the corresponding organic photoconductor are eliminated. These results establish a clear relationship between photochemistry and electrical fatigue. Electrochemical and electrophotographic studies reveal that the hole–transport properties of the DEH derivatives remain the same as DEH despite the structural modifications. Additionally, an X-ray crystal structure analysis of a novel DEH derivative, OMDEH, is reported.

Introduction

The hole-transport molecule *p*-(diethylamino)benzaldehyde diphenylhydrazone (DEH) undergoes a photochemically induced unimolecular rearrangement to an indazole derivative, 1-phenyl-3-(4-(diethylamino)-1-phenyl)-1,3-indazole, with a quantum efficiency of 0.4.[1,2] Because hydrazones such as DEH are commonly used in hole transport in organic layered photoconductors, this photocyclization reaction to an indazole derivative has deleterious consequences on the electrical properties of the organic photoconductor. In particular, photoinduced discharge curves reveal the evolution of residual surface charges on the organic photoconductor during light decay which require decay times as long as several tens of minutes or more before the photoconductor is completely discharged.[3] Clearly, such photoconductors will fail in electrophotographic applications which require photodischarge in several tens of milliseconds. This degradation of the initial electrical properties of organic photoconductors is referred to as"electrical fatigue".

The requirements for high-volume printing capabilities (5 × 10^5 copies/month) on organic layered photoconductors put stringent requirements on their durability.[4] Thus electrical fatigue of organic photoconductors is important, and in recent studies[3,5,6] we have related changes in the

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