Synthesis of Paramolybdate Intercalates of Hydrotalcite-like Compounds by Ion Exchange in Ethanol/Water Solution

Toshiyuki Hibino* and Atsumu Tsunashima

Materials Processing Department, National Institute for Resources and Environment,
16-3 Onogawa, Tsukuba, 305 Japan

Received February 26, 1997. Revised Manuscript Received August 1, 1997[⊗]

Highly ordered paramolybdate ($Mo_7O_{24}^{6-}$) intercalates of hydrotalcite-like compounds (HTlcs) were obtained through anion exchange performed on well-crystallized parent HTlcs in an ethanol/water solution. Aqueous solutions of paramolybdate are acidic, causing hydrolysis of HTlcs, but we found that an ethanol/water solution prevented dissolution of magnesium in the host layers and preserved the highly ordered layer structure of parent HTlcs during anion exchange. These highly ordered paramolybdate intercalates were found to change their structures easily at the usual drying temperatures, with the layer structure being transformed after dehydration of the interlayer water at 80 °C. Moreover, the (003) reflection of the XRD pattern for the paramolybdate intercalates obtained in this study was missing, although previous studies report that the (003) peak has been observed for poorly ordered paramolybdate intercalates. A model calculation proved that the (003) peak existed, but was very weak. The large atomic scattering factor of the molybdenum atoms in paramolybdates differentiates their XRD pattern from that of other HTlcs, such as those containing carbonate.

Introduction

Hydrotalcite, $[Mg_6Al_2(OH)_{16}]CO_3{\cdot}4H_2O$, is a member of the layered, double hydroxide group of minerals. Hydrotalcite, and many other related minerals and synthetic compounds known as hydrotalcite-like compounds (HTlcs), can be expressed by the general formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2][A^{n-}{}_{x/n}{\cdot}zH_2O]$, where M^{2+} = Mg, Ni, Fe, etc.; M^{3+} = Al, Fe, etc.; A^{n-} = CO_3^{2-}, OH^-, Cl^-, NO_3^-, etc.; and x generally lies between 0.2 (for M^{2+}:M^{3+} = 4:1) and 0.33 (for M^{2+}:M^{3+} = 2:1).[1−3] The structure of these materials consists of positively charged double hydroxide layers with the interlayer space filled by anions and water molecules. There is no limitation to the nature of the anion used for intercalation.

Intercalation of large polyoxometalates is currently attracting interest, and several methods have been developed for inserting polyoxometalates into the galleries of HTlcs: (a) direct synthesis;[4−5] (b) anion exchange with HTlcs in which the interlayer galleries are expanded by large organic anions;[6,7] (c) anion exchange with polyol-solvated HTlcs;[8,9] (d) anion exchange by use of a hot aqueous suspension of HTlcs that have a less basic host (Zn−Al HTlc);[10] (e) anion exchange by use of wet-starting HTlcs;[11,12] (f) reconstruction of calcined HTlcs in the presence of a polyoxometalate.[13]

Such polyoxometalate intercalates have been investigated as shape-selective catalysts.[9,14,15] Intercalates prepared under these different conditions vary in their surface areas and pore size distributions, both of which influence catalytic reactivity. Studies on differences in surface area and porosity, as well as differences in crystallinity and purity resulting from these different preparative routes, will also be important in electrochemical applications. Another area we consider to be of interest is the use of polyoxometalate intercalates as novel protonic conductors.[16−19]

Most polyoxometalate intercalates reported, however, have poor crystallinity and are of biphasic material with a broad reflection at about 1.0−1.1 nm in their X-ray diffraction (XRD) patterns. Pure, highly ordered polyoxometalate intercalates are needed for comparative studies. However, synthesizing these intercalates in a highly crystalline form is intrinsically difficult because HTlc host layers are basic, whereas polyoxometalate anions are acidic. Both HTlc host layers and polyoxometalate anions hydrolyze in aqueous solutions, and thus the products may be poorly ordered, or contain multicrystalline phases having different anions in the interlayers. The synthetic methods mentioned above are aimed at intercalating polyoxometalates readily and not at preventing the competing hydrolysis directly

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

(1) Ingram, L.; Taylor, H. F. W. *Mineral. Mag.* **1967**, 36, 465.
(2) Allmann, R. *Acta Crystallogr.* **1968**, *B24*, 972.
(3) Cavani, F.; Trifirò, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173.
(4) Narita, E.; Kaviratna, P. D.; Pinnavaia, T. J. *J. Chem. Soc., Chem. Commun.* **1993**, 60.
(5) Kooli, F.; Jones, W. *Inorg. Chem.* **1995**, *34*, 6237.
(6) Drezdzon, M. A. *Inorg. Chem.* **1988**, *27*, 4628.
(7) Twu, J.; Dutta, P. K. *J. Catal.* **1990**, 124, 503.
(8) Dimotakis, E. D.; Pinnavaia, T. J. *Inorg. Chem.* **1990**, *29*, 2393.
(9) Yun, S. K.; Constantino, V. R. L.; Pinnavaia, T. J. *Microporous Mater.* **1995**, 4, 21.
(10) Kwon, T.; Pinnavaia, T. J. *Chem. Mater.* **1989**, *1*, 381.
(11) Wang, J.; Tian, Y.; Wang, R.-C.; Clearfield, A. *Chem. Mater.* **1992**, *4*, 1276.
(12) Kooli, F.; Rives, V.; Ulibarri, M. A. *Inorg. Chem.* **1995**, *34*, 5122.
(13) Chibwe, K.; Jones, W. *Chem. Mater.* **1989**, *1*, 489.
(14) Kwon, T.; Tsigdinos, G. A.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 3653.
(15) Twu, J.; Dutta, P. K. *J. Phys. Chem.* **1989**, *93*, 7863.
(16) Itaya, K.; Chang, H.-C.; Uchida, I. *Inorg. Chem.* **1987**, *26*, 624.
(17) Moneyron, J. E.; De Roy, A.; Besse, J. P. *Hybrid Circuits* **1991**, *24*, 26.
(18) Keita, B.; Belhouari, A.; Nadjo, L. *J. Electroanal. Chem.* **1993**, *355*, 235.
(19) Qiu, J.; Villemure, G. *J. Electroanal. Chem.* **1995**, *395*, 159.

S0897-4756(97)00115-4 CCC: $14.00

(although easier intercalation will eventually help to minimize hydrolysis). We believed that hydrolysis would be inhibited if a medium other than water were used in ion exchange, because hydrolysis does not occur without water. Some polyoxometalates such as paramolybdate do not dissolve in solvents other than water. However, we expected that hydrolysis would be inhibited to some extent if a mixed medium consisting of a minimum amount of water to dissolve a polyoxometalate salt and a solvent other than water was used for ion exchange. Therefore, we used in this study an ethanol/water solution containing as much ethanol as possible. This is the first study using a medium other than water for anion exchange of HTlcs.

A Mg−Al system was chosen as the host layer and the atomic ratio of Mg:Al was varied. Dissolution of host layers makes intercalation more difficult. As pH declines, the magnesium in the host layers is more readily dissolved than the aluminum. For this reason, we expected the intercalation behavior of Mg−Al HTlcs at low pH to vary with the Mg:Al atomic ratio. Paramolybdate was selected as an intercalated anion to monitor the efficiency of the ethanol/water solution in inhibiting hydrolysis, because isopolyoxometalates are generally easier to hydrolyze than heteropolyoxometalates.

Finally, note that the (003) peaks of the XRD pattern of paramolybdate intercalates obtained in the present study were missing, whereas the (006) and (009) peaks were clearly observed. We modeled an intercalate structure, and confirmed that the XRD pattern calculated from the model structure fitted the observed patterns.

Experimental Section

Synthesis of Parent HTlcs. Two groups of parent HTlcs were prepared to examine whether intercalation of paramolybdate would result in different products depending on the size of the anions initially present in the HTlcs. Parent HTlcs containing large, organic adipate anions ($^{-}OOC(CH_2)_4COO^{-}$), and HTlcs containing small, simple chloride anions were synthesized by a coprecipitation reaction according to Miyata's procedure.[20] A hydrothermal treatment was performed on the coprecipitates to synthesize highly ordered forms. All steps in the synthesis, including washing and drying, were performed under nitrogen flow to avoid carbonate contamination from the air. The distilled water used for synthesizing and washing was decarbonated by boiling.

Adipate/NO₃−HTlcs. An aqueous solution of $Mg(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 9H_2O$ ($Mg^{2+} + Al^{3+} = 0.5$ mol L^{-1}) was continuously added to an aqueous solution of adipate:NaOH at a flow rate of 50 mL h^{-1}. The molar amount of adipate was twice that of aluminum. The mixture was maintained at pH 10 by dropwise addition of a NaOH solution while vigorously stirring. The resulting slurry was kept in a sealed Teflon container with the mother liquor at 150 °C for 24 h followed by cooling and washing several times with distilled water. The wet product was twice washed with ethanol and centrifuged to replace any remaining water with ethanol and then dried in N_2 at room temperature. The atomic ratios of Mg:Al in the initial solutions before coprecipitation were varied at 2:1, 3:1, and 4:1. As will be mentioned in the Results and Discussion section, not only adipate but also a certain amount of nitrate was incorporated into each product. Therefore, we refer to the products whose Mg:Al ratios in the initial solutions before coprecipitation were 2:1, 3:1, and 4:1, as adipate/NO_3−HTlc (2:1), adipate/NO_3−HTlc (3:1), and adipate/NO_3−HTlc (4:1), respectively.

Cl/NO₃-HTlcs. HTlcs containing chloride were prepared in the same way as the adipate/NO_3−HTlcs. Aqueous solutions of $Mg(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 9H_2O$ were added to aqueous solutions of NaCl. A large amount of nitrate, as well as chloride, was incorporated into each product, although it has been reported that the affinity of chloride to HTlcs is higher than that of nitrate.[11,21] Therefore, we refer to these products as Cl/NO_3−HTlc (2:1), Cl/NO_3−HTlc (3:1), and Cl/NO_3−HTlc (4:1).

In addition, we express the parent HTlcs with the same Mg:Al ratios in the initial solutions (before coprecipitation) collectively. For example, adipate/NO_3−HTlc (2:1) and Cl/NO_3−HTlc (2:1) are collectively represented as parent HTlcs having Mg:Al = 2:1.

Intercalation of Paramolybdate by Anion Exchange. *Anion Exchange in Ethanol/Water Solution.* Solutions of 0.17 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ dissolved in 50 mL of ethanol/water solution were prepared. (Ethanol/water ratio 1:1 v/v; ammonium paramolybdate would not dissolve in the mixed solution if a higher proportion of ethanol were used.) A 0.1 g portion of each parent HTlc was added to these mixed solutions. The amount of paramolybdate was more than twice that necessary for stoichiometric anion exchange. The mixtures were left at room temperature for more than 3 days, stirring at intervals. Washing was carried out with 1:1 (v/v) ethanol/water solution. Drying was carried out in the same way as for parent HTlcs. All anion exchange procedures were also performed under nitrogen flow.

Anion Exchange in Aqueous Solution. A 0.1 g portion of each parent HTlc was added to a 50 mL aqueous solution containing 0.17 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. Then the procedure described above for anion exchange in the ethanol/water solutions was followed. Washing was carried out with distilled water. Drying was carried out in the same way as for parent HTlcs, and all anion-exchange procedures were performed under nitrogen flow.

Thermal Decomposition of Paramolybdate Intercalates. Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) of samples was carried out in air at a heating rate of 10 °C min^{-1}. Paramolybdate intercalates were calcined at 50, 80, 100, 150, 250, and 350 °C, and their powder X-ray diffraction (XRD) patterns were observed with Cu $K\alpha$ radiation. Paramolybdate intercalates calcined at 80 °C were soaked in distilled water for 2 h, 1day, and 3days. Rehydration behavior of these samples was observed with XRD.

Chemical Analysis. Atomic ratios of Mg:Al or Mg:Al:Mo of HTlcs were obtained by X-ray microanalysis with an energy-dispersive spectrometer (EDS) attached to a transmission electron microscope (TEM). Adipate content was measured as carbon content determined by a combustion method. Nitrate and chloride contents were determined by gravimetric analysis after dissolving samples in dilute sulfuric acid. Nitrate from the dissolving samples was precipitated as nitron nitrate with Nitron ($C_{20}H_{16}N_4$), and chloride was precipitated as silver chloride at 60 °C with a silver nitrate aqueous solution.

Simultaneous equations were set up from measured values of the Mg:Al ratio, weight loss at 1000 °C, adipate or chloride content, and nitrate content. The structural formulas of the parent HTlcs were determined by solving the equations. In the formulas, it was assumed that any remaining positive charge in the host layer not compensated for by either adipate or chloride and nitrate anions was compensated for by hydroxide anions.

Model Calculation of XRD Pattern. Structure factors and Lorentz polarization factors were calculated from a model structure. They were multiplied together, and the intensities of the (00*l*) reflections were obtained as the products. Five reflections corresponding to successive orders of the basal spacing were calculated, because synthesized HTlcs usually show two or three basal reflections. The adequacy of this

---

(20) Miyata, S. *Clays Clay Miner.* **1980**, *28*, 50.

(21) Miyata, S. *Clays Clay Miner.* **1983**, *31*, 305.

Table 1. Elemental Data for Parent HTlcs

sample	*a*	*x*	*y*	*z*	*n*
$Mg_{1-a}Al_a(OH)_2\cdot[(^-OOC(CH_2)_4COO^-)xa/2\cdot(NO_3^-)ya\cdot(OH-)za]\cdot nH_2O$					
adipate/NO_3−HTlc (2:1)	0.36	0.88	0.06	0.06	0.87
adipate/NO_3−HTlc (3:1)	0.29	0.62	0.27	0.11	0.57
adipate/NO_3−HTlc (4:1)	0.23	0.15	0.75	0.11	0.45
$Mg_{1-a}Al_a(OH)_2\cdot[(Cl^-)xa\cdot(NO_3^-)ya\cdot(OH^-)za]\cdot nH_2O$					
Cl/NO_3−HTlc (2:1)	0.33	0.20	0.62	0.18	0.31
Cl/NO_3−HTlc (3:1)	0.27	0.29	0.54	0.18	0.48
Cl/NO_3−HTlc (4:1)	0.21	0.19	0.75	0.05	0.49

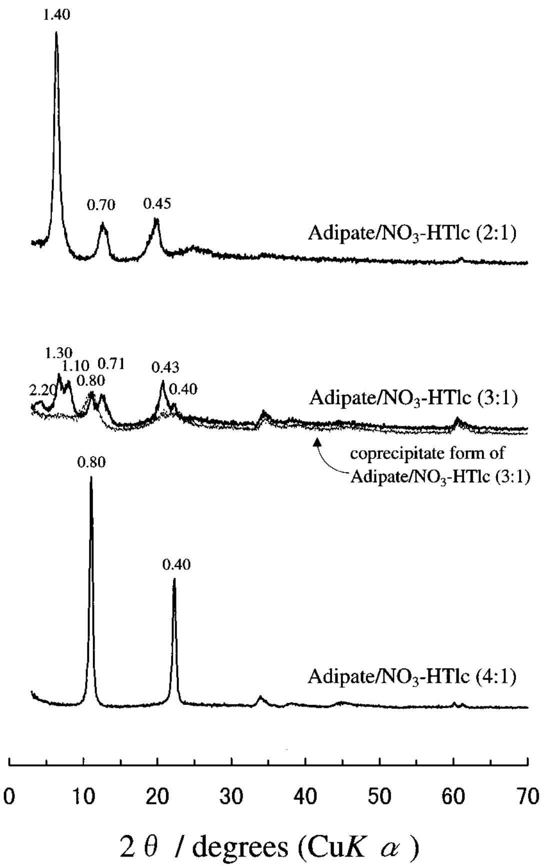

Figure 1. XRD patterns for adipate/NO_3−HTlcs. Numbers refer to *d* spacing values in nanometers. Scale of the XRD pattern for adipate/NO_3−HTlc (4:1) is reduced to half that of the others.

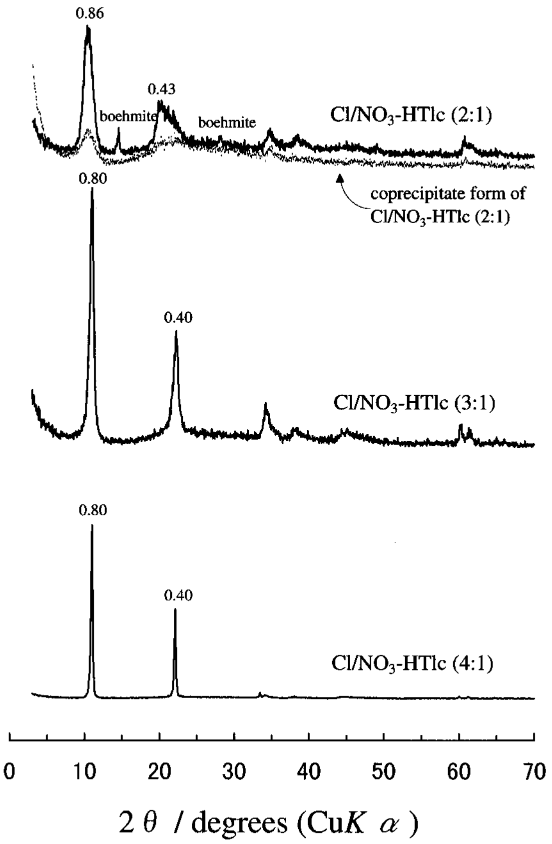

Figure 2. XRD patterns for Cl/NO_3−HTlcs. Numbers refer to *d* spacing values in nanometers. Scale of the XRD pattern for Cl/NO_3−HTlc (4:1) is reduced to one-tenth that of the others.

calculation was verified by calculating XRD patterns of carbonate forms of HTlc.

Results and Discussion

Parent HTlcs. The powder XRD patterns for adipate/NO_3−HTlcs and Cl/NO_3−HTlcs, and *d* values of basal reflections are given in Figures 1 and 2. The adipate/NO_3−HTlcs had different basal spacing depending upon the atomic ratio of Mg:Al. A basal spacing of 1.40 nm was observed for adipate/NO_3−HTlc (2:1), whereas 0.80 nm basal spacing was observed for adipate/NO_3−HTlc (4:1). The differences in basal spacing were well explained by the results of chemical analyses listed in Table 1. Adipate was the prevailing interlayer anion for adipate/NO_3−HTlc (2:1), and nitrate was the prevailing interlayer anion for adipate/NO_3−HTlc (4:1). Therefore, the magnitude of the basal spacing was determined by the size of the prevailing anions. However, adipate/NO_3−HTlc (3:1) showed complicated XRD reflections of basal spacing, and another HTlc prepared in the same way as adipate/NO_3−HTlc (3:1), omitting only the hydrothermal treatment (the coprecipitated form of adipate/NO_3−HTlc (3:1)), showed only a broad basal reflection at about 0.80 nm. The many basal reflections of adipate/NO_3−HTlc (3:1) resulted from the existence of different HTlc phases, such as adipate intercalate, nitrate intercalate, and interstratified phases. These phases were not crystallized and did not appear as reflections for the coprecipitated form of adipate/NO_3−HTlc (3:1), except for the phase having a basal spacing of about 0.80 nm.

Compared with adipate/NO_3−HTlcs, the basal spacing of Cl/NO_3−HTlcs did not change very much with the atomic ratio of Mg:Al, and neither did the molar ratio of interlayer anions. Nitrate was intercalated more than chloride, although it has been reported that chloride has a higher affinity for HTlcs than does nitrate.[11,21] Cl/NO_3−HTlc (2:1) included a boehmite (γ-AlOOH) phase as a coproduct, although the coprecipitated form of Cl/NO_3−HTlc (2:1) showed a broad basal reflection at 0.85 nm, and did not include any coproduct phase. When the Mg:Al ratio was 2:1 and nitrate and chloride coexisted in the interlayers, the high layer

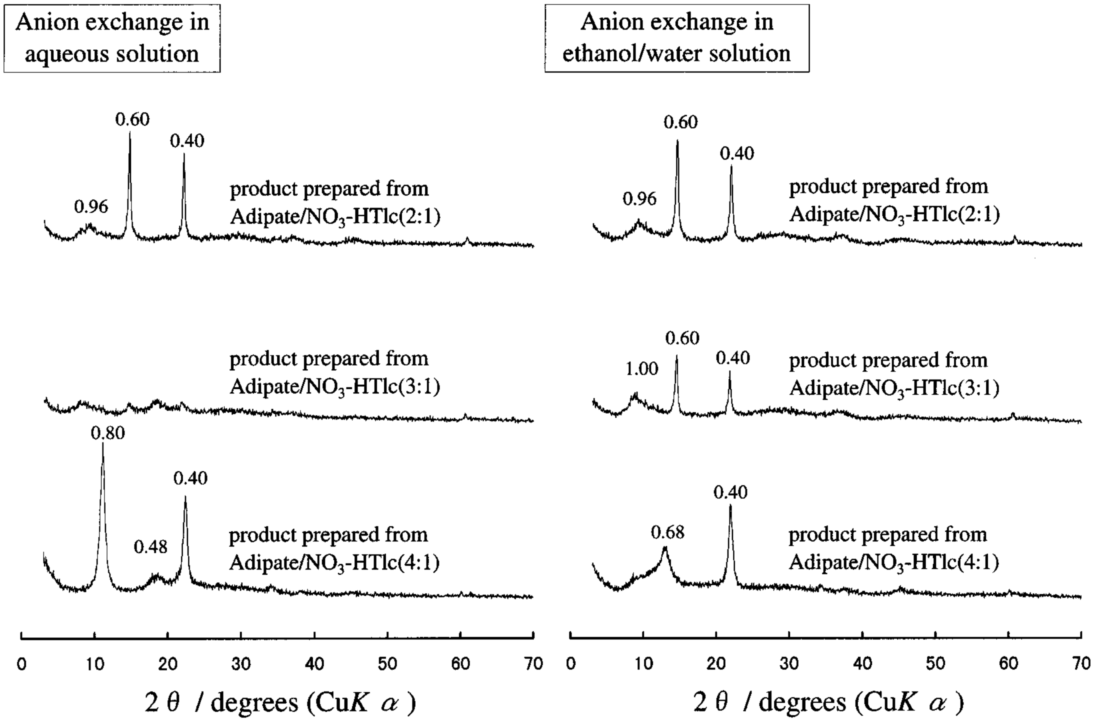

Figure 3. XRD patterns for products obtained by anion exchange with aqueous solution (left series) and with ethanol/water solution (right series). Numbers refer to *d* spacing values in nanometers.

Table 2. Elemental Data for Products after Anion Exchange

parent HTlc	Mg:Al atomic ratio before anion exchange	Mg:Al:Mo atomic ratio after anion exchange: aqueous solution	Mg:Al:Mo atomic ratio after anion exchange: ethanol/water solution
adipate/NO$_3$−HTlc (2:1)	1.82:1.00	1.77:1.00:0.79	1.75:1.00:0.79
adipate/NO$_3$−HTlc (3:1)	2.44:1.00	1.06:1.00:0.48	2.30:1.00:1.03
adipate/NO$_3$−HTlc (4:1)	3.39:1.00	1.22:1.00:0.17	2.78:1.00:0.75
Cl/NO$_3$−HTlc (2:1)	2.00:1.00	1.34:1.00:0.57	1.89:1.00:0.89
Cl/NO$_3$−HTlc (3:1)	2.72:1.00	0.77:1.00:0.34	2.13:1.00:1.03
Cl/NO$_3$−HTlc (4:1)	3.67:1.00	1.68:1.00:0.18	2.84:1.00:0.63

charge density would not be compensated for sufficiently by those anions because of repulsion. A small amount of aluminum might have been precipitated as a hydroxide in amorphous form to decrease the positive charge of the host layers, and crystallized as boehmite after subsequent hydrothermal treatment. The amount of boehmite in Cl/NO$_3$−HTlc (2:1) was very small (about 5 wt %), as measured by weighing the undissolved remainder when the sample was dissolved in acid solution. Because it contains a phase (boehmite) other than HTlc, even if only in a small amount, Cl/NO$_3$−HTlc (2:1) should not be used for intercalation of paramolybdate. We used it in order to examine the effect of anion size on intercalation. Fortunately, the boehmite in Cl/NO$_3$−HTlc (2:1) became undetectable by XRD after anion exchange, perhaps by becoming amorphous.

Intercalation of Paramolybdate. XRD analysis showed that adipate/NO$_3$−HTlcs and Cl/NO$_3$−HTlcs provided the same products after anion exchange, although the reflection peaks of the products prepared from adipate/NO$_3$−HTlcs were slightly sharper than those of the products prepared from Cl/NO$_3$−HTlcs. This indicates that paramolybdate can be intercalated, regardless of the relative size of the initial anion. Figure 3 shows XRD patterns for products obtained by anion exchange from adipate/NO$_3$−HTlcs in both aqueous and ethanol/water solutions. Reflection peaks observed at more than $2\theta = 30°$ for all samples were indexed as reflections of HTlcs other than basal reflections. Values of *d* spacing observed at less than $2\theta = 30°$, which are expected to be basal reflections, are given in Figure 3.

When anion exchange was performed in aqueous solutions, products with sharp basal reflections at 0.60 and 0.40 nm were obtained from parent HTlcs having Mg:Al = 2:1; mostly amorphous products were obtained from parent HTlcs having Mg:Al = 3:1; and products having the same reflections as parent HTlcs were obtained from parent HTlcs having Mg:Al = 4:1. Much of the magnesium in the host layers was dissolved by anion exchange performed in aqueous solutions (Table 2). Magnesium contents in paramolybdate intercalates prepared from parent HTlcs with Mg:Al = 3:1 and 4:1 were much less than the minimum Mg content for Mg−Al HTlcs (the ratio of Mg:Al is 2:1 at the minimum Mg content). The atomic ratio of Al:Mo = 1.00:1.17 would be required for all paramolybdate intercalates, if paramolybdate anions replace all the initial anions in the parent HTlcs. However, the Mo contents of paramolybdate intercalates obtained were less than that at the ratio of Al:Mo = 1.00:1.17. Paramolybdate anions were poorly intercalated when the Mg:Al ratio of the parent HTlc was 4:1.

When anion exchange was performed in the ethanol/water solution, products with sharp basal reflections at 0.60 and 0.40 nm were obtained from parent HTlcs having Mg:Al = 2:1 and 3:1, and products with basal reflections at 0.68 and 0.40 nm were obtained from parent HTlcs having Mg:Al = 4:1. When parent HTlcs

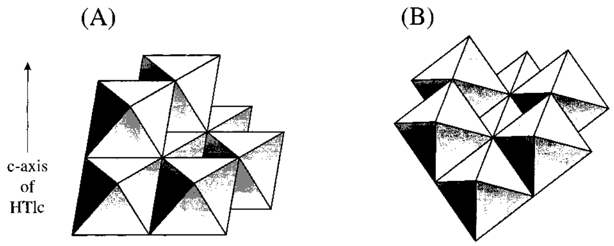

Figure 4. Two possible orientations (A, B) of paramolybdate anions in the interlayer. Octahedra represent MoO_6.

having Mg:Al = 2:1 were used, no differences were observed in chemical compositions and XRD pattern between paramolybdate intercalates prepared in aqueous solution and those prepared in ethanol/water solution. However, in the case of parent HTlcs having Mg:Al = 3:1 and 4:1, dissolution of Mg in ethanol/water solution was prevented, and their Mo contents were much higher than those of paramolybdate intercalates prepared in aqueous solutions. The ratio of Al:Mo was a better indicator to evaluate the extent of replacement by paramolybdate than either infrared spectra or carbon analysis for adipate. On the basis of the ratio indicator, the highest replacement was observed for paramolybdate intercalates prepared in ethanol/water solution from parent HTlcs having Mg:Al = 3:1.

Previous studies of intercalation of paramolybdate reported that paramolybdate intercalate has a basal spacing ($c/3$) of 1.20 nm.[6,13] Consequently, reflections at 1.20, 0.60 and 0.40 nm are expected as (003), (006), and (009) reflections. However, paramolybdate intercalates obtained in the present study showed different patterns and are discussed below.

It is noteworthy that a broad reflection at about 1.0 nm was observed for these paramolybdate intercalates. A similar phase has been observed in almost all previous reports on synthesis of polyoxometalate intercalates.[4,5,8,11,22,23] It has been suggested that this phase is a poorly ordered Mg–Al salt of polyoxometalates. However, we conclude that the phase obtained in the present study was a HTlc containing, perhaps as a mixture, other smaller anions such as OH^- or small molybdate anions derived from paramolybdate anions by hydrolysis, because (a) the broad reflection at about 1.0 nm was not observed when carbonate intercalate was exposed to the same ethanol/water solution that was used for anion exchange (carbonate intercalate did not change at all), (b) when paramolybdate intercalates were exposed to a Na_2CO_3 aqueous solution, the broad reflection at 1.0 nm disappeared, due to exchange for carbonate anions, and the XRD pattern showed only the carbonate forms of HTlc, and (c) no precipitate was obtained from mixed solutions of $Mg(NO_3)_2$, $Al(NO_3)_3$, and $(NH_4)_6Mo_7O_{24}$ at about pH 5.0 (the pH during anion exchange in the present study).

Although the broad reflection peak at about 1.0 nm was observed in the present study, its intensity was much weaker than that reported previously.[6,13] Paramolybdate intercalates obtained in the present study showed highly ordered forms.

Model Calculation of XRD Patterns. The highly ordered forms of paramolybdate intercalates we obtained exhibited two patterns that are different from those previously reported: a pattern with two basal reflections at 0.60 and 0.40 nm, respectively, that could be indexed as (006) and (009) reflections of basal spacing ($c/3$ = 1.20 nm); and another pattern with two basal reflections at 0.68 and 0.40 nm, respectively. In previous reports, reflections at 1.20, 0.60, and 0.40 nm, indexed as (003), (006), and (009) reflections, were observed for paramolybdate intercalates. However, those reported paramolybdate intercalates were poorly ordered, and their reflections of XRD patterns were vague.[6,13] Therefore, we modeled possible structures of paramolybdate intercalates and calculated their XRD patterns to determine the structures of the paramolybdate intercalates we obtained.

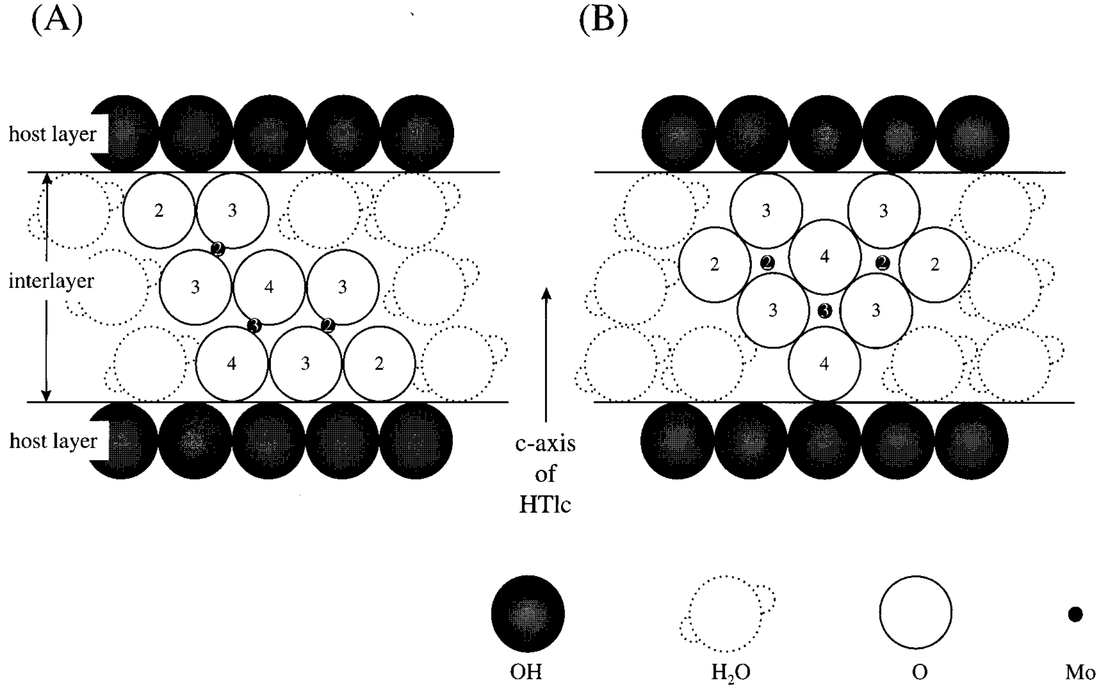

Figure 5. A atomic arrangement of two possible orientations (see Figure 4) of intercalated paramolybdate anions in the interlayer projected on a face perpendicular to the host layers. Numbers of superposed atoms are indicated.

Table 3. Data of Model Structures

	model structure (a)			model structure (b)		
	atom	numbers of atoms[a]	positions of atoms[b]	atom	numbers of atoms[a]	positions of atoms[b]
host layer	Mg	18	0.00	Mg	18	0.00
	Al	6	0.00	Al	6	0.00
	O	24	0.10	O	24	0.10
	O	24	0.90	O	24	0.90
	H	24	0.10	H	24	0.10
	H	24	0.90	H	24	0.90
$Mo_7O_{24}^{6-}$	O	7	0.30	O	5	0.30
	Mo	3.5	0.40	Mo	3.5	0.43
	O	10	0.50	O	7	0.43
	Mo	3.5	0.60	Mo	3.5	0.56
	O	7	0.70	O	7	0.56
				O	5	0.70
interlayer water	O	17	0.30	O	19	0.30
	O	14	0.50	O	12	0.50
	O	17	0.70	O	19	0.70
	H	34	0.30	H	38	0.30
	H	28	0.50	H	24	0.50
	H	34	0.70	H	38	0.70

[a] Numbers of atoms are calculated for one paramolybdate anion. [b] Positions of atoms in the direction of (00*l*) are expressed as fractions of the basal spacing (1.20 nm).

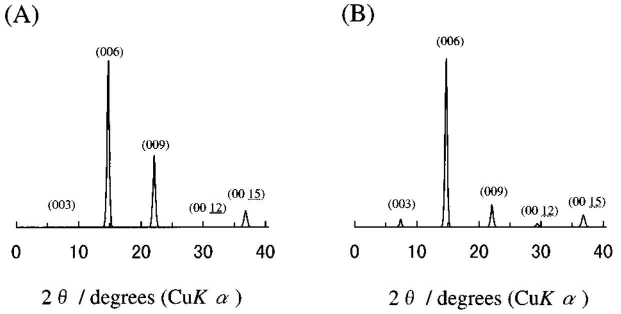

Figure 6. XRD patterns calculated on the basis of the orientations shown in Figure 4. Pattern A is calculated from Figure 4A, pattern B from Figure 4B.

Figure 4 shows two possible orientations of paramolybdate anions in the interlayer (inverted orientations in each case can occur equivalently). The height was 0.72 nm for either orientation, and the basal spacing was 1.20 nm when a value of 0.24 nm was used as the diameter of oxygen.

Before calculation of the XRD pattern, determination of both the position and amount of interlayer water is necessary. Calculation of these on the basis of sites present in the interlayer is possible, assuming a close-packed configuration of oxygen atoms. The number of interlayer water molecules per the formula ($[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2][A^{n-}{}_{x/n}{\cdot}zH_2O]$) was calculated by the following equation according to Miyata:[24]

$$z = 1 - Nx/n$$

where N = the number of sites occupied by the anion, n = the charge of the anion, and x = Al/(Mg + Al).

Atomic arrangements based on Figure 4 are illustrated in Figure 5. Atomic positions are projected along the *a*-axis, and the number of superposed atoms is indicated in each atom. Table 3 lists the positions and numbers of atoms. Thus, XRD patterns of paramolybdate intercalates on the basis of orientations in Figure 4 can be calculated. The calculated XRD patterns are shown in Figure 6, and calculated intensities of (00*l*) reflections are listed in Table 4. These results were calculated using the ratio Mg:Al = 3:1. When the ratios were 2:1 and 4:1, the calculated XRD patterns were almost the same.

Table 4. Intensity of XRD Reflections Calculated from Model Structures

model structure	*hkl*	2*θ*/deg (Cu Kα)	LP factor	structure factor $\|F\|^2$	intensity I/I_{max}
a	0 0 3	7.36	482.5	26	0.1
	0 0 6	14.72	118.9	95840	100.0
	0 0 9	22.08	51.6	101960	45.8
	0 0 12	29.44	28.2	834	0.2
	0 0 15	36.80	17.4	81802	12.4
b	0 0 3	7.36	482.5	1600	4.5
	0 0 6	14.72	118.9	145054	100.0
	0 0 9	22.08	51.6	47367	14.2
	0 0 12	29.44	28.2	13828	2.3
	0 0 15	36.80	17.4	89007	9.0

The calculated XRD pattern of Figure 6A fits both the XRD patterns of paramolybdate intercalates prepared from parent HTlcs having Mg:Al = 2:1 and 3:1 in ethanol/water solutions, and also the XRD patterns of paramolybdate intercalates prepared from parent HTlcs having Mg:Al = 2:1 in aqueous solutions. When intercalated anions do not contain atoms with large scattering factors, intensities of basal reflections of HTlcs are mainly governed by the X-ray intensity scattered by metals, such as magnesium and aluminum, in the host layers. However, because of the large scattering factor, molybdenum in paramolybdate anions intercalated in HTlcs can affect intensities of reflection lines. Indeed, the model calculation presented here demonstrates that the reflection of (003) essentially cannot be visible (the reflection is too weak to observe), as shown in Figure 6 (A). The lack of (003) reflection was reported also for decavanadate ($V_{10}O_{28}^{6-}$) intercalates of HTlc[23] and may be from the same cause, because the structure of decavanadate intercalates is similar to that of paramolybdate intercalates. Consequently, we attribute the observation of a (003) reflection for paramolybdate intercalates in previous studies to poor crystallinity.[6,13]

---

(22) Narita, E.; Kaviratna, P.; Pinnavaia, T. J. *Chem. Lett.* **1991**, 805.

(23) Ulibari, M.-A.; Labajos, F. M.; Rives, V.; Trujillano, R.; Kagunya, W.; Jones, W. *Inorg. Chem.* **1994**, *33*, 2592.

(24) Miyata, S. *Clays Clay Miner.* **1975**, *23*, 369.

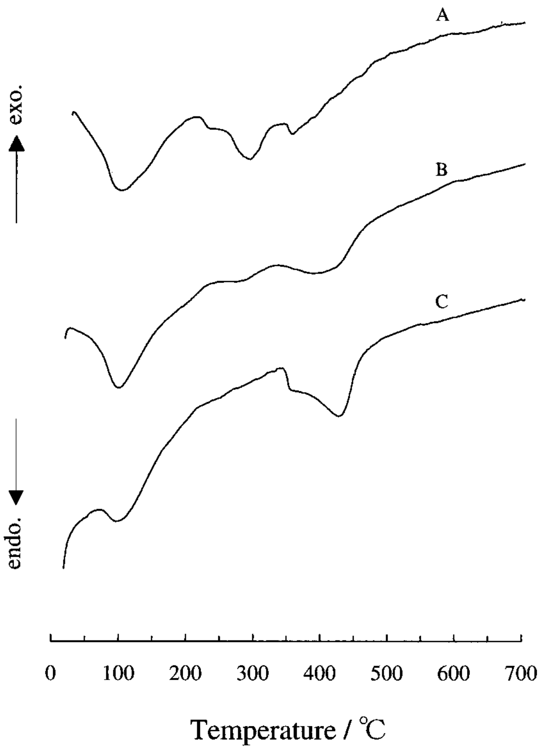

Figure 7. DTA curves of paramolybdate intercalates prepared from: (A) adipate/NO_3−HTlc (2:1); (B) adipate/NO_3−HTlc (3:1); and (C) adipate/NO_3−HTlc (4:1), each with ethanol/water solution.

In the present study, another XRD pattern of paramolybdate intercalate prepared from parent HTlcs having Mg:Al = 4:1 in an ethanol/water solution gave basal reflections at 0.68 and 0.40 nm, representing two phases. The reflection peak at 0.68 nm (phase 1) was broad, while that at 0.40 nm (phase 2) was sharp. The value of 0.40 nm is less than the host layer thickness of 0.48 nm. Thus, the reflection at 0.40 nm might be (006) reflection, and (003) reflection of phase 2 might be too small to observe. We found some candidate structures for these two phases. However, the intensity calculations for these structures contained many assumptions, and we could not reach a satisfactory conclusion.

Thermal Decomposition of Paramolybdate Intercalates. Using different parent HTlcs of adipate/NO_3−HTlcs and Cl/NO_3−HTlcs caused no difference in the thermal decomposition behavior of resulting paramolybdate intercalates. Also, no difference was observed between paramolybdate intercalates prepared in aqueous solution and those prepared in ethanol/water solution when the Mg:Al ratio of the parent HTlcs was 2:1. As mentioned above, when the Mg:Al ratio of parent HTlcs was 3:1 and 4:1, paramolybdate was not successfully intercalated into the HTlc structure in aqueous solution. Therefore, we describe here only the thermal decomposition behavior of paramolybdate intercalates prepared in ethanol/water solution from all parent HTlcs, and those prepared in aqueous solution from parent HTlcs having Mg:Al = 2:1, and focus on differences related to the different Mg:Al ratios of the parent HTlcs. Figure 7 shows DTA curves of these paramolybdate intercalates (Mg:Al = 2:1, 3:1 and 4:1), and Figure 8 shows XRD patterns of these intercalates heated to various temperatures.

Endothermic peaks that can be attributed to loss of interlayer water began at about 80 °C and peaked at about 100 °C for all paramolybdate intercalates. Due to this dehydration, structural transformations occurred at 80 °C for all the paramolybdate intercalates (Figure 8). Paramolybdate intercalates prepared from parent HTlcs with Mg:Al = 2:1 or 3:1 could be restored by exposure to water, but we could not rehydrate the paramolybdate intercalates prepared from parent HTlcs with Mg:Al = 4:1 at all, as shown in Figure 9.

Paramolybdate intercalate prepared from parent HTlc with Mg:Al = 2:1 changed its XRD pattern at 80 °C; basal reflections at 0.60 and 0.40 nm disappeared, and a new reflection at 0.48 nm appeared at this temperature. Also, the color of its powder was changed from white to yellow by heating at 80 °C. The phase obtained at 80 °C was restored to the initial phase by rehydration, and its color reverted to white. The XRD reflection peak

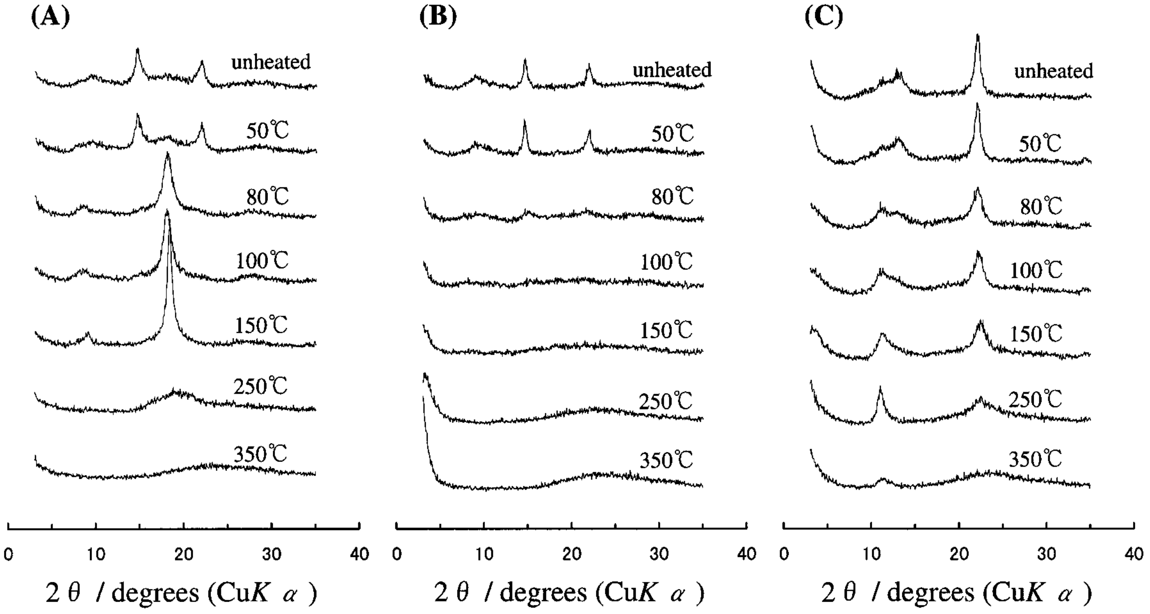

Figure 8. XRD patterns for paramolybdate intercalates prepared from: (A) adipate/NO_3−HTlc (2:1), (B) adipate/NO_3−HTlc (3:1); and (C) adipate/NO_3−HTlc (4:1), each with ethanol/water solution, when heated at the indicated temperatures.

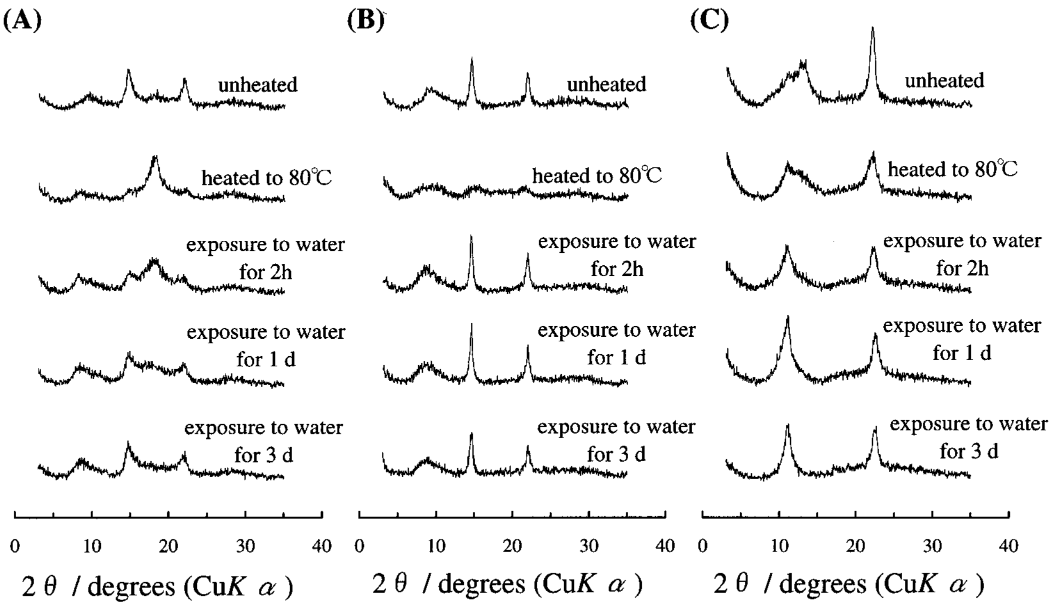

Figure 9. XRD patterns for paramolybdate intercalates prepared from (A) adipate/NO_3−HTlc (2:1); (B) adipate/NO_3−HTlc (3:1); and (C) adipate/NO_3−HTlc (4:1) each with ethanol/water solution, when heated at the indicated temperatures or when exposed to water for the indicated time after heating at 80 °C.

at 0.48 nm might result from a change of arrangement of anions in the interlayers, although the precise structure is unclear.

Paramolybdate intercalate prepared from parent HTlc with Mg:Al = 3:1 became amorphous at 80 °C, and its white color did not change. The amorphous phase obtained at 80 °C was also restored to its initial phase by exposure to water. The restoration was complete in 2 h compared to the 3 days required for paramolybdate intercalate prepared from parent HTlc with Mg:Al = 2:1, as shown in Figure 9.

When paramolybdate intercalate prepared from parent HTlc with Mg:Al = 4:1 was heated to 80 °C, an XRD reflection at 0.80 nm became prominent, the reflection at 0.64 nm disappeared, and the reflection at 0.40 nm decreased in intensity. The reflection at 0.80 nm might be the (003) peak of phase 2. Phase 1 might become amorphous at 80 °C, and thus the reflection at 0.64 nm would disappeared. The XRD pattern obtained at 80 °C did not return to the initial state upon exposure of the intercalate to water (Figure 9).

Conclusion

It is clear from the results presented here that an ethanol/water solution is very helpful in intercalating paramolybdate by preventing the host layers of HTlcs from dissolving during anion exchange with paramolybdate. Magnesium in the host layer dissolved during anion exchange in both aqueous solution and in ethanol/water solution. However, the decrease in magnesium after anion exchange in the ethanol/water solution was much less than that in the aqueous solution, especially when the Mg:Al ratios of the parent HTlcs were 3:1 and 4:1.

Anion exchange in aqueous solution produced the same paramolybdate intercalate as in ethanol/water solution only when the Mg:Al ratio of parent HTlcs was 2:1. In previous studies,[6,13] this was also the Mg:Al ratio of parent HTlcs used. Therefore, we believe that in those studies, paramolybdate anions were able to be intercalated in those works despite the use of aqueous solutions. The present study shows that the highest anion-exchange intercalation rate for paramolybdate is attained by anion exchange in ethanol/water solution with parent HTlcs having Mg:Al = 3:1.

Furthermore, the present study confirms that it is unnecessary for the interlayer gallery height to be expanded by large anions, such as large organic anions, in order to readily intercalate paramolybdate.

As for the paramolybdate intercalate itself, we have discovered two new properties: the structure of paramolybdate intercalate is transformed after dehydration of the interlayer water at about 80 °C. Moreover, highly ordered paramolybdate intercalates having 1.20 nm basal spacing clearly showed (006) and (009) peaks but did not show a (003) reflection at 1.20 nm, although previous works reported that a (003) peak. The model calculation in the present study shows that the (003) peak is very weak. Polyoxometalate intercalates could show XRD patterns very different from HTlcs containing carbonate because heavy metals, such as molybdenum atoms, have large atomic scattering factors.

CM970115A