

Preparation of New Useful Materials by Surface Modification of Inorganic Layered Compound

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We have obtained water-treated Zn-Al layered double hydroxides (LDHs) that were covered by hydroxyl groups between the layers. By reaction of the water-treated Zn-Al LDH with oxychloride, the surface modification of the Zn-Al LDH by esterification was attained. The reaction products were characterized by X-ray diffraction measurements and thermal analysis, and the esterification reaction was confirmed by an IR spectrum in which the peak intensity at 3400 cm^{-1} decreased and a new peak at 1550 cm^{-1} appeared. Interlayer spacing of the LDH increased by the esterification reaction. The esterified LDHs obtained in this work were hydrophobic. © 1995 Academic Press, Inc.

INTRODUCTION

There are various kinds of layered double hydroxides whose empirical formula is $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2](A^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where A^{n-} is an exchangeable anion. The crystal structure consists of positively charged brucite-like octahedral hydroxide layers, which are neutralized by the interlayer anions (1). Center metals are divalent metals like Zn, Mg, and part of the divalent metals were exchanged with trivalent metals like Al. Therefore, the layers have a positive charge and intercalate anions between the layers. The Mg-Al layered double hydroxide (LDH) is one of the naturally occurring minerals belonging to this group. Intercalation into the LDHs occurs by electrostatic interaction between the anionic charge of guest species and cationic sites in the clay layers. Therefore, only anion guest species could be intercalated into the LDHs. Certainly, many organic anions were intercalated by electrostatic interaction (2-4).

The carbonate LDH includes a carbonate ion between the layers. It is well known that the carbonate LDH decomposes to oxide solid by thermal treatment, and the calcined product can rehydrate and incorporate the carbonate anions in an aqueous solution to reconstruct the original LDH structure. Similarly, the calcined LDH is expected to find applications in the uptake of organic anions from aqueous solutions as shown in Scheme 1. In practice, we have already reported preferential intercala-

tion of isomeric organic anions with the same charge into the calcined LDH (5).

The calcined Mg-Al LDH and the calcined Zn-Al LDH were obtained by heat treatment at 500°C . Even with the calcined Mg-Al LDH standing in degassed water, a carbonate ion was incorporated into the Mg-Al LDH layers upon storage. However, in the case of the calcined Zn-Al LDH, no incorporation of a carbonate ion was confirmed by the same treatment with the calcined Mg-Al LDH. It indicated that the calcined Mg-Al LDH has a greater ability to absorb a carbonate ion than the calcined Zn-Al LDH (6).

In this study, we have succeeded in modifying the Zn-Al LDH surface by the esterification reaction of the hydroxyl groups with various organic compounds.

The new intercalation compounds have a hydrophobic field, as shown in Scheme 2.

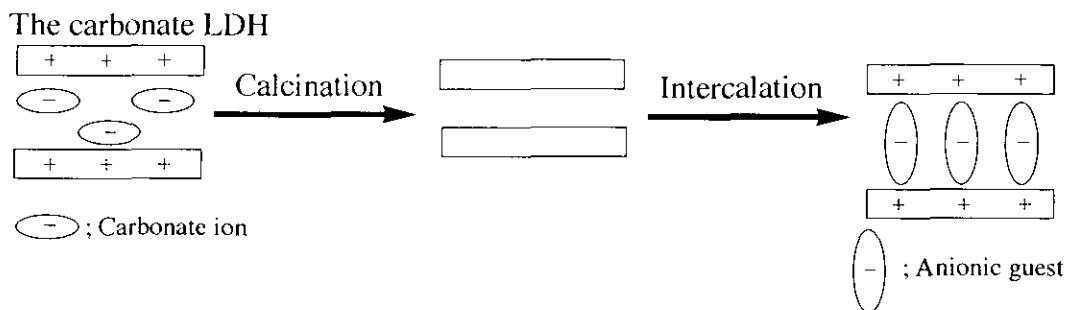
EXPERIMENTAL

Preparation of the Layered Double Hydroxides

The Mg-Al and Zn-Al LDHs were prepared by reaction of the mixture of $\text{Mg}(\text{NO}_3)_2$ or $\text{Zn}(\text{NO}_3)_2$ ($((1 - X)/2$ mole/liter) and $\text{Al}(\text{NO}_3)_3$ ($(X/2$ mole/liter) in a Na_2CO_3 solution, whose pH was adjusted to ca. 10 with NaOH solution, under a nitrogen atmosphere at 60°C for 2 hr. After being filtered, the products were each fully washed with an alkali solution and distilled water three times. The products were dried for 48 hr at 80°C , giving the carbonate LDH. The LDH was calcined at 500°C for 3 hr to prepare the Mg-Al or Zn-Al oxides. The oxides were amorphous.

Water Treatment of the LDHs

The water-treated Zn-Al LDH that contained hydroxyl groups in the interlayer space was prepared by the reaction of the calcined Zn-Al LDH (0.4 g) in degassed water (100 ml) with stirring under a nitrogen atmosphere for 2 hr at 60°C . After the sample was dried *in vacuo* at room temperature, the existence of hydroxyl groups was determined by TG/DTA, XRD, and FT-IR.



SCHEME 1. Traditional intercalation method of the LDH.

Reaction of the Water-Treated Zn–Al LDH with Acid Chloride

The powdered, water-treated Zn–Al LDH was reacted with half an equivalent, or with an excess amount of various acid chlorides in acetonitrile or ether for 5 hr under stirring at room temperature or at 40°C. The obtained powder was filtered, and fully washed with acetonitrile or ether to remove unreacted and physisorbed acid chloride. The amounts of reacted organic compounds were determined by elemental analysis. Obtained compounds were characterized by TG/DTA, XRD, and FT-IR.

Characterization of the LDHs

The XRD powder pattern of each sample was obtained using $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) at 20 mA and 40 kV.

Characterization of all samples were performed by FT-IR spectra on a Horiba FT-200 and TG/DTA on a Seiko SSC-5200.

RESULTS AND DISCUSSIONS

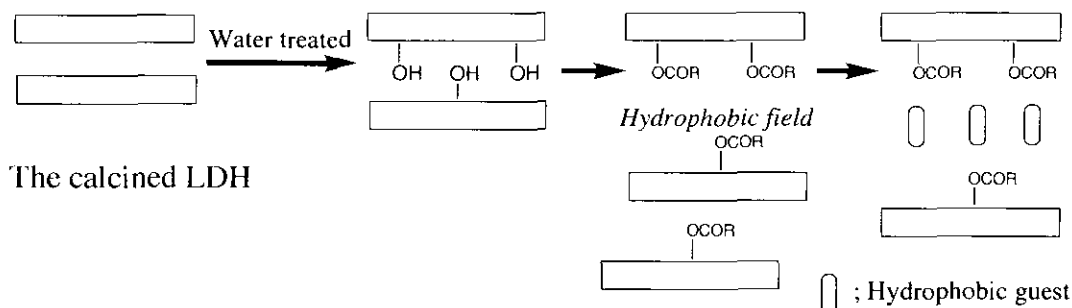
Preparation of the Water-Treated LDHs

The XRD pattern of the carbonate Zn–Al LDH is shown in Fig. 1a. The layer distances of the carbonate Zn–Al LDH and Mg–Al LDH are 7.6 and 7.8 Å, respectively.

Even with the carbonate LDHs standing in neutral water no hydroxyl ions were ion-exchanged into the LDHs. Upon heating of the LDHs at 500°C for 3 hr, the carbonate ion was decomposed to CO_2 and the calcined LDHs were obtained, as shown in Fig. 1b, where the peaks in the XRD patterns showed no distinct crystalline phase, only an amorphous phase. We have already confirmed the reversibility of desorption and adsorption of a carbonate ion of the LDH (4). The calcined Mg–Al and Zn–Al LDH were standing in degassed water under a nitrogen atmosphere at 60°C for 2 hr. In the case of Zn–Al LDH clear peaks reappeared as shown in Fig. 1c. From the peak, the interlayer spacing was estimated to be 7.6 Å.

It has been confirmed that interlayer water of the water-treated Mg–Al LDH was desorbed below 200°C, and structural water and carbon dioxide were desorbed below 400°C, as shown in Fig. 2 (7). The endothermic peak of 200°C corresponded to desorption of interlayer water, and another peak at ~380°C corresponded to desorption of structural water and carbon dioxide. In TG analysis of the water-treated Zn–Al LDH, only one clear endothermic peak at 200°C was observed, as shown in Fig. 3. The TG/MS spectrum indicates that the weight loss corresponded to desorption of interlayer water.

In the IR spectrum of the carbonate Zn–Al LDH a relatively sharp and strong line at 1360 cm^{-1} was observed, as shown in Fig. 4a, which is assigned to the ν_3



SCHEME 2. New intercalation method of the LDHs.

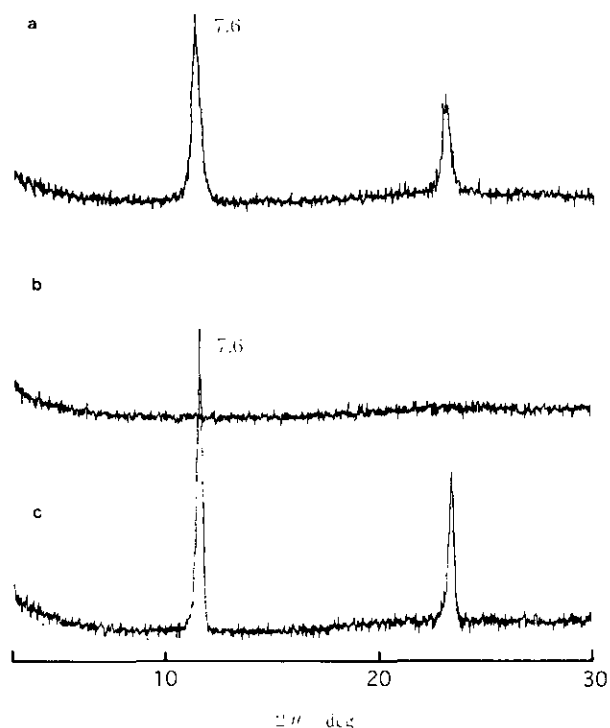


FIG. 1. XRD patterns of (a) the carbonate Zn-Al LDH, (b) the calcined Zn-Al LDH, and (c) the water-treated Zn-Al LDH.

vibration mode of a carbonate ion (8, 9). On the other hand, in the IR spectrum of the water-treated LDH, the peak of a carbonate ion was fairly small, as shown in Fig. 4c. TG analysis and the IR spectrum indicate that the interlayer expansion of the Zn-Al LDH by the water treatment is not caused by incorporation of a carbonate ion. In the case of the water-treated Mg-Al LDH, a peak

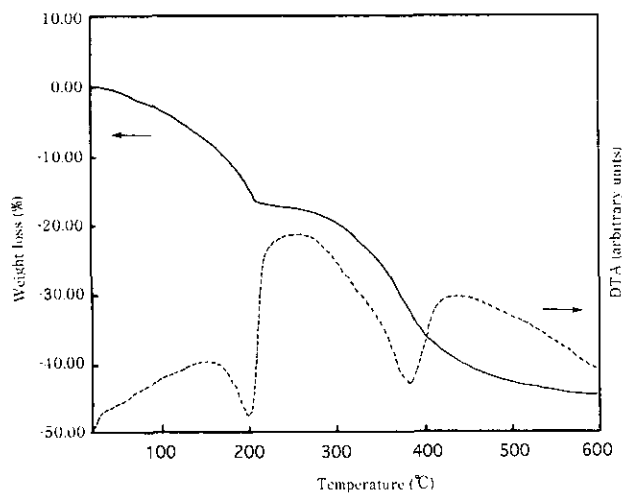


FIG. 2. Thermal analysis and differential thermal analysis of the water-treated Mg-Al LDH.

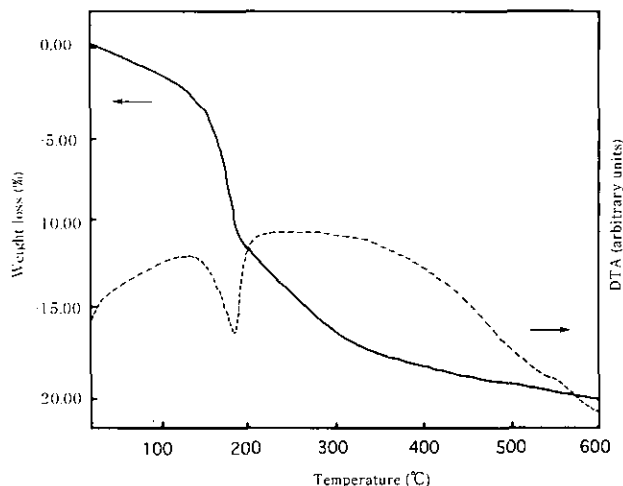


FIG. 3. Thermal analysis and differential thermal analysis of the water-treated Zn-Al LDH.

was observed at 1360 cm^{-1} stronger than that of the water-treated Zn-Al LDH. This indicates that the calcined Mg-Al LDH has a greater ability to absorb a carbonate ion than the calcined Zn-Al LDH.

From these results we concluded that the surface of the water treated Zn-Al LDH layer was covered by hydroxyl groups and water and the amount of carbonate ion between the layers was small. Scheme 3 shows a schematic representation of the water-treated LDH whose layer sur-

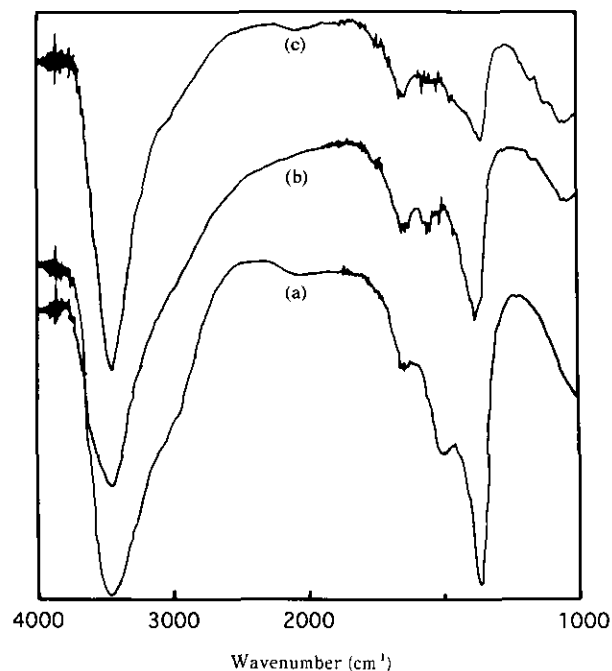
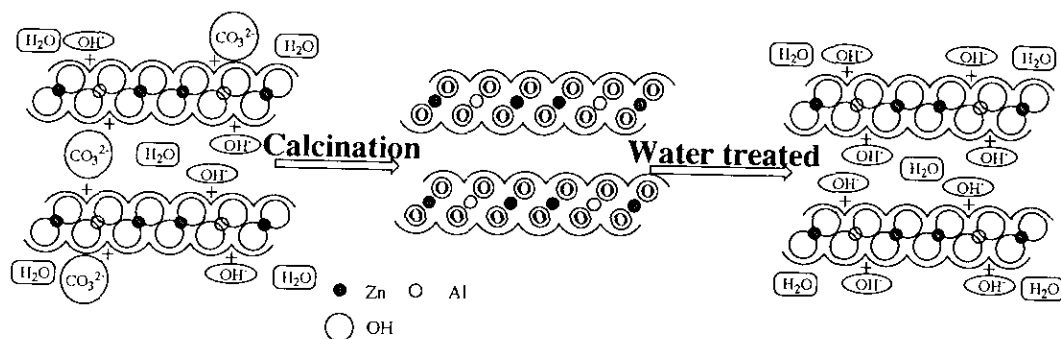


FIG. 4. IR spectra of (a) the carbonate Zn-Al LDH, (b) the water-treated Mg-Al LDH, and (c) the water-treated Zn-Al LDH.



SCHEME 3. Preparation of the water-treated Zn-Al LDH.

face was covered only by hydroxyl groups and water. In the case of the Mg-Al LDH, the similar compound was not obtained, as mentioned above. We could not determine the reason for the difference between the Mg-Al LDH and the Zn-Al LDH.

We also tried to prepare the water-treated LDH directly without the calcination step. The mixture of $\text{Zn}(\text{NO}_3)_2$ ((1 - X)/2 mole/liter) and $\text{Al}(\text{NO}_3)_3$ (X/2 mole/liter) in a Na_2CO_3 aqueous solution, whose pH was adjusted to ca. 10 with a NaOH solution, was refluxed under a nitrogen atmosphere for 2 hr. The IR spectrum of the obtained LDH did not show any evidence for the presence of a carbonate ion between the layers. This indicated that a carbonate ion was not intercalated between the LDH layers under the conditions of refluxing of water.

Reaction of the Water-Treated Zn-Al LDH with Organic Oxychloride

As mentioned above, the surface of the water-treated Zn-Al LDH layer was covered by hydroxyl groups. The water-treated Zn-Al LDH was reacted with organic oxychloride in an organic solvent and stirred at room temperature or 40°C for 5 hr. Four monochlorides and four dichlorides were reacted with the water-treated Zn-Al LDH as shown in Table 1. In the reaction we did not prevent the production of organic acid. In the reaction of sebacylchloride in acetonitrile, organic acid was not separated from the LDH. XRD patterns of the products were similar to those of sebamic acid. We have avoided the presence of acid by using ether, because sebamic acid was soluble in ether.

XRD patterns of the reaction products of the LDH with sebacylchloride in ether are shown in Fig. 5. In the reaction of the water-treated Zn-Al LDH with sebacylchloride, interlayer spacing of the water-treated LDHs increased from 7.6 to 13.8 Å. When the calcined Zn-Al LDH instead of the water-treated Zn-Al LDH was reacted with sebacylchloride, no reaction occurred. It indicated that the presence of inner surface hydroxyl groups

was essential for the esterification. In the reaction of the water-treated Zn-Al LDH with an excess amount of sebacylchloride, there were no clear peaks in the XRD pattern. It indicates that the reaction product of LDH with an excess amount of sebacylchloride was an amorphous phase.

The IR spectrum of the modified Zn-Al LDH by sebacylchloride was shown in Fig. 6. In the IR spectrum of the water-treated LDH a broad peak at 3400 cm^{-1} is observed, which is assigned to the O-H combination vibration. For the reaction of the water-treated Zn-Al LDH with oxychloride, the decrease in the peak at 3400 cm^{-1} and the appearance of a new peak at 1550 cm^{-1} , which was assigned to the adsorption peak of the ester combination vibration, were confirmed. The peak at 1550 cm^{-1} is assigned to the symmetric stretching vibration of carboxylate, and the peak at 1400 cm^{-1} is assigned to the asymmetric stretching vibration of carboxylate. Also, the IR spectrum of the reaction product of sebacylchloride was different from that of sebamic acid, indicating that there was no acid in the product. These results confirmed the occurrence of the esterification reaction of the Zn-Al LDH in the interlayer space, as shown in Scheme 4.

Interlayer spacing increased to 7.7–16.1 Å, depending on the size of the acid chloride, as shown in Table 1. Layer expansions were calculated from the thickness of the brucite layer and interlayer spacing. Table 1 also shows compositions that were calculated by elemental analysis. These results suggested that 6–85% of the hydroxyl groups reacted with mono- or diacid chlorides, yielding an ester.

From the values of the layer expansion and the molecular sizes of monochlorides, layer expansions were larger than expected. It suggests the bilayer formation of organic guests between the layers. In the case of dichlorides, layer expansions were smaller than the sizes of the dichlorides. We postulate a bridged structure in which the two ends of the guest have reacted with surface hydroxyl groups of opposing inner planes.

TABLE 1
Esterification of the Zn-Al LDH by Organic Acid Chlorides (G) Producing Intercalate
 $Zn_{0.75}Al_{0.25}(OH)_{0.25}(OH)_x(O-G)_y$ or $(O-G-O)_z$

Acid chloride (size, Å) ^a	<i>d</i> -Spacing (Å)			Layer expansion (Å)	<i>x</i> , <i>y</i> , <i>z</i> in Esterified LDH			(Solvent)
	of acid	in acetonitrile	in ether		<i>x</i>	<i>y</i>	<i>z</i>	
Butanoylchloride (4.7)	—	11.8	—	7.0	1.11	0.89		
Hexanoylchloride (7.2)	—	16.1	—	11.3	0.71	1.29		
Benzoylchloride (6.1)	10.9	11.2	—	6.4	1.45	0.55		
Phenylacetylchloride (6.1)	14.2	15.4	15.1	10.2	1.49	0.51		(in acetonitrile)
					1.88	0.12		(in ether)
Adipoylchloride (6.4) ^b	6.8	—	7.7	2.9	1.64		0.18	
Suberoylchloride (8.9) ^b	8.9	—	10.7	5.9	1.38		0.31	
Sebacoylchloride (11.4) ^b	11.2	11.2	13.8	9.0	0.31		0.85	(in acetonitrile)
					1.56		0.22	(in ether)
Dodecanedioylchloride (14.0) ^b	13.8	—	15.2	10.4	1.49		0.26	

^a Distance between carbonyl carbon and the furthest hydrogen from the carbon except sebacoylchloride.

^b Distance between two carbonyl carbons.

Thermal decomposition behavior of these compounds was determined by TG analysis. The TG analysis of sebacoylchloride alone, the water-treated LDH, and the surface-modified LDH that reacted with sebacoylchloride are shown in Fig. 7. The weight loss of sebacoylchloride itself occurred at 20 to 450°C. For the modified LDH that reacted with sebacoylchloride, a large weight loss started at over 300°C. The temperature was higher than that of the guest alone.

The esterified LDHs obtained in this work were partially soluble in organic solvent, and they floated on water.

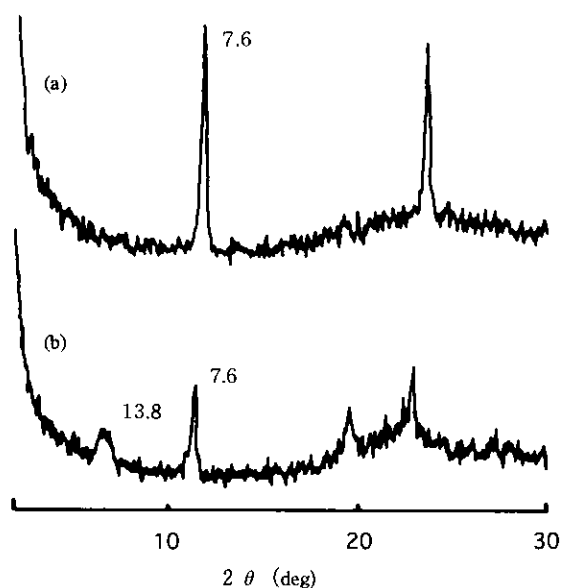


FIG. 5. XRD patterns of (a) the water-treated Zn-Al LDH and (b) the reaction product of (a) with sebacoylchloride.

It suggested that they are hydrophobic and have a hydrophobic field in interlayer spacing.

CONCLUSION

We have prepared water-treated Zn-Al LDH. It reacted with acid chloride and interlayer spacing increased. The IR spectrum of the new intercalation compound

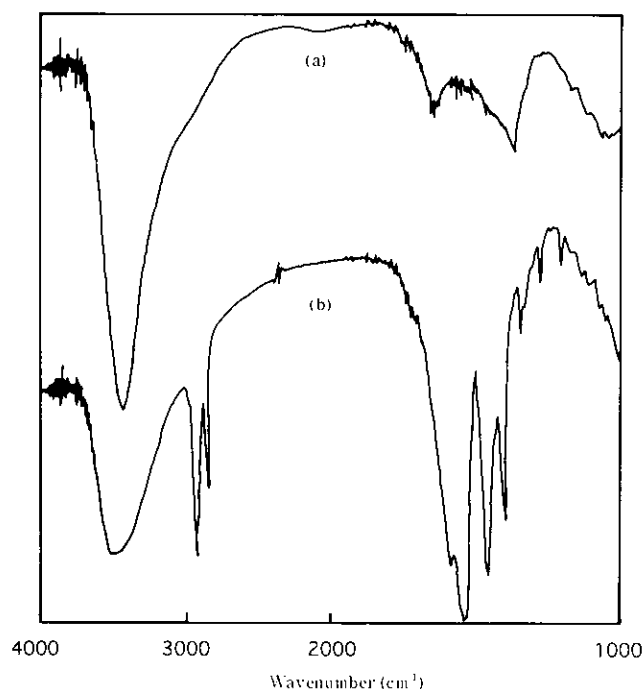
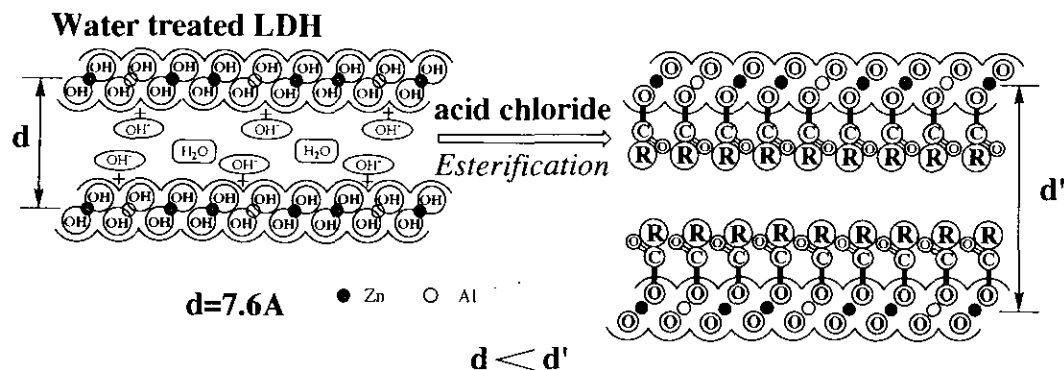


FIG. 6. IR spectra of (a) the water-treated Zn-Al LDH and (b) the reaction product of (a) with sebacoylchloride.



SCHEME 4. Reaction of the water-treated Zn-Al LDH with acid chloride.

showed that the number of hydroxyl groups decreased and the formation of ester groups was confirmed. From these results we concluded that the esterification reaction occurred at interlayer spacing. The obtained esterified LDHs were hydrophobic.

Various kinds of organic derivatives, including func-

tional organic compounds (10), can be obtained by the esterification of the water-treated LDH. For instance, derivatives of the LDH formed through reaction with optically active compounds could be used to separate racemic compounds. The esterified LDHs prepared in this study are candidates for new functional materials and catalysts.

ACKNOWLEDGMENTS

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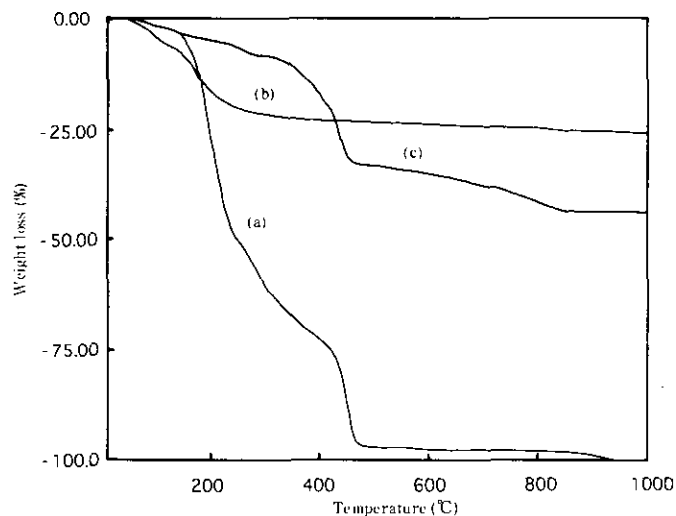


FIG. 7. Thermal analysis of (a) sebacylchloride, (b) the water-treated Zn-Al LDH, and (c) the reaction product of (b) with sebacylchloride.