Article

Preparation of Heteropolyacid-intercalated Layered Double Hydroxide

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Abstract

We prepared W-based heteropolyacid (HPA)-layered double-hydroxide (LDH) composites. The effects of the intercalation process on the composite characteristics and the Keggin structure stability were then investigated. The HPA-LDH composites were prepared using ion-exchange method on Zn-Al(NO₃) LDH and reconstruction method on Mg-Al(CO₃) LDH. In both cases, $d=1.47$ nm spacing, indicating HPA intercalation to LDH, was identified. [SiW₁₂O₄₀]⁴⁻ was hydrolyzed into [SiW₁₁O₃₉]⁸⁻ during ion change processing, thereby obtaining [SiW₁₁O₃₉]⁸⁻-LDH composites.

Key words: Heteropolyacids, LDH, Reconstruction, Ion-exchange

1 Introduction

Heteropolyacids (HPAs) have been investigated as acid catalysts.[1,2] They are also known as photocatalysts; recently, strong photo-oxidation power of W-based HPAs was reported.[3] The HPAs are highly soluble in water and in organic solvents. For that reason, they are commonly used as homogeneous catalysts. However, direct use of HPAs for photocatalytic purification presents an obstacle to their separation from treated water. Therefore, preparation of a heterogeneous catalyst system of HPAs has been investigated using host materials such as mesoporous silica and clays.[3,4]

Layered double hydroxides (LDH) are described as $M^{2+}_{1-x}M^{3+}_x(OH)_2A^{n-}_{x/n} \cdot mH_2O$; they are composed of octahedral $M^{2+}(OH)_6$ brucite-like layers and changeable interlayer anion. These materials possess a two-dimensional layer structure. The positive layer charge is controllable by changing the ratio of divalent and trivalent cations.[5] Ion-exchange method [6–8] and reconstruction method [9–11] are known as typical anion intercalation methods. Ion-exchange method is executed by merely soaking LDHs in an anion solution; reconstruction method includes heating LDHs at 500–600°C before soaking in an anion solution. The layered structure decomposes when LDHs are heated to 500–600°C. However, the layer structure is reconstructed by soaking it in water with a proper anion. This reconstruction process is used for large anion intercalation into LDH. To date, various polyacid and heteropolyacid anions have been shown to be intercalatable into the LDH host layer.[12]

Intercalation of anions into LDHs requires a proper balance of the charge amount and size. Hu et al. prepared a composite using W-based HPA and LDH with lacunary Keggin anion [SiW₁₁O₃₉]⁸⁻ and Zn-Al (NO₃) LDH.[13] However, Keggin-type anions such as [PW₁₂O₄₀]³⁻ and [SiW₁₂O₄₀]⁴⁻ are difficult to intercalate into the LDH layer because these anions possess a smaller negative charge and lower stability in high-pH water than lacunary

Keggin-type anions. In water with high pH, Keggin-type anions are commonly decomposed into lacunary Keggin ions by hydration.[14] However, intercalation-process-dependence of the stability of W-based Keggin-type anions is not well reported. For this study, we prepared LDHs of the Mg-Al(CO₃) system and Zn-Al(NO₃) system. In addition, HPA-LDH composites were prepared using ion-exchange method on Zn-Al(NO₃) LDH and reconstruction method on Mg-Al(CO₃) LDH using H₄SiW₁₂O₄₀. Then, the effects of intercalation process on the composite characteristics and stability of Keggin structure were investigated.

2 Experimental

2.1 LDH synthesis

All starting chemicals were of reagent grade (Wako Pure Chemical Industries Ltd., Tokyo, Japan). In this study, LDHs of the Mg-Al(CO₃) system (Mg/Al=2, 4) and Zn-Al(NO₃) system (Zn/Al=2) were prepared as in previous studies.[15,16] Solutions of Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O were mixed in the appropriate ratio and co-precipitated by adding mixed solutions of NaOH and Na₂CO₃. After mixing (24 h), centrifuging, washing in distilled water and ethanol, and drying, LDH powders of the Mg-Al(CO₃) system were obtained.

Solutions of Zn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O were mixed in the appropriate ratio and co-precipitated by adding mixed solutions of NaOH at pH 9.5. In this process, distilled water was used after degassing by N₂ bubbling. After refluxing in N₂ at 90°C for 18 h, centrifuging, washing in distilled water, and drying, LDH powder of the Zn-Al(NO₃) system was obtained.

2.2 Ion Exchange Method

Ion-exchange processing and reconstruction processing were carried out using ion changed water to avoid effects of CO₃²⁻. Interlayer NO₃⁻ in LDH powder of the Zn-Al(NO₃) system is exchanged with HPAs in a high-temperature aqueous solution.[12,17] In this work, ethylene glycol (EG) was used as a swelling agent. An aqueous solution of EG (H₂O:EG=1:1) was used to support interlayer space expansion. Subsequently, SiW₁₂O₄₀·26H₂O (0.20 g) was dissolved into EG solution (40 cm³) and LDH (0.40 g) was added to the solution. The mixture was stirred at 80°C for 2 h, then centrifuged at 8000 rpm for 20 min after cooling and washing with water. White powder was obtained after drying at 80°C for 24 h. For comparison, the same procedure was carried out using water only, instead of the EG solution.

2.3 Reconstruction method

The LDHs of Mg-Al(CO₃) system were calcined at 500°C for 12 h in air, and heat-decomposed LDHs were prepared. Then SiW₁₂O₄₀·26H₂O (0.68 g) was dissolved into water (200 cm³); the heat-decomposed LDHs were added to the solution. After stirring for 24 h, LDH powders were separated from the solution by centrifugation (8000 rpm, 20 min) and washed with water. White powder was obtained after drying at 80°C for 24 h.

2.4 Evaluation

Crystalline phases of the obtained powders were evaluated using X-ray diffraction (XRD, XRD-6100; Shimadzu Corp.). The specific surface area and pore structure were evaluated using N₂ adsorption and desorption isotherms at 77 K (Autosorb-1; Quantachrome Instruments). The specific surface area was calculated using BET method and the pore volume was obtained from the maximum amount of adsorption at a relative pressure (P/P_0) of 0.999. The pore size distribution was calculated using BJH method with the desorption isotherms. The average pore size was calculated from the specific surface area and pore volume. The chemical compositions of the LDHs were

analyzed for Mg, Al, and W using ICP-OES (Teledyne – Leeman Labs, USA). The infrared spectra (FT-IR 8600PC; Shimadzu Corp.) of the samples were recorded using the KBr disk method.

3 Results and Discussion

3.1 Ion-exchange method

Figure 1 shows XRD patterns of $\text{Zn}_2\text{Al}(\text{OH})_6(\text{NO}_3)\cdot 2\text{H}_2\text{O}$, the composites prepared in the EG solution, and that in water. In the EG solution, the ion-exchange ratio between NO_3^- and HPA was higher than that in water. The LDH layer thickness and the size of the Keggin anion are reported respectively as 0.48 nm and 0.98 nm. Basal spacing ($d=1.48$ nm, 003) and 00 l harmonics ($d=0.732$ nm, 006, 0.486 nm, 009) after ion-exchange show good agreement with the sum of LDH layer thickness and Keggin anion, implying that the ion-exchange process was attained. Furthermore, 1.48-nm spacing indicated that the gallery height was 0.98 nm. A salt-like impurity was detected as a broad peak at 1.16 nm. Many polyacid – LDH composites show such a characteristic impurity peak.[12]

In Fig. 1, the order of peak intensity by XRD on 00 l harmonics is, fundamentally, (009) > (006) > (003). This trend is common for both Keggin and lacunary Keggin ion intercalated LDHs such as $\text{H}_2\text{W}_{12}\text{O}_{40}\text{-Zn}_2\text{Al LDH}$ [5] and $[\text{SiW}_{11}\text{O}_{39}]^{8-}\text{-Zn}_2\text{Al LDH}$. [6] Therefore, the (003) peak is weaker than the (006) and (009) peaks.

Table 1 shows the result of ICP analysis. The expected atomic ratio (Al:Zn:W) calculated from the ion-exchange capacity is 1:2:1.38 if the interlayer NO_3^- is replaced completely with $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ in the $\text{Zn}_2\text{Al}(\text{OH})_6\text{NO}_3$ system. Practical values by ICP analysis were 1:1.4:0.52 for the composite using EG solution and 1:1.6:0.61 for the composite using water (Table 1), which implies that the ion-exchange capacities used for $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ were 37% (EG solution) and 44% (water). The composite ion-exchange in water exhibited higher W content. However, the presence of a salt-like impurity might affect the Zn:Al:W ratio. A part of the positive layer charge might be compensated by OH^- anion and the remaining NO_3^- ion.

Table 2 shows peak positions of IR spectra of the composite and K salt of HPAs. The composite peak positions differed from those on $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ ion, and peak patterns resembled those of $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ and its composite reported by Hu et al. The d -value and gallery height on $[\text{SiW}_{11}\text{O}_{39}]^{8-}\text{-Zn}_2\text{Al LDH}$ were reported respectively as 1.452 nm and 0.98 nm. Based on these results, the interlayer HPA might be lacunary $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ or a similar species. In solution, lacunary species possess higher charges than $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ ion. Moreover, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ is stable only when pH is less than 6. After reflux treatment, the pH of the solution was around 8. For that reason, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ was decomposed into $[\text{SiW}_{11}\text{O}_{39}]^{8-}$; then, selective intercalation occurred during the ion-exchange reaction.

Figure 1. XRD patterns of composites prepared using ion exchange. (a) After ion exchange in EG solution. (b) After ion change in water. (c) Zn-Al LDH before ion exchange. X: A salt-like impurity

Table 1. Chemical composition of Zn-Al LDH and composites

sample	Al	Molar ratio	
		Zn	W
ZnAl ₂ -NO ₃ LDH	1.0	2.1	—
After ion-exchange in EG solution	1.0	1.4	0.52
After ion-exchange in water	1.0	1.6	0.61

Table 2. IR peak positions of composites and HPA (cm⁻¹)

sample	Si-Oa	W=Od	W-Ob-W	W-Oc-W
Zn-Al LDH composite by EG solution	1000	952	908	
Zn-Al LDH composite by water	999	954	908	
Mg-Al LDH composite (Mg/Al=2)	1000	955	912	798
Mg-Al LDH composite (Mg/Al=4)	1000	954	908	
ZnAl ₂ -SiW ₁₁ * ¹	997	945	897	792, 728
SiW ₁₂ * ²	930	982	885	792
SiW ₁₁ * ²	1000	952	870	797, 725

*¹Hu et al. [6] *²K salt

Table 3. Porous properties of the LDHs

	Specific surface area (m ² / g)	Total pore volume (cm ³ / g)	Average pore size (nm)
ZnAl ₂ LDH	19	0.11	12
Zn-Al LDH composite by EG solution	57	0.12	4.3
Zn-Al LDH composite by water	43	0.11	5.2

Mg/Al = 2 **Mg/Al = 4** Figure 2. XRD patterns of composites prepared by reconstruction. (a) Reconstructed HPA-LDH composite. (b) Heat-decomposed LDH (c) Mg-Al-CO₃ LDH before heat treatment.

X: A salt-like impurity

The specific surface area, total pore volume, and average pore size of the obtained LDHs are listed in Table 3.

The order of the specific surface area is $\text{Zn}_2\text{Al}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} < \text{HPA-Zn}_2\text{Al LDH composite (ion-exchanged in water)} < \text{HPA-Zn}_2\text{Al LDH composite (ion-exchanged in EG solution)}$. Intercalated HPA anion worked as pillars and expanded the gallery height, thereby increasing the specific surface area.

3.2 Reconstruction method

Figure 2 shows XRD patterns of $\text{Mg}_2\text{Al}(\text{OH})_6(\text{CO}_3) \cdot 2\text{H}_2\text{O}$ and Mg-Al composites prepared using the reconstruction method. The layer structure of Mg-Al(CO_3) LDHs was destroyed and their peaks were eliminated by heat treatment at 500°C. After reconstruction, new peaks appeared. Although the peaks were broader than those of ion-exchange composites in Zn-Al LDH, basal spacing ($d=1.45$ nm, 003) and $00l$ harmonics ($d=0.735$ nm, 006 , 0.486 nm, 009) indicated that ion exchange was attained. A broad peak at 1.07 nm ($2\theta=8.3$ deg) indicates an impurity that is commonly observed in HPA-LDH composites.

Table 4. Chemical composition of Mg-Al LDH and composites

Sample	Al	Molar ratio	
		Mg	W
$\text{Mg}_2\text{Al-CO}_3\text{LDH}$	1.0	2.0	—
Mg-Al LDH composite (Mg/Al = 2)	1.0	1.7	1.12
$\text{Mg}_4\text{Al-CO}_3\text{LDH}$	1.0	4.0	—
Mg-Al LDH composite (Mg/Al = 4)	1.0	3.3	0.7

Table 5. Porous properties of Mg-Al- CO_3 LDHs and composites

Sample	Specific surface area (m^2 / g)	Total pore volume (cm^3 / g)	Average pore size (nm)
$\text{Mg}_2\text{Al-CO}_3\text{LDH}$	130	1.1	17
Mg-Al LDH composite (Mg/Al = 2)	<1	0.02	—
$\text{Mg}_4\text{Al-CO}_3\text{LDH}$	130	0.32	4.9
Mg-Al LDH composite (Mg/Al = 4)	85	0.09	2.1

Similarly to $\text{Zn-Al}(\text{NO}_3)_2$ LDH, the IR spectra imply that $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ was intercalated in this system. Table 4 shows the result of ICP elemental analysis. If reconstruction is attained completely with $[\text{SiW}_{11}\text{O}_{39}]^{8-}$, the ideal molar ratio (Al:Mg:W) of the Mg_2Al LDH system should be 1:2:1.38. In the case of the Mg_4Al system, the ideal ratio is 1:4:1.38. Compared with the ICP results shown in Table 4 (1:1.7:1.1 and 1:3.3:0.7), the ion-exchange capacity used for $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ was 81% in the case of $\text{Mg}_2\text{Al-LDH}$, and 50% in the $\text{Mg}_4\text{Al-LDH}$ system. The decrease of the Mg/Al ratio before and after ion exchange indicates leaching of LDH by HPA. The HPA- Mg_2Al composite contained a larger amount of W than the HPA- Mg_4Al composite. A larger layer charge is advantageous for HPA anion intercalation. The composite prepared using the reconstruction process exhibits a lower specific surface area than the original Mg-Al(CO_3) LDHs (Table 5). Gardner et al. reported that Zn-based LDH intercalated with a Keggin-type HPA ($\text{H}_2\text{W}_{12}\text{O}_{40}$) is nonporous after outgassing at 70°C.[12] They attributed this result to the poor accessibility to the interlayer space for N_2 and organic substances when it is occupied by solvated Keggin anion. In the present study, the Mg_2Al composite contained a larger amount of $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ than the $\text{Mg}_4\text{Al-LDH}$

composite and the Zn_2Al -LDH composite, which is one reason for the nonporous structure of the Mg_2Al composite. Incomplete ion exchange might be a key factor for preparation of the porous structure. Deposition of the salt-like impurity might also signal an important effect on the result of specific surface area.

Characterization of the interlayer $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ is carried out using XRD and IR spectra in this study. The gallery height of LDH is known to be equivalent to the interlayer polyacid size.[12,16,17] Other decomposed species of Keggin ion, e.g., $[\text{SiW}_9\text{O}_{34}]^{10-}$, are smaller than 1.0 nm. For that reason, D-spacing should decrease less than 1.48 if these anions were intercalated. The ratio between Si and W is important information that is useful to identify the HPA structure. However, interlayer $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ characterization by ICP analysis was almost impossible in this case because of the interference with Si contamination from the glass flask at LDH synthesis and existence of the salt-like impurity. At present, IR yields direct evidence of $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ intercalation. Detailed characterization of intercalated ions using other spectroscopic analyses is now underway.

4 Summary

In this study, we prepared W-based HPA-LDH composites; the effects of intercalation process on the composite character and the stability of the Keggin structure were investigated. The HPA-LDH composites were prepared using ion-exchange method on $\text{Zn-Al}(\text{NO}_3)$ LDH ($\text{Zn}/\text{Al}=2$) and reconstruction method on $\text{Mg-Al}(\text{CO}_3)$ LDHs ($\text{Mg}/\text{Al}=2, 4$). When $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ was used as a starting material for HPA, intercalation of HPA was confirmed into both LDHs by XRD. Both IR and chemical analyses suggested that $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ was hydrolyzed to $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ during ion change.

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