Synthesis and Adsorption Property of Calixarene-*p*-sulfonate-intercalated Layered Double Hydroxides

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(Received March 3, 2004; CL-040237)

The synthesis of the *p*-sulfonate[4]calixarene (CS4)/M^{2+}–Al layered double hydroxides (Mg–Al and Zn–Al/CS4/LDHs) has been investigated as well as their adsorption behavior of benzyl alcohol (BA) in aqueous solution. The CS4/LDHs were easily synthesized by the conventional coprecipitation method. The basal spacing of the CS4/LDHs was expanded to 1.33 (Mg–Al) and 1.61 nm (Zn–Al), which indicates that CS4 cavity axis was oriented vertically (Mg–Al) and parallel (Zn–Al) to the LDH basal layer, respectively. In particular, the Zn–Al/CS4/LDH was found to have 2 types of micro pore, the CS4 cavity and the intermolecular space. The adsorption of BA to the CS4/LDH was influenced by the amount and orientation of CS4 ion in the interlayer of the LDHs.

In recent years, much attention has been given to new families of microporous adsorbent resulting from the inorganic layerd compounds with polynuclear complex ions or bulky organic molecules.[1,2] The combination of layered material and intercalation technique will have a possibility of providing new nanohybrid materials. Layered double hydroxides (LDHs) are widely known as host–guest materials, anion exchangers, anionic clays, and hydrotalcite-like compounds. The chemical composition of LDHs is generally represented as $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2][A^{n-}{}_{x/n}\cdot yH_2O]$. LDHs consist of positively charged octahedral hydroxide layers and an exchangeable interlayer anion with water molecules. It was used as versatile material in medical science, catalysis, separation technology and nanocomposite materials engineering.[3]

Calixarenes are macrocyclic molecules of the metacyclophanes general class, consisting of several phenol units (usually four to eight) connected via methylene bridges in the ortho position with respect to the hydroxy group. Shinkai and co-workers synthesized water-soluble calixarenes carrying sulfonate groups in 1984.[4] The calixarene cavity is capable of molecular recognition in solution.[5,6] This property is of great interest for application in the remediation of contaminated groundwater and industrial effluents.

In this study, the intercalation of water-soluble *p*-sulfonate[4]calixarene (CS4) (Figure 3a) in the interlayer of the Mg–Al and Zn–Al LDHs ($M^{2+}/Al = 3$) by coprecipitation method has been investigated as well as the adsorption property of the resulting CS4/LDHs.

The CS4/LDHs was prepared by the coprecipitation method under N_2 atmosphere. $M^{2+}(NO_3)_2\cdot 6H_2O$ (M^{2+} = Mg or Zn) (1.5 mmol) and Al $(NO_3)_3\cdot 9H_2O$ (0.5 mmol) were dissolved in distilled water (20 cm^3) and added drop-wise over 1 h to a solution of CS4 (1 mmol) in water (100 cm^3). Solution pH was adjusted by addition of 0.1 mol/dm^3 NaOH solution (pH 10 for Mg–Al, pH 7 for Zn–Al), and the mixture was aged at 40 °C for 1 h. The precipitate was separated by centrifugation, washed with distilled water and dried at 40 °C for 24 h in vacuum. The surface area of the CS4/LDHs was measured by the BET method using N_2 gas.

Adsorption was carried out using the batch method. We selected benzyl alcohol (BA) ($pK_a = 15.4$) as adsorption compound which have no electrical interaction with LDH basal layer in the adsorption condition. CS4/LDH (0.05 g) was added to aqueous BA solution (10 cm^3), the concentration of which was two times CS4 in the LDH. The suspended mixture was shaken for 24 h set at a reciprocating shaker at 25 °C. The amount of BA

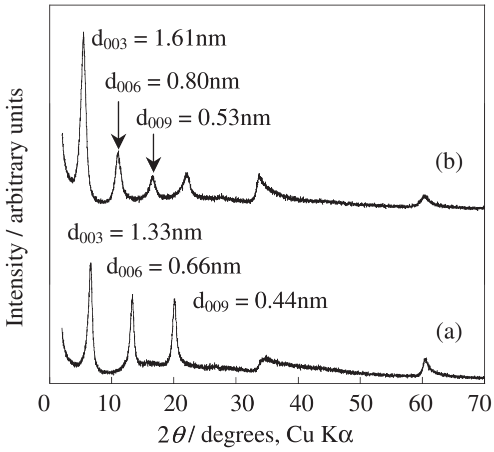

Figure 1. XRD patterns of (a) Mg–Al/CS4/LDH, (b) Zn–Al/CS4/LDH.

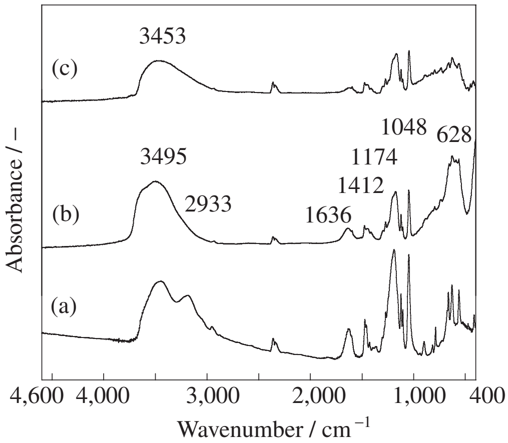

Figure 2. FT-IR spectra of (a) CS4, (b) Mg–Al/CS4/LDH, (c) Zn–Al/CS4/LDH.

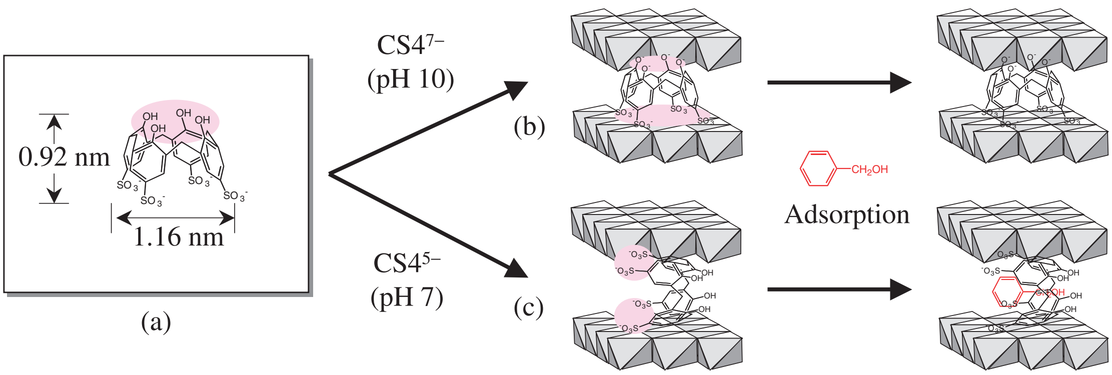

Figure 3. Schematic representation of structure models: (a) CS4, (b) High negative charge (Mg–Al/CS4/LDH), (c) Low negative charge or Zn–CS4 complexed (Zn–Al/CS4/LDH).

adsorbed was determined by using TOC and UV–vis.

The XRD patterns of the CS4/LDHs are shown in Figure 1. According to XRD, the solid products were found to have the expanded LDH structure. The basal spacing of the Mg–Al/CS4/LDH was expanded to 1.33 nm. The d-spacing indicates that CS4 are a monolayer thickness in CS4/LDHs. Considering the original brucite layer thickness of 0.48 nm, CS4 cavity axis was presumed to orient vertically to the LDHs basal layer. In the case of the Zn–Al/CS4/LDH ($d_{003} = 1.61$ nm), CS4 was thought to orient its cavity axis parallel to the LDHs basal layer. From chemical composition, only half of the Zn–Al/LDH interlayer space was occupied by CS4 molecules, with the CS4 rings stacked about 0.85 nm apart within the LDH interlayers. The FT-IR spectra of the CS4 and CS4/LDHs revealed that there was no changes in CS4 structure before and after the intercalation (Figure 2).

The weak absorption peaks of methylene bridges $-CH_2-$ were observed in the region 2915–2940 cm^{-1}, the strong absorption peaks of S–O were observed at 1037–1040 cm^{-1}. A broad absorption peak in the region 3000–3600 cm^{-1} was assigned to OH group stretches of both hydroxides for the basal layer and the interlayer CS4 molecule. In the ^{13}C CP/MAS NMR spectra, it was observed that C–O and C–S peaks shift to lower frequency regions. It suggests that an interaction of the intercalated guest anions with the host hydroxide layers was generated. However, the chemical shift was not influenced by a kind of the host metals.

The CS4/LDHs have two types of micropores, the CS4 cavity and the intermolecular space (Figure 3). We considered two reasons for the difference in conformation. First, the arrangement of CS4 in the interlayer space of the LDHs was presumed to change by the number of dissociated OH group ($pK_{a1} = 3.08$, $pK_{a2-4} > 11$),[7] namely the strength of the electrostatic force of attraction between the negative CS4 and the positive LDH basal layer. Synthesis pH of the Mg–Al/CS4/LDH (pH 10) is higher than that of the Zn–Al/CS4/LDH (pH 7). Therefore, CS4 molecules adopted a perpendicular monolayered arrangement within the Mg–Al/LDH interlayers. On the other reason, the formation of Zn–CS4 complexes would obstruct the interaction between the dissociated OH groups and the LDH basal layer. The lower rim contained OH groups in CS4 can be employed to bind transition metal ion,[8] however, CS4 hardly bind with Mg^{2+} ion. Therefore, CS4 was thought to orient its cavity axis parallel to the Zn–Al LDH basal layer. In the BET surface area measurement, the surface area of the Zn–Al/CS4/LDH was found to be four times than that of the Mg–Al/CS4/LDH (Table 1), indicating that the Zn–Al/CS4/LDH has higher adsorption capacity than the Mg–Al/CS4/LDH.

Table 1. BET surface area and compositional data for CS4/LDHs

Host	BET s. a. of CS4/LDH/m^2/g	Molar ratio of solid product		
		M^{2+}/Al	CS4/Al*	BA/CS4
Mg-Al	12.8	3.1	0.25	0.22
Zn-Al	52.7	3.0	0.12	2.10

*Theoretical molar ratio of the solid product: $CS4^{5-}/Al = 0.200$.

In the adsorption experiments, the resulting CS4/LDHs were found to adsorb BA in aqueous solution with keeping the LDH structure. The adsorption affinity of the Zn–Al/CS4/LDH was greater than that of the Mg–Al/CS4/LDH (Table 1). This result indicates that the adsorption of BA on the Zn–Al/CS4/LDH was related not only to the interlayer space, but also to the intercalated calixarene cavity. This suggests that CS4 molecular arrangement within the LDH interlayer mainly dominated the sorption of BA.

In summary, CS4/LDHs have 2 types of micropores, the CS4 cavity and the intermolecular space. CS4 molecular arrangement within LDH interlayer was changed by selecting host metal Mg–Al or Zn–Al, influenced on the adsorption of BA. Therefore, CS4/LDHs have considerable possibility as organic–inorganic hybrid new absorbent.

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Published on the web (Advance View) May 31, 2004; DOI 10.1246/cl.2004.790