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Synthesis of *p*-sulfonated calix[4]arene-intercalated layered double hydroxides and their adsorption properties for organic molecules

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Abstract

Calixarenes are macrocyclic organo anions, which cavity is capable of molecular recognition, while layered double hydroxides (LDHs) are widely known as hydrotalcite-like compounds, anion exchangers and host–guest materials. In this study, the intercalation of water-soluble *p*-sulfonated calix[4]arene (CS4) in the interlayer of the Mg–Al and Zn–Al LDHs (M^{2+}/Al ratio = 3) by the coprecipitation method has been investigated as well as the adsorption property of the resulting CS4/LDHs for benzyl alcohol (BA) and *p*-nitrophenol (NP). It was found that the CS4/LDHs with the molar ratio of CS4/Al = 0.25 (Mg–Al LDH) and 0.12 (Zn–Al LDH) were obtained as a single phase. The arrangement of CS4 in the LDH interlayer was different by the kind of the host metal ions as CS4 cavity axis perpendicular (Mg–Al LDH) and parallel (Zn–Al LDH) to the basal layer, influencing strongly on the BET surface area, N_2 adsorbed volume and adsorption property for BA and NP.
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1. Introduction

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 $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}[A_{x/n}{}^{n-}\cdot yH_2O]^{x-}$, where M^{2+} is a divalent cation such as Mg^{2+}, Zn^{2+}, Co^{2+}, Ca^{2+}, Cu^{2+}, etc., M^{3+} a trivalent cation such as Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Mn^{3+}, etc., A^{n-} an anion of charge ($n-$) such as OH^-, Cl^-, $NO_3{}^-$, $CO_3{}^{2-}$, $SO_4{}^{2-}$, etc.[1] LDHs consist of positively charged octahedral hydroxide layers and an exchangeable interlayer anion with water molecules.[2] It was used as versatile material in medical science, catalysis, separation technology and nanocomposite materials engineering.[3]

In recent year, much attention has been given to new families of microporous adsorbent resulting from the inorganic layered compounds with polynuclear complex ions or bulky organic molecules.[4,5] LDH is often used as an inorganic host material to synthesize the organic/LDH hybrid material. On the other hand, the intercalation of the macrocyclic molecules has great attractions.[6,7] As the molecular arrangement in hybrid material can be regulated by nanoscale level, it has the possibility to show the characteristic of not possessing in each organic substance or inorganic substance. The combination of layered material and intercalation technique will have a possibility of providing new nanohybrid materials.[8]

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 hydroxyl group as shown in Fig. 1. According to the reports on the applications of calixarenes, many fundamental studies with these supermolecules have been noted and the cylindral-shaped

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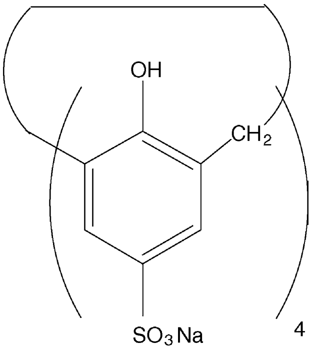

Fig. 1. Structure of CS4.

calixarenes of varying cavity sizes can form a variety of host–guest types of inclusion complexes similar to cyclodextrins. However, calixarene hostmolecules have a unique composition that includes benzene groups, which provide π–π interaction, and hydroxyl groups for hydrogen bonding. Shinkai et al. synthesized water-soluble calixarenes carrying sulfonate groups in 1984.[9] The calixarene cavity is capable of molecular recognition in solution,[10,11] which is of great interest for application in the remediation of contaminated groundwater and industrial effluents.[12,13]

In this study, the intercalation of water-soluble *p*-sulfonated calix[4]arene (CS4) 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 benzyl alcohol (BA) and *p*-nitrophenol (NP) adsorption properties of the resulting the CS4/LDHs.

2. Experimental

2.1. Intercalation of calix[4]arene for LDH

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 the solution was added drop-wise to a solution of CS4 (1 mmol) in water (100 cm^3) over 1 h. 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 oven.

2.2. Adsorption properties of calix[4]arene/LDH

Adsorption experiments were carried out by the batch method using BA ($pK_a = 15.4$) and NP ($pK_a = 7.15$) as adsorbates, non-anionic and anionic species in the adsorption condition, respectively. The adsorption properties of the CS4/LDHs were estimated by comparing the adsorption results for two organic adsorbates. The CS4/LDHs (0.05 g) were added to the aqueous adsorbate solution (10 cm^3), in which the amount of the adsorbate was two times for CS4 in the LDH. The suspended mixture was shaken at 25 °C for 24 h using a reciprocating shaker.

2.3. Characterization of solid product

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku Rint 2200 powder X-ray diffractometer, using Cu Kα radiation ($\lambda = 0.15405$ nm) at 20 mA, 40 kV, a scanning rate of 2 °/min, and a 2θ angle ranging from 2° to 70°. Fourier transform infrared (FT-IR) spectra were obtained using a JASCO WS/IR 7300 FT-IR spectrophotometer by the standard KBr disk method. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out in the temperature range 30–800 °C in flowing air at a heating rate of 10 °C/min using a Rigaku TG/DTA 320. Chemical analysis date for Al, Mg and Zn were obtained using a Shimadzu AA-6650 atomic adsorption spectrophotometer after dissolution of the solid products in 0.1 mol/dm^3 HCl solution. The adsorbates (BA and NP) concentration in supernatant solution was measured using a Shimadzu TOC-5000 total organic carbon analyzer (TOC) and a JASCO V-570 UV–vis/NIR spectrophotometer (UV–vis), respectively. Solid-State ^{13}C-CP/MAS NMR spectroscopy was performed at 125.7 MHz with a Varian Unity INOVA-500.

The surface area of the CS4/LDHs was measured by the BET method. The samples were outgassed at 100 °C for 2 h. The isotherms using the nitrogen adsorption/desorption were measured on a BEL JAPAN BELSORP mini.

3. Results and discussion

3.1. Intercalation of calix[4]arene for LDH by coprecipitation method

The XRD patterns of the CS4/LDHs are shown in Fig. 2. In these XRD patterns, the solid products were found to have

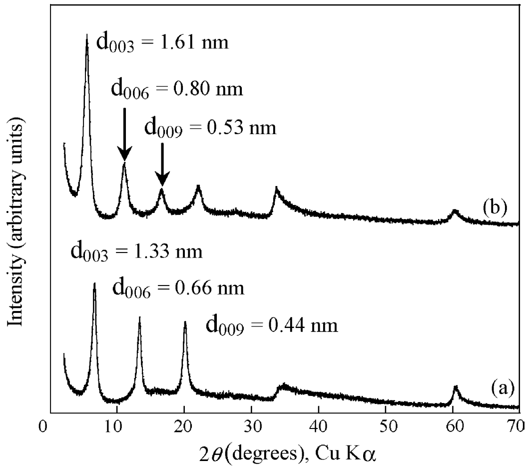

Fig. 2. XRD patterns of (a) Mg–Al/CS4/LDH and (b) Zn–Al/CS4/LDH.

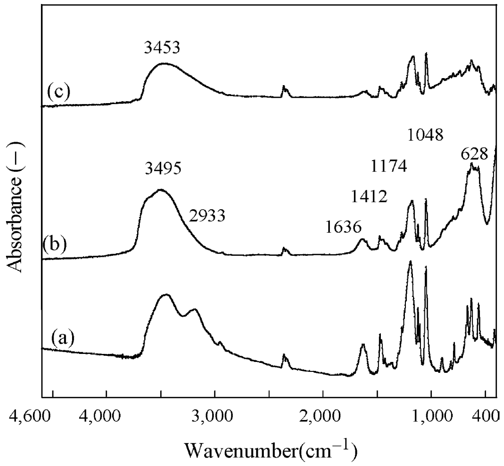

Fig. 3. FT-IR spectra of (a) CS4, (b) Mg–Al/CS4/LDH and (c) Zn–Al/CS4/LDH.

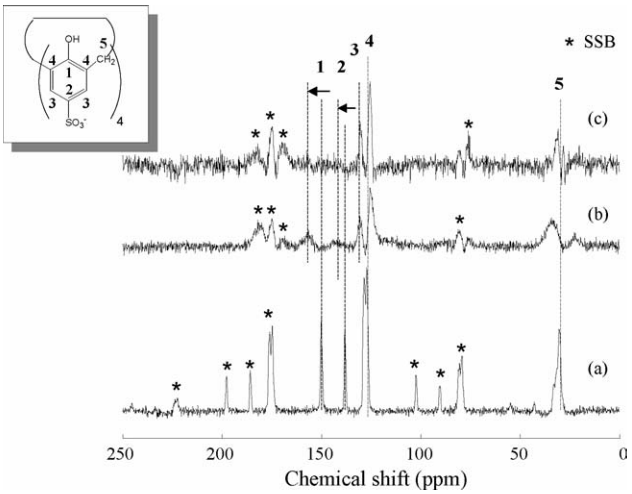

Fig. 4. ^{13}C-CP/MAS NMR spectra of (a) CS4, (b) Mg–Al/CS4/LDH and (c) Zn–Al/CS4/LDH.

the expanded LDH structure. The basal spacing, d_{003}, of the Mg–Al/CS4/LDH was expanded to 1.33 nm. It indicates that CS4 anions are a monolayer thickness in the CS4/LDH. Considering the original brucite layer thickness of 0.48 nm, CS4 cavity axis was presumed to orient vertically to the LDH 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, when CS4 rings stacked about 0.85 nm apart within the LDH interlayers.

The FT-IR spectra of the CS4/LDHs are shown in Fig. 3. The FT-IR spectra of CS4 and the CS4/LDHs reveal that there is no changes in CS4 structure after the intercalation. The weak absorption peaks of methylene bridges $-CH_2-$ was observed in the region 2915–2940 cm^{-1} and the strong absorption peaks of S–O was observed at 1037–1040 cm^{-1}. A broad absorption peak in the region 3000–3600 cm^{-1} is assigned to OH group stretches of both hydroxides for the basal layer and the interlayer CS4 molecule.

The ^{13}C-CP/MAS NMR spectra of the CS4/LDHs are shown in Fig. 4. In the ^{13}C-CP/MAS NMR spectra, C1(C–O) and C2(C–S) peaks shift to lower frequency regions was recognized. It suggests that an interaction of the intercalated CS4 with the host hydroxide layers was generated. Moreover, the resonance of the cointercalated CO_3^{2-} was observed at 180.2 ppm.

Fig. 5 shows the schematic representation of structure models of the CS4/LDHs. The CS4/LDHs have two types of micropores the CS4 cavity and intermolecular space. We considered two reasons for such difference in the CS4 conformation. First, the arrangement of CS4 in the interlayer space of the LDHs was presumed to be different by the number of dissociated OH group (p$K_{a1} = 3.08$, p$K_{a2-4} > 11$),[14] 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) was higher than that of the Zn–Al/CS4/LDH (pH 7). Therefore, CS4 molecules take a perpendicular monolayered arrangement within the Mg–Al/LDH interlayers as show in Fig. 5(b). Second reason, the formation of Zn–CS4 complexes would obstruct the interaction between the dissociated OH groups and the LDH basal layer. The lower rim combined OH groups in CS4 can

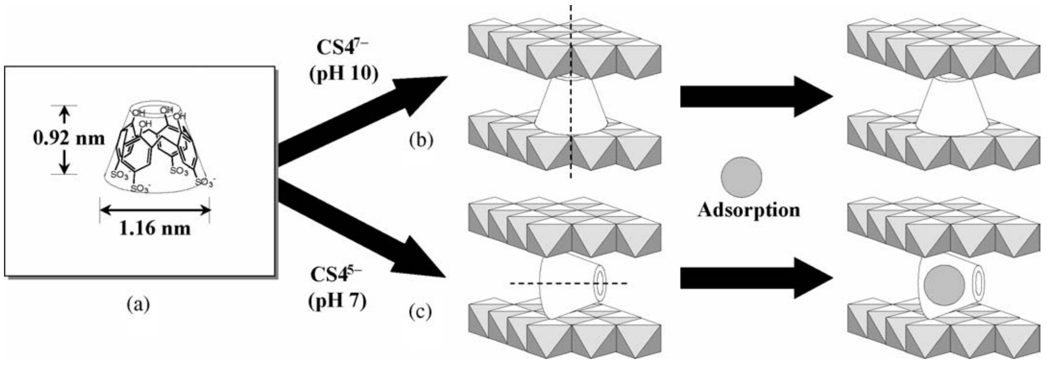

Fig. 5. Schematic representation of structure models: (a) CS4, (b) high negative charge (Mg–Al/CS4/LDH) and (c) low negative charge or Zn–CS4 complexed (Zn–Al/CS4/LDH).

Table 1
BET surface area and N_2 adsorbed volume and compositional data for the CS4/LDHs

Host	BET s.a ($m^2\ g^{-1}$)	N_2 adsored volume ($mm^3\ g^{-1}$)		Molar ration of solid product			
		Adsorption side	Desorption side	M^{2+}/Al	CS4/Al[a]	BA/CS4	NP/CS4
Mg–Al/CS4	22.4	49.6	43.3	3.1	0.25	0.22	0.76
Zn–Al/CS4	79.0	132	161	3.0	0.12	2.10	4.50

[a] Theoretical molar ratio of the solid product: $CS4^{5-}/Al = 0.20$ and $CS4^{7-}/Al = 0.14$.

be employed to bind transition metal ion[15]; however, CS4 hardly bind with Mg^{2+} ion. Therefore, CS4 was considered to orient its cavity axis parallel to the Zn–Al LDH basal layer as shown in Fig. 5(c).

3.2. Adsorption properties of calix[4]arene/LDH

The BET surface area and N_2 adsorbed volume of the CS4/LDHs are indicated in Table 1 and the adsorption–desorption curves of the CS4/LDHs are also displayed in Fig. 6. Both features of the CS4/LDHs can be classified the intermediate type between types II and IV. This result indicates that the CS4/LDHs have a mesopore as well as micropore. Fig. 7 shows the pore size distribution of the CS4/LDHs in which a sharp and high peak around 2.0 nm appears in the desorption curve. Entirely, the pore size distribution curve was broad and ranged to a micropore side. The N_2 adsorbed volume was found to be greater for the Zn–Al/CS4/LDH than for the Mg–Al/CS4/LDH. The result can be explained by the difference in the CS4 arrangement in the interlayer space of the LDH. In the BET surface area measurement, the surface area of the Zn–Al/CS4/LDH was four times than that of the Mg–Al/CS4/LDH, expecting that the Zn–Al/CS4/LDH has higher adsorption capacity than the Mg–Al/CS4/LDH. As a reference, the same measurement was carried out using the NO_3/LDHs, no difference between Mg–Al and Zn–Al/LDHs was observed.

Compositional data for the CS4/LDHs obtained after the adsorption in aqueous solutions are also indicated in Table 1.

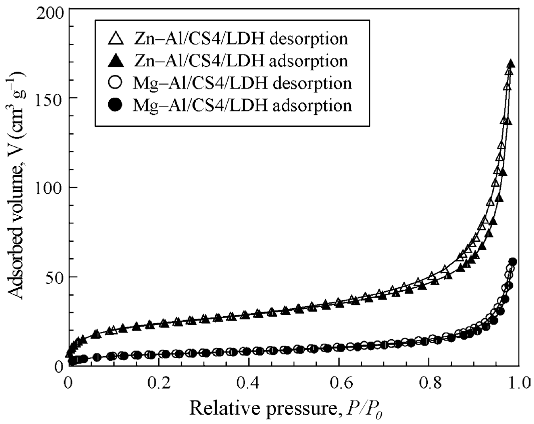

Fig. 6. N_2 adsorption/desorption isotherms for the CS4/LDHs.

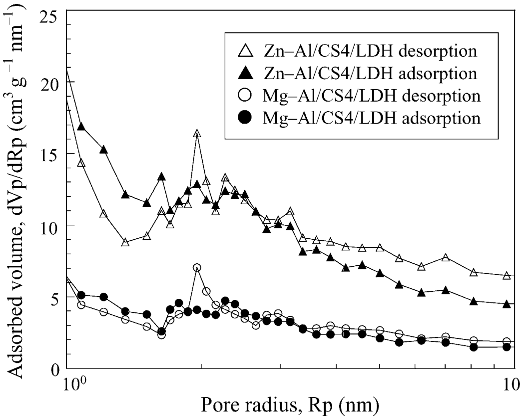

Fig. 7. Pore size distributions of the CS4/LDHs.

In the adsorption experiments, the CS4/LDHs were found to adsorb BA and NP in each aqueous solution with keeping the LDH structure. The amount of CS4 in the CS4/LDHs was not changed before and after the adsorption. For each adsorbates, the adsorption ability of the Zn–Al/CS4/LDH was much greater than that of the Mg–Al/CS4/LDH. This result was similar to the N_2 gas adsorption data.

The adsorption of BA for the Zn–Al/CS4/LDH was considered to relate not only to the interlayer space, but also to the intercalated calixarene cavity. As no adsorption of BA for the LDHs incorporating inorganic guest anions was observed in the preliminary experiments, the driving force of BA adsorption was thought to be based on the presence of CS4 in the LDH interlayer. In the adsorption of NP, the CS4/LDHs indicated the same tendency. In addition, the adsorbed amount of NP was higher than that of BA, because NP can be attracted not only by CS4, but also by the LDH basal layer. The results suggest that the CS4/LDHs are possible to adsorb organic non-anionic and anionic molecules. Strict interaction between CS4 molecular and organic adsorbates in the LDH interlayer is as yet unclear.

4. Conclusions

The investigation has led to a new finding for the intercalation of a water-soluble macrocyclic molecule, CS4, in the interlayer of LDHs. Some of the important findings of this study can be summarized as follows. (I) The Mg–Al and Zn–Al/CS4/LDHs were synthesized by the coprecipitation method. (II) The amount and arrangement of CS4 was different by the kind of the host metal ions, as CS4 cavity axis perpendicular (Mg–Al LDH) and parallel (Zn–Al LDH) to the basal layer. (III) The BET surface area and N_2 gas adsorbed pore volume were larger in the Zn–Al/CS4/LDH than in the Mg–Al/CS4/LDH. (IV) The adsorption ability for BA and NP in aqueous solution were also larger in the Zn–Al/CS4/LDH than in the Mg–Al/CS4/LDH, because of effective use of the parallel arranged CS4 cavity only in the Zn–Al/CS4/LDH. (V) The CS4/LDHs have a considerable possibility as new organic–inorganic hybrid adsorbents for many organic molecules.

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