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Na-dodecylsulfate modification of hydrocalumite and subsequent effect on the structure and thermal decomposition

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Abstract Hydrocalumite (CaAl-Cl-LDH) has the similar structure to layered double hydroxide (LDH). The effects of Na-dodecylsulfate (SDS) on the structure, morphology, and thermal property of CaAl-Cl-LDH have been investigated. Through ion exchange, CaAl-Cl-LDH had been modified with SDS at two concentrations: 0.005 mol L^{-1} and 0.2 mol L^{-1}. Two different adsorption behaviors were observed through Fourier transform infrared (FTIR) spectra and X-ray diffraction (XRD) patterns. When the SDS concentration was 0.005 mol L^{-1}, surface anion exchange was the major process. When the SDS concentration was 0.2 mol L^{-1}, anion exchange intercalation occurs, with the interlayer distance expanded to 3.25 nm, and the particle morphology from regular hexagons to irregular platelets. The thermal analysis (TG–DTA) showed that dehydration and dehydroxylation occur at a lower temperature when hydrocalumite was intercalated with dodecylsulfate. All these observations revealed that the property of CaAl-Cl-LDH has been changed by SDS modification.

Keywords Hydrocalumite · Na-dodecylsulfate adsorption · Anion exchange · Thermal analysis

Introduction

Layered double hydroxides (LDHs), also called as hydrotalcites or hydrotalcite-like compounds, have received increasing attention in recent years, because of their wide applications as anion exchangers, adsorbents, catalysts, and catalyst supports [1–4]. LDHs have a general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]\ A_{x/n}\cdot yH_2O$, where M^{2+} and M^{3+} are metal cations, and A^{n-} denotes the interlayer anions [5]. LDHs are a class of clay minerals with positively charged metal hydroxide sheets compensated by anions in the interlayer. The anion may be inorganic or organic. Recently, LDHs are found to be functional fillers in developing polymer nanocomposites [6, 7]. However, due to the hydrophilic property of LDH surfaces, LDHs will not be well dispersed within the hydrophilic polymer matrices. A possible solution is to change the hydrophilic nature of inorganic-LDHs into hydrophobic one with an anionic surfactant. For example, dodecylsulfonate anions intercalation into LDHs changed the surface property from hydrophilicity to hydrophobicity [8]. The surfactant adsorbed on LDH particle surface acts as a bridge linking the hydrophilic LDH nanoparticles and hydrophobic polymers [9]. In addition, the LDH-surfactant materials are able to absorb non-ionic organic compounds [10, 11]. Zhao et al. [12] introduced SDS into the interlayer of MgAl-Cl-LDH to trap chlorinated organic pollutants in water, and the removal effect was increased to four times as that of other clay-derived sorbents.

Hydrocalcumite ($[Ca_2(Al, Fe)(OH)_6]^{+}X^{-}\cdot mH_2O$), expressed as AFm conventionally, has the same layer structure as natural hydrotalcite, where X^{-} is an anion, such

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as OH^-, Cl^-, SO_4^{2-}, and CO_3^{2-}. Hydrocalcumite can easily form in the hydrated cement paste, and thus can be cheaply prepared [13, 14]. In particular, $Ca_2Al(OH)_6Cl(H_2O)_2$ (CaAl-Cl-LDH) is a major hydration product found in concrete submerged in seawater and is subjected to Cl^- corrosion [15]. Cl^- in CaAl-Cl-LDH has less affinity for hydrocalumite, so the exchange with SO_4^{2-}, CO_3^{2-}, or many anionic surfactants is very possible.

In this study, we investigated the modification of CaAl-Cl-LDH with an anionic surfactant, Na-dodecylsulfate (SDS) under two different conditions, and examined the subsequent effect on the structure and the thermal decomposition behaviors.

Experimental

Materials preparation

The CaAl-Cl-LDH was prepared by heating freshly synthesized tricalcium aluminate (C_3A) with $CaCl_2$ solution. First, C_3A was synthesized through the solid phase reaction. In brief, reagent grade $CaCO_3$ and low-alkali Al_2O_3 at a molar ratio of 3:1 were heated at 1300–1350 °C. The heating process was conducted in quartz crucibles and continued until X-ray powder diffraction and a modified Franke test showed that the free lime content was reduced to below 0.5%. The as-prepared C_3A was then mixed with $CaCl_2{\cdot}6H_2O$ solution in double distilled CO_2-free water. During the process, the suspension was continuously shaken for more than 18 h under N_2 gas atmosphere and at the temperature of 55 ± 1 °C. After cooling to room temperature, the suspension was filtered and extensively washed by double distilled CO_2-free water until the filtrate was free of Cl ion ($AgNO_3$ test). The product was dried at 105 °C, ground and stored in a glass container.

Modification of CaAl-SDS-LDH hydride materials

The CaAl-Cl-LDH was modified with SDS at different concentrations in the following typical procedure. In brief, 50 mL of a surfactant solution containing 0.005 or 0.2 mol L^{1} SDS was mixed with 0.2 g CaAl-Cl-LDH and shaken at 150 rpm in a thermostatic bath shaker at 25 ± 1 °C for 24 h. After stirring, the mixture was aged at 60–70 °C for 24 h further. The slurry was then collected and washed with distilled water via filtration, and dried at 70 °C overnight. The resulting materials were referred to as CaAl-SDS 0.005 and CaAl-SDS 0.2, respectively.

Materials characterization

Powder X-ray diffraction (XRD) patterns were collected at room temperature with a D/max RBX diffractometer with Cu Kα (40 kV, 100 mA) radiation. All the samples were scanned in a step of 6° per minute in $2\theta = 5°$ to 65°. In particular, these samples were carefully scanned in $2\theta = 2°$ to 15° at a scanning rate of 2° per minute using silts 1/6 (divergence), 1/6 (anti-scattering), and 0.15 (receiving). Fourier transform infrared (FTIR) spectra were recorded by the Thermo Nicolet AVATAR 370 in the range 400–4000 cm^{-1} with 4 cm^{-1} resolution by measuring the absorbance of KBr disk containing 1–2 wt% samples.

Thermal analysis (TG–DTA) was carried out by NETZSCH Simultaneous TG–DTA/DSC Apparatus STA 449C/4/G Jupiter-QMS 403C Aeolos in pure N_2 atmosphere at a heating rate of 10 °C/min within 40–1000 °C. Samples of 10–15 mg were used in each measurement with sintered α-Al_2O_3 as the reference.

The morphology of the products was examined with scanning electron microscopy (SEM) with an S-2360 microscope (Hitachi). Before loading, the sample was ultrasonically dispersed in ethanol solution.

Results and discussions

FTIR spectra

The FTIR spectra of as-synthesized CaAl-Cl-LDH powder and the samples with SDS (CaAl-SDS 0.005 and CaAl-SDS 0.2) are shown in Fig. 1. For CaAl-Cl-LDH, the strong overlapping bands at 3480 and 3636 cm^{-1} are attributed to the stretching vibrations of lattice water and –OH groups in CaAl-Cl-LDH, respectively. The peak at 1621 cm^{-1} is also due to the H–O–H bending vibration of the interlayer water molecule. The stretching and deformation vibrations of M–OH are reflected by peaks at 785 cm^{-1} and at 532 cm^{-1}. Compared to the FTIR spectrum of CaAl-Cl-LDH, sample CaAl-SDS 0.005 further shows the bands of dodecylsulfate

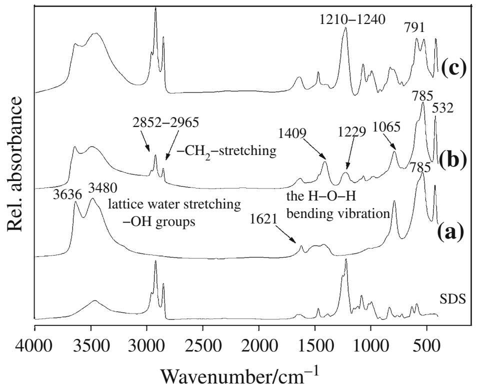

Fig. 1 FTIR spectra of samples of pure SDS, CaAl-Cl-LDH (**a**), CaAl-SDS 0.005 (**b**), and CaAl-SDS 0.2 (**c**)

(DS), such as C–H stretching and bending (2852–2965 cm^{-1} and 1409 cm^{-1}), $–OSO_3^-$ stretching and bending (1229 and 1065 cm^{-1}). These bands are identical with those bands of pure SDS, indicating that DS is adsorbed on the surface of CaAl-Cl-LDH. Moreover, these peaks are obviously intensified in CaAl-SDS 0.2, indicating more DS is intercalated into and/or adsorbed on the LDH. It is presumed that SDS has successfully been intercalated into LDH at the SDS initial concentration of 0.2 mol L^{-1}. It is worth mentioning that CaAl-SDS 0.005 and CaAl-SDS 0.2 have a strong IR band at 1229 cm^{-1}, indicating the sulfate group has a C_{3v} symmetry. However, pure SDS shows two split bands (1240 and 1210 cm^{-1}), due to the symmetry reduction of sulfate group in SDS solid. This further indicates that SDS was successfully intercalated into the interlayer of CaAl-Cl-LDH.

X-ray diffraction

The XRD patterns of as-synthesized CaAl-Cl-LDH powder and samples CaAl-SDS 0.005 and CaAl-SDS 0.2 are depicted in Fig. 2. In the case of CaAl-Cl-LDH, The XRD patterns are identical to that recorded on PDF 78-1219 in the database of the International Centre for Diffraction Data. This reveals that the synthesized compound is a typical hydrocalumite, with a nominal chemical formula of $Ca_2Al(OH)_6Cl(H_2O)_2$. It is observed that the basal spacing (d_{002}) is 0.78 nm, so the calculated interlayer spacing is 0.3 nm if subtracting the thickness of the LDH hydroxide layer (0.48 nm) [16]. In the case of CaAl-SDS 0.005 sample, the main diffraction peaks found in the XRD pattern were similar to that of CaAl-Cl-LDH, yet there was a weak peak at $2\theta = \sim 3°$. While in the case of CaAl-SDS 0.2, the main diffraction peaks found in the XRD pattern are typical of organo-LDHs composite [17]. After intercalation of DS^-, the $d_{(002)}$ peak shifted toward $2\theta = 2.7°$, and with the second diffraction peak at 6.0°, with the result that the interlayer d-spacing is expanded to 3.25 nm. The sharp and intense (00l) reflections demonstrate a well-crystallized DS-intercalated LDH compound, similar to those found for DS intercalated Mg-Al-LDHs [18] and Zn-Al-LDHs [19]. Due to the increase of the basal spacing of the layered materials, the diffraction peak being responsible for the interlayer spacing shifts to a lower 2θ value [22]. This has also suggested that very limited amount of DS enters the interlayer space of CaAl-Cl-LDH when the SDS concentration is 0.005 mol L^{-1}. Usually, the conformation of intercalated anions in the interlayer of LDHs can be deduced from the d-spacing value of the resultant materials. Theoretically, the length of SDS anion is 1.78 nm, a basal spacing of 2.26 and 4.04 nm would be observed for monolayer and bilayer models with perpendicular orientation of the DS in the interlayer, respectively [20]. In this study, the basal spacing of CaAl-SDS 0.2 was observed as 3.25 nm, thus the conformation of DS in the interlayer is neither monolayer nor bilayer, but a inter-penetrating bilayer model [8].

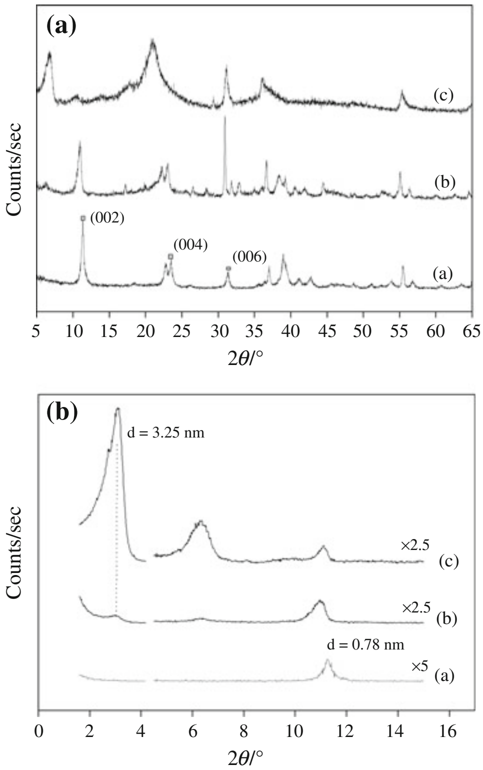

Fig. 2 XRD patterns of samples of CaAl-Cl-LDH (**a**), CaAl-SDS 0.005 (**b**), and CaAl-SDS 0.2 (**c**)

SEM characterization

The SEM micrographs of CaAl-Cl-LDH and the sample of CaAl-SDS 0.2 are shown in Fig. 3. The SEM image demonstrates the approximately hexagonal platy crystallites of CaAl-Cl-LDH with sharp particle edge and similar particle size (Fig. 3a). The resulting sample treated with SDS reveals significant changes in morphology. There are many small and aggregated particles observed in CaAl-SDS 0.2 (Fig. 3b), and the particle edge is not as sharp as that of CaAl-Cl-LDH, suggesting that there might be some DS traps over the external surface of the intercalate particles, as reported previously by other authors [21].

Thermal analysis

The thermal analysis revealed further evidence of the different adsorption behaviors of modified CaAl-Cl-LDH. The TG–DTA curves of CaAl-Cl-LDH and these samples of CaAl-SDS 0.005 and CaAl-SDS 0.2 are shown in Fig. 4. For CaAl-Cl-LDH, three loss steps are observed (Fig. 4a). The first mass loss of 10.38% before 240 °C corresponds to dehydration of water molecules (adsorbed and lattice),

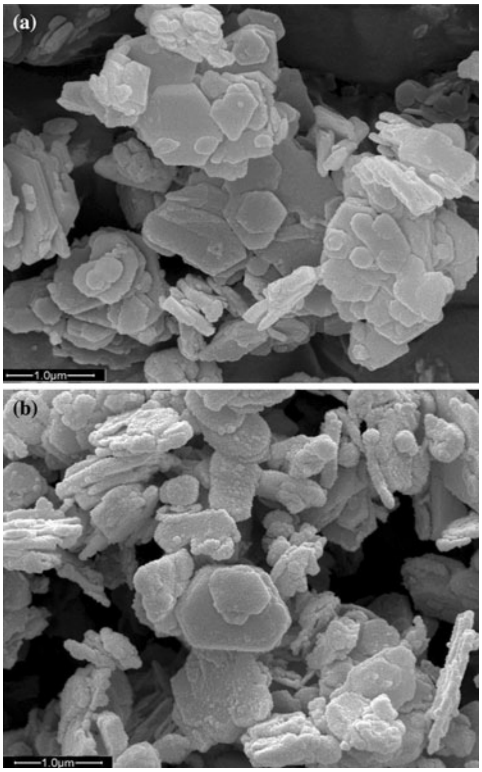

Fig. 3 SEM micrographs of CaAl-Cl-LDH (**a**) and CaAl-SDS 0.2 (**b**)

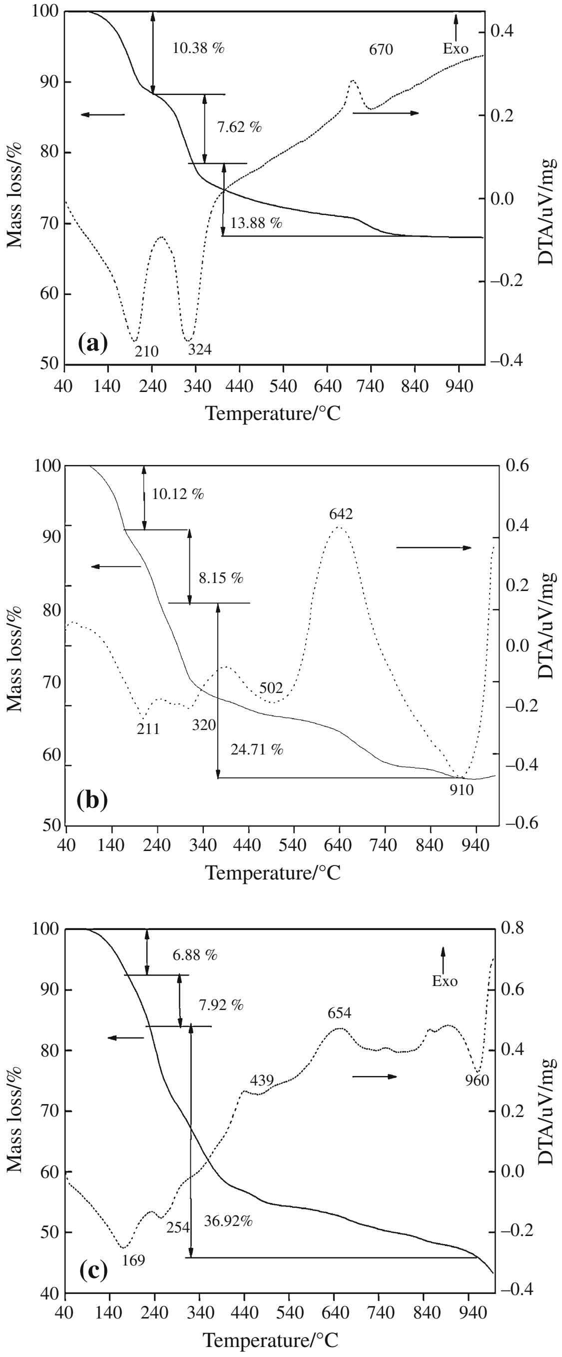

Fig. 4 TG and DTA curves of CaAl-Cl-LDH (**a**), CaAl-SDS 0.005 (**b**), and CaAl-SDS 0.2 (**c**)

which is slightly lower than that of other LDHs, such as Mg-Al-LDH, Zn-Al-LDH [19, 22]. The second mass loss (7.62%) takes place at about 324 °C due to the dehydroxylation of CaAl-Cl-LDH. The mass loss at ca. 670 °C, related to an exothermic peak in DTA curve, is attributed to generate a new product $11CaO{\cdot}7Al_2O_3{\cdot}CaCl_2$ [22]. The total mass loss is 31.9% at 900 °C

Compared to CaAl-Cl-LDH, the thermal decomposition of sample of CaAl-SDS 0.005 is almost identical (Fig. 4b). The total weight loss of sample CaAl-SDS 0.005 is 43.0%, 11.1% more than that of CaAl-Cl-LDH. This increase in mass loss is resulted from the loading of SDS, whose decomposition is reflected by the mass loss in 400–900 °C and the exothermal peak at 642 °C. As shown in Fig. 4(c), thermal degradation of sample CaAl-SDS 0.2 also takes place in several steps, corresponding to loss of adsorbed and interlayer water, dehydroxylation, and decomposition of DS. The temperature of interlayer water loss seems to be lower than that of CaAl-Cl-LDH and CaAl-SDS 0.005, indicating the changes of LDH structure. It could be caused by the fact that DS intercalated into interlayer of CaAl-Cl-LDH reduces the interactions of water with the environment in CaAl-Cl-LDH. In other words, SDS intercalated into CaAl-Cl-LDH could increase hydrophobic nature of interlayer surface [23, 24]. The decomposition of DS in the interlayer is also evidenced by the peak at 654 °C. Moreover, a new endothermic peak occurs at 960 °C, which is due the decomposition of (Ca, Al) sulfate that is formed during decomposition of DS. The total mass loss is 51.7%.

Based on the results of FTIR, XRD, SEM, and the thermal analysis, it was concluded that the anion exchange behavior may occur in two ways: (1) when SDS concentration was 0.005 mol L^{-1}, only surface adsorption of DS occurred; (2) adsorption coupled with intercalation of DS into CaAl-Cl-LDH at the SDS concentration of 0.2 mol L^{-1}.

Conclusions

In this study, DS modified CaAl-Cl-LDHs were synthesized at two SDS concentrations through the ion exchange method. Combining the results measured from FTIR, XRD, TG–DTA, and SEM techniques, we could conclude that DS was intercalated into the interlayer spacing of CaAl-Cl-LDH at the DS concentration of 0.2 mol L^{-1}, which expanded the interlayer spacing to 3.25 nm. When DS concentration was 0.005 mol L^{-1}, surface adsorption of DS was the major anion exchange event.

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