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Synthesis and characterization of Cd–Cr and Zn–Cd–Cr layered double hydroxides intercalated with dodecyl sulfate

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Abstract

Cd–Cr and Zn–Cd–Cr layered double hydroxides (CdCr-LDH and ZnCdCr-LDH) containing alkyl sulfate as the interlamellar anion have been prepared through a coprecipitation technique. The resulting compounds were characterized using X-ray diffraction, infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy. Magnetic property measurements indicate that antiferromagnetic interactions occur between the chromium ions in the two compounds at low temperatures. The introduction of zinc influences the ligand field of Cr^{III} and the Cr^{III}–Cr^{III} interactions in the LDH compound. It is found that both CdCr-LDH and ZnCdCr-LDH can be delaminated by dispersion in formamide, leading to translucent and stable colloidal solutions.

Keywords: Layered double hydroxide; Chromium; Cadmium; Zinc; Magnetic properties

1. Introduction

Inorganic layered compounds are useful host materials between sheets of which guest species can be intercalated and novel composites with various functions can be obtained through intercalation [1–3]. Among the layered compounds, layered double hydroxides (LDHs) have received considerable attention due to their interesting properties and wide applications as catalysts, catalyst precursors or catalyst supports, adsorbents, anion exchangers, medicine stabilizers, ionic conductors and polymer stabilizers [4–15]. LDHs can be represented by the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}A^{m-}_{x/m}\cdot nH_2O$, where M^{II} stands for a divalent cation, M^{III} a trivalent cation and A^{m-} an anion [16]. From the structure point of view, the metallic cations in an LDH material are located in octahedral $[M(OH)_6]$ units which share edges to form $M(OH)_2$ layers with the brucite ($Mg(OH)_2$) structure, and the partial substitution of the divalent cations by trivalent ones results in positive charges in the inorganic layers which are balanced by anions sandwiched between the layers [17–19]. The compositions of LDHs are versatile and it is possible to modulate the properties of LDHs by changing the M^{II} and M^{III} cations, their molar ratio, and the nature of the compensating anions [20]. In addition, the synthesis of LDHs containing three or more cations in the layers and the introduction of various anions between the layers are also feasible. Although a variety of LDHs have been synthesized with divalent metals such as Mg, Mn, Fe, Co, Ni, Cu, Zn, and Ca and trivalent metals such as Al, Cr, Mn, Fe, Co, La, and Y [18–21], only a few systems containing Cd appeared in the literature. Miyata and Kumura described the preparation of LDH containing Cd as the divalent metal, but it seemed that the obtained material was a mixture of the desired product and $CdCO_3$ [22]. Later on, Bao synthesized $[Mg_6Al_2(OH)_{16}][CO_3]\cdot 4H_2O$ in which Mg^{II} was partially substituted by Cd^{II} ions in the hydrotalcite, but no product was prepared with Cd alone as the divalent metal [23] untill 1997 when Vichi

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and Alves reported the well-crystallized LDHs with Cd as the divalent metal and Al as the trivalent metal and nitrate and carbonate as the counter anions [17].

In this paper, we present the preparation of a new LDH compound containing Cd as the divalent metal and Cr as the trivalent metal (CdCr-LDH) and a ternary (Zn, Cd, Cr) metal hydroxide with the LDH structure (ZnCdCr-LDH) through a coprecipitation technique. Dodecyl sulfate (DS) has been used as the anion to intercalate the layers of these two compounds, which exhibit high structural order and can be exfoliated into single layers in formamide solution, providing new precursors to be used in assembly chemistry. Antiferromagnetic interactions between the Cr^{III} centers have been observed for the as-prepared CdCr-LDH and ZnCdCr-LDH.

2. Experimental

2.1. Preparation

All reagents for synthesis were commercially available and used as received without further purification. The method of preparation of the LDHs was based on that described previously [24]. For the synthesis of CdCr-LDH, a solution of 0.02 mol $Cd(NO_3)_2 \cdot 4H_2O$ and 0.01 mol $Cr(NO_3)_3 \cdot 9H_2O$ with a Cd^{II}/Cr^{III} ratio of 2/1 in 15.8 mL H_2O was mixed with a solution of DS surfactant (0.02 mol sodium DS in 85 mL H_2O). To the resulting solution was added dropwise a solution of 2 mol L^{-1} NaOH until a particular pH (8.0) was reached and the system was aged at room temperature for 2 h. Subsequently, a gray-blue suspension was formed and the solid product was separated by centrifugation from the suspension, washed with distilled water and dried under vacuum. For the synthesis of ZnCdCr-LDH, a mixture of 0.02 mol $Zn(NO_3)_2 \cdot 6H_2O$, 0.01 mol $Cd(NO_3)_2 \cdot 4H_2O$ and 0.01 mol $Cr(NO_3)_3 \cdot 9H_2O$ in 15.8 mL H_2O was used as the cation solution, and the final pH was adjusted to 8.0 using a 2 mol L^{-1} NaOH solution as well. The rest of the preparation procedure was the same as that for the CdCr-LDH material. The resulting product appeared light pink in color. Exfoliation of the layered double hydroxides (CdCr-LDH and ZnCdCr-LDH) was realized through dispersion of 0.15 g as-prepared LDH material in 50 mL formamide with stirring at room temperature. The exfoliation process was completed in about three days and a clear colloidal solution was obtained.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer with Cu$K\alpha$ ($\lambda = 1.5418$ Å) radiation. The FT-IR spectra of the samples dispersed in KBr pellets were obtained within 4000–500 cm^{-1} wavenumber region on a Nicolet Impact 410 FTIR spectrometer. The thermogravimetric (TG) analyses were conducted on a Netzsch STA 449C thermal analyzer under a flow of dry air at a heating rate of 20 K min^{-1}. The C, H, N, S elemental analysis was performed on a Perkin-Elmer 2400 elemental analyzer, whereas the metal contents were determined by inductively coupled plasma (ICP) analysis on a Perkin-Elmer Optima 3300DV ICP spectrometer. The UV-vis powder diffuse reflectance spectra were measured on a Perkin-Elmer Lambda 20 spectrometer. The scanning electron microscope (SEM) images were taken on a JEOL JSM-6700F electron microscope and the temperature-dependent magnetic susceptibility data were collected on a Quantum Design MPMS-XL-5 SQUID magnetometer under an applied field of 1000 or 10,000 Oe over the temperature range 2–300 K. To confirm the exfoliation of LDHs in the colloidal solution, atomic force microscope (AFM) images were obtained at room temperature in the tapping mode using a Digital Instruments Nanoscope IIIa AFM. Prior to imaging, the colloidal solution was diluted and dropped onto a mica substrate and dried under vacuum.

3. Results

Fig. 1 shows the SEM images for the two as-prepared LDHs compounds. It is seen that both compounds appear as irregular plate-like particles characteristic of sheet structure, and the particle diameter varies from 0.3 to 2 μm for CdCr-LDH and from 2 to 70 μm for ZnCdCr-LDH.

The powder XRD patterns for the as-synthesized samples are displayed in Fig. 2. As can be seen, both materials exhibit high structural order, and the typical diffraction peaks correspond to intercalated LDHs with layer separations in good agreement with those reported previously [24]. The basal spacings calculated from the XRD patterns are presented in Table 1. CdCr-LDH has a basal spacing of 26.9 Å whereas ZnCdCr-LDH has one of 27.4 Å. The introduction of the DS surfactants in the interlayer space of LDH is evidenced by IR spectroscopy and elemental analysis. Fig. 3 shows the FT-IR spectra of the samples. Besides a broad absorption band at around 3500 cm^{-1} due to the presence of hydroxyl groups of LDH, the existence of C–H stretching at 2919, 2844 cm^{-1} and C–H bending at around 1469 cm^{-1} confirms the presence of the DS molecules in the sample. As expected, the absorption bands of the sulfate ion at 1255, 1226, 1083, 998, and 593 cm^{-1} are also observed in the two LDH compounds. Absorption bands of nitrate (1380 cm^{-1}) and carbonate (1450 cm^{-1}) ions are not observed for CdCr-LDH and