

Easily Oxidizable Polysulfide Anion Occluded in the Interlayer Space of Mg/Al Layered Double Hydroxide

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(Received May 12, 2004; CL-040541)

Magnesium–aluminum layered double hydroxide containing polysulfide anions was prepared by a hydrothermal reaction from magnesium and aluminum hydroxides. Thioacetamide was used as the sulfide source. The product exhibits light green color corresponding to the S_2^- and S_3^- ions and turns to colorless when the sample was stored in air for several days or heat treated in air at 120 °C. The color change showed that the occluded polysulfide anions were oxidized to sulfate anion by atmospheric oxygen.

Host–guest complexation has extensively been investigated to control the physicochemical characteristics of both host and guest and to construct hybrids with unique functions to which both host and guest alone cannot access.^{1–3} The states of the immobilized guest species, stabilization and destabilization of guest species by host–guest complexation are a topic of interest. Stabilization of dyes by complexation with sepiolite,⁴ which is a microporous silicate, and that of the photochemically formed viologens in the layered host–guest systems⁵ are notable examples.

Here we report a unique state of polysulfide anions in the interlayer space of a layered double hydroxide. Layered double hydroxides (LDHs; the general formula of $M^{2+}_{1-x}M^{3+}_x(OH)_2(A^{n-})_{x/n} \cdot mH_2O$) are a class of layered materials consisting of positively charged brucite-like layers and the charge compensating interlayer exchangeable anions.⁶ The introduction of guest species into the interlayer space of LDHs has been reported.^{6–9} Small and highly charged anions preferentially occupy the LDH interlayers.^{5,10–12} According to this guest selectivity sequences,^{11,12} the selectivity of sulfide anions (S^{2-}) should be very high because of its small size (1.84 Å) and bidentate nature. However, to our knowledge, there is only one report on the Mg/Al LDH including sulfide anion and the detailed characterization of the sulfide containing LDH was not reported.¹³ In order to address the point, we examined the preparation and characterization of sulfide anion-containing LDH and found that polysulfide anions, which are important blue and yellow chromophores,^{14–18} were successfully incorporated in the interlayer space of Mg/Al LDH.

Hydrothermal reaction using magnesium and aluminum hydroxides (brucite and gibbsite) as the inorganic sources was employed for the synthesis of the sulfide anion-containing LDHs. This method was originally developed for the synthesis of the LDH-deoxycholate intercalation compounds.¹⁹ Following is a typical synthetic procedure; brucite (116.6 mg), gibbsite (39.0 mg) powders and 751.2 mg of thioacetamide (Mg:Al:S = 4:1:20 in molar ratio) were mixed in 100-mL distilled water with vigorous magnetic stirring. The mixture was transferred into a Teflon-lined autoclave and heated at 150 °C for 1 day. The precipitate was separated by centrifugation, washed with deionized water thoroughly and dried under reduced pressure.

Light green colored precipitates were obtained by the reactions. Figure 1a shows the XRD pattern of the product prepared by the reaction. A sharp diffraction peak with the d value of 8.1 Å accompanying higher reflections was observed in the X-ray diffraction pattern, indicating the formation of a layered material.

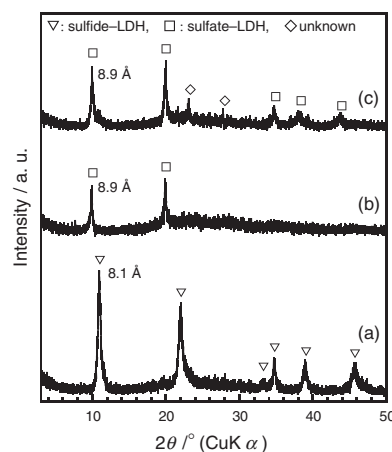


Figure 1. X-Ray powder diffraction patterns of the products. (a) As-synthesized, (b) stored in air for 2 weeks, and (c) heat treated in air at 120 °C.

The product was composed of finite platy particles with the lateral size of around a few μm as shown by SEM. The chemical composition of the precipitate was Mg: 20.1, Al: 11.2, S: 16.4 mass%. From the chemical composition, the molar ratio of Mg:Al in the product was determined to be 2:1. All these observations confirmed the successful formation of sulfide anion containing LDH.

Sato et al. reported the synthesis of a sulfide anion containing Mg/Al LDH with a d value of 7.9 Å, which is slightly smaller than that of our present sample.¹³ They did not describe the color and the properties of the product. We thought that the slight difference in the d value, 8.1 and 7.9 Å observed in the present study and in the report by Sato et al.,¹³ was due to the formation of polysulfide anions in the interlayer space of LDH in the present study.

Polysulfide anions such as S_2^- and S_3^- are known chromophores of blue ultramarine pigment and its natural counterpart lapis lazuli.¹⁶ These chromophores are stabilized in sodalite cage as sodium salts. Ultramarine pigments are synthesized under reducing conditions where sulfur was used as the sulfide source. Polysulfide anions have also been formed in glasses and in solution from elemental sulfur by chemical and electrochemical reduction. In the present synthesis, thioacetamide should be the polysulfide source. These species have been characterized by using electronic transition (visible absorption), Raman, and ESR

spectroscopies. The visible absorption spectrum (Figure 2a) of the as-synthesized product was recorded by using an integrated sphere. Absorption bands were observed at around 406, 533, and 646 nm. Similar absorption bands have been observed for the blue ultramarine pigment and lapis lazuli.¹⁵ According to the assignments,¹⁵ the observed absorption bands at 406 and 646 nm were ascribed to $1\pi \rightarrow 1\pi_g$ transition of S_2^- and $1a_2 \rightarrow 2b_2$ transition of S_3^- , respectively. Thus, the precipitate was thought to be a polysulfides anion-containing LDH. During the hydrothermal treatment, thioacetamide was hydrolyzed to give sulfide anion (S^{2-}) and the sulfide anions were oxidized to polysulfide anions (S_2^- and S_3^-) subsequently.

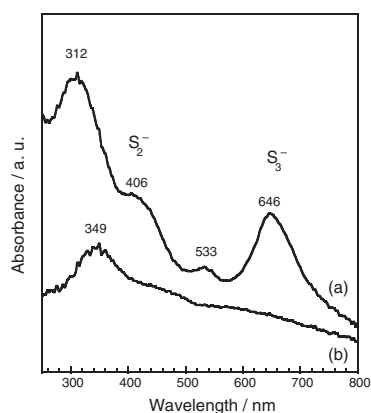


Figure 2. Visible absorption spectra of the products (a) as-synthesized and (b) stored (a) in air for 2 weeks.

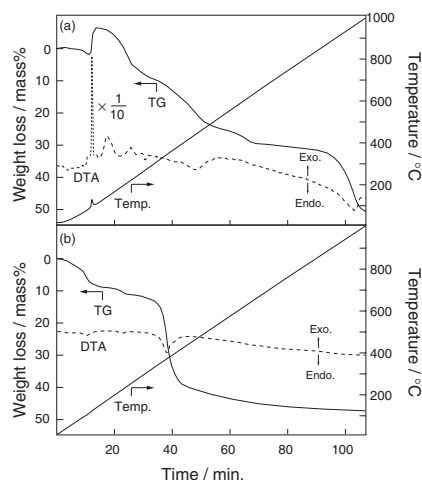


Figure 3. TG-DTA curves of the sulfide anion-containing LDH recorded in Air (a) and in He (b).

It is worth noting that the light green color faded out upon heating the sample. TG-DTA curves of the as-synthesized product are shown in Figure 3a. An exothermic peak was observed at around 100–200 °C, which accompanied a weight gain (ca. 8.0 mass%) in the corresponding TG curve. On the contrary, the exothermic reaction was absent when TG-DTA was conducted in He as shown in Figure 3b. After the heat treatment, absorption bands due to sulfate anion (SO_4^{2-}) appeared in the infrared spectra of the product. The basal spacing changed from

8.1 to 8.9 Å during the color fading, which is consistent with the value reported for the sulfate containing Mg/Al LDH. These observations suggested that the sulfide anion occluded in the interlayer space of the Mg/Al LDH was oxidized by atmospheric oxygen at this temperature range. The infrared absorption bands due to carbonate anions observed for the as-synthesized sample disappeared by the heat treatment. The removal of carbonate anions can compensate the charge balance to some extent, though the detailed charge balance is required.

The color was also faded out when the sample was stored in air even at room temperature for several days. The IR spectrum and the XRD pattern also changed in a same manner as mentioned above. These observations indicate that the interlayer polysulfide anions were oxidized by atmospheric oxygen to sulfate anion at room temperature. The polysulfide in ultramarine blue and lapis lazuli are very stable toward atmospheric oxygen. On the contrary, polysulfide anions in solutions are very sensitive to atmospheric oxygen. The present oxidation of polysulfide anion in the interlayer space of LDH is a unique example of the stability of interlayer guest species controlled by the shielding of host layer. The observed oxidation behavior also suggests the possible uses of the present compound as an oxygen-sensing materials.

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