Incorporation of CoS into the Interlayer Space of Montmorillonite by Solid-solid reaction

ABSTRACT

Metal sulfide, CoS, was synthesized in the interlayer space of montmorillonite by solid-solid reaction between Co(II)-montmorillonite and Na$_2$S at room temperature and subsequent heat treatment at 200°C for 1 h. The heat treated Co(II)-montmorillonite-Na$_2$S was characterized by powder X-ray diffraction, thermal analysis, UV-visible and photoluminescence spectroscopies. The basal spacing of heat treated product was ca. 1.2 nm, corresponding to the interlayer expansion of ca. 2-3 Å. No luminescence band of CoS was observed for the product after the heat treatment. When the heat treated Co(II)-montmorillonite-Na$_2$S was allowed to stand in desiccator at room temperature for 4 months, the luminescence band was observed at 440 nm. The weak luminescence intensity of intercalation compound was ascribed to the quenching impurities including iron in montmorillonite.

Key Words: CoS, Montmorillonite, Solid-solid reaction
Intercalation of organic and inorganic guest species into inorganic layered solids has been investigated from a wide range of scientific and practical view points, partly because of the well-confined nanostructure of the resulting intercalation compounds. Smectite including montmorillonite, which is a typical 2:1 type layered clay mineral, has been known to accommodate various guest species in its interlayer space to form the intercalation compounds due to its advantage properties such as swelling behavior, ion exchange property, adsorptive property and large surface area (Van Olphen, 1977). As a consequence, the synthesis, properties and possible applications of the intercalation compounds have been extensively reported (Theng, 1974; Ogawa & Kuroda, 1995, 1997). Solid-solid reaction, which means the formation of compounds through solid-solid interfaces, has been used because of the facile operation and possibility to prepare compounds not accessible from solutions (Patil et al., 1984; Toda et al., 1987). Solid-state intercalations of organic guest species into the interlayer spaces of layered clay minerals have been reported so far (Ogawa et al., 1992, Bujdák & Slosiariková, 1992). Incorporation of 2,2'-bipyridine (Ogawa et al., 1991), 4,4'-bipyridine (Khaorapapong et al., 2000, 2001), 1,2-di(4-pyridine)ethylene (Khaorapapong et al., 2001), thioacetamide (Khaorapapong et al., 2002a), 8-hydroxyquinoline (Khaorapapong et al., 2002b; Khaorapapong & Ogawa, 2007a, 2007b) and sodium sulfide (Khaorapapong et al., 2007) in smectites through solid-solid reactions and in situ formation have been investigated.

Metal sulfides including cobalt sulfide (CoS) have widely used for electroluminescence (Lou et al., 2003) and nonlinear optical devices (Chin et al., 2001) because of their excellent physical and optical properties. Much effort has been made to improve these properties by immobilizing metal sulfides on solid surfaces, since the properties are sensitive to size and shape of the nanocrystals (Zhang et al., 2003; Wang et al., 2005; Zhang et al., 2006). The incorporation of metal sulfides into zeolites (Iacomi et al., 2005; Zhang et al., 2006) and layered metal oxides (Shanguan & Yoshida, 2002) has been extensively investigated.

In this article, in order to prepare novel photofunctional host-guest systems, we utilized solid-solid reaction between Co(II)-montmorillonite and sodium sulfide at room temperature to form cobalt sulfide in the interlayer space of montmorillonite. The formation of CoS in the interlayer space may affect the optical properties.

Experimental

Materials

Sodium-montmorillonite (Kunipia F, Kunimine Industries Co., Ltd., the reference clay sample of the Clay Science Society of Japan) was used as a host material. The cation exchange capacity (CEC) of sodium-montmorillonite was 119 meq/100 g of clay. Sodium sulfide (Na₂S·xH₂O, analytical grade) was obtained from Aldrich Co., Ltd. Cobalt chloride (analytical grade) was supplied by Univar Co., Ltd. All chemicals were used without further purification.

Sample preparation

Co(II)-montmorillonite was prepared by a conventional ion exchange method. An aqueous solution of sodium-montmorillonite was mixed with an aqueous solution of cobalt chloride and the mixture was magnetically stirred at room temperature for 24 h. After the ion exchange reaction, the resulting solid was collected by centrifugation and washed with deionized water repeatedly until a negative AgNO₃ test was obtained and dried at 40°C for 3 days. The amount of adsorbed cation was determined by inductively coupled plasma emission spectroscopy (ICP) to confirm the quantitative cation exchange. The amount of exchanged cation in montmorillonite was 118 meq/100 g of clay. The intercalation of Na₂S into the interlayer space of Co(II)-montmorillonite was carried out by solid-solid reaction according to the method described in our previous reports (Khaorapapong et al., 2000, 2001, 2002a, 2002b, 2007; Khaorapapong & Ogawa, 2007a, 2007b). The mixture of the host and guest species was ground manually with an agate mortar and pestle at room temperature for 10-15 min. The molar ratio of sulfide ion (from Na₂S) to the interlayer cation of montmorillonite was 1:1.

Characterization

Powder X-ray diffraction data were collected on a Bruker D8 ADVANCE diffractometer using monochromatic CuKα radiation. Diffuse reflectance spectra of the solid sample were recorded with a Shimadzu UV-VIS-NIR-3101PC scanning spectrophotometer using an integrated sphere. TG-DTA curves were performed with a Perkin Elmer Pyris Diamond TG-DTA instrument at a heating rate of 10°C min⁻¹ under dry air flow using α-alumina (α-Al₂O₃) as a standard material. Inductively couple plasma emission spectroscopic (ICP) data were taken with a Perkin Elmer Optima 2100DV.
spectrometer. Luminescence spectra were recorded on a Shimadzu RF-5310PC spectrofluorophotometer in the wavelength range of 300-900 nm with the excitation at 340 nm.

Results and discussion

Solid-state intercalation of Na$_2$S into the interlayer space of Co(II)-montmorillonite

As a result of solid-state reaction between Co(II)-montmorillonite and Na$_2$S, the color of hydrated montmorillonite was changed from pink to black. The change in the color of the product confirmed the change in the coordination state of the interlayer cation. The basal spacing of Co(II)-montmorillonite-Na$_2$S was 1.25 nm (Fig. 1c). The gallery height was determined to be 0.29 nm by subtracting the thickness of silicate layer (0.96 nm) from the observed basal spacing. In the XRD pattern of Na$_2$S (not shown), the strong diffraction peaks located at $d = 0.19, 0.30, 0.31$ and 0.93 nm were observed. No diffraction peak due to Na$_2$S crystal was detected in the XRD pattern of Co(II)-montmorillonite-Na$_2$S (Fig. 1c). When the loading amount of Na$_2$S was increased (2:1 for the molar ratio of sulfide ion to interlayer cation of montmorillonite), the basal spacing did not increase further and the diffraction peaks due to unreacted Na$_2$S were detected in the X-ray diffraction pattern of the product. Since the gallery height of Co(II)-montmorillonite-Na$_2$S (ca. 1.3 nm) was not so much different from that of Co(II)-montmorillonite (ca. 1.5 nm) (Fig. 1d), the increase in the basal spacing may due to the hydration of montmorillonite occurred by humidity in air atmosphere and/or hydrated Na$_2$S during the solid-solid reaction.

By the heat treatment at 200°C for 1 h in air atmosphere, the basal spacing of heat treated product was slightly decreased to 1.19 nm which corresponds to the gallery height of 0.23 nm (Fig. 1b), suggesting the dehydration of adsorbed water. When the heat treated product was allowed to stand in air at room temperature for 4 months, the basal spacing of the heat treated sample was detected almost at the same $d$ value (1.19 nm) (Fig. 1a). The increase in the basal spacing and the change in the color of the intercalation compound suggested the intercalation of sulfide ion in the interlayer space of montmorillonite.

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\begin{align*}
\text{(a)} & : 1.25 \text{ nm} \\
\text{(b)} & : 1.19 \text{ nm} \\
\text{(c)} & : 1.48 \text{ nm} \\
\text{(d)} & : 1.25 \text{ nm}
\end{align*}
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Fig. 1 XRD patterns of Co(II)-montmorillonite-Na$_2$S (a) after storage for 4 months, (b) after heat treatment, (c) after reaction and (d) Co(II)-montmorillonite

The TG-DTA curve of Co(II)-montmorillonite-Na$_2$S is shown in Fig. 2 together with those of Co(II)-montmorillonite and Na$_2$S. The derivative of the TG curve, DTG curve, was also performed to show the change in the TG slope that may not be clear from the TG curve. Endothermic peaks owing to melting and vaporization of Na$_2$S at around 52, 91 and 194°C (Fig. 2f) were absent in the DTA curve of intercalation compound (Fig. 2e), implying that unreacted Na$_2$S were not contained in the intercalation compound. In the TG curve (Fig. 2b), three steps of weight losses were observed. The initial weight loss was observed from room temperature to 149°C for Co(II)-montmorillonite-Na$_2$S (Fig. 2b). In the corresponding DTA curve, the endothermic peaks at 46 and 77°C (Fig. 2e) were interpreted to the desorption of adsorbed and/or coordinated water. The second weight loss between 149 to 519°C was ascribed to the dehydration of retained water in the interlayer space of the intercalation compound. In the last weight loss between 519 to 793°C without significant endothermic or exothermic peak in the DTA curve (Fig. 2e) was attributed to the thermal decomposition of CoS (Qian et al., 1998) and the dehydroxylation of structural OH group (Guggenheim & Van Groos, 2001). In the corresponding DTG curve of intercalation compound (not shown), the last mass loss showed two processes of mass losses, indicating the oxidative decomposition of CoS and dehydroxylation of structural OH group of
montmorillonite. While the last mass loss at the same temperature range of Co(II)-montmorillonite (not shown) appeared only one process of mass loss, confirming the dehydroxylation caused by breaking of the hydroxyl group of montmorillonite. Thermal analysis results confirmed the intercalation of CoS in the interlayer space.

**Fig. 2** TG-DTA curves of (a, d) Co(II)-montmorillonite, (b, e) Co(II)-montmorillonite-Na$_2$S and (c, f) Na$_2$S

In situ formation and optical properties of CoS particle

The optical properties of the product were studied by UV-visible absorption and photoluminescence spectroscopies. The absorption spectra of the heat treated Co(II)-montmorillonite-Na$_2$S is shown in Fig. 3 together with that of the heat treated product after storage for 4 months. The diffuse absorption spectrum of heat treated Co(II)-montmorillonite-Na$_2$S (Fig. 3a) revealed the onset at 317 nm. When the heat treated intercalation compound was allowed to stand for longer period in air atmosphere at room temperature, the absorption spectrum appeared small absorption peak at 366 nm (Fig. 3b). It has been reported that a shoulder absorption of CoS particle revealed at 288 nm (Wang et al., 2005). Consequently, the band observed for the heat treated product can be attributed to CoS formed in the interlayer space of montmorillonite.

![Figure 3](image_url) Diffuse reflectance absorption spectra of heat treated Co(II)-montmorillonite-Na$_2$S (a) after heat treatment (200°C) and (b) after storage for 4 months

The photoluminescence spectra of heat treated intercalation compound after the heat treatment and after storage for 4 months are shown in Fig. 4. No luminescence band was observed for the intercalation compound (not shown) and heat treated intercalation compound (after the heat treatment) (Fig. 4a). After storage for 4 months, the emission band of the product was observed at 440 nm. While the non heat treated one, which was stored for the same period, did not demonstrate any new emission band. The appearance of photoluminescence band of the heat treated intercalation compound after storage for 4 months confirmed the formation of CoS particle in the interlayer space. The luminescence intensity of the product was weak, indicating that the impurities such as iron quenched the luminescence of CoS particle in montmorillonite (Ogawa & Kuroda., 1995).
Fig. 4 Photoluminescence spectra of heat treated Co(II)-montmorillonite-Na₂S (a) after heat treatment (200°C), (b) after storage for 4 months

Conclusions
CoS particle was formed in the interlayer space of montmorillonite via a solid-solid reaction between Co(II)-montmorillonite and sodium sulfide as well as subsequent heat treatment at 200°C. The appearance of UV-visible and PL bands was attributed to the formations of CoS incorporated in the interlayer space of montmorillonite. The novel synthetic route has been proved to be a facile and low temperature method to synthesize CoS in montmorillonite.

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References


