Applied Clay Science 43 (2009) 238–242

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Formation of MnS- and NiS-montmorillonites by solid-solid reactions

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ARTICLE INFO

Article history:
Received 11 April 2008
Received in revised form 19 July 2008
Accepted 22 July 2008
Available online 3 August 2008

Keywords:
Manganese sulfide
Nickel sulfide
Montmorillonite
Optical properties
Solid–solid reaction

ABSTRACT

MnS and NiS, which are a class of material used as a phosphor in thin film electroluminescence devices, formed in the interlayer spaces of montmorillonite by solid–solid reactions between powder of Mn(II)- or Ni(II)-montmorillonite and sodium sulfide at room temperature. The intercalation compounds were characterized by powder X-ray diffraction, transmission electron microscopy, thermal analysis, thermogravimetric-mass spectroscopy analysis, and Raman, UV–visible and luminescence spectroscopies. The present solid-state intercalation and *in situ* formation of metal sulfides in the interlayer spaces of montmorillonite are a feasible synthetic route to prepare metal sulfide-montmorillonite hybrid materials with novel nanostructure and properties.

1. Introduction

The intercalation of guest species into layered inorganic solids has attracted great interest in a wide range of fundamental scientific and application viewpoints (Whittingham, 1982; Ogawa, 2004). It is well known that organic and inorganic guest species can be easily penetrated into the interlayer spaces of smectites, a group of 2:1 layered clay minerals, to give intercalation compounds (van Olphen, 1977). As a consequence, the preparations, properties and possible applications of organically modified smectites have been extensively reported (Theng, 1974; Ogawa and Kuroda, 1995, 1997). Solid–solid reaction, which occurs between powders in the solid state, has been used partly because of the facile operation. Solid-state intercalation of both nonionic and cationic guest species into the interlayer spaces of layered clay minerals has been reported so far (Ogawa et al., 1991, 1992a,b, Bujdák and Slosiariková, 1992; Ogawa et al., 1993). Incorporations of diimines (2,2′-bipyridine (Ogawa et al., 1991), 4,4′-bipyridine (Khaorapapong et al., 2000, 2001) and 1,2-di(4-pyridine)ethylene (Khaorapapong et al., 2001)), thioacetamide (Khaorapapong et al., 2002a), 8-hydroxyquinoline (Khaorapapong et al., 2002b; Khaorapapong and Ogawa, 2007, 2008) and sulfide ion (Khaorapapong et al., 2008a,b) into smectites through solid–solid reactions and *in situ* complex formation with the interlayer exchangeable cations have been achieved.

Here, we report the formation of manganese sulfide (MnS) and nickel sulfide (NiS) into the interlayer spaces of montmorillonite. Metal sulfides nanomaterials have been attracted considerable interests due to their unique optical and electrical properties, and a wide variety of potential applications for electroluminescence (Lou et al., 2003) and nonlinear optical devices (Chin et al., 2001). Because the physical and optical properties of metal sulfides depend on their shape and size, the immobilization of metal sulfide particles in a spatially confined environment is a way to control the photophysical and photochemical properties of the formed particles as a result of morphological control. Accordingly, the encapsulation of MnS in a clinoptilolite, one of the most abundant natural zeolite, was conducted by the ion exchange reaction of Mn^{2+} and subsequent sulfidation with aqueous Na_2S solution at room temperature (Iacomi et al., 2003). NiS nanoparticles were also prepared in Y-zeolite by the ion exchange reaction of nickel ion and subsequent hydrothermal reaction between Ni-zeolite and thioacetamide (Zhai et al., 2002). The incorporation of CdS, ZnS and/or PbS into mesoporous silica (Chen et al., 1998; Zhang et al., 2001; Gao et al., 2001), layered metal oxides (Shangguan and Yoshida, 2002) and layered metal phosphate (Cao et al., 1991) has been reported so far. Besides the shape and size of the particles, their location and population should be controlled precisely, further study on the preparative method and characterization of the nanoparticle immobilized solid supports is worth conducting. In the present work, we utilized solid–solid reactions between Mn(II)- or Ni(II)-montmorillonite and sodium sulfide at room temperature and subsequent heat treatment to form MnS and NiS particles in the interlayer spaces of montmorillonite.

2. Experimental

2.1. Materials

Sodium montmorillonite (the reference sample of the Clay Science Society of Japan, JCSS-3101, Kunipia F, obtained from Kunimine, Japan)

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doi:10.1016/j.clay.2008.07.027

was used as a host material. The cation exchange capacity (CEC) was 1.19 meq/g. Sodium sulfide ($Na_2S{\cdot}xH_2O$) was obtained from Aldrich Co., Ltd. Manganese(II) chloride and nickel(II) chloride were purchased from Fluka Co., Ltd. and Univar Co., Ltd., respectively. All chemicals are analytical grade and were used as received.

2.2. Sample preparation

Mn(II)- and Ni(II)-montmorillonites were prepared from sodium montmorillonite by conventional ion exchange reactions using an aqueous solution of manganese(II) or nickel(II) chloride. The dispersion was allowed to react at room temperature for 24 h. The solids were washed repeatedly with deionized water (until the $AgNO_3$ test was negative) and dried at 40 °C for 3 days. Quantitative cation exchange of manganese(II) and nickel(II) ions was confirmed by inductively coupled plasma emission spectroscopy (ICP). The amounts were 0.99 and 0.93 meq/g for Mn(II)- and Ni(II)-montmorillonites, respectively. The intercalation of Na_2S into Mn(II)- or Ni(II)-montmorillonite was carried out by solid–solid reactions according to the method described in our previous works (Ogawa et al., 1991; Khaorapapong et al., 2000, 2001, 2002a,b, 2008a,b; Khaorapapong and Ogawa, 2007, 2008). The mixture of Mn(II)- or Ni(II)-montmorillonite and Na_2S was ground manually in an agate mortar at room temperature for 10–15 min. The molar ratio of sulfide ion (from Na_2S) to the interlayer cation of montmorillonite was 1:1. After the solid–solid reactions, all products were heated at 200 °C for 1 h in air atmosphere and allowed to stand in desiccator at room temperature for 4 months.

2.3. Characterization

Powder X-ray diffraction data were obtained on a Bruker D8 ADVANCE diffractometer using monochromatic CuKα radiation. TEM images were performed on a JEOL JEM-2010 transmission electron microscope with an accelerating voltage of 200 kV. Raman spectra were measured on a Jobin Yvon T64000 System Raman spectrometer with a 30 mW argon ion laser operating at 514 nm for excitation. Diffuse reflectance absorption spectra of the solid samples were collected on a Shimadzu UV–VIS–NIR-3101PC scanning spectrophotometer using an integrated sphere. TG–DTG–DTA curves were recorded with a Perkin Elmer Pyris Diamond TG–DTA instrument at a heating rate of 10 °C/min under a dry air flow using α-alumina (α-Al_2O_3) as a standard material. Thermogravimetric-mass spectroscopy analysis was performed on a Rigaku ThermoMass thermogravimetric-mass spectrometer (TG-DTA-MS) at a heating rate of 10 °C/min under a He flow. Inductively coupled plasma emission spectroscopic (ICP) data were taken with a Perkin Elmer Optima 2100DV spectrometer. Luminescence spectra were carried out on a Shimadzu RF-5301PC spectrofluorophotometer in the wavelength range of 300–900 nm with the excitation at 340 nm.

3. Results and discussion

The color of Ni(II)-montmorillonite due to the hydrated interlayer transition metal ion was changed from pale green to green by solid–solid reaction between Ni(II)-montmorillonite and Na_2S at the molar ratio of 1:1 (Ni^{2+}:S^{2-}). As reported in our previous study after the reaction with Na_2S, the color of Mn(II)-montmorillonite changed from brown to dark brown (Khaorapapong et al., 2008b) due to the change in the coordination state of the Mn(II) interlayer cations. The change in the color of the intercalation compound by solid–solid reaction was thought to be caused by the change in the coordination state of the interlayer exchangeable cations. The two intercalation compounds were referred to as Mn-montmorillonite–Na_2S and Ni-montmorillonite–Na_2S. The basal spacing of Mn-montmorillonite–Na_2S and Ni-montmorillonite–Na_2S (Table 1) was 1.27 and 1.28 nm, respectively. The gallery heights were 0.31 (Mn-montmorillonite–Na_2S) and 0.32 nm (Ni-montmorillonite–Na_2S) by subtracting the thickness of the silicate layer (0.96 nm) (Clementz et al., 1973) from the observed basal spacings. The XRD pattern of sodium sulfide (not shown) showed strong reflections due to crystalline Na_2S at $d = 0.19$, 0.30, 0.31 and 0.93 nm. No reflections of Na_2S were seen in the XRD patterns of the products. When the loading amounts of sulfide ions were increased (Mn^{2+} or Ni^{2+}:S^{2-} = 1:2), the basal spacing did not increase further and the reflections of unreacted Na_2S were detected in the X-ray diffraction patterns of the products. The increase in the basal spacing caused by the intercalation of Na_2S and/or the formation of MnS or NiS did not affect the interlayer spacing of the hydrated Mn(II)-montmorillonite or Ni(II)-montmorillonite. The basal spacing of hydrated smectites (from 1.2 to 1.8 nm) is depending on the amount of adsorbed water in the interlayer spaces. The basal spacings of 1.5–1.8 nm were related to bilayers of adsorbed water and those of 1.2–1.4 nm were ascribed to monolayers (Clementz et al., 1973). Since the basal spacing of Mn-montmorillonite–Na_2S (1.27 nm) and Ni-montmorillonite–Na_2S (1.28 nm) was not so much different from those of Mn(II)-montmorillonite (1.48 nm, Fig. 1c) and Ni(II)-montmorillonite (1.48 nm, Fig. 1d), the increase in the basal spacing may be due to the change in the hydration of montmorillonite.

By the heat treatment at 200 °C for 1 h in air atmosphere, the basal spacing of Mn-montmorillonite–Na_2S and Ni-montmorillonite–Na_2S (Table 1) was close to those of the as-synthesized intercalation compounds. The observed basal spacing of the heated Mn-montmorillonite–Na_2S was 1.25 nm as reported in the preliminary communication (Khaorapapong et al., 2008b). The expansion of the interlayer space was 0.29 nm. After the heat treatment, the basal spacing of Ni-montmorillonite–Na_2S was 1.22 nm, corresponding to a gallery height of 0.26 nm. When the heated Mn-montmorillonite–Na_2S and Ni-montmorillonite–Na_2S were allowed to stand in air at room temperature for 4 months (Fig. 1a, b and Table 1), the basal spacings of the samples did not change (ca. 1.2 nm). We concluded that the increase in the basal spacings and the change in the colors of the products were caused by the intercalation of Na_2S and the *in situ* formation of MnS and NiS in the interlayer spaces of montmorillonite.

Table 1
Basal spacings of as-synthesized, heated (200 °C) and stored (4 months) samples

Sample	Basal spacing (nm)		
	After reaction[a]	After heat treatment	After 4 months
Mn(II)-montmorillonite	1.48	–	–
Ni(II)-montmorillonite	1.48	–	–
Mn-montmorillonite–Na_2S	1.27	1.25	1.23
Ni-montmorillonite–Na_2S	1.28	1.22	1.23

[a] At room temperature.

TEM images of heated Mn– and Ni-montmorillonite–Na_2S (Fig. 2a and b) after storage for 4 months showed the edge of silicate layers with embedded MnS or NiS particles. The MnS or NiS particles showed a darker contrast than the silicate layer due to diffraction effects. The presence of some particles on the external surface of the montmorillonite was also observed. The single MnS or NiS particles in the interlayer spaces were round shaped with an average size of 2–6 nm and the particles were accumulated to form larger MnS or NiS aggregate. Since the microenvironments of MnS and NiS formed in the interlayer spaces of montmorillonite are different from those of the MnS (Lu et al., 2001; Zhang et al., 2006) or NiS free particles (Sadjadi et al., 2006), the distribution and accumulation of the particle size are still difficult to elucidate. Taking the gallery height of the heat-treated product (ca. 0.3 nm) and the estimated size of ca. 2–6 nm, the MnS or NiS particles with the height of ca. 0.3 nm and diameter (length/width) of ca. 2–6 nm probably were arranged in monolayers with the length/width plane parallel to the silicate layer.