Research paper

Preparation of copper oxide in smectites

Nithima Khaorapapong [a,*], Nuttaporn Khumchoo [a], Makoto Ogawa [b]

[a] Department of Chemistry, and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand
[b] Department of Earth Sciences, and Graduate School of Creative Science and Engineering, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan

ARTICLE INFO

ABSTRACT

Copper oxide nanoparticles were prepared in the interlayer spaces of sodium- and cetyltrimethylammonium–smectites by a titration of an aqueous solution of copper nitrate at 70 °C in the presence of dispersed smectites. The resulting hybrids were characterized by powder XRD, SEM, TEM, TG-DTA, as well as FT-IR and UV–visible spectroscopies. A massive blue shift (from 490 nm to 232–478 nm) of the UV–visible absorption observed for the hybrids confirmed the formation of nanometer-sized copper oxide (3–7 nm) in the interlayer spaces. A small amount of larger CuO particle with the size of around 0.6–2.9 μm formed at the external surface of clay mineral particles. The nature of the broad absorption band (at around 490 nm) of pure copper oxide and the hybrids with high copper oxide loading was attributed to the overlapping of the Cu^{2+} to O^{2-} charge transfer as well as d–d transition of copper oxide. The interactions with smectites played a role in stabilizing and protecting the formed copper oxide nanoparticles.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The interests in the preparation of organic–inorganic and inorganic–inorganic hybrid materials, aiming to combine the advantages of the two components as well as to modify the properties of components, have been significantly increased in the fields of materials chemistry (Ogawa et al., 1998; Ogawa, 2004). The hybridization (intercalation) of layered solids and appropriate guest species offers a promising way for developing hybrids with desired functions. (Ogawa and Kuroda, 1995; Ogawa and Kuroda, 1997; Lagaly et al., 2006; Okada and Ogawa, 2011; Okada et al., 2012; Ide et al., 2013; Ogawa et al., 2014) Among possible layered inorganic solids, smectite, a 2:1 layered clay mineral, has been used to accommodate various functional species for constructing nanohybrids because of its useful characters such as large surface area, swelling behavior, ion exchange and adsorption for the guest accommodation (van Olphen, 1977; Lagaly et al., 2006).

Among available host–guest complexes of smectite, those with inorganic nanoparticles on and in the layered structure are materials investigated extensively for the applications as adsorbents and catalysts. (Gil et al., 2010) Because the size and shape of the nanoparticles are sensitive to the surrounding environment during their preparation, the immobilization of nanoparticles on various smectites and under different conditions has been conducted so far (Lagaly et al., 2006) to optimize the structures and properties of smectite-nanoparticle hybrids. The preparation of hybrids of smectites containing metal oxide and metal chalcogenide nanoparticles have been reported so far (Dékány et al., 1999; Németh et al., 2003; Kun et al., 2006; Khaorapapong and

Ogawa, 2011; Khaorapapong et al., 2011; Ontam et al., 2011, 2012a, 2012b).

In the present study, the preparation of copper oxide with varied loading amounts in the presence of sodium and cetyltrimethylammonium–smectite was investigated as a way of morphology controlled synthesis of copper oxide. Copper oxide, a p-type semiconductor with a narrow band gap (1.2 eV), has received attention over the past decades because it exhibits a wide range of useful properties for the applications in electronic and optoelectronic devices, such as solar cell, gas sensor, photocatalyst, and magnetic storage media (Li et al., 2004; Liu et al., 2006a, 2006b; Zhang et al., 2006; Yang et al., 2007). The nanosized copper oxide has been prepared from a solution by such elaborated methods as microwave irradiation, precipitation method and hydrothermal reaction, using fashionable instruments or hazardous solvents (Wang et al., 2002; Zhu et al., 2004; Liu et al., 2006a, 2006b). The incorporation of copper oxide in mesoporous silicas has been reported by ion exchange and subsequent calcination to control the size and morphology of copper oxide within the pore for the optimized catalytic functions (Li and Gao, 2003; Hao et al., 2006; Maji et al., 2010; Suh and Ihm, 2010; Wang et al., 2012; Wang et al., 2012; Nezamzadeh-Ejhieh and Karimi-Shamsabadi, 2013, 2014). The immobilization on solid supports may improve the stabilities of the guest.

The introduction and catalytic activity of CuO complexed with such clay minerals as sepiolite and attapulgite have also been reported (Cao et al., 2008; Chen et al., 2011). The immobilization of CuO in layered materials, which are expandable along the z axis, may lead to a variety of unique structure and properties. The complexation of CuO with layered double hydroxide (LDH) has been reported so far (Carja, et al., 2013). Recently, the preparation of CuO–montmorillonite by thermal decomposition of $CuSO_4 \cdot 3Cu(OH)_2$–montmorillonite and its antibacterial

* Corresponding author. Tel.: +66 4320 2222 41x12370 2; fax: +66 4320 2373.
E-mail address: nithima@kku.ac.th (N. Khaorapapong).

activity was reported (Sohrabnezhad et al., 2014). These successes motivated us to investigate the preparation of CuO–smectites using smectites with different types and modification, and with varied CuO amounts, which is a way for the optimization of material performances in various applications.

2. Experimental

2.1. Materials

Na-montmorillonite (a reference clay mineral sample of the Clay Science Society of Japan, JCSS-3101; Kunipia F, which is a natural montmorillonite and a product of Kunimine Industries Co., Japan) and Na-saponite (a reference clay mineral sample of the Clay Science Society of Japan, JCSS-3501; Sumecton SA, which was synthesized hydrothermally by Kunimine Industries Co., Japan) were used as the host materials. The cation exchange capacity (CEC) was 1.19 and 0.70 meq/g of montmorillonite and saponite, respectively. Copper nitrate ($Cu(NO_3)_2 \cdot 2.5H_2O$) was purchased from Univar and sodium hydroxide was supplied by Carlo Erba Regenti. Cetyltrimetylammonium bromide (CTAB) was obtained from Fluka. All chemicals were used as received and all experiments were carried out using deionized water.

2.2. Sample preparation

Copper oxide (CuO) was prepared by the reaction between an aqueous solution of copper nitrate and a sodium hydroxide solution, which was done with magnetic stirring at 70 °C in air atmosphere for 3 h. The black solid sample was collected by centrifugation and washed repeatedly with deionized water to get rid of excess reactants. The molar ratio of Cu^{2+}:OH^- in the aqueous solutions of the CuO precursors (copper nitrate and sodium hydroxide) was 1:10. Organically modified smectites (CTA-montmorillonite and CTA-saponite) were obtained by cation exchange of sodium–smectites using an aqueous CTAB with the amount of CTAB equal to the cation exchange capacity (1.19 and 0.70 meq/g of clay minerals for montmorillonite and saponite, respectively). The hybridization of CuO with smectites was done by adding an aqueous solution of copper nitrate and a sodium hydroxide solution into the colloidal dispersion of the hosts. The mixture was stirred at 70 °C in air atmosphere for 3 h. The loading amount of Cu^{2+} was 1, 3 and 12 times with respect to the CEC of smectites. After the reactions, the black or gray solids were separated by centrifugation, washed repeatedly with deionized water to remove the excess surfactant, as well as bromide and nitrate ions that might be contained, and then dried at 40 °C for 3 days. Hereafter, the products were named as CuO@montmorillonite(n), CuO@saponite(n), CuO@CTA-montmorillonite(n) and CuO@CTA-saponite(n), where n denoted the CuO loading (versus CEC).

2.3. Characterization

Crystalline structure of the samples was studied by powder X-ray diffraction technique using a Bruker D8 ADVANCE diffractometer with monochromatic CuKα radiation in a 2θ range of 2–80°. TG-DTA curves were recorded on a Rigaku Thermoplus TG 8120 at a heating rate of 10 °C min^{-1} under a dry air flow using α-alumina (Al_2O_3) as the standard material. Fourier transform-infrared spectra were performed on a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr pellet in the wavenumber range of 400–4000 cm^{-1}. Particle morphology of the products was examined with a Hitachi S-2380N scanning electron microscope. TEM images were taken on the Tecnai G^2 20 LaB6 with an accelerating voltage of 200 kV. Diffuse reflectance spectra of the solid samples were recorded on a Shimadzu UV–vis-NIR-3101PC spectrophotometer using an integrated sphere. Nitrogen adsorption–desorption isotherms were measured on a BELSORP mini instrument, BEL Japan, Inc., after the sample was degassed at 120 °C under a vacuum for 3 h.

3. Results and discussion

3.1. Hybridization of CuO with smectites and CTA-smectites

As a result of the reaction between sodium smectites or CTA-smectites and the aqueous solutions of copper salt, black and gray colored solids were obtained (the color is shown in Fig. 1), which indicated the formation of CuO. The color variation observed for the hybrids was assumed to the difference of the amount as well as size and shape of formed CuO.

The XRD pattern of the as-prepared CuO (Fig. S1) was characterized by three main reflections located at $d = 0.25$, 0.23 and 0.18 nm, which were indexed as (110), (002), and (111) planes of monoclinic phase of CuO (JCPDS No. 48-1548) (Xia et al., 2009). No other reflections due to the starting materials and such impurities as oxides and hydroxides of copper were seen in the XRD pattern, indicating that the added copper ion was transformed into CuO.

The basal spacings of the hybrids (CuO@montmorillonite(n), CuO@saponite(n), CuO@CTA-montmorillonite(n), and CuO@CTA-saponite(n)) are summarized in Table 1 (XRD patterns of all products are also shown in Figs. 2 and S2). The (001) reflections of CuO@montmorillonites, CuO@saponites, and CuO@CTA-saponites were ca. 1.4–1.5 nm, while those of CuO@CTA-montmorillonites were ca. 2 nm. The expansions of the interlayer spaces of the hybrids were obtained by subtracting the thickness of silicate layer (0.96 nm) from the observed basal spacings, which are also summarized in Table 1. The XRD patterns of CuO@smectite(1) and CuO@CTA-smectite(1) obtained with the lowest CuO loading did not show any reflections due to monoclinic phase of CuO, indicating that the expansion of the interlayer space was affected by the intercalated species including CuO and/or CTA cation. CuO crystal possibly formed on the external surfaces of smectites, however, the quantity was too small to be detected by present powder XRD analysis of CuO@smectite(1) and CuO@CTA-smectite(1).

On the contrary, the XRD patterns of CuO@smectite(3), CuO@smectite(12), CuO@CTA-smectite(3), and CuO@CTA-smectite(12) showed the (110), (002), and (111) reflections ascribable to monoclinic CuO, showing the presence of CuO crystals on the external surface of smectites. The CuO@CTA-montmorillonite(1), (3), and (12) showed the larger expansion of interlayer spaces (ca. 2 nm), which was thought to be caused by the co-existence of CTA cation with the formed CuO. The interlayer CTA cations were thought to arrange as pseudo-trimolecular layers in montmorillonite ($d_{001} \sim 2.0$ nm). The CTA ion tend to orient as a lateral monolayer or a partial distortion of the alkyl chain to the silicate layers of saponite ($d_{001} \sim 1.3$–1.5 nm) (van Olphen, 1977; Lagaly et al, 2006; Bisio et al., 2011). The interlayer space of the hybrids did not expand further after the formation of CuO, implying that the CuO nanoparticle was embedded at the free space around the CTA cation. Though, it is very difficult to characterize the interactions between CuO and CTA as well as the detailed conformation of CTA close to the CuO, it was thought that the CuO formed by the intercalation of the CuO precursors (Cu^{2+} and OH^-) to form CuO subsequently in the interlayer space. The intercalated CuO nanoparticles, which have a smaller size than the ones formed on the external surface, may exhibit unique optical property and stability due to the nano-size and nano-confinement effects.

Due to the low surface area of sodium montmorillonite (ca. 10 m^{2}g^{-1}), after the intercalation of CTA and/or CuO, the BET surface area did not change so much. Saponite showed the larger BET surface area than montmorillonite. The surface area of saponite (199 m^{2}g^{-1}) dramatically decreased after the reaction with CTA and CuO to be 43 m^2 g^{-1} for CuO@CTA-saponite(12), 25 m^2 g^{-1} for CuO@CTA-saponite(1), and 15 m^2 g^{-1} for CuO@CTA-saponite(3), which was much smaller than that of pristine saponite (ca. 199 m^2 g^{-1}). Because of the card-house structure, the BET surface area of sodium saponite and the hybrids of CuO with sodium saponite were determined to be around 199 and 140–150 m^2 g^{-1}.