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Note

Surfactant intercalated α-hydroxides of cobalt and nickel and their delamination-restacking behavior in organic media

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Abstract

Dodecyl sulfate and dodecylbenzene sulfonate intercalated α-hydroxides of nickel and cobalt were synthesized by ammonia precipitation. These solids delaminate to give a colloidal dispersion of layers in organic solvents such as 1-butanol. The dispersed layers could be reassembled either by evaporation of the colloid or by coagulation by the addition of a polar solvent.

Keywords: α-Nickel hydroxide; α-Cobalt hydroxide; Intercalation; Delamination; Colloidal dispersion

1. Introduction

Delamination of layered solids leads to highly dispersed phases, which form the basis of synthesis of novel layered composites and mesoporous solids with unique properties [1,2]. Usually delamination is carried out in solvents, where intercalation of a large number of solvent molecules between the layers increases the distance between the layers to such an extent that each layer behaves like an independent particle. By vigorous stirring, complete separation of layers could be achieved to form colloidal dispersion of layers. This colloidal dispersion is thermodynamically unstable with respect to reflocculation but may be stabilized by appropriate choice of solvent and/or pH [3].

Delamination of different types of layered solids has been studied extensively [3]. Exfoliation of layered structures such as graphite [4], MS_2 (M = Mo, W, Ti) [5], layered phosphonates [6,7], and clays [8] has been achieved by manipulation of interlayer interactions.

Among the clays, cationic clays, also known as smectites, which consist of negatively charged aluminosilicate layers and interlayer cations swell and delaminate readily in aqueous medium due to their low layer charge density. Anionic clays that consist of positive metal hydroxide layers and interlayer anionic species do not delaminate in aqueous medium due to their high layer charge density. Dense interlayer hydrogen bonding leads to tight stacking of the layers, making delamination difficult.

Exchange of interlayer inorganic anions of anionic clays for organophilic anions takes place readily [9]. Introduction of such species weakens the stacking of the layers and favors interaction with organic solvents, thus enhancing delamination in organic media. Adachi-Pagano et al. first reported the delamination of surfactant intercalated layered double hydroxides (LDHs) in organic media [10,11]. Following this work, delamination of different LDHs in organic media by various approaches has been reported [12–14].

We are interested in investigating the organic-delaminable anionic clays. We have recently reported the delamination behavior of hydroxy double salts, which are similar in struc-

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ture to LDHs [15]. In this work, we study the delamination behavior of α-hydroxides, another class of compounds that can be considered as anionic clays.

Hydroxides of divalent metals, especially those of the first transition series, crystallize as layered structures. Divalent hydroxides of the formula $M(OH)_2$ [M = Ni, Co, Fe] are isostructural with the mineral brucite, $Mg(OH)_2$, and consist of hexagonal packings of hydroxyl ions with M^{2+} ions occupying alternate rows of octahedral sites [16]. The hydroxides of Co(II) and Ni(II) are extensively studied as they are widely employed as electrode materials in alkaline secondary batteries [17,18]. Studies on the delamination behavior of these solids will form the basis of developing novel composites with enhanced electrochemical properties.

The hydroxides of nickel and cobalt crystallize in different polymorphic modifications, mainly the β- and the α-form [19,20]. The β-form is of the formula $M(OH)_2$ and it is an ordered stacking of neutral layers of the composition $[M(OH)_2]$ with an interlayer spacing of 4.6 Å. The α-form is a hydroxyl-deficient compound and consists of a stacking of positively charged layers of composition $[M(OH)_{2-x}(H_2O)_x]^{x+}$, which intercalate anions such as NO_3^-, Cl^-, OAc^-, SO_4^{2-} along with water molecules in the interlayer region to restore charge neutrality [21]. Consequently, the α-hydroxides have a larger interlayer spacing, which varies with the size of the interlayer anion.

In this paper, we describe the synthesis of surfactant-intercalated α-hydroxides of nickel and cobalt, delamination of these α-hydroxides in organic solvents, and restacking of dispersed layers to recover the parent solids.

2. Experimental

2.1. Synthesis

Surfactant-intercalated α-divalent metal hydroxides were prepared by the addition of 35 ml of a solution containing metal acetate, $M(OAc)_2$ [M = Ni, Co], and the surfactant [dodecylsulfate (DS) or dodecylbenzene sulfonate (DBS)] in the mole ratio 1:0.9 in 50 ml of 0.5 M NH_3 solution with constant stirring. The solid product formed was immediately centrifuged, washed free of anions with water followed by acetone, and dried in air at room temperature.

2.2. Delamination and restacking

The delamination of the DS or DBS intercalated α-hydroxide was carried out by subjecting a mixture of 25 mg of the sample and 100 ml of the solvent (1-butanol, 1-octanol, or 1-decanol) to sonication at 80 °C for 2 h. The dispersion was then centrifuged at 2000 rpm to remove any undispersed solid and the stability of the resulting translucent colloidal dispersion was studied by allowing it to stand undisturbed for several days at room temperature.

The dispersed monolayers of α-hydroxides were restacked by adding 100 ml of acetone to 100 ml of the colloidal dispersion. Coagulation occurs slowly and most of the solid settles down within 24 h. The settled product is washed with acetone and dried in air at room temperature. Restacking was also carried out by slowly evaporating the colloidal dispersion at 65 °C until the solvent was removed completely.

2.3. Characterization

All the samples were characterized by chemical analysis, powder X-ray diffraction (Philips X'pert Pro, Cu$K\alpha$ radiation, secondary graphite monochromator, 2° 2θ per minute), infrared spectroscopy (Nicolet Impact 4000 FTIR spectrometer, KBr pellets, resolution 4 cm^{-1}), and thermogravimetry (Mettler Toledo STAR^e SW 7.01, under N_2 flow, 5 °C per minute). The as-prepared and restacked samples were also characterized by transmission electron microscopy (JEOL 200CX) operated at 160 kV. In situ X-ray diffraction of the colloidal dispersions was carried out in order to understand the nature of the colloids.

3. Results and discussion

The pXRD patterns of the as-prepared surfactant-intercalated α-hydroxides are shown in Fig. 1. DS and DBS intercalated α-cobalt hydroxides (Figs. 1a and 1b) are moderately ordered along the layer stacking direction, as we observe in a number of 00ℓ reflections. The basal spacings calculated from these reflections are 25.82 and 30.19 Å, respectively for DS and DBS intercalated α-cobalt hydroxides. These values confirm the incorporation of the surfactant anions. The alkyl

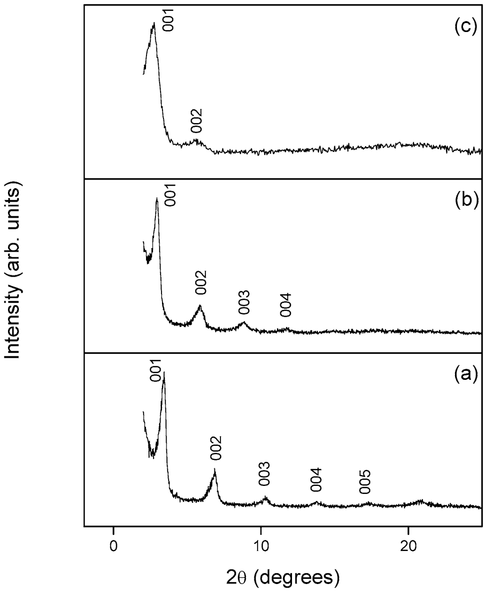

Fig. 1. pXRD patterns of the as-prepared DS (a) and DBS (b) intercalated α-cobalt hydroxides and DS intercalated α-nickel hydroxide (c).