

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], MS₂ (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 re-stacked 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, $CuK\alpha$ radiation, secondary graphite monochromator, $2^\circ 2\theta$ 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

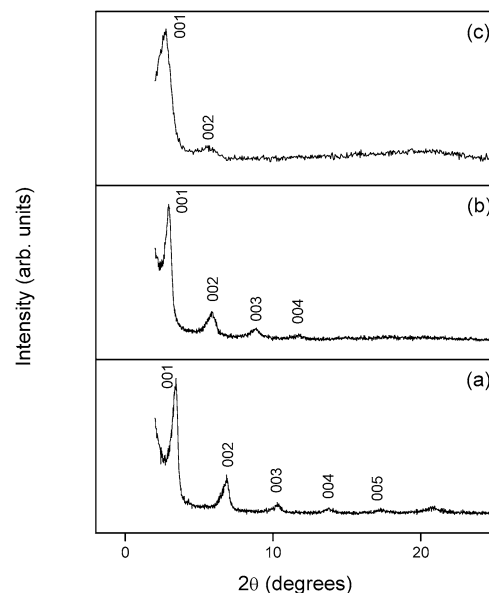


Fig. 1. pXRD patterns of the as-prepared DS (a) and DBS (b) intercalated α -cobalt hydroxides and DS intercalated α -nickel hydroxide (c).

chains of the anions are approximately perpendicular to the slabs and these chains of adjacent layers interpenetrate each other. DS intercalated α -nickel hydroxide (Fig. 1c) shows only two $00l$ reflections, unlike the cobalt analogue, suggesting that this sample is very poorly ordered along the stacking direction. All efforts to improve the crystallinity failed. The basal spacing is 31.5 Å, which is ~ 6 Å larger than the cobalt analogue. It is possibly due to stacking disorders and presence of extra water molecules in the interlayer region. The wet chemical analysis of the samples yields the nominal formula $M(\text{OH})_{1.67}(\text{surf})_{0.33}\cdot m\text{H}_2\text{O}$, where $M = \text{Ni}$ or Co , $\text{surf} = \text{DS}$ or DBS , and $m = 1.1$ for Co samples and 1.5 for Ni samples.

Fig. 2 shows the IR spectra of DS (Fig. 2a) and DBS (Fig. 2b) intercalated α -cobalt hydroxides. In both the cases, we observe strong and broad absorption at 3500 cm^{-1} due to hydrogen-bonded hydroxyl groups. C–H stretching vibrations of alkyl chains of the surfactant and S=O stretching vibrations of the sulfate group are observed around 2850–2920 and 1200 cm^{-1} , respectively. The absorption bands at 1000, 1010, and 1100 cm^{-1} are due to the *para* disubstituted aromatic ring in case of the DBS intercalated α -cobalt hydroxide. The nature of the C–H stretching absorption band suggests that the alkyl chains take up an all *trans* confirmation [22]. We observe strong peaks at 2850 and 2920 cm^{-1} . If the chains were disordered, the peak at 2920 cm^{-1} will be broad and almost absent.

The thermogravimetric curves along with the respective derivative curves for the DS and DBS intercalated α -cobalt hydroxides are shown in Fig. 3. The DS intercalated sample (Fig. 3a) shows a four-step weight loss pattern. The first step, which occurs from 50 to 150°C , may be attributed to the loss of adsorbed and interlayer water and the remaining steps correspond to the decomposition of the hydroxyl and the surfactant. The thermogravimetric curve for the α -nickel

hydroxide (Fig. 3b) shows three steps, the first step corresponding to the removal of adsorbed and interlayer water and the other steps corresponding to the decomposition of the hydroxyl lattice and the interlayer surfactant anion. The net weight losses observed in both cases match well the nominal formulae of the compounds.

Delamination of the surfactant anion intercalated α -hydroxide in organic solvents such as 1-butanol, 1-octanol, and 1-decanol was observed after sonication at 80°C . The translucent colloids thus obtained were found to be stable for a few weeks. About 0.25 g of the layered solid could be dispersed through delamination in 1 L of 1-butanol. The extent of delamination and the stability of the colloid obtained were the same for both the DS and DBS intercalated Ni and Co hydroxides. Though the extent of ordering along the *c*-direction is different for Ni and Co hydroxides, these solids showed identical delamination behavior, indicating that the order or the lack of it along the stacking direction does not influence the delamination behavior strongly in these systems. Similar colloids were obtained when either the sample was stirred at room temperature for 24 h in the solvent or when the sample was refluxed in the solvent for 4 h. Though the extent of dispersion in these methods was comparable to that in sonication, the colloids obtained were less stable. While the colloids obtained through sonication are stable for a few weeks, those obtained through refluxing in the solvent or stirring with the solvent at room temperature are stable only for a few hours. The in situ XRD of the colloid obtained by dispersing DS intercalated α -cobalt hydroxide is shown in Fig. 4a. The complete absence of $00l$ reflections confirms that the layers have come apart and behave as independent particles.

The parent layered solid could be obtained from the colloidal dispersions either by evaporation of the colloid or by flocculation through addition of a polar solvent such as ace-

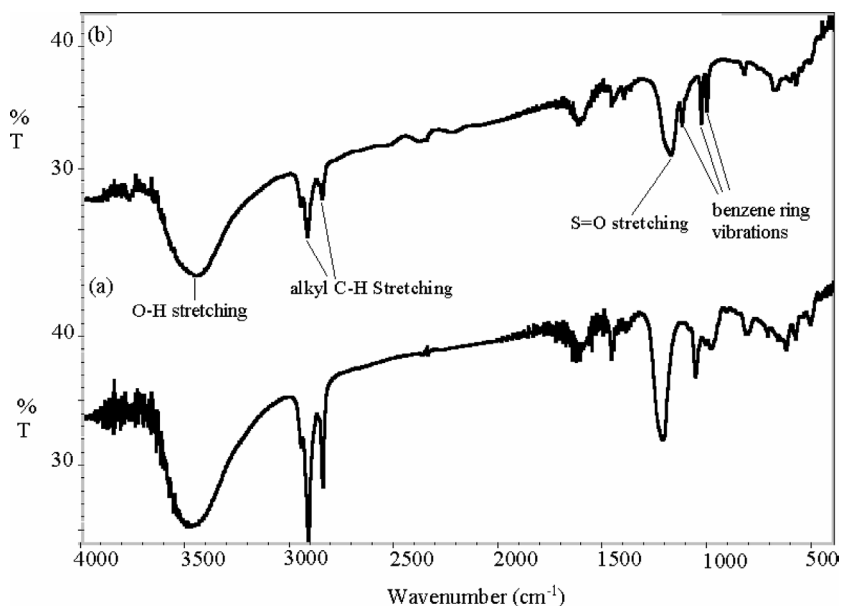


Fig. 2. IR spectra of the as-prepared DS (a) and DBS (b) intercalated α -cobalt hydroxides.

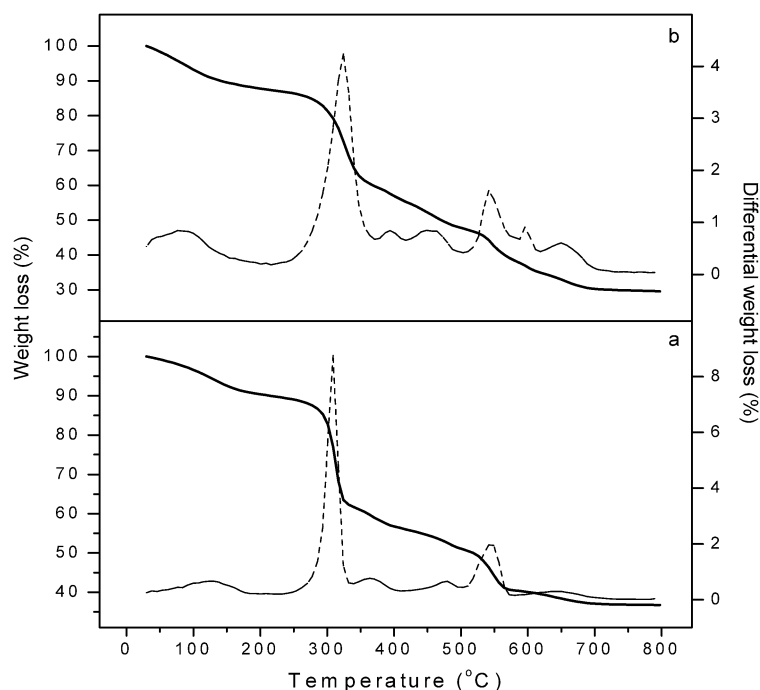


Fig. 3. Thermogravimetry curves (along with the derivative curves) of the as-prepared DS intercalated α -cobalt hydroxide (a) and α -nickel hydroxide (b).

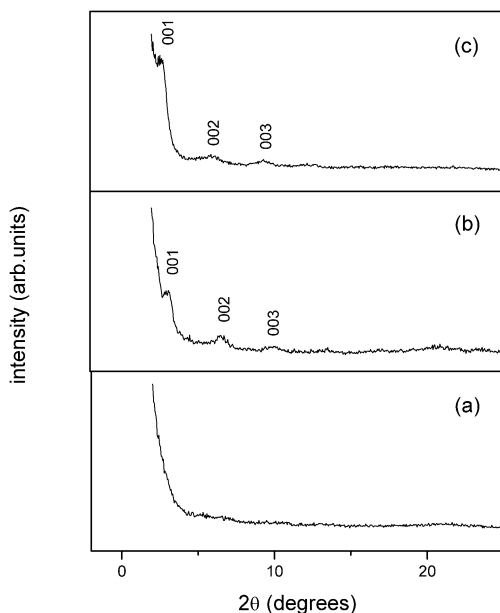


Fig. 4. In situ XRD pattern of the colloidal dispersion of DS intercalated α -cobalt hydroxide (a) and the pXRD patterns of the reassembled samples obtained by adding acetone into the colloids formed from DS intercalated α -cobalt hydroxide (b) and DBS intercalated α -cobalt hydroxide (c).

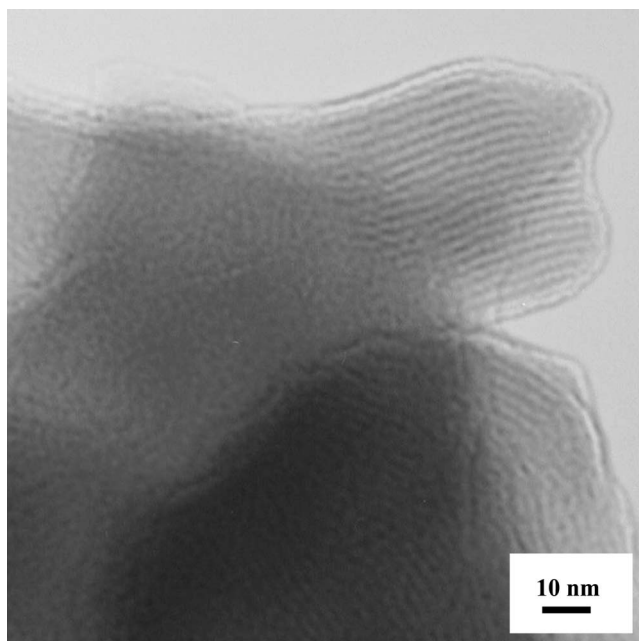
tone. The pXRD patterns of the reassembled DS and DBS intercalated α -cobalt hydroxide samples obtained by flocculation using acetone shown in Figs. 4b and 4c are identical to that of the parent solids, except that the samples are less ordered along the stacking direction, as indicated by the absence of many $00l$ reflections and higher broadening of the observed $00l$ reflections.

TEM investigations were carried out to observe the nature of layer stacking of the compounds. Figs. 5a and 5b are bright field images from an as-prepared sample and a delaminated and restacked DS intercalated α -cobalt hydroxide sample, respectively. Fig. 5a shows that the as-prepared sample is well ordered and shows a layer spacing of about 2.6 nm, which is consistent with the spacing obtained from pXRD. The restacked sample, on the other hand, shows considerable disorder and the size of the ordered regions is on the order of a few tens of nanometers. This is also in agreement with the XRD results, which show poor ordering and broadening of the $00l$ lines.

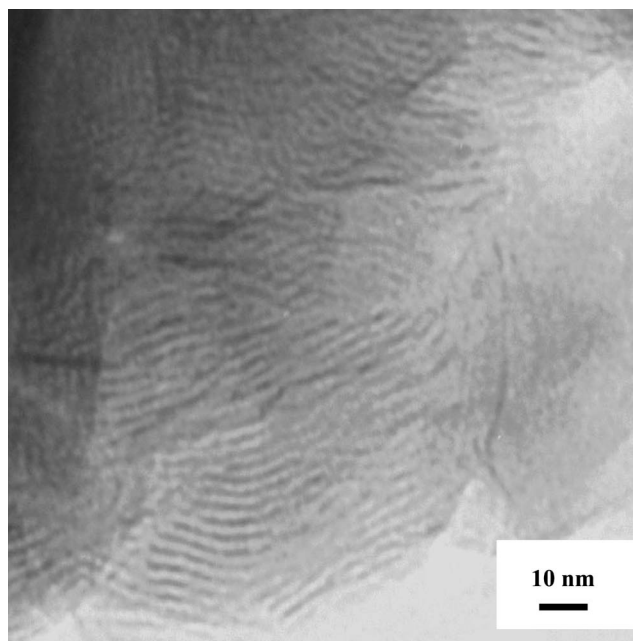
In conclusion, surfactant-intercalated α -hydroxides of cobalt and nickel show delamination-restacking behavior like that of surfactant intercalated LDHs, but here the restacked samples are poorly ordered. This may be attributed to the fact that α -hydroxides are not as stable as LDHs. The colloidal dispersions obtained from these metal hydroxides are made of independent monolayers. The colloidal dispersions of hydroxides obtained here are potential precursors for oxide nanoparticles and composites such as $\text{Ni}(\text{OH})_2$ -graphite and $\text{Ni}(\text{OH})_2$ - $\text{Co}(\text{OH})_2$, which would find applications in alkaline batteries.

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(a)



(b)

Fig. 5. TEM images of (a) as-prepared and (b) restacked DS intercalated α -cobalt hydroxide samples.

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