Controlling of morphology of Ni/Al-LDHs using microemulsion-mediated hydrothermal synthesis

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Abstract. A quaternary microemulsion, cetyltrimethylammonium bromide (CTAB)/water/*n*-hexane/*n*-hexanol, was selected for the synthesis of Ni/Al-layered double hydroxides (LDHs). Ni/Al-LDHs with nanowire-, spherical-, rod- and tube-like morphologies were prepared via the microemulsion-mediated hydrothermal synthesis. The CTAB concentration played an important role in determining the morphology of Ni/Al-LDHs. The structure, composition and morphology of the obtained Ni/Al-LDH nanostructures were investigated by X-ray diffraction, inductively coupled plasma emission spectroscopy, infrared spectrometer and transmission electron microscopy. A possible formation mechanism of Ni/Al-LDH nanostructures is proposed.

Keywords. Nanostructures; chemical synthesis; TEM; microstructure.

1. Introduction

Layered double hydroxides (LDHs) are a group of synthetic anion clays, characterized by the formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$ (where M = metal and A = anion) (Cavani *et al* 1991; Bellotto *et al* 1996; Jayashree *et al* 2002). They have a layered structure, with positively charged brucite-like sheets, where M^{II} and M^{III} are octahedrally coordinated. The excess charge is balanced by anions as CO_3^{2-} , SO_4^{2-} , NO_3^- situated in the interlayer. LDHs themselves have attracted a great deal of interest as anion exchangers, ionic conductors, and additives for various polymers and other functional materials (Cavani *et al* 1991; Zhao *et al* 2003). Mixed oxides obtained from the LDH precursors have been found to have application as adsorbents, catalysts, and pigments, as well as usefulness in sensor and magnetic technologies (Lee and Lee 2002; Zhao *et al* 2002, 2005). Due to the importance of composition, size and morphology on these functions, it is of particular importance that research into the nanostructure of the LDHs be performed.

Microemulsion systems have been widely used as an ideal media for the preparation of nanoparticles (Feng *et al* 2000; Chen and Wu 2002). In particular, a water-in-oil (w/o) microemulsion has been used, consisting of a transparent and isotropic liquid medium with nanosized water pools, dispersed in a continuous phase and stabilized by surfactant and cosurfactant molecules at the water/oil interface. These water pools offer ideal microreactors for the formation of nanoparticles. Furthermore, many compounds in 1D nanostructures such as ZnO, BaCO₃,

CdS have also been prepared using various microemulsion methods (Zhang *et al* 2002; Zhang and Gao 2003; Cao *et al* 2003).

In this paper, microemulsion-mediated hydrothermal synthesis of Ni/Al-LDHs is explored, along research into the controllability of the morphology of Ni/Al-LDHs. Furthermore, the relationship between percentage of surfactant and the morphology of LDHs is also investigated.

2. Experimental

2.1 Synthesis of Ni/Al-LDHs

A quaternary microemulsion, cetyltrimethylammonium bromide (CTAB)/water/*n*-hexane/*n*-hexanol, was selected for the synthesis of Ni/Al-LDHs. As a typical synthesis, a solution was prepared by dissolving 1.45–1.75 g of CTAB in 34 ml of *n*-hexane and 4 ml of *n*-hexanol. The solution was stirred for 30 min until it became transparent. Next, 2 ml of 0.1 M solution containing the sulfates of the elements (Ni/Al = 3/1 (molar ratio)) and 2 ml of 0.3 M urea aqueous solution were added to the solution. After substantial stirring, the resulting microemulsion solution was then transferred into a 50 ml stainless Teflon-lined autoclave and heated at 200°C for 12 h, then cooled to room temperature. The final precipitate was centrifuged, washed with propanone and ethanol, and then dried.

2.2 Characterization methods

Powder XRD patterns of Ni/Al-LDHs were recorded on a Rigaku XRD-6000 diffractometer under the following

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Table 1. Selected data for Ni/Al-LDHs.

CTAB concentration (wt%)	3.5	3.8	4.2	4.4
Ni/Al molar ratio	2.68 : 1	2.71 : 1	2.71 : 1	2.55 : 1
d_{003} (nm)	0.7973	0.7866	0.7961	0.7985
d_{006} (nm)	0.3913	0.3906	0.3903	0.3921
d_{009} (nm)	0.2594	0.2588	0.2579	0.2584
d_{110} (nm)	0.1513	0.1509	0.1512	0.1512
Lattice parameter, a (nm)	0.3026	0.3018	0.3024	0.3024
Lattice parameter, c (nm)	2.3699	2.3517	2.3651	2.3741

Figure 1. XRD patterns for Ni/Al-LDHs prepared using different CTAB concentrations: a. 3.5 wt%, b. 3.8 wt%, c. 4.2 wt% and d. 4.4 wt%. **Figure 2.** IR spectrum for Ni/Al-LDHs prepared using 4.2 wt% of CTAB.

conditions: 40 kV, 20 mA, $\text{CuK}\alpha$ radiation. The samples, as unoriented powders, were step-scanned in steps of 0.04°

(2θ) in the range of $5\text{--}80^\circ$ using a count time of 10 s per step.

The TEM micrographs were recorded on a Hitachi H-800 TEM instrument.

Elemental analyses were performed by ICP emission spectroscopy (LEEMAN, Prodigy, ICP-OES).

IR spectra were recorded on a FT-IR Spectrometer of Perkin-Elmer Instruments LLC using KBr pellets.

3. Results and discussion

Powder XRD patterns for Ni/Al-LDHs prepared using different CTAB concentrations are shown in figure 1. In each case, the XRD patterns exhibit characteristic reflections of a LDH material with a series of (00 l) peaks appearing as narrow symmetric lines at low angles, corresponding to basal spacing and higher order reflections. Higher diffraction intensities are observed for Ni/Al-LDHs synthesized using 3.8 wt% and 4.4 wt% of CTAB concentration.

Table 1 lists the elemental chemical analysis data for metals of Ni/Al-LDHs. The results are lower than the values used in the reaction stoichiometries. This deviation in the molar ratio from those existing in the starting solutions can be due to different precipitation rates of the various hydroxides.

Assuming a rhombohedral 3R stacking sequence and using the positions of the (003), (006) and (110) reflections, the lattice parameters a and c may be calculated. As shown in table 1, the variation of CTAB concentration does not give rise to deep changes in the parameters, a , which is the average distance between metal ions in the layers, and c , which represents three times the distance from the centre of one layer to the next.

IR spectral analysis of Ni/Al-LDHs prepared using 4.2 wt% of CTAB can be found in figure 2. The bands at 1107.6 cm^{-1} and 617.0 cm^{-1} are attributed to ν_3 and ν_4 bands of the SO_4^{2-} ions, respectively, indicating that the interlayer anions of the Ni/Al-LDHs are SO_4^{2-} ions.

Observations of the size and morphology of the Ni/Al-LDHs synthesized using different CTAB concentrations were performed using the Hitachi H-800 TEM instrument. As shown in figure 3a, products prepared using 3.5 wt% concentrations of CTAB maintain a nanowire morphology

Figure 3. TEM micrographs for Ni/Al-LDHs prepared using different CTAB concentrations: a. 3.5 wt%, b, c. 3.8 wt%, d, e. 4.2 wt% and f. 4.4 wt%.

that is uniform in shape and size. Figure 3b shows that flower-like or spherical structures are obtained when CTAB concentration is 3.8 wt%. By observation of figure 3c, it is clear that the flower structure is assembled with nanowires similar to figure 3a. In the case of 4.2 wt% of CTAB concentration, TEM micrograph shows a clear rod-like structure (figures 3d and e) and many Ni/Al-LDH aligned nanorods self-assemble into well-ordered bundles. A tube structure is also observed in the sample obtained at 4.4 wt% of CTAB concentration, as shown in figure 3f. From this, it is clear that the morphology of Ni/Al-LDHs strongly depends on CTAB concentration.

In a quaternary microemulsion made up of cetyltrimethylammonium bromide (CTAB), water, *n*-hexane, and *n*-hexanol, nanosized water pools were dispersed in a continuous oil phase and stabilized by surfactant and co-surfactant molecules at the water/oil interface. These

water pools offer ideal microreactors for the formation of Ni/Al-LDHs. Since different CTAB concentrations lead to different morphologies of Ni/Al-LDHs, it can deduce that the morphology of Ni/Al-LDHs is controlled by the assembling shape of the surfactant, which is related to the concentration of CTAB in the microemulsion system. When CTAB concentration is low (3.5 wt%), micelle of small size form due to the gathering of CTAB molecules. Due to the preferential adsorption of cationic surfactant CTAB headgroups, uniform nanowires with a preferential growth direction may be formed within the water pools of reverse micelles under hydrothermal conditions. However, increasing the CTAB concentration to 3.8 wt% causes the micelle concentration to become supersaturated, with the assembling of small micelle resulting in the formation of spherical micelle of large size. From these, spherical Ni/Al-LDHs are able to be obtained. It

appears that with further increase of CTAB content, formation of rod-like micelle becomes responsible for Ni/Al-LDHs with rod-like and tube-like structures.

4. Conclusions

In summary, the formation of Ni/Al-LDH nanostructures via microemulsion mediated hydrothermal synthesis was investigated. It was found that the morphology of Ni/Al-LDHs can be controlled using different concentrations of CTAB. Furthermore, nanowires are found to form in lower CTAB content, while a spherical morphology is obtained with higher concentration. Nanorods are found to grow preferentially with increasing CTAB concentration to a greater extent. As a result, a growth mechanism based on the micelle morphology has been proposed for the formation of Ni/Al-LDH nanostructures.

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