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In situ synthesis of surfactant/silane-modified hydrotalcites

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Abstract

In this study, anionic surfactant and silane-modified hydrotalcites were synthesized through a soft chemical in situ method. The resulting materials were characterized using X-ray diffraction (XRD), high-resolution thermogravimetric analysis (HRTG), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and N_2 adsorption–desorption. The Mg–Al hydrotalcite (LDH) and the only surfactant-modified hydrotalcite (LDH-2) display similar XRD patterns while both surfactant and silane-modified hydrotalcite (LDH-3) show two distinct series of reflections, corresponding to hydrotalcite and smectite-like materials, respectively. The smectite-like materials show a series of regular (001) reflections with $d_{001} = 12.58$ Å. Further supporting evidence was obtained from FTIR and TG, for example, the vibration at 1198 cm^{-1} corresponds to Si–O–Si-stretching mode and the mass loss at ca. 861 °C to dehydroxylation. In LDH-2, the loaded surfactants are located in both the interlayer space and the interparticle pores with a "house of cards" structure as supported by FTIR, TG, and N_2 adsorption–desorption isotherms. Both electron microscopy (SEM and TEM) micrographs and N_2 adsorption–desorption isotherms show that in situ modification with surfactant and silane has a significant influence on the morphology and porous parameters of the resulting hydrotalcite materials.

Keywords: Hydrotalcite; In situ synthesis; Anionic surfactant; Silane; Nanochemistry

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1. Introduction

Layered double hydroxides (LDHs) are a family of anionic clays. The structure of hydrotalcite can be derived from a brucite structure ($Mg(OH)_2$) in which, e.g., Al^{3+} or Fe^{3+} (pyroaurite–sjögrenite) substitutes a part of the Mg^{2+}. This substitution creates a positive layer charge on the hydroxide layers, which is compensated by interlayer anions or anionic complexes [1].

Similar to cationic clay minerals (e.g., smectites), the interlayer anions in LDHs can be replaced by organics, resulting in the formation of organic hydrotalcites with different interlayer arrangement models [2]. These materials are attractive sorbents for anionic or acidic contaminants such as phenols, acidic pesticides, and anionic detergents [3–8].

In the last decades, the synthesis and application of organoclays have attracted great attention since organoclay-based nanocomposites exhibit remarkable improvement in properties when compared with virgin polymer or conventional micro- and macrocomposites. These improvements include increased strength and heat resistance, decreased gas permeability and flammability, and increased biodegradability of biodegradable polymer [9]. Unfortunately, little attention was paid to the application of the organohydrotalcites in the synthesis of nanocomposites. However, when compared with smectites, several advantages can be found if hydrotalcite is used to synthesize nanocomposites. Firstly, hydrotalcite has more water content than smectite minerals (brucite is a widely used flame retardant); hence, using hydrotalcite to synthesize nanocomposites can improve the flame-retarding property of the resulting materials. Secondly, hydrotalcite can be synthesized under facile experimental conditions whereas almost all the used montmo-

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rillonites are natural and organoclays are prepared through ion exchange. Surfactant-modified hydrotalcite can be in situ prepared in the preparation course of hydrotalcite and this can reduce the cost of the synthesized materials. More recently, the synthesis and application of silane-grafted clays in the synthesis of nanocomposites have attracted great interest in which silanes may be introduced onto the clay intrasurface [10,11], external surface [12], and edges of the clay sheets [13]. The last case can greatly accelerate the intercalation of big organic molecules into the clay interlayer space and improve the chemical–physical properties of the resulting materials [13]. In the synthesis procedure of hydrotalcite, the silane-grafted hydrotalcite can be in situ synthesized when the silane is added in the reaction system [14].

Hence, the main aim of this research is to explore the in situ synthesis of anionic surfactant-modified and silane-grafted hydrotalcites. The microstructure of the resulting products was investigated using various techniques, including X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TG), scanning electronic microscopy (SEM), transmission electronic microscopy (TEM), and N_2 adsorption–desorption. Some new insights were obtained including a novel synthesis route to in situ preparation of organohydrotalcite and the microstructure of the resulting products. This is of fundamental importance for synthesis and application of hydrotalcite-based materials.

2. Materials and methods

2.1. Materials

All the chemicals used in this study are of analytical grade. $Mg(NO_3)_2{\cdot}6\,H_2O$, NaOH $Al(NO_3)_3{\cdot}9H_2O$, and $C_{12}H_{25}OSO_3$-Na were provided by Sigma Pty Ltd., Australia, and C_6H_5Si-$(OCH_3)_3$ was provided by Aldrich, USA.

2.2. Synthesis of Al–Mg hydrotalcite

A mixed solution of aluminum and magnesium nitrates ($[Al^{3+}] = 0.25$ M and $[Mg^{2+}] = 0.75$ M) and a mixed solution of sodium hydroxide ($[OH^-] = 2$ M) were placed in two separate vessels and purged with nitrogen for 20 min (all compounds were dissolved in freshly decarbonated water). The cationic solution was added to the anions via a peristaltic pump at 40 ml/min. The resulting precipitate was then filtered thoroughly with room temperature decarbonated water to remove nitrates and left to dry in a vacuum desiccator for several days. The resulting hydrotalcite was referred to as LDH.

2.3. In situ synthesis of anionic surfactant-modified hydrotalcite

Two hundred milliliters of water was first decarbonated via boiling. The aluminum and magnesium nitrates were dissolved in 100 ml of the decarbonated water (referred to as solution 1). NaOH and Na-dodecyl sulfate (SDS) were dissolved in 100 ml of the decarbonated water (referred to as solution 2). Solution 1 was added into solution 2 via the peristaltic pump with rapid stirring and refluxing. The mixture was stirred at room temperature overnight (ca. 20 h). Then, the resulting product was washed with decarbonated water and ethanol for three times, respectively, and dried in a desiccator. The resulting hydrotalcite was referred to as LDH-2.

2.4. In situ synthesis of anionic surfactant and silane-modified hydrotalcite

Two hundred milliliters of water was first decarbonated via boiling. The aluminum and magnesium nitrates and phenyltrimethoxysilane (PTMS) were dissolved in 100 ml of the decarbonated water (referred as solution 1); NaOH and Na-dodecyl sulfate (SDS) were dissolved in 100 ml of the decarbonated water (referred to as solution 2). Solution 1 was added into solution 2 via the peristaltic pump with rapid stirring and refluxing. The mixture was stirred at room temperature overnight (ca. 20 h). Then, the resulting product was washed with decarbonated water and ethanol for three times, respectively, and dried in desiccator. The resulting hydrotalcite was referred to as LDH-3.

2.5. Characterization

X-ray diffraction (XRD) patterns of LDH and the modifying products were recorded using Co$K\alpha$ radiation ($\lambda = 1.78897$ Å) on a Philips PW1050 diffractometer at 40 kV and 32 mA with 1° divergence slit, 1° antiscatter slit, between 2.5 and 75° (2θ) at a step size of 0.02° 2θ. LDH and the modifying products were pressed in stainless-steel sample holders.

Thermogravimetric analyses of the samples were obtained using a TA Instruments Inc. Q500 high-resolution TGA operating at ramp 10 °C/min with resolution 6.0 °C from room temperature to 1000 °C in a high-purity flowing nitrogen atmosphere (80 cm^3/min). Approximately 40 mg of finely ground sample was heated in an open platinum crucible. Repetitive analyses were undertaken.

FTIR spectra using the ATR technique were recorded on Nicolet Nexus 870 Fourier transform infrared spectrometer with a diamond attenuated total reflectance (ATR) smart accessory. Then 128 scans were collected for each measurement over the spectral range of 525–4000 cm^{-1} with a resolution of 4 cm^{-1}.

For TEM observation, small drops of dilute suspensions of 0.1 g of the samples in 5 cm^3 of doubly distilled water were placed on Cu mesh grids that had been coated with a thin carbon film. The grids were air-dried and then briefly placed in a 60 °C oven to ensure complete drying prior to insertion into the instrument. The specimens were examined in a Philips CM200 transmission electron microscope operated at an accelerating voltage of 200 kV. The surface morphology of the prepared samples was examined by SEM. Small amounts of the dried powders (approximately 0.01 g) were placed on sticky carbon tape on standard Al mounts and then sputter-coated with a thin conductive layer of gold. The samples were viewed in an FEI Quanta 200 scanning electron microscope at 20 kV.