



Research paper

Synthesis and thermal decomposition of metal hydroxide intercalated saponite

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ABSTRACT

Chlorite-like nanocomposites in which the anionic clay layers are intercalated between the cationic clay layers were prepared by mixing an aqueous colloidal dispersion of exfoliated layers of copper hydroxysalt or α -cobalt hydroxide with an aqueous colloidal dispersion of exfoliated saponite layers. The nanocomposites showed a different thermal decomposition behavior compared to the parent layered solids. The thermal decomposition of the chlorite-like nanocomposites resulted in nanocomposites in which metal oxide ($\text{CuO}/\text{Co}_3\text{O}_4$) nanoparticles are uniformly distributed in saponite matrix. The particle size of the oxide nanoparticles in the nanocomposite could be varied by varying the decomposition parameters such as the temperature and duration of decomposition.

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1. Introduction

Layered nanocomposites comprising two or more different kinds of layered solids exhibit synergistic properties (Carja et al., 2007; Fang et al., 1999; Kim et al., 1997; Komarneni, 1992; Li et al., 2007; Nethravathi et al., 2007; Sasaki et al., 2001; Venugopal et al., 2007, 2008). These find applications as sorbents (Bentouami and Ouali, 2006; Hu et al., 2007), catalysts (Lau et al., 2006), stabilizers in emulsions (Abend and Lagaly, 2001) and adsorbents (Seredych et al., 2008). Layered nanocomposites can also be used as precursors to a number of metal/metal oxide nanoparticle-layered solid nanocomposites for varied applications (Han et al., 2005; Kun et al., 2006; Liu et al., 2007; Oliveira et al., 2003; Tsoufis et al., 2008; Venugopal et al., 2006).

Layered nanocomposites comprising both the anionic and cationic clay layers closely resemble the 'chlorite' mineral which has metal hydroxide layers intercalated between 2:1 aluminosilicate layers (Butruille and Pinnavaia, 1996; Letaief and Ruiz-Hitzky, 2003; Murray, 2007; Sudo, 1981). Chlorite-like layered nanocomposites of varied compositions can be used as catalysts and precursors to metal/metal oxide pillared clay materials (Butruille and Pinnavaia, 1996; Murray, 2007). Due to the versatile applications of chlorite-like compounds and their derivatives, a number of nanocomposites of cationic and anionic clays have been prepared in the recent past (Feng et al., 2000; Hornok et al., 2005; Lagaly et al., 2001). In these reports hydroxides of various metals

were intercalated into clay to obtain sandwich nanocomposites. Metal hydroxide-clay nanocomposites were also prepared by precipitating metal hydroxide in clay dispersions (Yamanaka and Brindley, 1978), by heterogeneous coagulation of clay dispersion with peptized colloid of magnesium-aluminum layered double hydroxide (LDH) (Lagaly et al., 2001) and by layer-by-layer coatings of the clay and LDH dispersions on a glass substrate (Hornok et al., 2005). Layered nanocomposites prepared from non-delaminated precursors resulted in materials with non-homogeneous distribution of properties (Lagaly et al., 2001) and the intercalated metal hydroxide layers in some of these nanocomposites metamorphose into some other form or get leached out on aging (Hsu, 1968; Hsu and Bates, 1964). Therefore, in order to prepare nanocomposites with a more or less alternating arrangement of oppositely charged clay layers, it is necessary to use well segregated/delaminated layers of the precursor layered solids.

This work describes the synthesis of layered nanocomposites of a synthetic smectite, saponite, with two structurally distinct anionic clays, α -cobalt hydroxide and copper hydroxysalt by the spontaneous flocculation of the delaminated layers of the precursor layered solids. α -Hydroxides and hydroxysalts [or basic salts] are anionic clays with positively charged metal hydroxide layers and charge compensatory interlayer anions. The positive charge in the former arises due to the partial protonation of the layer hydroxyl ions (Rajamathi et al., 2001) while in the latter; the deficiency of the hydroxyl ions is coped up by the anions that get directly 'grafted' to the lattice metal ion (Newman and Jones, 1999). The saponite- α -cobalt hydroxide [saponite-Co(OH)] and saponite-copper hydroxide [saponite-Cu(OH)] nanocomposites could be decomposed to get CuO and Co_3O_4 nanoparticle dispersed saponite

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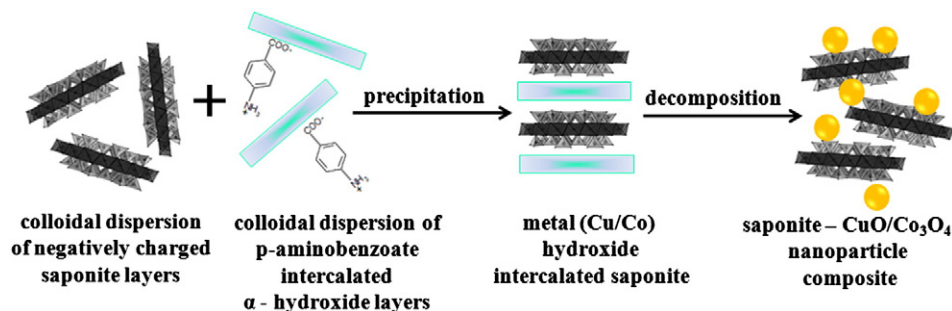


Fig. 1. Schematic illustration of the steps involved in the synthesis of metal hydroxide intercalated saponite and their decomposition to saponite-metal oxide nanoparticle nanocomposite.

respectively. The steps involved in the formation of the chlorite-like nanocomposites and their conversion to metal oxide nanoparticle-saponite nanocomposites is shown schematically in Fig. 1.

2. Materials and methods

2.1. Preparation of colloidal dispersion of saponite

1 g of Na⁺-saponite of the composition, NaMg₆(Si₇Al)O₂₀(OH)₄ synthesized by a procedure reported by Kawi and Yao (1999) was added to 1000 ml of water and stirred at room temperature for 3 days. The translucent colloidal dispersion was divided into two equal halves and used in two different nanocomposite preparations.

2.2. Preparation of p-aminobenzoic acid intercalated copper hydroxysalt and its colloidal dispersion

Solution of Cu(NO₃)₂·3H₂O (0.3092 g dissolved in 8 ml of water) is added with continuous stirring to 13 ml of 0.5 M NH₃ solution containing 0.0880 g of p-aminobenzoic acid (PABA) (Nethravathi et al., 2010). The nominal composition of the obtained copper hydroxysalt is Cu₂(OH)₃(PABA)·H₂O [hereafter referred to as Cu(OH)(PABA)]. The bluish-green solid obtained was separated by centrifugation and washed several times with water. As the pH neared ~7 the solid formed a colloidal dispersion due to delamination. The solid was washed continuously to get it entirely into the colloidal dispersion state.

The preparation of Cu(OH)(PABA) was repeated and the precipitate was washed with water till it started forming colloidal dispersion. At this stage the solid was washed a few times with acetone and dried in air at room temperature. The solid thus obtained was used for further characterization.

2.3. Preparation of saponite-Cu(OH) nanocomposite

The entire Cu(OH)(PABA) dispersion obtained in the previous step was added to 500 ml of Na⁺-saponite dispersion containing 0.5 g of Na⁺-saponite with continuous stirring on a magnetic stirrer. The colloidal mixture was stirred for a further 15 min and then left undisturbed for 30 min. The highly swollen flocculated mass of solid settled quantitatively at the bottom of the beaker was separated by centrifugation, washed with water followed by acetone and dried in air at room temperature.

2.4. Preparation of PABA intercalated α-cobalt hydroxide and its colloidal dispersion

α-Cobalt hydroxide of the nominal composition Co(OH)_{1.67}(PABA)_{0.33}·H₂O [hereafter referred to as α-Co(OH)(PABA)] was prepared by the addition of 0.5646 g of Co(NO₃)₂·6H₂O dissolved in 12 ml of water to 20 ml of 0.5 M NH₃ solution containing 0.2394 g of PABA with continuous stirring (Nethravathi et al., 2012). The green

solid obtained was processed in the same way as in the case of Cu(OH)(PABA) to get a dispersion that was used in nanocomposite preparation.

The preparation of α-Co(OH)(PABA) was repeated and the green solid was washed with water till the pH was ~7. The solid was then washed with acetone and dried in air at room temperature. The solid thus obtained was used for further characterization.

2.5. Preparation of saponite-Co(OH) nanocomposite

The entire α-Co(OH)(PABA) colloidal dispersion obtained in the previous step was added to 500 ml of Na⁺-saponite dispersion containing 0.5 g of Na⁺-saponite with continuous stirring on a magnetic stirrer. The stirring was continued for another 15 min and the mixture was left undisturbed for 30 min. The solid was separated and processed as in the case of saponite-Cu(OH) nanocomposite.

2.6. Preparation of nitrate intercalated α-cobalt hydroxide and Cu₂(OH)₃(NO₃)·H₂O

Nitrate intercalated α-cobalt hydroxide and basic copper hydroxide were prepared by procedures reported elsewhere (Newman and Jones, 1999; Rajamathi et al., 2000) with slight modifications. α-Cobalt hydroxide was prepared by adding 2.9104 g of Co(NO₃)₂·6H₂O dissolved in 35 ml of water to 50 ml of 0.5 M NH₃ solution with continuous stirring. The green solid obtained was washed immediately with water, acetone and was dried in air at room temperature. Cu₂(OH)₃(NO₃)·H₂O was prepared by the drop-wise addition of 50 ml of 0.75 M NaOH

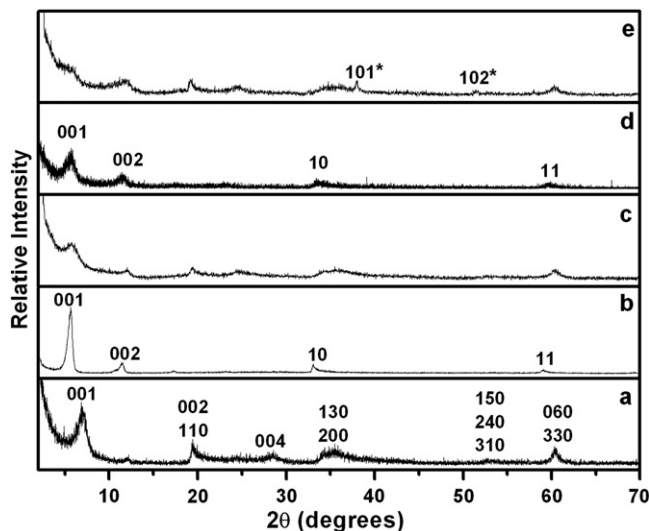


Fig. 2. PXRD patterns of Na⁺-saponite (a), Cu₂(OH)₃(PABA)·H₂O (b), saponite-Cu(OH) nanocomposite (c), α-Co(OH)_{1.67}(PABA)_{0.33}·1.1H₂O (d) and saponite-Co(OH) nanocomposite (e). [* reflections due to β-Co(OH)₂].

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