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Ultrasound-assisted reconstruction and delamination studies on CaAl layered double hydroxides

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ABSTRACT

Two kinds of CaAl layered double hydroxides (CaAl-LDHs) were synthesized with chloride and nitrate anions by co-precipitation method. The samples were calcined and finally reconstructed by rehydration using ultrasounds, in the presence of NaCl or $NaNO_3$. Reconstructed samples presented smaller lamella size than the parent ones. All samples were characterized by X-ray powder diffraction, FT-IR spectroscopy, thermogravimetric analysis and TEM microscopy. Delamination was not achieved by mechanical stirring for 2 days, whereas most samples underwent delamination by the use of ultrasounds. Additionally, a hybrid CaAl-LDHs with CdTe quantum dots was synthesized by reconstruction of a calcined CaAl-LDHs in the presence of the quantum dots.

1. Introduction

Layered double hydroxides (LDHs), also known as hydrotalcite-like materials, have general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}_{1/n})m\,H_2O$, where M(II) and M(III) are divalent and trivalent cations and A^{n-} an anion. They consist of positively charged octahedral sheets, alternated with anions and water molecules in the interlayer space where electrostatic interactions and hydrogen bonds take place (Evans and Slade, 2006).

CaAl layered double hydroxides (CaAl-LDHs) are a subgroup of LDHs in which the divalent metal is calcium and the trivalent metal is typically aluminum. Other trivalent metals can be also found in this subgroup of LDHs. A number of anions can be host in the interlayer space, and for the most common a specific nomenclature is used. This is the case for Friedel's salt and Kuzel's salt, with chloride and sulfate anions, respectively (Renaudin et al., 1999; Mesbah et al., 2011).

LDHs present a variety of cation and anion compositions. This versatility explains why these materials have been proposed for a wide range of applications: catalysts, ion exchange hosts, cement additives and fire retardants, among others (Cavani et al., 1991). LDHs can be found in nature or synthesized in laboratory by inexpensive procedures (Costantino et al., 1998; Othman et al., 2009). Co-precipitation method is very common, starting from the appropriate salts in alkaline solutions.

Another method to obtain LDHs, which has been widely studied, is the reconstruction of calcined LDHs or mixed oxides. After calcination at moderate temperatures (in the range 673–873 K), anions and water are removed as gases and the layered structure of LDHs collapses in a mixture of metal oxides (Cavani et al., 1991). Because of the so-called *memory effect*, in the presence of water, calcined LDHs can be rehydrated and reorganized in a layered structure again (Abelló et al., 2005; Sharma et al., 2010; Xu et al., 2013). As an example, the rehydration of tricalcium aluminate ($3CaO\cdot Al_2O_3$), an important phase in Portland cement, is a common route to synthesize CaAl-LDHs (Zou and Plank, 2012; Zhang et al., 2014).

Valente and co-workers studied the thermal decomposition and reconstruction of LDHs prepared by sol–gel and co-precipitation processes (Valente et al., 2010). They claimed that the properties of the final materials mainly depended on the conditions used for reconstruction. Abelló and co-workers synthesized reconstructed LDHs using sonication (Abelló et al., 2005), and similar materials were studied by Álvarez and co-workers (Álvarez et al., 2013). Reconstructed LDHs have been widely used as precursors for a range of materials, from catalysts to adsorbents (Rojas, 2012; Rives et al., 2014). Tao and co-workers synthesized silylated

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LDHs through reconstruction of calcined LDHs without using surfactants (Tao et al., 2010). Zhao and co-workers compared the properties of as-synthesized and reconstructed LDHs with europium to detect changes in the luminescence properties (Zhao et al., 2012). They reconstructed calcined LDHs using mechanical stirring in the presence of water. Pavel et al. (2010, 2011) correlated the memory effect of catalysts based on calcined LDHs for the cyanoethylation reaction and the removal of the aging step in the synthesis of the catalyst precursors. More recently, Lee and co-workers used reconstructed LDHs for the isomerization reaction of glucose to fructose (Lee et al., 2014). They compared catalysts reconstructed by sonication at different times and by mechanical stirring.

Delamination of LDHs has received increasing attention in the last years. Producing positively charged platelets is of great interest for nanocomposite synthesis, multilayer films and to enhance the accessibility to the interlayer region of LDHs (Wang and O'Hare, 2012). LDHs face complications for being delaminated because of the high density of the layers and the interlayer electrostatic interactions (Ma et al., 2006). A valid route is the use of particular solvents: i) Adachi-Pagano and co-workers first delaminated LDHs intercalated with surfactants like dodecyl sulfate (LDHs-DDS) in the presence of butanol, refluxing at 393 for K 16 h (Adachi-Pagano et al., 2000); ii) Jobbágy and Regazzoni (2004) studied exfoliation of LDHs-DDS with CCl_4 whereas Naik et al. (2011) performed the same process in toluene; iii) Hibino and Jones (2001) were the first to report delamination of LDHs in formamide at room temperature. They investigated several solvent combinations and found the system LDHs-glycine along with formamide as the most successful. Lately, in another study, other amino-acids and several polar solvents were tested (Hibino, 2004); iv) Several authors reported then the use of formamide for delaminating LDHs together with the use of mechanical stirring or ultrasounds (Li et al., 2005; Liu et al., 2006; Wu et al., 2007; Stoica et al., 2012); v) Gordijo et al. (2007) reported that Mg–Al–CO_3 LDHs can be exfoliated with a mixture of ethanol:N,N-dimethylformamide. Finally, Leroux and co-workers studied the exfoliation of LDHs in polyester aiming at polymer nanocomposite applications (Swanson et al., 2013). To the best of our knowledge, there are no studies reporting CaAl-LDHs delamination.

There is also an increasing interest in the synthesis of LDHs with optical properties (Gunjakar et al., 2011; Zheng et al., 2014); the incorporation of quantum dots (QDs) in LDHs, for instance, prevent them from aggregation and keep their optical properties unchanged (Dong et al., 2013). Hybrid LDHs with QDs have a potential use as photocatalysts, sensors and different devices, among others (Dong et al., 2013; Cho et al., 2014; Tang et al., 2014).

The aim of this work is to report the synthesis of two kinds of CaAl layered double hydroxides calcined and reconstructed by the use of ultrasounds in the presence of NaCl or $NaNO_3$. Chloride and nitrate, respectively, act as counter anions of the LDHs structure. Delamination studies of samples synthesized by co-precipitation and reconstructed in the presence of formamide were carried out. A hybrid CaAl-LDHs was synthesized by reconstruction of a calcined CaAl-LDHs in the presence of CdTe QDs.

All CaAl-LDHs have been characterized by X-ray powder diffraction (XRPD), FT-IR spectroscopy, thermogravimetric analysis (TGA) and TEM microscopy. Delamination tests were performed by Tyndall effect, X-ray powder diffraction and AFM microscopy. The hybrid CaAl-LDHs was characterized additionally by optical spectroscopic techniques.

2. Materials and methods

2.1. Synthesis of chloride and nitrate CaAl layered double hydroxides

The two CaAl-LDHs were synthesized by co-precipitation method. The selected Ca/Al ratio of the starting salts was 2, for both samples. The synthesis details for the chloride CaAl-LDHs (in this work labeled as HC-Cl) can be found elsewhere (Pérez-Barrado et al., 2013). After the addition of the salts, the chloride CaAl-LDHs was aged using conventional heating and refluxing for 24 h at 333 K. For the nitrate CaAl-LDHs (HC-NO_3), the details are reported elsewhere (Grover et al., 2010). When the addition of the salts was completed, the samples were aged for 24 h at room temperature (RT).

2.2. Calcination and reconstruction of CaAl layered double hydroxides

Calcination was performed with synthetic air at 723 K for 8 h in a tubular furnace. Samples were place in a quartz reactor. When calcination was completed, samples were stored in a desiccator. In an initial stage calcination was performed in a muffle under static air, but was later discarded since a phase attributed to $CaCO_3$ is present in the final product. Calcined samples are called cHC-Cl and cHC-NO_3.

Rehydration was performed in an ultrasound bath, using a formerly reported methodology published before (Abelló et al., 2005). 0.25 g of sample was placed in a 2-necked round-bottom flask with 50 ml of a 0.01 M solution of the suitable salt (either NaCl or $NaNO_3$). The reconstruction was performed by refluxing the solution at 333 K for 2 h under an inert atmosphere of N_2 in order to prevent the incorporation of CO_2. The solution was filtered and washed with ethanol. Finally, it was dried in an oven at 353 K overnight. The nomenclature for reconstructed samples is shown in Table 1.

2.3. Delamination process

Samples were diluted in formamide at a concentration of 1 mg/ml. Delamination was performed in a similar procedure to that of Palomares et al. (Stoica et al., 2012). In an ultrasound bath (Ultrasons-H, P Selecta, 40 kHz) at RT in cycles of 60 min of ultrasonication followed by 50 min of rest. Around 6 and 8 cycles were needed. In parallel, samples were also agitated vigorously for 2 days at RT, using a mechanical shaker (SB5, 700 rpm), in a purged and sealed Erlenmeyer, as described before (Ma et al., 2006), in order to compare these methods. Delamination tests were done several times to check the reproducibility of the process.

2.4. Synthesis of a hybrid CaAl layered double hydroxide

A CaAl-LDHs was synthesized with thiol-capped CdTe QDs from reconstruction of a calcined sample, following the above mentioned procedure. 0.25 g of sample cHC-Cl, a solution of 0,01 M ammonium thioglycolate and 250 μl of the CdTe QDs colloidal solution ($1 \cdot 10^{-5}$ M) were added to a round-bottom flask. The size of the quantum dots ranged between 2.5 and 5 nm. The sample was recovered by centrifugation at 4000 rpm and stored in a desiccator. The nanoparticles were supplied by Centro Nanosistemi, in Alessandria (Italy). This sample is labeled as hrHC-Cl-AM.

2.5. Characterization

XRPD measurements were made using a Siemens D5000 diffractometer (Bragg–Brentano parafocusing geometry and vertical–goniometer) fitted with a curved graphite diffracted-beam monochromator and diffracted-beam Soller slits, a 0.06° receiving slit, and scintillation counter as a detector. The angular 2θ diffraction range was between 5° and 70°. Sample was dusted on to a low background Si(510) sample holder. The data were collected with an angular step of 0.05° at 3 s per step and

Table 1
Reconstructed samples.

Reconstructed sample	Calcined parent sample	Salt added to the solution
rHC-Cl–Cl	cHC-Cl	NaCl
rHC-Cl-NO_3	cHC-Cl	$NaNO_3$
rHC-NO_3-Cl	cHC-NO_3	NaCl
rHC-NO_3–NO_3	cHC-NO_3	$NaNO_3$