



# Effect of post-synthesis microwave–hydrothermal treatment on the properties of layered double hydroxides and related materials

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## ABSTRACT

The effect of microwave–hydrothermal treatment (MWHT) on the properties of Mg,Al-layered double hydroxides with the hydrocalcite-like structure intercalated with carbonate and organic anions (terephthalate, adipate and dodecyl sulphate) and on their thermal decomposition products is studied. All solids have been characterised by element chemical analysis, powder X-ray diffraction, FT-IR spectroscopy, thermal analysis, transmission electron microscopy, specific surface area determination by N<sub>2</sub> adsorption at –196 °C and particle size distribution. The MWHT yielded a larger improvement of the crystallinity for carbonate-containing samples than for the organic-intercalated ones; however, although the crystallinity is not greatly modified for the latter, the thermal properties and particle size distribution are significantly affected by the ageing treatment.

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## 1. Introduction

Hydrocalcite-like compounds (HTLcs), anionic clays or layered double hydroxides (LDHs) are the names commonly used to describe a class of layered materials with general chemical formula  $[M_1^{2+}_x M_2^{3+}_y (\text{OH})_z] (A_{x/n}^{n-})_m \text{H}_2\text{O}$  (Cavani et al., 1991; Rives, 2001; Evans and Duan, 2006). The presence of a wide range of cations and anions in the HTLcs structure have led to their application in specific fields, such as catalysis (Basile and Vaccari, 2001; Albertazzi et al., 2004; Kannan, 2006) and decontamination (Ullibarri and Hermosín, 2001; Park et al., 2004; Cornejo and Celis, 2008) and more recently as polymer stabilizers or modifiers (Leroux and Besse, 2004; Taviot-Guého and Leroux, 2006; Utracki et al., 2007; Goh et al., 2008). The physico-chemical properties of these materials (crystallinity, specific surface area, particle size and thermal stability) play an important role on their application. For instance, when used as adsorbents large specific surface areas are required (Carriazo et al., 2007); if they are employed as catalysts or precursors of catalysts, together with the specific surface area, the basicity or the distribution of the active phase should be controlled. Finally, preparation of HTLcs/polymer nanocomposites is influenced by small and homogeneous particle size.

The final properties of the materials can be modulated during the synthesis process (Rives, 2001; He et al., 2006) or by applying a post-synthesis treatment (Sheida et al., 2002; Xu and Lu, 2005; Xu et al., 2006). Microwaves (MW) can be used as a heating source during the synthesis of HTLcs. Their interaction with materials produces dipole

reorientation in dielectric materials (dielectric heating) and ionic conduction if ions can be drift under the field exist. In this way, it is possible to achieve a uniform bulk heating of the materials – volumetrically distributed heating – reducing thermal gradients. Since Komarnemi et al. (1996) reported in 1996 for the first time the use of microwave radiation coupled to hydrothermal treatment (the so called microwave–hydrothermal treatment, MWHT), several teams have studied in the last decade the application of microwave radiation during the processing of HTLcs (Rao et al., 1999; Kannan and Jasra, 2000; Tichit et al., 2002; Climent et al., 2004; Rivera et al., 2006; Benito et al., 2006a,b, Bergarda et al., 2007; Herrero et al., 2007). The use of microwaves as a source of heating during ageing of the slurry obtained by coprecipitation permits to increase the crystallinity of the solids in short periods of time modifying the properties of the as-prepared layered materials or after calcination.

In a previous work (Benito et al., 2009b) the authors reviewed the results obtained during the microwave-assisted synthesis of HTLcs with carbonate anions in the interlayer, but different chemical composition in the layers. In this work, we summarize the effect of MWHT on the properties of Mg,Al-HTLcs intercalated with carbonate (Benito et al., 2006b) and organic anions (terephthalate, adipate and dodecyl sulphate) (Benito et al., 2009a; Herrero et al., 2009), as prepared and after thermal treatment, in order to establish a relationship between the chemical nature of the interlayer region and the microwave post-treatment. Carbonate containing HTLcs are used as adsorbents (Carriazo et al., 2007; Cornejo and Celis, 2008), precursors of catalysts (Tichit et al., 2002, 2006) and catalysts (Albertazzi et al., 2004; Kannan, 2006). The insertion of organic anions in the interlayer space improves the compatibility of these lamellar materials with polymers for preparation of HTLcs/polymer

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nanocomposites (Costa et al., 2005; Qiu et al., 2005, 2006; Wang et al., 2009). In this sense, the intercalation of dodecyl sulphate (DS) ( $C_{12}H_{25}(SO_4^-)$ ) (Newman and Jones, 1998), a monovalent surfactant containing sulphate groups ( $SO_4^-$ ), would permit the sorption of many types of organic molecules due to the organophilic nature of the surfactant; moreover, the layer spacing distance will greatly extend, which facilitates the intercalation and dispersion of organic molecules or polymer chains (Lv et al., 2009). Another route to prepare HTlc/nanocomposites can be the intercalation of a monomer precursor to promote the *in situ* polymerization. Thus, adipate (AD) ( $C_4H_8-1,4-(COO^-)_2$ ) and terephthalate (TA) ( $C_6H_4-1,4-(COO^-)_2$ ) were chosen as anions to be intercalated. Adipate and terephthalate are dicarboxylic anions; while the former is an aliphatic compound, the later contains an aromatic ring. Adipate, when intercalated in the HTlc, usually stands with the two  $COO^-$  groups anchored to the adjacent brucite-like layers and the hydrocarbon chains are slightly tilted, whereas for terephthalate the aromatic ring stands erect in the interlayer with the anionic groups toward hydroxyl layers (Carlino, 1997). However, it should be remarked that the orientation can change depending on the lamellar charge (Carlino, 1997) and the hydration degree (Newman et al., 1998).

As reported above, the main aim of this work is to study the effect of the MWHT treatment. To our knowledge, few reports are found in the literature about the conventional hydrothermal treatment of organo-intercalated HTlcs. Crepaldi et al. (2000, 2002) observed that the effect of the hydrothermal treatment on Zn,Cr HTlcs intercalated with DS was dependent on the Zn/Cr ratio and on the presence of other anions different to DS in the interlayer region. Kooli et al. (1996) observed that terephthalate-intercalated HTlcs were thermally unstable after hydrothermal treatment, and Vucelic et al. (1995) reported that the synthesis at high temperature and pressure results in the destabilization of the layer expansion. Regarding the use of microwaves in the intercalation of HTlcs, few reports are found in the literature. Hussein et al. (2000, 2002) reported that Zn,Al HTlc intercalated with anionic surfactants (dodecyl sulphate and naphthaleneacetate) were synthesized faster by a microwave-assisted method compared to a conventional method, but the resulting nanocomposites showed no significant differences.

## 2. Experimental

### 2.1. Synthesis

The solids were synthesized by coprecipitation; a detailed description of the preparation of these materials has been described elsewhere (Benito et al., 2006b; Herrero et al., 2009; Benito et al., 2009a). Briefly, an aqueous solution containing nitrates of metal cations ( $Mg^{2+}$  and  $Al^{3+}$ ) in the desired amounts (molar  $M^{2+}/M^{3+}$  ratio = 2/1) was mixed with an aqueous solution of the desired anion (carbonate, terephthalate, adipate or dodecyl sulphate). The molar amount of organic anion was twice that of aluminium. The pH of the reaction mixture was kept at a preselected value (pH = 10) by adding 1 M NaOH. Then, the samples were submitted to microwave-hydrothermal treatment (MWHT) at 125 °C for different periods of time. MWHT was carried out in a Milestone Ethos Plus multimode cavity microwave oven. The samples were placed in teflon digestion vessels, sealed and mounted on a turntable in the microwave oven. Temperature during the irradiation was continuously monitored with a thermocouple introduced in a reference vessel. The software dynamically controls the temperature profile adjusting the delivered power at any time. The duration of the treatment period was changed (from 10 to 180 min) in order to study the progress of crystallisation under MWHT conditions. The precipitates were separated and washed by centrifugation with distilled water until complete removal of the excess of charge balancing anions and cations in the starting salts was achieved, and dried in air, the carbonate system, or in vacuo,

the systems containing organic anions. In order to study whether the MWHT affected the physico-chemical properties of the solids obtained upon calcination of the HTlc, the Mg,Al- $CO_3$  samples were calcined at 10 °C/min up to 250, 550 and 1000 °C and the compounds intercalated with organic anions at 225 °C.

Samples were named as follows: the carbonate intercalated samples were named as MA-HWt and the organic-intercalated series as MA-X-HWt, where X stands for the interlayer anion (AD, TA or DS for adipate, terephthalate or dodecyl sulphate, respectively) and t for the MW irradiation time, in minutes. The non-aged samples were named as MA-0, MA-AD-0, MA-TA-0 and MA-DS-0. Where applicable, a label c1, c2 and c3 was added to indicate the calcination temperature (c1 = 250 or 225 °C, c2 = 550 °C and c3 = 1000 °C).

## 3. Methods

Element chemical analysis for metal ions was carried out by atomic absorption in a Mark 2 ELL-240 apparatus, in Servicio General de Análisis Químico Aplicado (University of Salamanca, Spain). The content of C, S, and N were determined using a Leco CHNS-932.

Powder X-ray diffraction (PXRD) patterns were recorded in a Siemens D-500 instrument using Cu-K $\alpha$  radiation ( $\lambda = 1.54050 \text{ \AA}$ ) and equipped with Diffrac AT software. Identification of the crystalline phases was made by comparison with the JCPDS files. Crystallite sizes were calculated by the Scherrer equation from the width of the (00*l*) diffraction maximum; the Warren correction for instrumental line broadening was also considered, but the possible contribution of disorder effects and/or lattice strains to the peak broadening were ignored.

The FT-IR spectra were recorded in a Perkin-Elmer FT1730 instrument, using KBr pellets; 100 spectra (recorded with a nominal resolution of  $4 \text{ cm}^{-1}$ ) were averaged to improve the signal-to-noise ratio.

Thermogravimetric (TG) and differential thermal analyses (DTAs) were carried out in TG-7 and DTA-7 instruments, respectively, both from Perkin-Elmer, in flowing oxygen, at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ .

Specific surface area assessment was carried out in a Gemini instrument from Micromeritics. The sample (ca. 80–100 mg) had been previously degassed in flowing nitrogen at 110 °C for 2 h in a FlowPrep 060 apparatus, also from Micromeritics, in order to remove physisorbed water, and the data were analysed using published software (Rives, 1991).

The transmission electron photographs were taken in Servicio General de Microscopía Electrónica (University of Salamanca, Spain) with a ZEISS-902 Microscope. The samples were dispersed in acetone by ultrasounds, and some drops of this suspension were deposited on a copper grid previously impregnated with an amorphous carbon film with a voltaic arc.

The particle size analysis was carried out on a Malvern Mastersizer 2000 apparatus equipped with two lasers as excitation sources and interfaced to a PC computer equipped with commercial Mastersizer software. Analyses were carried out using the Lorenz–Mie theory and attributing refraction indexes of 1.33 and 1.52 to water and the LDH material, respectively. Samples were first dispersed in distilled water and the volume distribution percentage of the sample was plotted versus the particle size. Then, ultrasounds were applied until the shape of the curve did not change any longer, i.e. until total dispersion, or deaggregation, of the solid particles was attained.

## 4. Results

### 4.1. Coprecipitated samples

Element chemical analyses were carried out for all HTlcs (data not shown here). The  $M^{2+}/M^{3+}$  experimental ratio for all samples were in agreement with the ratios existing in the starting solutions. Only small differences from the expected values were detected, depending on the

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