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Research paper

Fast aging treatment for the synthesis of hydrocalumites using microwaves

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ABSTRACT

Friedel's salt $[Ca_2Al(OH)_6]Cl\cdot 2H_2O$, commonly known as hydrocalumite, was synthesized by co-precipitation following different aging treatments, using microwave irradiation or conventional heating and by refluxing or in autoclave, with the aim of decreasing the aging times (24 h) employed when aging by conventional heating or at room temperature. Hydrocalumites were characterized by XRPD, FT-IR, N_2 physisorption, ICP-OES, TEM, TEM-electron diffraction and TGA techniques. The use of microwaves favors a faster crystalline growth in the stacking direction whereas the use of autoclave improves the lamellar crystallinity. The highest crystallinity was found for the sample aged with microwave irradiation by autoclaving at 453 K for 1 h. This sample presented the highest crystallite size in the stacking direction (76 nm), the largest lamellar crystals (4000 nm) with *R3c* symmetry, and the highest dehydration- and dehydroxylation temperatures.

1. Introduction

Layered double hydroxides (LDH) are anionic clays widely reported in literature. They are versatile materials with many applications in science: additives in polymers, catalysis, environmental treatments, medicine, etc (Del Hoyo, 2007; Guo et al., 2010). LDH have general formula $[M(II)_{1-x}M(III)_x(OH_2)^{x+}(A^{n-}_{x/n})]mH_2O$, where M(II) and M(III) are divalent and trivalent cations and A^{n-} the anion. The layers are positively charged due to trivalent cation substitution, which are compensated by the presence of anions in the interlamellar region, where water molecules are also located. In general, they form a mixture of oxides after calcination and have memory effect, which allows them to be reconstructed after calcination (Cavani et al., 1991). Hydrotalcites, with Mg and Al as divalent and trivalent cations, respectively, have been extensively studied, and used in many applications (Cavani et al., 1991; Figueras, 2004; Li and Duan, 2006; Tichit and Coq, 2003). However, in this study, we focus our attention into Friedel's Salt, also called hydrocalumite (HC). Hydrocalumites have general formula $[Ca_2Al(OH)_6]Cl\cdot 2H_2O$, where the metal cations are usually calcium and aluminum (Rousellot et al., 2002). Typically, they play a significant role in cement and concrete industry in the composition of "AFm" phases, which contain hydrocalumite-like compounds expressed as hydrated calcium aluminates (Matschei et al., 2007; Raki et al., 2004; Raki et al., 2010). Interestingly, because of their basicity before and after calcination, they can be used as basic heterogeneous catalysts (Campos-Molina et al., 2010; Cota et al., 2010; Mora et al., 2010). Recently, their use as absorbents for environmental purposes (Grover et al., 2010) and as inorganic framework for ceramic pigments has been reported (Domínguez et al., 2011).

Hydrocalumites can be synthesized with several types of anions in the interlamellar space, although chloride and nitrate anions are the most used (Frost et al., 2011; Vieille et al., 2003). In "AFm" phases, it is possible to find a wide range of anions: carbonate, sulphate, bromide, iodide and chromate (Mesbah et al., 2011). According to the structure, the interlamellar distance and stability of the hydrocalumite can change depending on the anion. In view of the anion exchange capacity of LDH, HC with different anions can be used for different adsorbent applications (Zhou et al., 2012). The presence of carbonate ($-CO_3^{2-}$)- as interlamellar anion difficults greatly the anion exchange and delamination processes (Ma et al., 2006). An appropriate methodology for HC synthesis should always avoid the incorporation of carbonate in the interlamellar space and the calcite ($CaCO_3$) formation.

Recently, different approaches to synthesize HC have been reported. Sánchez-Cantú et al. prepared them from purchased hydrated lime and boehmite (Sánchez-Cantú et al., 2012). However, it was possible to identify boehmite and calcite phases in the final product; Kuwahara et al. recycled blast furnace slag as a precursor to obtain HC (Kuwahara et al., 2010) but they identified the presence of minor metals (Fe, Mn, Si and Ti) in the final chemical composition.

The most common synthetic procedure is the co-precipitation of Ca & Al salts at constant pH followed by an aging treatment at room temperature or by conventional heating; 353 K for 12 h (Radha et al., 2005), 333–338 K for 24 h (Campos-Molina et al., 2010; Vieille

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et al., 2003), room temperature (RT) for 24 h (Grover et al., 2010) or RT for 48 h (Domínguez et al., 2011). Zhang et al. have optimized the modification of experimental variables such as pH, time, temperature and solvent for the production at a large-scale for the cement industry (Xu et al., 2011). They found the best results for samples aged at 343 K for 24 h that later were successfully scaled-up using SNAS (separate nucleation and aging steps) method at pH in the range of 10.5–11.5.

The use of microwave irradiation in the aging process could be an excellent solution to decrease the long time of synthesis of hydrocalumites, since microwaves not only reduce enormously aging times but also provide much more crystallinity in the final material, as observed when applied to the synthesis of zeolitic materials and hydrotalcites (Ayala et al., 2011; Benito et al., 2006; Bergadà et al., 2007; Stoeger et al., 2012) or in the preparation of clays (hectorites and saponites among others), where aging times have been remarkably decreased (Sánchez et al., 2012; Trujillano et al., 2010; Vicente et al., 2010).

The aim of this work was to synthesize Ca_2Al–Cl hydrocalumites by different aging treatments. In pursuit of finding a fast aging treatment that can lead to more crystalline hydrocalumites, we compare microwave irradiation versus conventional hydrothermal heating, and autoclave versus reflux conditions, at different times and temperatures.

2. Experimental

2.1. Synthesis of Ca_2Al–Cl hydrocalumites (HC)

Several hydrocalumites were synthesized by coprecipitation method at constant pH (Vieille et al., 2003) with a Ca/Al molar ratio of 2 and Cl^- as anion. In a typical synthesis, the samples were prepared with vigorous stirring, under N_2 atmosphere and using decarbonized water to prevent from $-CO_3^{2-}$ incorporation. A solution of 250 ml ethanol/water mixture (2:3 v/v) was placed into a 500 ml 4-neck round-bottom flask in an oil bath at 333 K. A 100 ml solution with the salts was prepared by mixing the appropriate amounts of 0.66 M $CaCl_2 \cdot 2H_2O$ (Sigma-Aldrich) and 0.33 M $AlCl_3 \cdot 6H_2O$ (Riedel-de Haën) solutions. Another solution of 2 M NaOH (Panreac) was used to keep pH constant at 11.5. The pH electrode and the two compensated pressure funnels for addition of the salts and the NaOH solution respectively, were connected to 3 of the necks of the round-bottom flask. N_2 was bubbled through neck number 4 to avoid CO_2 incorporation. After complete addition of the salts, several aging procedures were performed using conventional or microwave heating and reflux or autoclave as recipients (Table 1). Samples were named starting with letters HC, corresponding to hydrocalumite, followed by letters R or A (refluxing or autoclave) for conventional heated samples and by RMW or MW (refluxing or autoclave) for microwaved samples. Finally, a number in subscript indicates the time of aging in hours whereas the number between parentheses is the temperature of aging. Additionally, another sample was synthesized at the same preparation conditions than those employed for synthesizing sample $HCRMW_3(353)$ but without using inert atmosphere during the hydrothermal treatment ($HCRMW_3(353)B$). This sample was characterized by XRPD and FT-IR spectroscopy in order to detect the carbonate species bands. All samples were compared to $HCR_{24}(333)$, which was aged as reported in literature, by refluxing at 333 K for 24 h with conventional heating.

Table 1
Aging treatments for hydrocalumites synthesis.

Nomenclature	Heating	Recipient	Temperature (K)	Time (h)
	Conventional/ Microwaves	Reflux/ Autoclave		
$HCR_{24}(333)$	Conventional	Reflux	333	24
$HCR_3(353)$	Conventional	Reflux	353	3
$HCRMW_3(353)$	Microwaves	Reflux	353	3
$HCA_3(353)$	Conventional	Autoclave	353	3
$HCA_1(453)$	Conventional	Autoclave	453	1
$HCMW_1(353)$	Microwaves	Autoclave	353	1
$HCMW_6(353)$	Microwaves	Autoclave	353	6
$HCMW_1(453)$	Microwaves	Autoclave	453	1

2.2. X-ray powder diffraction (XRPD)

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 2° 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 sample rotation. CuKα radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA.

2.3. Infrared spectroscopy (FTIR)

Infrared spectra were recorded on a Bruker-Equinox-55 FTIR spectrometer. Spectra were acquired by accumulating 32 scans at 4 cm^{-1} resolution in the range of 400–4000 cm^{-1}. Samples were prepared by mixing the powdered solids with pressed KBr disks in a mass ratio of 1:250, and dried in an oven before measurements.

2.4. Inductively coupled plasma-atomic emission spectroscopy (ICP-OES)

Ca/Al ratio has been analyzed in an ICP-OES analyzer (Induced Coupled Plasma-Optical Emission Spectroscopy) from Spectro Arcos. For the measurements, samples were introduced as a diluted solution into the analyzer. The powders (50 mg) were solubilised with HNO_3 (2 ml), heated if necessary and brought to 25 ml volume. 1 ml of the solution was diluted into 25 ml. Standards were used to perform calibration curves. All analyses were made by triplicate.

2.5. N_2 physisorption

N_2-adsorption–desorption isotherms were recorded at 77 K using a Quantachrome Quadrasorb SI surface analyzer. Prior to analysis samples were outgassed at 363 K. In a typical test, 0.2 g of sample was used for analysis. Specific surface areas were calculated from BET (Brunauer–Emmett–Teller) method. Average pore size was calculated from BJH (Barrett–Joyner–Halenda) method. External surface area was calculated from t-plot (statistical thickness) method.

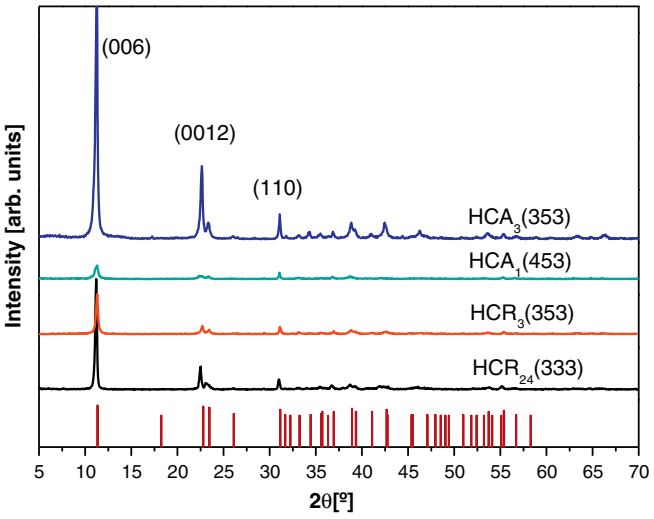

Fig. 1. XRPD of the samples synthesized by conventional heating a) $HCR_{24}(333)$, b) $HCR_3(353)$, c) $HCA_1(453)$ and d) $HCA_3(353)$. Hydrocalumite pattern: [JPDCS file: 035-0105].