



Fast microwave synthesis of hectorite

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ABSTRACT

Hectorite has been synthesized by aging the gel precursor by microwave–hydrothermal treatment at 393 K for 16 h. This hectorite had higher purity (60%) than hectorite prepared by conventional heating (45%). The effect of brucite used, aging temperature and time under microwaves on the resulting hectorite has been studied by XRD, N₂ adsorption, and SEM techniques. Higher proportions of hectorite with higher crystallinity were achieved at longer aging time, higher temperature, and by using a more crystalline brucite.

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1. Introduction

In hectorite $M_x[Li_xMg_{6-x}Si_8O_{20}(OH)_4]$ ($M=Na, Li, NH_4$) all octahedral sites are occupied with either Mg^{2+} or Li^+ . Hectorites used in many important fields such as catalysis (Körosi et al., 2004), synthesis of polymer-based nanostructured materials (Alexandre and Dubois, 2000), adsorption (Zielke and Pinnavaia, 1988), ionic exchange (Laudelout, 1987), and environmental issues (Pieper et al., 2006). Smectites can be extracted from natural resources; however they must be synthesized to obtain an impurity-free reproducible solid. Classical methods of synthesis involve the use of high temperatures (>623 K) or long aging times (from several days to several weeks) (Granquist and Pollack, 1959; Decarreau, 1980; Klopogge et al., 1999; Higashi et al., 2002).

Microwave technology has been used from 80s in different research fields, such as solid dehydration, and promotion of both organic and inorganic reactions (Komarneni et al., 1992; Kingston and Haswell, 1997). In the last years, there is an increasing interest in using microwaves to synthesize mesoporous materials (Newalkar et al., 2001), not only due to the particular characteristics that the synthesized solids can achieve, but also to decreased synthesis time with the subsequent energy saving. Therefore, microwave reactions constitute valuable processes in Green Chemistry. Microwaves have never been used to synthesize hectorite (or other smectites), but the noteworthy amount of publications reporting synthesis of hydroxalclites (Komarneni et al., 1996; Tichit et al., 2002; Rivera et al., 2006;

Bergadà et al., 2007), or synthesis of zeolites (Pilter et al., 2000; Romero et al., 2004), motivated us to take into account this new method.

We report a faster synthesis of hectorite by microwave–hydrothermal treatment.

2. Experimental

2.1. Synthesis

Hectorite was prepared according to the method reported by Granquist and Pollack (1959) in which brucite sheets are proposed to act as crystallisation nuclei of hectorite. Preparation was carried out as follows: 50 ml of a slurry composed by 0.8 g of SiO₂ (Aerosil 380 from Degussa), 0.3 g of freshly prepared brucite Mg(OH)₂ and 46 mg of LiF was vigorously stirred for 1 h. The slurry contained 3 wt.% solids and the molar ratio of the reactants was SiO₂:Mg(OH)₂:LiF=4:3:1. The samples were aged by autoclaving in laboratory microwave equipment (Milestone Ethos Touch Control), at 373 K for 4 and 8 h (samples H1–H2, Table 1) or at 393 K for 4, 8 and 16 h (samples H3–H6, Table 1). One hectorite sample was aged in an autoclave inside a conventional oven, to compare conventional aging with microwave hydrothermal treatment (sample H7). Brucite was synthesized by two different ways: the first consisted on rehydrating commercial magnesia by refluxing for 2 h (sample Brh); the second by precipitation from an aqueous solution of MgCl₂ with ammonia (Brp).

2.2. X-ray diffraction (XRD)

XRD measurements were made using a Siemens D5000 diffractometer (Bragg–Brentano parafocusing geometry and vertical θ – θ)

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Table 1
Relative integrated intensities for hectorite and amorphous SiO₂

Sample	Absolute integrated intensity			Relative integrated intensity (%)	
	Hectorite	SiO ₂	Brucite	Hectorite	SiO ₂
H1	5537	3573	685	60.78	39.22
H2	8539	4577	202	65.10	34.90
H3	6926	3580	26	65.92	34.08
H4	6908	5205	0	57.03	42.97
H5	6652	6012	0	52.53	47.47
H6	8934	6083	0	59.49	40.51
H7	6769	4870	0	58.16	41.84

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. Cu_{Kα} radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA.

The X-ray diffractogram was analyzed using the Fundamental Parameters Approach convolution algorithm (Cheary and Coelho, 1992) as implemented in the program TOPAS 3.0 (Coelho, 2005). This approach calculates the contribution to the peak width produced by a specific instrument configuration. The crystallite size was calculated from the net integral breadth of the peaks, β_i, (Stokes and Wilson, 1942) according to the following formula that comes from the Scherrer expression: β_i = λ/εcosθ where λ is the X-ray wavelength, ε is the crystallite size and θ is the Bragg angle. The diffraction peaks of hectorite presents an anisotropic peak broadening due to the plate shape of hectorite particles: (001) peaks usually presents different width than (hk0) peaks. Reflection (001) was selected to determine the basal spacing of the samples, and to estimate the crystallite size in the stacking direction. Reflection (060) was used to calculate the crystallite size of the sample sheets.

The starting cell parameters of hectorite were *a*: 5.2401 Å, *b*: 9.0942 Å, *c*: 10.7971 Å and β: 99.207° with the space group C2/m (Breu et al., 2003). The crystal structure of hectorite was not used for quantitative analysis because it was described with heavy cations that are not present in the current samples. For brucite, we took the cell parameters of ICDD card 44-1482: *a*: 3.1442 Å and *c*: 4.777 Å with the space group P-3m1.

For amorphous SiO₂, we used an isolated broad peak located at ~22.83° 2θ. The 2θ position of this amorphous halo was previously adjusted with a pure sample of amorphous SiO₂.

The refined parameters that were allowed to vary with the individual profiles included cell parameters, constrained peak position of amorphous SiO₂, linear background function, zero error, and the integral breadth of a Lorentzian profile to describe the extent of particle size induced broadening. The anisotropic peak broadening of hectorite was modelized fitting a spherical harmonic function implemented in the software. Fig. 1 shows one example of refined diffractogram.

The mass fraction of hectorite, brucite and SiO₂ was indirectly derived from the integrated intensity of all reflections that appear in the 2-theta range measured (Table 1). We related the relative integrated intensity of hectorite and amorphous SiO₂ with previous chemical analysis in such a way that a direct relationship was found between intensity and chemical analysis.

2.3. X-ray fluorescence (XRF)

Elemental analyses of the samples were obtained with a Philips PW-2400 sequential XRF analyzer with Phillips Super Q software. Analyses were made by triplicate for each sample.

2.4. N₂ adsorption

N₂-adsorption-desorption isotherms were recorded at 77 K using a Micromeritics ASAP 2000 surface analyzer. Prior to analysis samples were outgassed at 423 K. Specific surface areas were calculated from BET method.

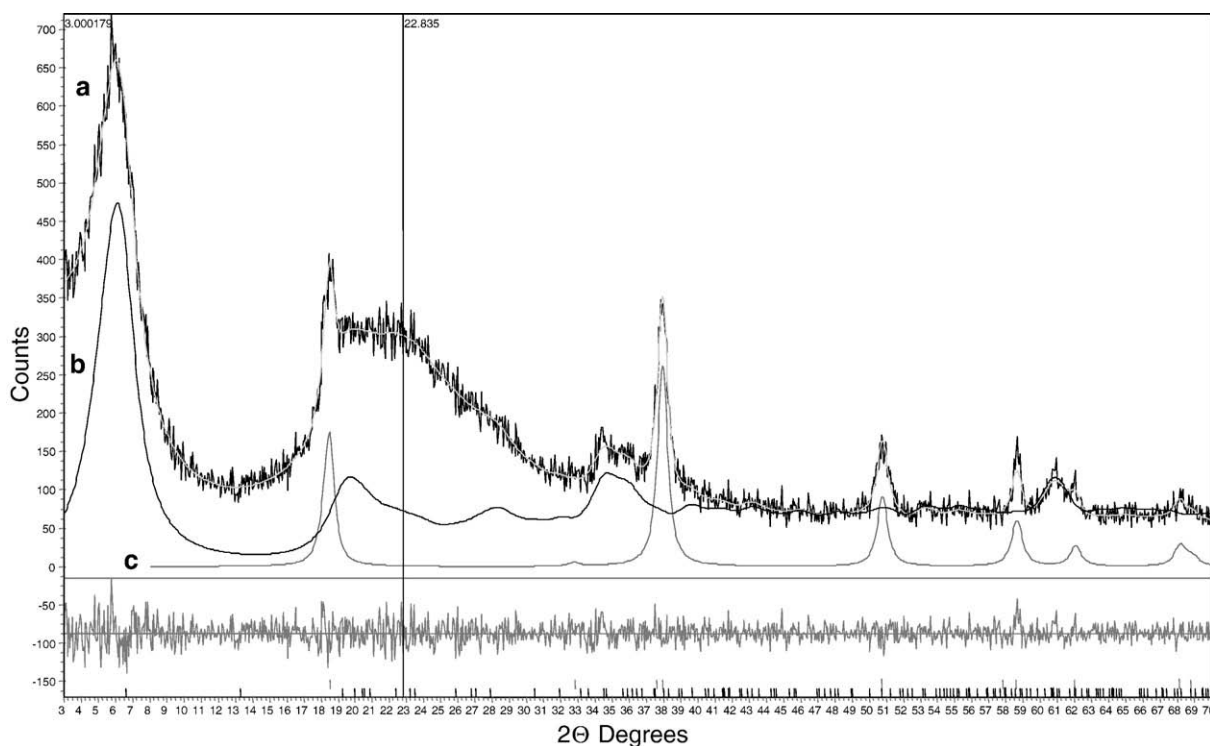


Fig. 1. (a) XRD pattern of one hectorite sample, (b) hectorite contribution, (c) brucite contribution, and amorphous SiO₂ (vertical line at 22.835° 2θ).

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