



Research paper

Use of polymer as template in microwave synthesis of saponite. Study of several factors of influence



Fiseha B. Gebretsadik, Pilar Salagre*, Yolanda Cesteros

Facultat de Química, Universitat Rovira i Virgili, C/Marcel·lí Domingo s/n, 43007 Tarragona, Spain

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ABSTRACT

Several saponites were synthesized at pH = 8 by microwaves or conventional hydrothermal aging with different slurry dilutions (H₂O/Si molar ratios of 250, 125 and 50) at 453 K under autogenic pressure. The influence of using a polymer as template, during the synthesis, and its molecular mass was investigated. The saponite prepared with medium dilution slurry by microwaves had the best incorporation of Al³⁺ in tetrahedral positions (Al^T/Al^O = 9.2), in agreement with its highest C.E.C. (0.87 mEq/g). Additionally, this sample showed the highest surface area (461 m²/g). In general, the increase of the slurry concentration and the presence of polymer improved the order in the tetrahedral sheet and decreased the amorphous silica content. The effect of polymer, on the stacking, was low but depended on the dilution and heat source (microwaves or conventional). The use of polymer and its molecular mass modified the saponite porosity and the incorporation of Al³⁺ in the tetrahedral sheet.

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1. Introduction

Saponites are trioctahedral 2:1 layer phyllosilicates of the smectite group with general formula M_x[Mg₆Al_xSi_{8-x}O₂₀(OH)₄] (M = Na, Li, NH₄). The layer consists of an octahedral sheet sandwiched between two tetrahedral ones (TOT type clay mineral). In the tetrahedral sheet, Si⁴⁺ and Al³⁺ are four-fold coordinated with oxygen. The octahedral sheets are composed of Mg²⁺ cations six-fold coordinated with oxygen and/or hydroxyl groups.

An isomorphous substitution of Si⁴⁺ in the tetrahedral position by Al³⁺ results in a negative layer charge in the sheet. However, substitution can also occur in the octahedral position whereby Al³⁺ substitutes Mg²⁺ with an atomic ratio of 2:3 without affecting the layer charge (Suquet et al., 1981) or in a 1:1 ratio with the generation of a positive layer charge, which compensates the negative one of the tetrahedral sheet. Additional negative charge in the layer could appear due to the presence of octahedral vacancies, as detected during the synthesis of hectorites at short reaction times (Iwasaki et al., 1989; Sánchez et al., 2013). The resulting negative charge is compensated by interlayer hydrated exchangeable cations such as Na⁺, K⁺, Ca²⁺, or even NH₄⁺, obtaining, in the latter case, a Brønsted acid material after decomposition.

Smectites are currently used for composite preparation (Ishimaru et al., 2003; Liu and Breen, 2005; Xue and Pinnavaia, 2008). Additionally,

acidity of smectites combined with the possibility of modulating composition makes this material attractive for heterogeneous catalysis (Casagrande et al., 2005; Gandía et al., 2005; Mata et al., 2007; Trujillano et al., 2011; Varma, 2002; Velasco et al., 2011). Nevertheless, the natural porosity of smectites is limited to microporosity. This gives restricted access to their interlayer space for bulky reactants in catalytic applications. The swelling capacity of smectites could solve this problem for reactions performed in the liquid phase, but one more general solution could be the generation of mesopores by pillar formation in their interlayer space (Carniato et al., 2011; Yao et al., 2004), or by delamination (Iwasaki et al., 1998).

Smectites and composites with modified properties have been prepared (Bisio et al., 2011; Auerbach et al., 2004) by the intercalation of bulky organic and inorganic cationic species and neutral polar compounds (Yui et al., 2002) taking advantage of the swelling capacity of smectites.

Delamination of clays has been widely used for the synthesis of composites. However, there are only few reports in the literature about the synthesis of delaminated mesoporous smectites. Thus, delaminated mesoporous hectorites were prepared by in-situ hydrothermal aging of a gel containing polyvinylpyrrolidone (Carrado and Xu, 1999) or quaternary ammonium salt (Iwasaki et al., 1998; Sánchez et al., 2012) followed by removal of the template by calcinations. Delamination of saponites was noticed by Vicente et al. (2010) during the preparation of saponites using microwaves for the aging treatment, and by Costenaro et al. (2012) for saponites prepared from highly diluted slurries (H₂O/Si molar ratio > 150). In these two references, low C.E.C. values (<60 mEq/g) and the presence of some residual amorphous silica were reported. These low values can be related to the presence of Al³⁺ in the

* Corresponding author at: Universitat Rovira i Virgili, Dpt. Química Física i Inorgànica, C/Marcel·lí Domingo s/n, 43007 Tarragona, Spain. Tel.: +34 977559571; fax: +34 977559563.

E-mail address: pilar.salagre@urv.cat (P. Salagre).

octahedral sheet, by compensation of the tetrahedral sheet charge, and in the interlamellar space, thus making more difficult the exchange.

The aim of this work was to study the influence of several parameters in the characteristics of ammonium saponites synthesized at pH = 8 using ultrasounds for reagent mixing and microwave irradiation or conventional heating during the aging treatment. The parameters studied were: slurry dilution by preparing three blocks of samples with H₂O/Si molar ratios of 250, 125, and 50, influence of using a polymer (polyvinylpyrrolidone) as template during the saponite synthesis and its molecular mass. The comparative effect of these parameters when applying microwaves or conventional heating during aging was also investigated. Samples were characterized by XRD, EDX, TEM, FT-IR, C.E.C. determination, N₂ physisorption and ²⁷Al-MAS-NMR techniques.

2. Experimental

2.1. Saponite preparation

The synthetic protocol previously reported by our research group for the synthesis of saponites (Vicente et al., 2010) was adopted with some modifications: incorporation of template, sequence of reagent addition and the use of tip probe ultrasound for reagent mixing. Two blocks of ammonium saponites, with and without template, were prepared at pH = 8 with different dilution slurries and using microwave irradiation or conventional heating for the aging treatment. The preparation conditions and the nomenclature of the synthesized samples are summarized in Table 1.

The reagents used in the synthesis were fumed silica (Sigma Aldrich), Mg(CH₃CO₂)₂ (Sigma Aldrich) and Al(OH)(CH₃CO₂)₂ (Panreac) as silicon, magnesium and aluminum sources, respectively. Saponites targeted have theoretical formula, Si_{6.8}Mg₆Al_{1.2}(NH₄)_{1.2}O₂₀(OH)₄.nH₂O.

Slurry was prepared in 150 ml of an aqueous ammonia solution with excess of ammonia with respect to that required from the theoretical formula. The reagent amounts were varied to make slurries with H₂O/Si molar ratios of 250, 125 and 50. Stoichiometric amounts of aluminum, silicon and magnesium sources were gradually dispersed one after the other in the same order while the slurry was mechanically stirred for half an hour between each addition. For the synthesis of samples with template (Table 1), polyvinylpyrrolidone (Sigma) was the first reagent added to the aqueous ammonia solution at 20% loading with respect to the mass of the other solid reagents. Polymer was used with two different molecular masses of 40,000 g/mol (P1) and 360,000 g/mol (P2) to investigate the effect of this parameter. After addition of the template, the procedure of addition of the rest of the reagents was the same as for the samples synthesized without template. For all samples (with and without template), the final mixing of the gel was carried out with a tip probe ultrasound for 30 min and the pH of the resulting slurry was 8. Then, the resulting gel was distributed in 3 Teflon reactors of 100 ml and finally the reactors were sealed previous to the hydrothermal treatment. The treatment

was performed at 453 K and autogenic pressure by conventional heating for 72 h or by microwaves (Milestone Ethos Touch Control) at the same temperature for 6 h. Samples were washed by centrifugation to neutrality with double distilled water and dried overnight at 363 K. For the samples prepared with polymer, the template was removed by calcination in a quartz tube reactor first by heating at 500 °C in an air flow of 2 ml/s for 12 h followed by a second step at 550 °C under an oxygen flow of 2 ml/s for 12 more hours.

2.2. X-ray diffraction (XRD)

XRD measurements of samples were made in a Siemens D5000 diffractometer equipped with a CuKα radiation (λ = 1.54 Å) source. Sample was dusted onto a low background Si (510) sample holder and data were collected with an angular step of 0.05° and at rate of 3 s per step. Measurement was done in 2θ diffraction angle between 5 and 70°. Integral breadth estimated from the (060) reflection by applying TOPAS 3.1 was used to calculate the crystallite sizes (Stokes and Wilson, 1942) using the Scherrer equation, considering a shape factor of 0.89 and removing the instrumental contribution with the standard LaB₆ SRM660a. Additionally, the position in the pattern of (060) reflection was employed to determine the preferential occupation of Mg²⁺ in the octahedral positions (trioctahedral character) comparing with the theoretical value of 1.53 Å. Reflection (001) was selected to compare the relative degree of delamination between the samples.

2.3. Infrared spectroscopy (FTIR)

Transmission infrared spectra of pellets (1 mg of sample with 250 mg IR grade KBr, Sigma Aldrich) dried at 353 K for 2 h before measurement were recorded on a Bruker-Equinox-55 FT-IR spectrometer. The spectra were acquired by accumulating 32 scans at 4 cm⁻¹ resolution in the range of 400–4000 cm⁻¹.

2.4. Energy dispersive X-ray (EDX)

Surface Si, Mg and Al contents of samples were quantified by energy dispersive X-ray experiments (EDX). EDX was performed on a scanning electron microscope, JEOL JSM6400, operating at accelerating voltage of 15 kV and working distance of 15 mm. All samples were covered with a graphite layer and accumulation time was 120 s.

2.5. N₂ physisorption

Micromeritics ASAP 2000 apparatus was used for measurement of nitrogen adsorption–desorption isotherms. Samples were degassed under vacuum at 383 K overnight before measurement. Specific surface areas and external surface area were determined from the BET and t-plot methods, respectively. Pore size distribution was calculated by applying the BJH method.

2.6. ²⁷Al-MAS-NMR

²⁷Al-MAS-NMR spectra were obtained on Varian Mercury Vx 400 MHz spectrometer. A 7 mm CPMAS probe was used with the samples spun at 4 kHz at the magic angle, using pulses at a duration of 2 μs with a time between pulses of 5 s and accumulation time of 3 h. Chemical shifts are given in ppm relative to [Al(H₂O)₆]³⁺ (0 ppm) using high purity Al(NO₃)₃·9H₂O (Sigma-Aldrich) as reference.

2.7. Transmission electron microscopy (TEM)

Transmission electron micrographs of the samples were obtained with a JEOL 1011 transmission electron microscope operating at an accelerating voltage of 100 kV and magnification of 200k. Samples were prepared by dispersing 0.1 mg of clay in 50 μl ethanol and applying a

Table 1

The nomenclature and preparation conditions of the synthesized samples.

Nomenclature	H ₂ O/Si molar ratio	Template	Aging
SC250	250	–	Conventional
SM250	250	–	Microwaves
SM250P1	250	P1	Microwaves
SM250P2	250	P2	Microwaves
SC250P1	250	P1	Conventional
SC125	125	–	Conventional
SM125	125	–	Microwaves
SM125P1	125	P1	Microwaves
SM125P2	125	P2	Microwaves
SC50	50	–	Conventional
SM50	50	–	Microwaves
SM50P1	50	P1	Microwaves
SM50P2	50	P2	Microwaves

P1: polyvinylpyrrolidone (40,000 g/mol); P2: polyvinylpyrrolidone (360,000 g/mol).

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