



Research paper

Microwave synthesis of delaminated acid saponites using quaternary ammonium salt or polymer as template. Study of pH influence



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ARTICLE INFO

Article history:

Received 29 January 2015

Received in revised form 27 April 2015

Accepted 4 May 2015

Available online 21 May 2015

Keywords:

Saponite

Microwave

Surfactant

Mesoporous

Delamination

Post-synthesis modification

ABSTRACT

Mesoporous saponites were prepared at pH 8 and 13 without and with template (surfactant or polymer) at 453 K and autogenic pressure using microwaves or conventional oven during the hydrothermal ageing treatment. Acidity was obtained by calcination of the NH_4 -form. The effect of dilution ($\text{H}_2\text{O}/\text{Si}$ molar ratios of 250, 125 and 50) was studied for the samples prepared at pH 8 with surfactant. In order to compare the effect of introducing surfactant during or after saponite synthesis, several samples prepared at pH 13 were modified after synthesis by refluxing or by stirring at room temperature in a surfactant solution. Preparation of samples at pH 13 favoured the ordering in the stacking direction, improved $\text{Al}^{\text{IV}}/\text{Al}^{\text{O}}$ ratio and led to samples with lower amorphous siliceous material content. The use of microwaves and surfactant for the synthesis at pH 13 afforded a saponite with the highest surface area ($603 \text{ m}^2/\text{g}$) and the smallest lamellae crystallite size (about 4 nm). The properties of the samples synthesized at pH 8 with surfactant depended on the dilution. Thus, the degree of delamination, the BET area and the $\text{Al}^{\text{IV}}/\text{Al}^{\text{O}}$ ratio increased whereas the amorphous siliceous material content decreased at lower slurry dilution. The incorporation of the surfactant by post-synthesis resulted in some degree of delamination especially when using refluxing. However, the degree of delamination was higher for the saponites prepared with the addition of the surfactant during the hydrothermal synthesis.

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1. Introduction

Some reactions and processes in the industry are catalysed by corrosive and polluting solution acid catalysts (Taguchi and Schüth, 2005). Their use is posing safety, health, environmental, economic and etc. concerns due to problems related to catalyst loss, separation and disposal (Busca, 2007). Important efforts were made to find benign and recoverable acid catalysts (Gładysz, 2002). The emergence of zeolite as solid acid catalyst brought a lot of benefits (Corma, 1997). However, many reagents in the fine and petrochemical industries were excluded by the microporous structures of zeolites (Ocelli et al., 2002).

Solid acid catalysts with wider pore structure and high thermal stability were reported (Beck et al., 1992; Kresge et al., 1992). Researchers at Mobil came up with a family of mesoporous aluminosilicates called M41S exhibiting large and uniform pores, high specific surface area and pore volume (Karge et al., 1994; Vartuli et al., 1994). Subsequently, attempts were made to modify and control the pore geometry, acidity and thermal stability of mesoporous materials (Selvam et al., 2001).

Preparation methods based on incorporation of bulky polyoxocations of Al, Ce, Cr, Ga, La, Si, Ti, and Zr (Kloprogge et al., 2005) and silicate (Torii and Iwasaki, 1988) as pillars were developed to prepare stable clays with accessible pores. The use of transition metal oxides as pillars also increased Lewis acid or redox characteristics (Ming-Yuan et al., 1988).

Clay minerals are cheap, easily available materials widely used in catalysis and adsorption (Busca, 2007). Surface area and acidity of natural clays are low and acid treatment and delamination were used to increase surface area (Vaccari, 1999). Among clay minerals, smectites have comparatively high surface area, acidity and swelling capacities making them good adsorption and catalytic materials (Dentel et al., 1995; Breen et al., 1997; He et al., 2001; Alther, 2003).

Saponites are trioctahedral clays of the smectite family with TOT structure (Griffen, 1992). The isomorphous substitution of Si^{4+} by Al^{3+} occurs in the tetrahedral sheets causing a negative layer charge. Hence, hydrated exchangeable cations are incorporated in the interlayer space to maintain electrical neutrality. The possibility of exchanging the interlayer cations with others gave clays with modified properties (Mortland et al., 1986; Boyd et al., 1988; Jaynes and Boyd, 1991). The exchange by H^+ could provide acid properties. When cations were exchanged by organic cations of long alkyl chains, hydrophobic composites with high adsorption capacity for organic contaminants could be obtained (Ray and Okamoto, 2003).

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One way of preparation of mesoporous clay minerals involved the use of bulky organic polymers and surfactants as void fillers or galleries, which upon calcination left porous structure behind. For example, mesoporous hectorite was prepared by in-situ hydrothermal crystallization of gel containing cationic surfactant (Iwasaki, et al., 1989) or neutral polymer (Carrado and Xu, 1999). Moreover, the use of different technologies and manipulation of the synthesis conditions allowed some degree of control over the pore structure of materials (Costenaro et al., 2012). Saponites with large pores were prepared by microwaves from gels of high slurry dilution (H_2O/Si molar ratio 250) (Vicente et al., 2010; Gebretsadik et al., 2014). The use of microwaves in preparation also afforded samples with higher delamination and reduced reaction time with subsequent energy saving (Bergadà et al., 2007). Ultrasound technology resulted in highly dispersed particles with homogeneous morphology and high surface area (Suslick and Price, 1999).

In this work, we report the use of microwaves, ultrasounds and template (polymer or surfactant) in the preparation of high surface area acid mesoporous saponites. Various preparation parameters such as pH, effect of template, type of template and use of surfactant during or after saponite synthesis were investigated in order to establish their effect.

2. Experimental

2.1. Saponite preparation

Two groups of saponites with theoretical formula $(M)_{1.2}Si_{6.8}Al_{1.2}Mg_6O_{20}(OH)_4 \cdot nH_2O$ ($M = Na^+, NH_4^+$), determined from the masses of the precursor compounds added in the slurry preparation, were prepared at pH = 8 and 13, with and without template (Table 1). The preparation of the slurry for the synthesis of sodium saponites at pH = 13 (4 samples) was carried out following the method described by Trujillano et al. (2011) with some modifications. A CO_3^{2-}/HCO_3^- buffer, pH 13, was prepared by dissolving 3.63 g of NaOH and 6.56 g of $NaHCO_3$ in 50 mL double distilled water. Solution **A** was prepared in the buffer by adding 5.6 mL sodium silicate solution ($SiO_2 \cdot NaOH$, SiO_2 27 wt.%, density 1.39 g/mL, Aldrich) and stirring the mixture mechanically for 10 min. Some samples were prepared in the presence of template, dodecyl trimethylammonium chloride surfactant (AS) (Acros) or polyvinylpyrrolidone polymer (P) (Sigma-Aldrich) with molar mass of 40,000 g/mol. For these samples, the surfactant or the polymer (AS or P) was added before the silicate solution at 20 wt.% loading with respect to the mass of the other solid reagents. In another beaker, solution **B** was prepared by dissolving 2.31 g $Al(NO_3)_3 \cdot 9H_2O$ (Aldrich) and 7.91 g $Mg(NO_3)_2 \cdot 6H_2O$ (Aldrich) in 5 mL double distilled water. Solution **B** was added drop by drop into solution **A** while under mechanical stirring. The slurry was mixed for 30 min and submitted to a final mixing in a tip ultrasound sonicator for 30 more min. All

samples of pH 13 were prepared at slurry dilution (H_2O/Si molar ratio) of 125.

Ammonium saponites (5 samples), with the same theoretical formula as pH 13 samples, were prepared from a slurry of initial pH = 8 with and without template by modifying the protocol previously reported by our research group (Gebretsadik et al., 2014). In 50 mL of a 3 wt.% ammonia solution, for the samples prepared with template, this was added at 20 wt.% loading with respect to the mass of the other solid reagents. Then, stoichiometric amounts of $Al(OH)(ac)_2$ (Aldrich), fumed silica (Aldrich) and $Mg(ac)_2 \cdot 4H_2O$ (Panreac) were added one after the other in the same order while stirring the solution for 30 min between each addition. The amount of the precursor (Si, Mg and Al) salt was varied with respect to the amount of water so that slurries at H_2O/Si molar ratios of 250, 125 and 50 were prepared. These slurries were mechanically stirred for 30 min followed by sonication for 30 min more.

The slurries of the samples prepared at pH 8 and 13 were then transferred into an autoclave, sealed and aged with microwaves (Milestone ETHOS-TOUCH CONTROL equipped with a temperature controller) at 453 K for 6 h or in a conventional oven at 453 K for 72 h. The resulting solution was filtered; the solid was washed with double distilled water until neutrality and dried overnight in an oven at 363 K. For the samples prepared with template, this was removed by calcination in air (1 mL/s) into a quartz tube reactor at 773 K for 12 h. When the template removal was not complete (sample appeared black or grey), calcination was continued for another 12 h at 823 K under an oxygen flow (1 mL/s).

The sodium saponite synthesized at pH 13 was transformed to their NH_4 -form by exchanging the sodium interlayer cation with saturated NH_4NO_3 solution at room temperature for 36 h (1 g of sample in 50 mL solution). The acid form was then obtained by calcination of the NH_4 -form in air at 723 K for 5 h.

Finally, two saponites prepared without template at pH 13 and aged with microwaves or by conventional heating were modified after synthesis by exchanging the sodium interlayer cation of the precursor sodium saponite with a dodecyl trimethylammonium chloride (AS) solution. In a typical experiment, 1 g of sample was stirred in 50 mL of double distilled water to favour its swelling and 0.4 g of surfactant was added. The mixture was stirred at room temperature or refluxed for 24 h. The sample was filtered and washed rigorously with double distilled water, dried overnight in an oven at 363 K and calcined and transformed into their acid form as previously described.

The nomenclature of the samples appears in Table 1. The letter S means saponite, the letter M or C indicated the heating source used during ageing, microwaves or conventional heating, respectively. The templates used were designated as P for the polymer and AS for the quaternary ammonium salt. The numbers 8 and 13 in the nomenclature

Table 1
The nomenclature and preparation conditions of the synthesized samples.

Nomenclature	H_2O/Si molar ratio	Template	% of template loading ^a	Mode of template addition	Ageing
SM13	125	—	—	—	Microwaves
SM13P	125	Polymer	20	During synthesis	Microwaves
SM13AS	125	Surfactant	20	During synthesis	Microwaves
SC13	125	—	—	—	Conventional
SM8(125)	125	—	—	—	Microwaves
SM8(125)P	125	Polymer	20	During synthesis	Microwaves
SM8(250)AS	250	Surfactant	20	During synthesis	Conventional
SM8(125)AS	125	Surfactant	20	During synthesis	Microwaves
SM8(50)AS	50	Surfactant	20	During synthesis	Microwaves
SM13AS _{PSM}	125	Surfactant	40	Post-synthesis	Microwaves
SC13AS _{PSM}	125	Surfactant	40	Post-synthesis	Conventional
SM13AS _{PSM} R	125	Surfactant	40	Post-synthesis	Microwaves
SC13AS _{PSM} R	125	Surfactant	40	Post-synthesis	Conventional

^a The amount of template was calculated with respect to the mass of the sample for the samples prepared by post-synthesis while for the samples in which the surfactant was added during synthesis, the amount of template was calculated with respect to the mass of the other solid reagents.

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