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Mechanical and textural properties of extruded materials manufactured with AlFe and AlCeFe pillared bentonites

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ABSTRACT

Extrudates were developed on AlFe and AlCeFe pillared bentonites shaped as pellets, Raschig rings and monoliths were prepared with Na- or Ca-bentonite as binder. The AlFe and AlCeFe poly(hydroxo metal) bentonites were tested as catalyst in the oxidation of phenol.

The mechanical stability of the extrudates, measured as breaking force was evaluated as a function of thermal treatment (105, 400 and 500 °C) together with the stability to water immersion. Calcination at 500 °C was needed to obtain water stable materials.

Specific surface area, micro- and mesopore volume of the extrudates depended on the calcination temperature. The conversion rate for phenol oxidation with extrudates was generally lower than for powders, due to an increased induction period and diffusion limitations.

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1. Introduction

Clay minerals have received much attention with respect to their possible application as catalytic materials. However, these solids inherently have the disadvantage of poor access to their active surface, which decreases their efficiencies for catalytic reactions. Nevertheless, by pillaring the clay minerals an improved porous catalytic material is formed with wide pore distribution, high thermal stability and, for some reactions, specific catalytic properties.

Numerous studies on the synthesis of pillared clay minerals, also called Pillared Interlayered Clays (PILC's) are cited in the literature, treating various applications in catalytic processes such as cracking (Wenyang et al., 1991; González et al., 1999; Bodman et al., 2002; Bodman et al., 2003; Gyftopoulou et al., 2005), hydrogenation of naphthalene (Colín et al., 2005), acylation of alcohols (Akçay, 2004), dehydrogenation of ethylbenzene (González and Moronta, 2004), catalytic wet peroxide oxidation (Barrault et al., 1998, 2000; Guélou et al., 2003; Carriazo et al., 2003, 2005a, 2008), selective catalytic reduction of nitrogen oxides (Valverde et al., 2003; Chmielarz et al., 2004; Qi et al., 2004;), phenol hydroxylation (Letaïef et al., 2003) and conversion of methanol (Sun Kou et al., 2003), among others.

However, the use of pillared clay minerals as a catalysts has not yet been extended to commercial levels, mainly because it has been difficult to perform the laboratory synthesis procedure at industrial scale, requiring the large volumes of water and long swelling times necessary (Vaughan, 1988). Many efforts have been made to optimize the synthesis, including those of Aouad et al. (2005), who developed a procedure for pillaring clay mineral with poly(hydroxo aluminum) cations, minimizing the processing time and the amount of water used, thus facilitating its extension to an industrial level. This is done by mixing montmorillonite without purification or chemical pretreatment with a solid precursor (Al_{13}^{7+}, basic aluminum nitrate) in a dialysis membrane.

The commercialization of PILC based catalysts not only depends on the optimization of the synthesis, but also on the ability to shape the powder material into conformed products (pellets, agglomerates, monoliths, etc.). These materials should keep their chemical properties and reactivity and maintain stability in the reaction medium. The manufacture of pellets, Raschig rings and monoliths that involve pillared montmorillonites has basically been accomplished by use of extrusion techniques (Mohino et al., 2005).

Most of the available literature on the manufacture of extrudates is related to ceramic monoliths such as cordierite, sepiolite, mullite, cordierte–mullite, α- and γ- alumina, zirconia, titania, zeolites and mixtures of these materials (Forzatti et al., 1998; Avila et al., 2005). However, there is very little biographical information related to the manufacture of extrudates based on pillared clays, which remains an essential aspect for these materials to be used at an industrial level. Mohino et al. (2005) studied aspects related to the composition of the paste in the production of monoliths of Al–PILC, together with the effect of temperature and pH on the physicochemical properties of the formed monoliths. The materials retained the properties of pillared clay (high specific surface area, acidity and reactivity) and showed

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good mechanical stability and resistance to changes in temperature and pH.

The ceramic mixtures for extrusion must meet the following requirements: mouldability, only experience a weak contraction during the drying process, be conformed before calcination, to permit handling without distortion, to attain a certain mechanical strength by calcination, while maintaining the intended textural and chemical properties of the original material.

The systems AlFe–PILC and AlCeFe–PILC synthesized in a diluted media were found to be active for phenol oxidation (Carriazo et al., 2003, 2005a, b, 2007a, 2008). Here we report on syntheses of similar pillared bentonites but in a highly concentrated media with ultrasound assistance for the intercalation (Sanabria et al, 2009). This was performed with the aim of achieving a significant decrease in the volume of water and the time periods involved in the synthesis. Once the intercalated clay mineral was obtained, the formulation of a paste included the poly(hydroxo metal) bentonite, bentonites (exchanged with sodium and calcium ions) as binding agents and water. The composition of the extrusion mixture was selected based on the assessment of mechanical strength and stability in an aqueous medium. The structural and textural changes of extrudates were evaluated by X-ray diffraction (XRD) and N_2 adsorption at 77 K. The catalytic activity of the extrudates was evaluated by phenol oxidation in a dilute aqueous medium.

2. Experimental

2.1. Synthesis of pillared bentonites

The starting clay was a bentonite from Valle del Cauca – Colombia (Carriazo et al., 2007b). The fractionated bentonite was exchanged with 0.5 M $CaCl_2$, washed in distilled water until a conductivity of <20 µS/cm was reached, dried at 60 °C and finally ground and sieved to 100 mesh. The polymeric precursor AlFe in aqueous solution was synthesized as described before in the previous study (Sanabria et al., 2008, 2009) with the Fe/Al molar ratio of 0.05 and the OH/metal ratio of 2.46. The polymeric precursor AlCeFe was synthesized in a manner similar to that of AlFe, with the Fe/Al molar ratio of 0.05 and the Ce/Al ratio of 0.02. The OH/metal molar ratio was 2.46. The optimal molar ratios of Fe and Ce were obtained from preliminary tests.

The mixture of bentonite and the solid pillaring agent (ratio of 20 meq metal/g bentonite) (Carriazo et al., 2003, 2005a, 2007a) was dialyzed in distilled water for 3 h then subjected to an ultrasound bath (50 kHz) for 30 min (Sanabria et al., 2009). The modified material was separated by centrifugation, washed until a conductivity near that of distilled water was reached, dried at 60 °C (poly(hydroxo metal) bentonite), ground and sieved to 100 mesh. Samples were calcined at 400 °C during 2 h with a heating ramp of 2 °C/min (pillared bentonites). The bentonite was noted as B and the pillared bentonites as B–AlFe and B–AlCeFe, respectively.

2.2. Extruded pillared bentonites

The mixtures to extrude were: AlFe or AlCeFe poly(hydroxo metal) bentonite, calcium and sodium bentonite and water. The solids were mixed before water was added. The paste was mixed with a spatula, placed into a 20 mL plastic syringe and, after eliminating air bubbles by extruding the mixture and feeding it back into the syringe for at least 3 times, the final cylindrical extrudates were obtained with a diameter similar to the syringe nozzle (2.5 mm). These samples were dried at room temperature, cut in to 2 cm long pieces and heated to 105, 400 and 500 °C for 2 h after reaching the target temperature using a heating ramp of 1.5 °C/min. Chemical and mechanical stabilities (water immersion) were then determined.

Furthermore, the final formulations were also extruded into pellets, Raschig rings and cylindrical monoliths with square cells, using a Bonnot extruder with an extrusion speed of 13.5 rpm. The extruded materials were dried at room temperature for 3 days then calcinated for 4 h at 500 °C, with a heating ramp of 1 °C/min. Subsequently, the mechanical strength and stability in water were determined. The extruded pellets with a diameter of 1.96 mm were cut to lengths of around 6 mm. The Raschig rings with an external diameter of 4.25 mm, and an internal diameter of 2.40 mm were cut to a length of 6 mm. The cylindrical monoliths had an outside diameter of 16.25 mm, a wall thickness of 0.85 mm and the square open channels were 1.72 mm. This gave a cell density of 11.7 cells/cm^2. These monoliths were cut to lengths of 15 mm.

2.3. Characterization

Chemical analysis of the bentonite and pillared bentonites was accomplished by X-ray fluorescence using a Magix Pro Philips PW2440 instrument. The amount of leached metal (after reaction) was determined by atomic absorption spectrometry using a PerkinElmer 400 spectrophotometer.

X-ray diffraction (XRD) patterns of bentonite, pillared bentonites and extrusion mixtures were determined in a LabX Shimadzu XRD-6000 diffractometer using Cu Kα radiation (steps of 0.01° 2θ and 2 s/step).

The thermal analysis was performed in a STA 409 Netzsch instrument with a 75 cm^3/min air flux and heating speed of 10 °C/min.

The mechanical strength of the extruded materials was evaluated with a TA-TX Plus universal texture analyzer. Variations of the exact force transversally confined to the axis until fracture were determined based on the force–time graph (Fig. 1). A cylindrical stainless steel probe of 2 mm in diameter with a trigger force of 0.5 kg was used for these tests. To establish the accuracy of the instrument, 10 measurements of exact load were performed on three samples of extruded material calcined at 105, 400 and 500 °C. A maximum standard deviation of 1.5 N was achieved.

Nitrogen adsorption–desorption isotherms of bentonite, pillared bentonites and extruded samples were determined in a Micromeritics ASAP 2020 instrument at 77 K after outgassing the samples for 1 h at 90 °C followed by 3 h at 400 °C at a vacuum of $<10^{-2}$ Pa.

2.4. Measurement of catalytic activity

The catalytic activity was evaluated for the oxidation of phenol in water, using a previously reported procedure (Carriazo et al., 2003, 2005a,b, 2007a, 2008). In the tests with pellets and Raschig rings, a 250 mL glass semibatch reactor thermostated at 25 °C was used, with 4 plastic mesh baskets attached to a stainless steel shaft connected to a motor.

Tests with monoliths were performed in a fixed bed reactor with recirculation. The 7.5 cm long glass reactor had a 2.1 cm internal diameter and the monolith was packed between two layers of glass Raschig rings. The phenol recirculation flow was 150 mL/min.

For the reaction, 250 mL of a 5×0^{-4} M phenol solution, 1.25 g of the pillared bentonite (2.08 g of the extruded material), a solution of 0.1 M H_2O_2 (20 mL, 2.22 mL/h) hydrogen peroxide was used and the

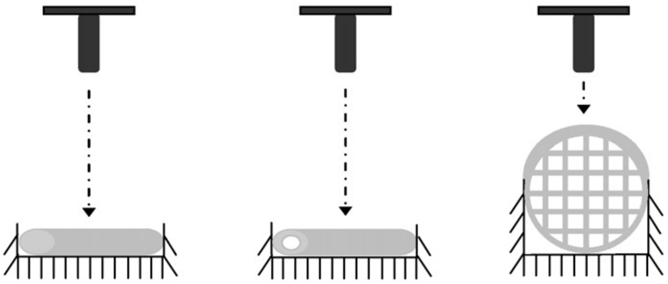

Fig. 1. Diagram of mechanical strength measurements.

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