



Pillared clays with Al–Fe and Al–Ce–Fe in concentrated medium: Synthesis and catalytic activity

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ABSTRACT

This paper proposes a new methodology for the modification of clays with the mixed Al–Fe and Al–Ce–Fe systems, which involves the synthesis of solid polymeric precursors and their use as pillaring agents in the modification of clays. The process of intercalation of clay with Al₁₃, Al₁₃ + Fe and Al₁₃ + Ce + Fe nitrate was performed using ultrasound. The pillaring agents Al₁₃, Al₁₃ + Fe and Al₁₃ + Ce + Fe were characterized by XRF, XRD, SEM and ²⁷Al NMR techniques, and pillared clays were characterized by XRF, XRD and N₂ adsorption to 77 K. The catalytic properties of pillared clays were evaluated using catalytic wet peroxide oxidation of phenol in dilute aqueous medium, demonstrating activity comparable to that of solids modified by the conventional method.

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1. Introduction

Synthesis of pillared clays (PILC) at the laboratory level primarily entails the suspension of diluted clay (2 wt.%) within a pillaring solution (typically 0.25 M), and it involves considerable contact time and large amounts of water [1–3]. To expand the pillaring process to an industrial scale, there is a need for simplification of procedures and optimization of the unit operations involved, particularly to decrease the relative volume of water. From a technical and economical point of view, Vaughan [1] lays down three conditions for the synthesis of pillared clays at a commercial scale:

- Minimum treatment of clay for purification.
- No prior requirement of clay exchange with sodium solutions.
- The use of concentrated suspensions of clay.

Current research into the process of pillaring is focused on the synthesis with concentrated suspensions, both of clay and of the pillaring agent. In this regard, Aouad et al. [2] developed a procedure for pillaring clays with aluminum, which minimizes the processing time and the amount of water used, allowing its extension to an industrial scale. To simplify the preparation of Al-PILC, natural clay is used without purification or chemical

pretreatment, so the clay powder and solid Al₁₃ nitrate come into contact in a dialysis membrane. The solid pillared by means of the aforementioned method has features similar to those of the solid synthesized by the conventional procedure that uses dilute suspensions [2].

In contrast, the chemical structure of the pillar can be modified through synthesis of so-called mixed pillars, which are derived from the hydrolysis of solutions containing two or more metal cations. The pillaring of clay with mixed metal complex of Al and Fe has been reported in detail by Lee et al. [4], who determined by Mössbauer spectroscopy that Fe is located preferentially on the surfaces of the pillars of alumina. Pálinkó et al. [5,6] analyzed by FTIR and Mössbauer spectroscopy the nature of the mixed species Al–Fe generated in pillared clays, as well as in pillaring agents precipitated as sulfates. They have concluded that there is no tetrahedral or octahedral isomorphous substitution of Fe in the Keggin structure of Al₁₃, which indicates the presence of co-hydrolysis and co-pillaring during the modification.

The clays modified by means of mixed pillars offer great potential as catalysts in various reactions of industrial interest due to the introduction of metal cations with catalytic properties. The decomposition of hydrogen peroxide in the presence of ions Fe³⁺/Fe²⁺ (Fenton system) is an important example, which prompted the proposal of a similar system with iron species supported in clays for oxidation reactions of organic compounds [7–9]. In order to improve the distribution of the active phase and increase the catalytic properties of the Al–Fe–PILC, some authors reported the addition of cerium to the mixed system [10–12].

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In this article, we report the synthesis of Al_{13} , $\text{Al}_{13} + \text{Fe}$ and $\text{Al}_{13} + \text{Ce} + \text{Fe}$ sulfate as precursors of Al_{13} , $\text{Al}_{13} + \text{Fe}$ and $\text{Al}_{13} + \text{Ce} + \text{Fe}$ nitrate, respectively. We used a procedure similar to that developed by Furrer et al. [13] for basic aluminum sulfate and nitrate, but we included Fe and Ce as second and third cations. The intercalation of clay powder with the Al_{13} , $\text{Al}_{13} + \text{Fe}$ and $\text{Al}_{13} + \text{Ce} + \text{Fe}$ nitrate was carried out using a dialysis membrane, applying ultrasound to promote diffusive processes and reduce synthesis time.

2. Experimental

2.1. Synthesis of the pillaring agent

The polymeric precursor in an aqueous solution was synthesized using the methodology of Furrer et al. [13] for basic aluminum chloride [13], but adding Fe and Ce as second and third metals. From $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and NaOH, three pillaring solutions were prepared: first, the Al solution; second, Al–Fe with 5 mol% of Fe; and third, Al–Ce–Fe with 2 mol% of Ce and 5 mol% of Fe. The OH/metal hydrolysis ratio was 2.46. Once hydrolysis was completed, the solutions were aged for 4 h at 60 °C.

Aqueous solutions of Al_{13} , $\text{Al}_{13} + \text{Fe}$ and $\text{Al}_{13} + \text{Ce} + \text{Fe}$ chlorides were added to 0.1 M solution of Na_2SO_4 , with a molar ratio of metal/ SO_4 of 1.0, while maintaining agitation at 700 rpm for 2 h. The mixture was then allowed to stand for 36 h. After this time, the precipitate was separated from the suspensions by centrifugation; successive washings with a buffer solution of citric acid/sodium citrate were made in order to dissolve the hydrolyzed iron not associated to the Keggin structure.

The Al_{13} , $\text{Al}_{13} + \text{Fe}$ and $\text{Al}_{13} + \text{Ce} + \text{Fe}$ sulfates were dried at 60 °C, dissolved in a solution of $\text{Ba}(\text{NO}_3)_2$, and subjected to ultrasound for 4.5 h [13]. Finally, the solution was separated from the solid (BaSO_4) by centrifugation and evaporated at 60 °C in an oven until crystals of Al_{13} , $\text{Al}_{13} + \text{Fe}$ and $\text{Al}_{13} + \text{Ce} + \text{Fe}$ nitrates were obtained. These nitrates were ground and sifted in a 100 mesh to then be used as pillaring agents in the modification of clays.

2.2. Synthesis of pillared clays

The starting clay was a natural bentonite from Valle del Cauca, Colombia, which was segregated by particle size (fraction $< 2 \mu\text{m}$) following the gravimetric sedimentation procedure [14]. The fraction of clay was homoionized with CaCl_2 [15], washed with distilled water until reaching a $< 20 \mu\text{S}/\text{cm}$ conductivity, dried at 60 °C and finally ground and sifted in a 100 mesh.

Solids were synthesized at a ratio of Al_{13} , $\text{Al}_{13} + \text{Fe}$ and $\text{Al}_{13} + \text{Ce} + \text{Fe}$ nitrates to clay of 20 meq metal/g clay. This ratio produced solids with good textural properties and excellent catalytic activity in the oxidation reaction of phenol in a dilute aqueous medium [8,10–12,16]. In a dialysis membrane, metal nitrate was mixed with calcium clay. The membrane was covered with distilled water and agitated for 3 h, allowing the passage of water through it. Subsequently, the container with the membrane was left in an ultrasound bath at 50 kHz for a period of 30 min.

The intercalated solids were removed from the membrane, centrifugally washed until reaching a conductivity near that of distilled water, dried at 60 °C, ground and sifted in a 100 mesh. Finally, the solids were heated to 400 °C at 2 °C/min and calcined for 2 h.

2.3. Characterization of the pillaring agent

Al_{13} , $\text{Al}_{13} + \text{Fe}$ and $\text{Al}_{13} + \text{Ce} + \text{Fe}$ sulfates as well as Al_{13} , $\text{Al}_{13} + \text{Fe}$ and $\text{Al}_{13} + \text{Ce} + \text{Fe}$ nitrates were characterized by X-ray fluorescence (XRF) on a Philips Magix Pro PW2440 instrument, with

samples prepared as pearls. For the X-ray diffraction, a Shimadzu LabX XRD-6000, which operates with Cu K α radiation (steps of 0.01 °2 θ and 2 s/step), was used. The scanning electron microscopy (SEM) was performed on a Jeol JSM-5400 equipment, using samples that were previously gold coated. The NMR spectra were taken on a Bruker DRX400 spectrometer with a magnetic field of 9.36 T and equipped with a multinuclear probe. Powdered samples were packed in 4 mm zirconia rotors and spun at 10 kHz. ^{27}Al NMR spectra were recorded at 104.26 MHz with a $\pi/20$ pulse width of 1.6 μs and delay time of 1 s. The chemical shift is reported in ppm from 0.1 M solutions of AlCl_3 .

2.4. Characterization of pillared clays

The starting clay and pillared clays were characterized by X-ray fluorescence (Philips Magix Pro PW2440), X-ray diffraction (Shimadzu LabX XRD-6000, with Cu K α radiation, powder samples, steps of 0.05 °2 θ and 2 s/step) and N_2 adsorption to 77 K. Textural properties were studied by N_2 adsorption measurements at liquid nitrogen temperature. The experiments were carried out in a Micromeritics ASAP 2020 equipment, where samples were degassed for 1 h at 90 °C and 3 h at 300 °C in vacuum.

2.5. Catalytic activity

The catalytic activity of the solids was evaluated in the oxidation reaction of phenol in a dilute aqueous medium by the procedure reported in previous works [8,12,16]. For each test, the reactor was loaded with 100 ml of a 5×10^{-4} M phenol solution, 0.5 g of the catalyst, a 0.1 M hydrogen peroxide solution and brought to a pH of 3.7. Monitoring of the phenol conversion with time and for the appearance of subproducts in the oxidation reaction were carried out by high performance liquid chromatography (HPLC) using a Hitachi D-7000 (LaChrom) instrument equipped with a Lichrosphere 60 Select B column. The assessment for total organic carbon (TOC) was carried out by means of an AnaTOC instrument. In all tests, a relative error less than 4% was estimated in the ranges from 60 to 240 min for the phenol conversions and from 120 to 240 min for TOC conversions [12].

3. Results and discussion

3.1. Characterization of pillaring agent

Table 1 summarizes the results of chemical analysis for Al_{13} , $\text{Al}_{13} + \text{Fe}$ and $\text{Al}_{13} + \text{Ce} + \text{Fe}$ sulfates and nitrates. The atomic ratio Al:Na:S 13:0.1:3.55 for basic aluminum sulfate with a crystalline monoclinic system was established by Klopogge et al. [17] based on an ICP-AES analysis, which corresponds to the structural formula $\text{Na}_{0.1}[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SO}_4)_{3.55} \cdot x\text{H}_2\text{O}$. The basic aluminum sulfate with crystalline cubic system, described by Johansson [18], corresponds to the formula $\text{Na}[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SO}_4)_4 \cdot x\text{H}_2\text{O}$, while the one indexed by Parker et al. [19] has the chemical formula $\text{Na}[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SO}_4)_4 \cdot 10\text{H}_2\text{O}$.

According to the values in Table 1, the atomic ratios of Al/Na and S/Na for sulfates synthesized in this work are lower than those obtained by Johansson [18] and near those of Parker et al. [19]. Differences in values may be associated with the method of analysis, since the atomic ratio in this case was obtained by X-ray fluorescence with a semi-quantitative application.

Taking into account the nominal amounts of Fe and Ce used in the synthesis, the incorporation of these two metals accounted for 22.3% of Fe in $\text{Al}_{13}\text{-SO}_4 + \text{Fe}$, and, for 23.8% and 0.94% of Fe and Ce, respectively, in $\text{Al}_{13}\text{-SO}_4 + \text{Ce} + \text{Fe}$. In $\text{Al}_{13}\text{-NO}_3 + \text{Fe}$ and $\text{Al}_{13}\text{-NO}_3 + \text{Ce} + \text{Fe}$, the percentage of incorporated Fe and Ce is much lower than in sulfates, given that, in the SO_4/NO_3 exchange process,

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