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Synthesis of pillared bentonite starting from the Al–Fe polymeric precursor in solid state, and its catalytic evaluation in the phenol oxidation reaction

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Abstract

A new methodology for the modification of a bentonite via pillaring was evaluated in this work, employing a mixed Al–Fe polyhydroxocation and clay powder, placing the two solid materials in contact into a dialysis membrane. The modified solids were characterized by X-ray diffraction (XRD) and elemental chemical analysis and their catalytic activity is probed on the phenol oxidation reaction in diluted aqueous phase. The results show that pillared clay with the solid Al–Fe polyhydroxocation has similar properties to the solid modified by the conventional method, which involves the use of a large quantity of water in the synthesis (clay suspension 2% and dilute pillaring solution). The catalytic tests with the modified solids show, in all cases, 100% of phenol conversion after 2 h and total organic carbon (TOC) elimination between 49 and 53%, in 4 h of reaction, results which can be compared with pillared bentonite from diluted suspensions.

Keywords: Al–Fe polyhydroxocation; Pillared clays; Catalytic wet peroxide oxidation

1. Introduction

Barrer and MacLeod (1955) were the first to introduce the concept of transformation of laminar solids in porous structures by the insertion of molecules in the laminar spacing of clay-like minerals of the smectite type. The terms ‘‘pillared’’ and ‘‘pillaring’’ originated from the works of Brindley and Semples (1977) and Vaughan and Lussier (1980), who found that inorganic robust molecules could be intercalated between layers in clays through an ionic exchange mechanism, followed by the removal of the solvent [1]. During calcination, the metal polyhydroxocation is transformed into an oxide which fixes itself to the clay in a strong manner [1–3]. The introduction of pillars, besides increasing the material's resistance and stability, provides porosity, a greater surface area, access to acid areas existing in natural clay, and the presence of potentially active species for a specific reaction [4,5].

The pillared clays synthesis method (PILC's) at the laboratory level is essentially based on the mixture of a clay dilluted suspension (2%) with a pillaring solution, a process generally involving considerable time and high volumes of water [6]. So that the pillaring process can be scaled at the industrial level, simplification of the procedures and optimization of the unitary operations involved are required, particularly the reduction in the water volume.

The current trend in the pillaring process focuses on the synthesis of concentrated suspensions, both for clay and for the pillaring agent. Schoonheydt and Leeman synthesize Al-saponite through the addition of clay dust to the aluminium pillaring solution [7]. Storaro et al. use a solid pillaring agent (solid chlorhydrol) and clay suspensions in acetone [8]. Recently, Vicente and Lambert have described a new synthetic pillaring path, by using a dialysis membrane, clay dust and small volumes of a pillaring solution [9]. Aouad et al. have developed a procedure for the pillaring of clays with aluminium, which minimizes the time of the process and the amount of water used, allowing for its extension to the industrial level. To simplify the Al-PILC synthesis, natural clay is used without purifying, besides solid Al_{13} nitrate, both

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contained in a dialysis membrane. The solid pillared through this method has similar characteristics to the one synthesized by the conventional method using diluted suspensions [6].

On the other hand, clays modified with mixed pillars offer a great potential as catalysts in several reactions of environmental interest, due to the possibility of introducing metal cations with properties leading to the desired reaction. In this way, recent works point out the possibility to eliminate highly refractory compounds at room temperature and atmospheric pressure, by using hydrogen peroxide as an oxidating agent, whose activation is catalyzed by Fe in a clayish matrix [10,11]. Research on the treatment of industrial wastewaters has been reinforced in the past few years, particularly regarding low cost methods for their recuperation. Catalytic wet peroxide oxidation (CWPO) is one of the most promising emerging processes for the treatment of waters polluted by organic matter [12–14].

In this work, the synthesis of mixed Al–Fe polyhydroxocations in solid state was made as an extension to the method developed by Furrer et al. for the aluminium polymer [15], but including iron as a second cation. The intercalation of clay dust and the mixed pillaring agent in the previously synthesized solid form was performed in a dialysis membrane, following a procedure similar to the one used by Aouad et al. [6]. The solids obtained were characterized by chemical analysis and X-ray diffraction, and the catalytic activity was assessed in the phenol oxidation reaction in aqueous phase. In addition, the Fe content in the leaching of the reactions was quantified by atomic absorption.

2. Experimental

2.1. Synthesis of the Al–Fe polyhydroxocation

The polymeric precursor in aqueous solution was prepared based on the procedure described by Raythatha et al., according to which discrete species are formed with the formula $[Al_xFe_y(OH)_{24}]Cl_7$, where by x and y depend on the Al and Fe proportion [16]. Starting from $AlCl_3{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$ and Na_2CO_3 three solutions were prepared with the following proportion: $[Al_{12.5}Fe_{0.5}(OH)_{24}]Cl_7$, $[Al_{11.7}Fe_{1.3}(OH)_{24}]Cl_7$ and $[Al_{10}Fe_{3.0}(OH)_{24}]Cl_7$ with 3.9, 10 and 23% molar Fe, considering the molar ratio as $100n_{Fe}/(n_{Fe}+n_{Al})$ and a hydrolysis ratio OH/metal = 2.0. The three aqueous solutions of discrete species were submitted to the process of crystallization with Na_2SO_4 and $Ba(NO_3)_2$, according to the methodology proposed by Furrer et al. for obtaining Al_{13} nitrate [15].

2.2. Synthesis of pillared clays

The starting clay is a commercially available, natural bentonite issued from Valle del Cauca, Colombia, provided by Bentocol (Colombia), which has been previously separated by particle size (<2 μm) and homoionized with a 0.5 M solution of calcium chloride [17,18]. The homoionized clay dust and the Al–Fe polyhydroxocation in powder are mixed and placed in the dialysis membrane (Spectra/Por, flat width 45 ± 2 mm, diameter 29 mm) in a ratio of 2 g of the blend per 1 cm of the membrane. The clay and Al–Fe polymeric precursor ratio used in the synthesis of all solids was 20 mequiv. metal/g clay. The membrane is then put into a beaker with the minimum quantity of distilled water to cover it, and the whole system is kept under constant agitation for 60 h not allowing any contact between the agitator and the membrane. Then, six washings with distilled water are performed in the same container where intercalation took place until conductivity is lower than 20 μS/cm. The intercalated clay suspensions are dried at 60 °C for 48 h, then sifted through a 100 mesh and then calcinated at up to 400 °C, with a heating ramp of 100 °C/h and for 2 h at 400 °C.

The solids obtained are labelled: B1-AlFe, B2-AlFe and B3-AlFe, where B refers to bentonite; 1, 2 and 3 refer to the three mole ratios of Fe/metal used in the Al–Fe polymer synthesis (3.9, 10 and 23%). As a reference material, natural bentonite calcinated at 400 °C is taken, whose chemical analysis and catalytic behavior have been documented in the existing literature [10,11].

2.3. Characterization of the solids

The X-ray diffraction analysis is carried out by means of a Bruker D8 Advance diffractometer (Cu Kα radiation) in Bragg–Brentano geometry, graphite secondary monochromator, steps of 0.05° 2θ at 2 s/step. The chemical analysis was performed by X-ray fluorescence (Philips MagiX Pro PW2440, samples prepared in pearls).

2.4. Catalytic evaluation

Solids modified with the solid Al–Fe polymeric precursor were evaluated in the phenol oxidation reaction in diluted aqueous medium according to the catalytic test procedure reported in prior works [12,13], using a 5×10^{-4} M phenol solution, 0.5 g catalyst, a solution of hydrogen peroxide 0.1 M and pH 3.7. Monitoring of the phenol conversion in time and the appearance of subproducts in the oxidation reaction are carried out by high performance liquid chromatography (HPLC) by means of a Hitachi D-7000 (LaChrom) appliance fitted with a self sampler L-7200, using an RP-18 Lichrosphere 60 Select B column, absorbance detector UV–vis L-7400 and as a mobile phase, a mixture of water, H_3PO_4 and methanol [19]. To assess the selectivity of catalysts towards CO_2 and H_2O, total organic carbon analysis was used (TOC), by means of an AnaTOC piece of equipment.

3. Results and discussion

Through chemical analysis by X-ray fluorescence, the effective incorporation of Al and Fe in the modified solids was established (Table 1). In general, the higher the content of Fe used in the synthesis, the greater the amount of this metal incorporated to the final solid.

X-ray diffraction patterns for the three modified solids (Fig. 1) reveal the effective introduction of the metal

Table 1
Chemical analysis of modified solids

Sample	Chemical analysis (%)			
	CaO	SiO_2	Al_2O_3	Fe_2O_3
B-Ca	2.5	51.2	16.8	7.6
B1-AlFe	0.4	47.8	26.2	10.1
B2-AlFe	0.4	46.1	26.6	10.9
B3-AlFe	0.4	45.2	23.9	15.0

polyhydroxocations and the later formation of oxides in the cations used (Al–Fe) in the interlamellar spacing (formation of pillars). Shifting of reflection d_{001} corresponding to a basal spacing of 13.8 Å for the starting clay (B-Ca not calcined) to 16.8 Å (B1-AlFe) and 17.6 Å (B2-AlFe) confirms the modification via pillaring of these solids. Regarding the B3-AlFe sample, we can appreciate the disappearance of the characteristic signal for clay, and a wide, little defined signal is revealed, suggesting a modification in the solid structure, without confirming the presence of pillars.

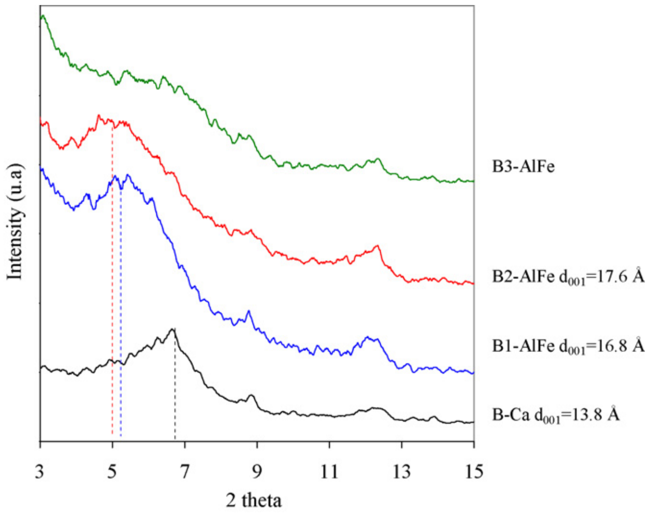

Fig. 1. XRD patterns of the natural bentonite and modified clays.

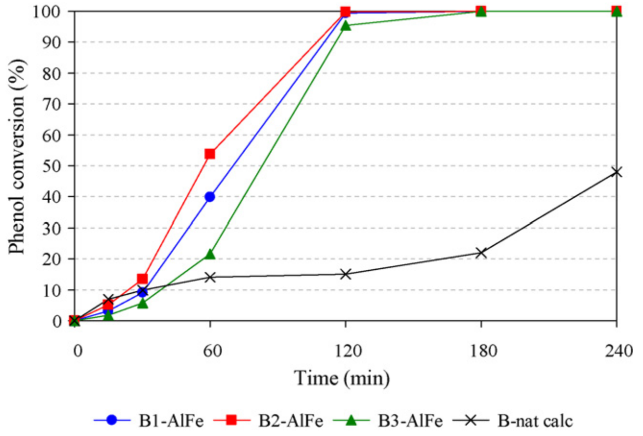

Fig. 2. Catalytic activity of the modified solids in the phenol oxidation reaction.

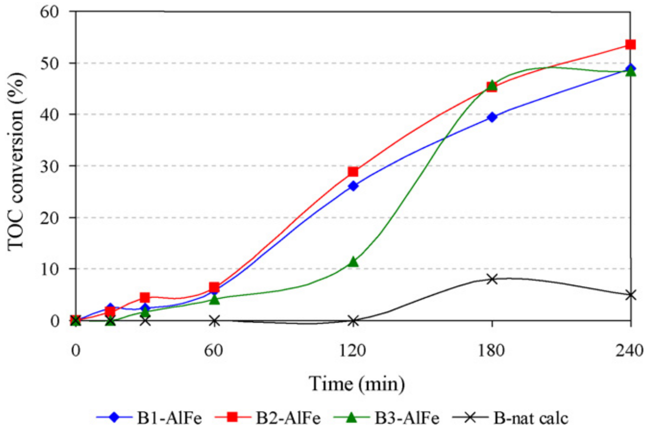

Fig. 3. TOC elimination by the modified clays in the phenol oxidation reaction.

The results of the catalytic assessment of pillared clays support the beneficial effect of introducing iron species in the solids, both in phenol conversion (Fig. 2) and in the one for total organic carbon, TOC (Fig. 3). The three solids modified achieve 100% of phenol conversion after 2 h of reaction, showing the catalytic potential of Al–Fe modified bentonites as compared with natural bentonite calcinated at 400 °C. Solid B2-AlFe shows greater phenol and COT conversion than solids B1-AlFe and B3-AlFe, confirming that the Fe ratio used in the synthesis (10% Fe molar) is the one leading to the formation of solids with a greater activity [11], probably due to better dispersion of the active metal than in the material with a higher Fe content (B3-AlFe).

Fig. 3 assesses the selectivity of solids in the oxidation reaction towards CO_2 and H_2O. All modified solids (B1-AlFe, B2-AlFe and B3-AlFe) show conversion values a lot higher than those of natural clay calcinated at 400 °C. The COT conversion percentage for modified solids ranges between 49 and 53%, and it is larger for solid B2-AlFe.

It is worth highlighting that the catalytic results obtained in this work by synthesizing pillared clays from the solid precursor in a concentrated medium are comparable with those obtained by making use of conventionally modified clays; that is, in highly diluted suspensions (2% clay and polymer solution) [11].

The amount of iron leached in the reaction medium is 0.39 ppm for B1-AlFe, 0.36 ppm for B2-AlFe and 0.27 ppm for B3-AlFe, values which are lower than the maximum allowed by the Colombian legislation for this metal in sewage waters and which, according to previous tests, do not contribute to the catalytic response obtained [20].

4. Conclusions

It is possible to modify bentonite starting from the polymeric precursor of solid Al–Fe, with chemical characteristics and chemical activity similar to those of the solid obtained by conventional synthesis (clay diluted suspensions and pillaring agent). The catalytic activity, assessed as conversion of phenol and total organic carbon confirms the positive effect of introducing iron in solids. The low iron content in the reaction leached indicates that, independently from the amount of this metal used in the synthesis of the mixed polyhydroxocation, the species exchanged are stable in the reaction medium. With this new methodology, the intercalation procedure is simplified, and the water volume is reduced, both essential requirements to allow the pillaring process to be up-scaled to the industrial level.

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