

A study on Al and Al–Ce–Fe pillaring species and their catalytic potential as they are supported on a bentonite

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Abstract

This work describes the synthesis and characterization by XRD of pillaring species in solid state, obtained from Al or Al–Ce–Fe polyhydroxocationic solutions, the modification of a bentonite via pillaring by ionic exchange with such solutions and the catalytic activity of the pillared clays in the phenol oxidation reaction in diluted aqueous medium with hydrogen peroxide. Results indicate the formation of boehmite from the Al³⁺ polyhydroxocationic solution and the presence of three different crystalline structures (boehmite, α -Fe₂O₃ and CeO₂) into the solid synthesized from the Al–Ce–Fe polyhydroxocationic solution. The EPR analysis confirms the formation of iron oxide particles and the likely inclusion of isolated Fe³⁺ species into the alumina matrix. On the other hand, the clay modified with Al–Ce–Fe is a very active (100% of phenol conversion in the first hour of reaction) and selective (55% of selectivity to CO₂) catalyst in the total oxidation of phenol, at 20 °C and atmospheric pressure.

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1. Introduction

Currently, great efforts are being made worldwide to enforce strict control on wastewaters from household, agricultural and industrial activities, which in many instances contain highly toxic organic compounds in diluted form (for example, phenol, substituted phenols, oxalic acid, acetic acid, pesticides and herbicides among others [1–4]) and which exert a greater oxygen demand on natural ecosystems.

Among the alternatives proposed for the elimination of organic matter in aqueous solution, we find the use of catalysts which are effective in increasing the oxidation capacity in wet oxidation processes (WO) [5–7], which in turn offer greater advantages through the use of hydrogen peroxide (CWPO: catalytic wet peroxide oxidation). The CWPO process lies within the range of advanced oxidation processes (AOP), having in common the generation of •OH radicals and the use of their oxidizing capacity [8–10]. These radicals are not very selective and they degrade most organic molecules to CO₂ and

H₂O. One of the most important processes in the generation of hydroxyl (•OH) and perhydroxyl (HO₂•) radicals is achieved through the Fenton system, which uses iron salts and hydrogen peroxide [3,11]. The use of iron species (II or III), supported on an appropriate solid, offers a positive alternative in the generation of a “modified Fenton” process [1,2,12].

On the other hand, pillared clays containing Fe(III), generally introduced as a polyhydroxocation, are highly promising catalysts to be used in the CWPO reaction. In this type of solids, the efficiency of incorporated active species of iron(III) is enhanced through the modification of the initial phyllosilicate through Al–Fe mixed polyhydroxocationic solutions, since the incorporation of Al³⁺ polyhydroxocations facilitates the pillaring of the solid and increases its microporosity. In addition, previous works [12,13] report that the incorporation of species of Ce favours catalytic activity (CWPO reaction) of the Fe(III) incorporated in pillared clays, probably due to the fact that the cerium oxide formed in the solids enhances the textural properties of the solid, the dispersion and/or the redox properties of active species [14–17].

Although the real form in which active iron species are found(III) in Al–Fe-pillared clays is still the object of some

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controversy [13,18–22], our work has been formulated on the hypothesis that active iron species are preferably oxides and not Fe(III) incorporated through isomorphic substitution. The incorporation of the third cation (cerium) has been studied even less in this system. In this sense, more elaborate knowledge on the cationic species incorporated into Al–Ce–Fe-pillared clays will make it possible to redirect and enhance synthesis processes for these catalysts to be employed in modified Fenton-type processes. It is thus fundamental to research on which chemical species can be formed in solid state starting from mixed Al–Ce–Fe polyhydroxocationic solutions during the pillaring process.

Throughout this work, the synthesis of Al- and Al–Ce–Fe-pillared clays and their catalytic evaluation in the phenol oxidation reaction are carried out, emphasizing the synthesis and characterization (XRD and EPR) of modifying solid species from Al and Al–Fe–Ce polyhydroxocationic solutions.

2. Experimental

2.1. Synthesis of solids

2.1.1. Pillared clay

The starting clay is a commercially available natural bentonite from Valle del Cauca, Colombia, supplied by Bentocol (Colombia), which has been previously separated by particle size (<2 μm) and homoionized with a 1N sodium chloride solution [12,13]. In order to modify the clay, two intercalating polyhydroxocationic aqueous solutions are prepared: an Al–Ce–Fe solution, with 10% Fe and 10% Ce expressed as molar percentages of Fe/(Fe + Al + Ce) and Ce/(Fe + Al + Ce), respectively, and another polyhydroxocationic solution containing only Al. The solutions are prepared starting from the corresponding nitrates and through the slow addition (dropwise) of NaOH (0.2 M) over the Al (0.2 M) or Al–Ce–Fe (0.2 M Al³⁺, 0.025 M Ce³⁺ and 0.025 M Fe³⁺) cations aqueous solution at room temperature (20 °C), until a ratio OH/metal = 2 is obtained. The resulting solutions were aged for 2 h at 60 °C.

The pillaring process is carried out as reported in previous works [12,13]. The resulting solids are labelled B-AlCe(10)Fe(10) and B-Al.

2.1.2. Pillaring species

Solid pillaring species are synthesized starting from Al and Al–Ce–Fe pillaring (polyhydroxocationic) solutions previously described. The solutions obtained are aged for 2 h at 60 °C and then submitted to crystallization. Finally, crystallized solids are washed with methanol, dried at 60 °C and then calcined at 400 °C for two hours. The resulting solids are labelled Al-Poly and AlCeFe-Poly.

2.2. Catalytic assessment

Al- and Al–Ce–Fe-pillared clays are assessed in the phenol oxidation reaction in diluted aqueous medium according to the procedure reported in previous works [12,13], using a

5×10^{-4} M phenol solution, 0.5 g of the catalyst, a 0.1 M hydrogen peroxide solution and pH 3.7. In order to follow up on phenol conversion and the by-products formation in the reaction, a HPLC Hitachi D-7000 (LaChrom) equipment is used as well as a Lichrosphere 60 Select B column. The assessment for total organic carbon (TOC) was carried out by means of an AnaTOC equipment. In all tests a relative error lower 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.

2.3. Characterization of solids

The X-ray diffraction study was performed by using a Philips PW 1820 diffractometer (K α radiation of Cu) in 2θ geometry and Bragg–Brentano configuration, using the forced powder technique, a step size of 0.05 and a step time of 2 s. The EPR spectra were taken with Bruker ESP 300 equipment at a temperature of 100 K, with a field modulation of 100 kHz and a frequency of 9.44 MHz (X band).

3. Results and discussion

3.1. Characterization and catalytic activity of modified clay

By means of X-ray fluorescence chemical analysis, the introduction of Al, Fe and Ce in the modified solids was verified (Table 1). The XRD analysis on modified clays reveals the introduction of the metal polyhydroxocations and the resulting formation of oxides or oxyhydroxides, of the cations employed, in the interlayer spacing of the material. The shifting of d_{001} basal spacing from 14.7 Å (natural clay) to 16.5 Å (B-Al) and 17.7 Å (B-AlCe(10)Fe(10)) confirms the modification via pillaring (Fig. 1).

The catalytic behaviour of the solids (Fig. 2) reveals the beneficial effect of introducing iron species into the materials, both in phenol elimination (a) and in the degradation of total organic carbon (TOC) (b). The non-negligible catalytic activity obtained for “natural calcined” clays and for clays pillared with Al only, can be explained by the initial contents of iron oxides found in natural clay [13], and the great difference found in the catalytic behaviour of these two solids can be the resulting consequence of the generation of microporosity in the pillared clay, which enhances access of the reacting species to and from the active sites [12].

For natural clay, the phenol conversion starts from 6% because of the adsorption phenomenon is presented previous to the reaction. In the experimental procedure, the catalyst is

Table 1
Chemical analysis and basal spacing (d_{001}) for natural clay and modified solids

Solid	Al (%)	Fe (%)	Ce (%)	d_{001} (Å)
Natural (not calcined) clay	9.83	6.03	38 ppm	14.7
B-Al	12.00	5.90	–	16.5
B-AlCe(10)Fe(10)	11.90	8.55	0.1	17.7

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