Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 107–108 (2005) 126–132

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Synthesis of pillared clays containing Al, Al-Fe or Al-Ce-Fe from a bentonite: Characterization and catalytic activity

J. Carriazo [a], E. Guélou [b], J. Barrault [b], J.M. Tatibouët [b],
R. Molina [a], S. Moreno [a,*]

[a] *Departamento de Química, Facultad de Ciencias, Centro de Catálisis Heterogénea,*
Universidad Nacional de Colombia, Carrera 30 No. 45-03, Bogotá, Colombia
[b] *Laboratoire de Catalyse en Chimie Organique, ESIP, 40 Avenue du Recteur Pineau,*
86022 Poitiers Cedex, France

Abstract

A Colombian bentonite was successfully pillared with solutions of Al, Al-Fe or Al-Ce-Fe polyhydroxocations under moderate conditions of synthesis in order to obtain active catalysts for the wet peroxide oxidation of organic pollutants from industrial wastewaters. The catalysts were very efficient in the phenol oxidation reaction in diluted aqueous medium under mild experimental conditions (298 K and atmospheric pressure). The addition of Ce in the synthesis step of the inorganic polycations yielded a favorable effect in the pillaring of the materials allowing the increase of the basal spacing and enhancing the catalytic activity of the solids. Besides, the characterization by TEM, EPR and chemical analysis techniques confirms the nanocluster formation of iron species, while no evidence of mixed pillars with isomorphic substitution of Fe for Al was obtained.

Keywords: Catalytic wet peroxide oxidation; Advanced oxidation processes; Al-Ce-Fe exchanged pillared clay

---

1. Introduction

As a relatively new class of microporous substrates, the pillared interlayer clays show interesting properties towards adsorption and catalysis. The application fields of these substrates are very broad because of the possibility to intercalate different types of pillars making them suitable for specific adsorption and catalytic processes [1]. The introduction of inorganic pillars in the natural clay improves its resistance and stability, increases its micro porosity and provides larger surface area and accessibility to its acid sites (Brönsted and Lewis sites) [2,3].

The intercalation of clays using solutions containing two cations has also been studied. The main cation used for this purpose is Al^{3+}. The addition of small molar fractions of a second cation is done in order to improve the thermal properties, as well as the adsorption and/or catalytic properties of the end product [4]. As reported by Gil et al. [4], these pillared clays obtained from mixed polycationic solutions have been used in various catalytic applications.

Various works have been reported on the synthesis of pillared clays with mixed systems of Al-Fe, but until now it is not absolutely clear how the iron species exist in the resulting solids. Some authors [5], referring to the synthesis with mixed polycationic solutions of Al-Fe and based on chemical analysis, have proposed the formation of mixed pillars of Al-Fe through the isomorphic substitution of Fe in the aluminum pillar. By using XPS techniques, other authors have studied pillared clays containing Al-Fe, which have allowed them to establish the existence of iron in the form of oxide [6,7]. Lee et al. [8], equally working on the mixed system Al-Fe and using Mössbauer spectroscopy, concluded that Fe is found preferably, ‘‘decorating’’ the alumina pillar. Other investigations on the same system Al-Fe [9], in which

---

* Corresponding author. Fax: +57 1 3165220.
E-mail address: smorenog@unal.edu.co (S. Moreno).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.07.157

infrared spectroscopy and Mössbauer techniques are used, do not give evidence of isomorphic substitution of the Fe in the alumina pillars.

In environmental catalysis there is a great interest in obtaining pillared clays containing iron (oxides or oxyhydroxides) species for use in the catalytic wet peroxide oxidation (CWPO) of toxic organic compounds since many industrial processes yield a variety of organic contaminants which are poured into natural water sources with a negative impact on ecosystems and humans (toxicity, carcinogenic and mutant properties) [10]. Among these pollutants contained in industrial residual waters we can highlight phenol, substituted phenols (clorophenol, nitrophenol), oxalic acid, acetic acid, pesticides and herbicides [10–13]. Phenol is particularly considered as one of the most toxic organic contaminants and it is commonly chosen as ‘‘model’’ molecule on catalytic oxidation of organic compounds studies in diluted aqueous medium.

This work shows the synthesis of solid catalysts, clays pillared with Al, Al-Fe and Al-Ce-Fe, in which iron is introduced as an active phase (activation sites for hydrogen peroxide as well as organic molecules) in order to develop a modified Fenton process on the surface of the solids that leads to the complete oxidation of organic molecules as an application of the catalytic wet oxidation with hydrogen peroxide, which is included within the set of *advanced oxidation processes* (AOP), which in turn have in common the $^{\bullet}OH$ radicals generation and the utilization of their oxidative capacity [14,15], as indicated in Fig. 1. These radicals are not very selective and they attack the majority of the organic molecules causing their oxidation to CO_2 and H_2O. Ce is introduced in order to improve the metallic dispersion properties [16], to increase the pillars resistance [17–19] and to favor the redox properties of the active metallic phase [16,20].

2. Experimental

2.1. Catalysts preparation

The starting clay was a natural Colombian bentonite, extracted from the ‘‘Valle del Cauca’’ region. The clay was previously homoionized with a sodium chloride solution (1N). Subsequently, it was exchanged with a 10% (expressed as molar percentage of Fe/(Fe + Al)) Al-Fe aqueous solution or with 0, 1, 5, 10% (expressed as molar percentage of Fe/(Fe + Al + Ce)) aqueous solutions of Al-Ce-Fe and keeping constant the molar percentage of cerium (20% = Ce/(Fe + Al + Ce)). Additionally, a polyhydroxicationic solution was prepared just containing Al. These solutions were prepared from the respective nitrates and through slow addition, at constant temperature (333 K), of 0.2 M NaOH to the solution containing the Al, Al-Fe or Al-Ce-Fe cations until a OH/metal = 2 ratio was obtained. The obtained solutions were allowed to stand for 3 h at room temperature.

The exchange process of the clay, carried out with each of the previously aged polymeric solutions of Al, Al-Fe or Al-Ce-Fe, was done keeping a relation of 20 miliequivalents of metal per gram of clay. The intercalating solution was slowly added to an aqueous suspension of clay (2%) at room temperature. The clay was previously ‘‘swollen’’ through continuous stirring of the suspension for 24 h. After the exchange, the suspensions were left stirring for 3 h at room temperature. The obtained solids were washed by centrifugation until nitrate-free, and then they were dried at 333 K and finally calcined at 673 K for 2 h. The solids are designated as: Al-Pilc, AlFe(10%)-Pilc, AlCe-Pilc, AlCeFe(1%)-Pilc, AlCeFe(5%)-Pilc, AlCeFe(10%)-Pilc, according to the molar percentages of the active phase (iron) in the precursor solutions.

2.2. Characterization of the catalysts

The chemical analysis of the solids was carried out by X-ray fluorescence (SDX, Siemens SRS 330). For the determination of surface areas (BET) a Micromeritics Flowshorb II 2300 device was used, in which the samples were previously out gassed at 573 K for 3 h. The X-ray diffraction (XRD) study was done in a Bruker AXS D5005 device, which operates with Cu Kα radiation. The electron microscopy analysis was performed in a Philips CM 120 (120 kV) transmission microscope with EDX analyzer.

The EPR spectra were recorded on a Bruker ESP-300E spectrometer with the following settings: central field 4100

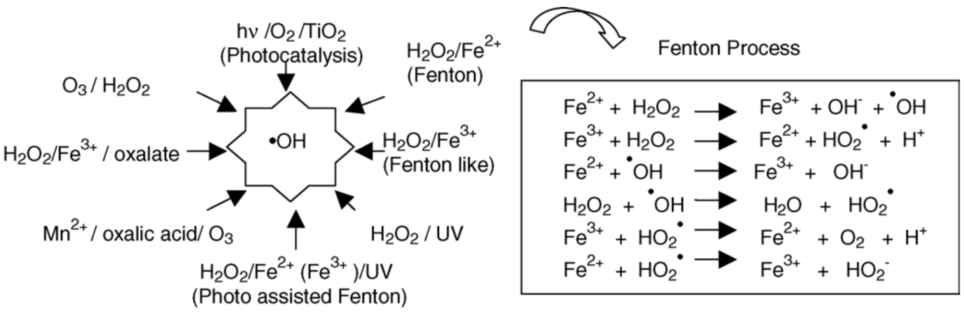

Fig. 1. Advanced oxidation processes (AOP).

G, swept width 8000, microwave frequency 9.25 GHz (X band), modulation amplitude 10.25 G, time constant 40.96 ms and gain 2×10^3. The ESR spectra were recorded at 77 K under vacuum after out gassing at room temperature for 1 h.

2.3. Catalytic activity

The catalytic oxidation reaction of phenol in a diluted aqueous medium was carried out in a semi batch glass reactor (pyrex) with a capacity of 250 ml, open to the atmosphere, thermostated at 298 K, thoroughly stirring and constantly monitoring and registering the pH variations by means of an electrode. The device featured an automatic dosimeter (Dosimat 725 Metrohm) for the continuous addition of the oxidizing agent (hydrogen peroxide solution).

For each test the reactor was loaded with 100 ml of a phenol solution (5×10^{-4} M) and 0.5 g of catalyst. The hydrogen peroxide solution (0.1 M) was added at a 2 ml/h flow and during a reaction time of 4 h. The pH was continuously adjusted to 3.7 and a flow of air was introduced in the reactor at 2 l/h. The course of the phenol conversion and the appearance of the intermediate compounds was followed by high performance liquid chromatography (HPLC) by means of a Waters 600E liquid chromatographer equipped with an aminex HPX 87 H (Biorad) column. The evaluation of the total organic carbon (TOC) was carried out with a Dohrman DC-190 device.

At the end of each trial, a solution was separated from the reactive medium by filtration in order to determine the leaching of iron during the reaction. The analysis of iron in solution was done by atomic absorption, using a Perkin-Elmer 3300 spectrometer.

3. Results and discussion

3.1. Characterization

Table 1 summarizes the results of the chemical analysis, surface area and basal spacing ($d_{0\,0\,1}$) obtained by X-ray diffraction. The elemental analysis indicates that the starting clay was effectively modified in its chemical composition. A tendency to increase the Fe content is verified as its content increases in the pillaring solution. Also a decrease of the aluminum content is evident as the Fe content increases, while that of Ce remains practically constant. This result could be related to a ‘‘competition’’ between iron and aluminum, which is not given between iron and cerium. As it has been established, the iron has the possibility to be found taking part in the aluminum pillar, decorating the pillar or in isomorphic substitution [4]. Nevertheless, a proportional relation between introduced Fe quantities and the decrease in the Al quantities (Fig. 2) was not observed, which indicates that it is not very probable that the pillar synthesis be developed through the isomorphic substitution of Fe by Al, or that at least it is not the only way in which the introduction of Fe in the solids has been carried out. If the introduced iron would have been found only in isomorphic substitution, the decrease in the Al content would correspond approximately to the molar content of introduced Fe, and therefore the relationship shown in the Fig. 2 should be close to the ideal line for an isomorphic substitution.

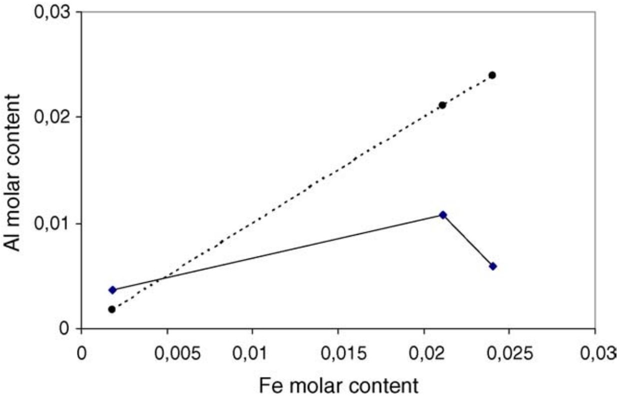

Fig. 2. Variation of Al and Fe contents in the solids (continuous line). The discontinuous line represents the ideal form when only isomorphic substitution has occurred.

The construction of Fig. 2 was done on a calculation basis (100 g of solid) such that the weight percentages from Table 1 are assumed to be the mass values of each one of the elements (Fe or Al) used to calculate the number of moles. To each solid the aluminum mass contribution (9.3%) from the natural clay was subtracted as a good experimental

Table 1
Characterization of the solids: chemical analysis, DRX and surface area

Solid	Fe (%)	Al (%)	Ce (%)	Al/Ce (molar ratio)	BET area (m^2/g)	$d_{0\,0\,1}$ (Å)
Al-Fe (10%)	8.76	11.72	–		129.8	17.0
Al-Ce-Fe (10%)	8.68	11.83	0.10	103.86	147.7	18.2
Al-Ce-Fe (5%)	7.34	11.99	0.13	86.28	121.8	18.0
Al-Ce-Fe (1%)	6.16	12.28	0.13	97.87	126.8	19.0
Al-Ce-Pilc	6.06	12.38	0.14	94.59	116.0	18.4
Al-Pilc	6.06	12.48	–	–	114.1	17.7
Non-calcinated natural clay	6.03	9.83	38 ppm	–	51.7	14.7
Calcinated natural clay	6.61	–	–	–	57.0	12.1

approach for the mass estimation of aluminum introduced in the final solid during the synthesis. Therefore, the introduced Al quantity is expressed as moles of Al. For the determination of the Fe mass introduced by the synthesis, the iron percentage (6.06%) found in the solids AlCe-Pilc and Al-Pilc (close to the value 6.03 in the natural clay) was subtracted in all cases as the best way to estimate the iron mass contribution from the starting material. Finally, the variations in the number of moles of Al (Δ moles Al) as well as in the number of moles of Fe (Δ moles Fe) were determined.

Taking about the low cerium quantities introduced in the synthesis process this could be explained from the structure proposed for the Al-Ce polycation, different from the simple structure for the keggin ion [4,18,21] in which a Ce atom in tetrahedral coordination is surrounded by four Al_{13} units, giving the possibility of generating pillars with a low Ce content. The molar ratio Al/Ce, in all cases greater than 52, indicates that the Ce was introduced in quantities less than the maximum possible according to the structure proposed for the Al-Ce polyhydroxocation, with which possibly part of the Al in solution was exchanged in the simple way from the keggin cation.

The transmission electron microscopy results (Fig. 3) show the iron species formation (probably iron oxides or oxyhydroxides). The particle sizes for this species were carefully measured between 15 and 25 nm, showing a better distribution (smaller particle sizes) for the solids containing cerium. As such species (clusters) are larger than the pillars, the results confirm that at least a fraction of Fe added during the synthesis is introduced in an independent form of any isomorphic substitution. On the other hand, the EDX results do not give evidence of the presence of Ce, which is evident by X-ray fluorescence analysis. This indicates that Ce, besides being present in small quantities is also very well dispersed throughout the solids.

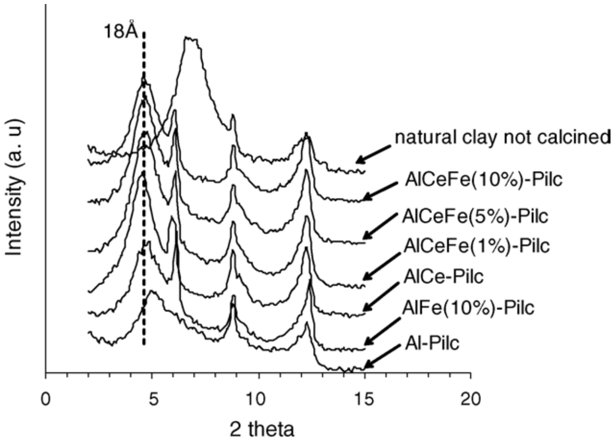

Fig. 4. X-ray diffraction patterns of the natural bentonite and of the clay modified with Al, Al-Fe and Al-Ce-Fe.

The XRD results indicate that the modification carried out on the clay leads, in all cases, to the successful pillaring of the material (Fig. 4). In Table 1, it is observed that the addition of Ce in the synthesis leads to a greater basal spacing of the solids. Besides, Fig. 4 clearly shows that the signal $d_{0\,0\,1}$ around 18 Å is well defined and symmetric for the solids synthesised with Al-Ce-Fe, which is not evident for Al-Pilc and AlFe(10%)-Pilc, which show wider peaks

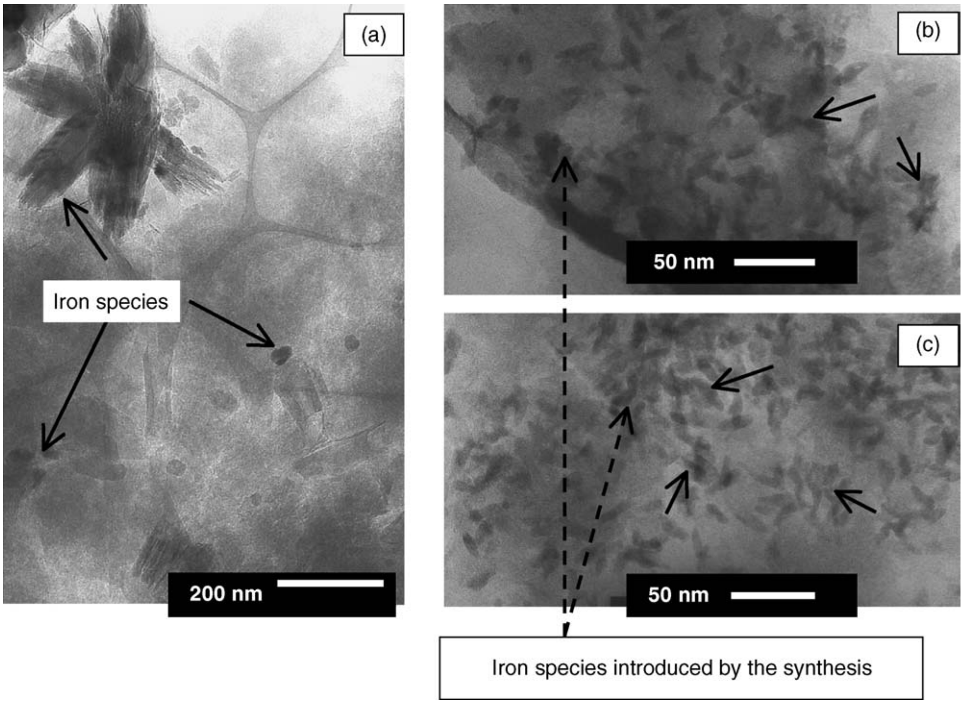

Fig. 3. Transmission electron microscopy: (a) natural bentonite, (b) AlFe (10%)-bentonite, (c) AlCeFe (10%)-bentonite.

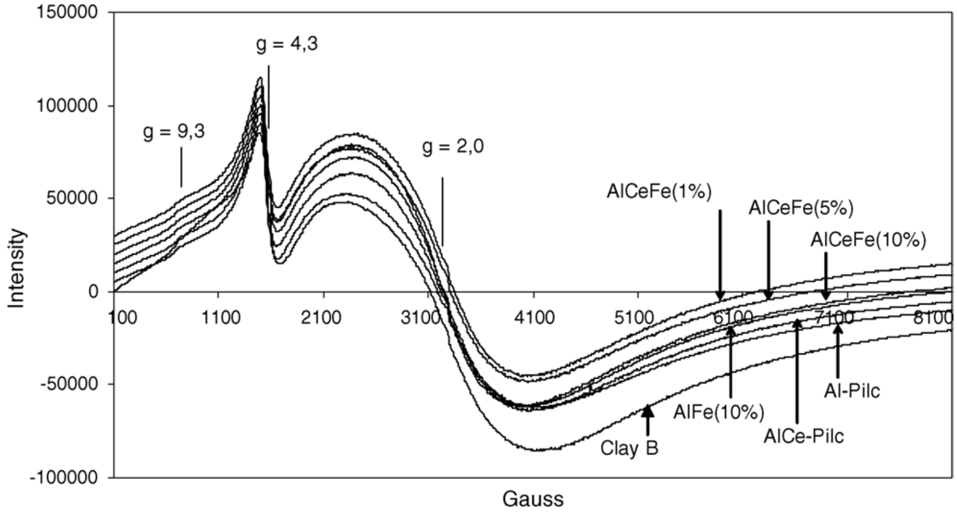

Fig. 5. EPR spectra of the natural bentonite and of the clay modified with Al, Al-Fe, Al-Ce and Al-Ce-Fe.

and are less intense. The presence of a wide signal $d_{0\,0\,1}$ is related to the heterogeneity in the size of the pillars. The above considerations reveal the favorable effect of cerium in the pillaring process of the clay, which agrees with what was reported by Hernando et al. [17,18].

The surface area values agree with the X-ray diffraction results. The over 100% increases in the BET areas in all cases is a result of the pillaring of the clay with the consequent formation of micro and mesopores.

The EPR analysis (Fig. 5) reveals the presence of two characteristic Fe^{3+} signals in smectite type minerals [22] to values of $g = 4.3$ and 2.0. Besides this, a weak signal at $g = 9.3$ which has been associated with the signal of $g = 4.3$. The signal at $g = 4.3$ is assigned to the presence of isolated Fe^{3+} [23–26] in tetrahedral or octahedral coordination, which in the case of the smectite minerals corresponds to the iron located in the interior of the clay sheets (iron substituting aluminum in the octahedral layers). On the other hand, the signal at $g = 2.0$ is associated to the presence of clusters of iron [23–25]. In this work, this last signal is modified (keeping the signal invariable at $g = 4.3$), with the general tendency to increase its intensity as the iron content introduced by the synthesis increases as well. The observed increase in the intensity of the signals is in the order 8.68%Fe [AlCeFe(10%)] > 6.16%Fe [(AlCeFe(1%)] > 6.06%Fe [(AlCe-Pilc)] > 7.34%Fe [(AlCeFe(5%)] > 6.06%Fe [Al-Pilc] = 6.03%Fe [Clay B]. This indicates that the iron species introduced in the clay are preferably found in nanocluster form (oxides or oxyhydroxides of Fe).

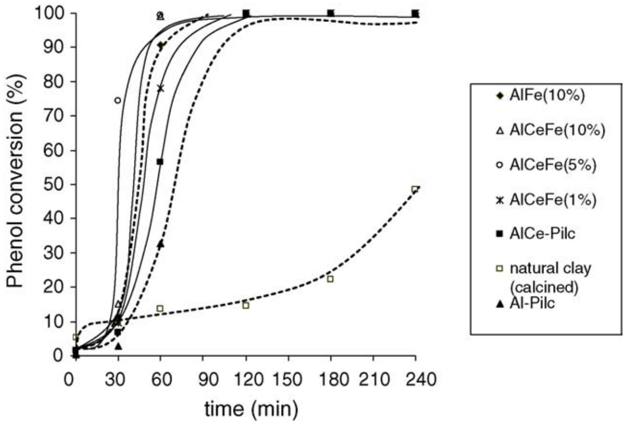

Fig. 6. Catalytic activity of the modified clays in the phenol oxidation reaction in diluted aqueous medium, at 298 K and atmospheric pressure.

3.2. Catalytic activity

The catalytic tests effectively show that the solids prepared by pillaring of the Colombian bentonite with Al, Al-Ce or Al-Ce-Fe are catalysts with excellent properties to be used in the reaction of phenol oxidation in diluted aqueous medium (Figs. 6 and 7). The phenol conversions reached by these catalysts are 100%, and in some cases (AlCeFe(10%)-Pilc and AlCeFe(5%)-Pilc) such a conversion is reached in the first hour of reaction. The levels of the

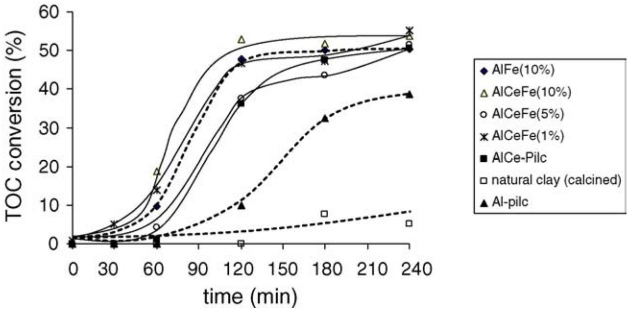

Fig. 7. TOC elimination by the modified clays in the phenol oxidation reaction in diluted aqueous medium, at 298 K and atmospheric pressure.

TOC conversion (total mineralization of the organic substance) are equally important, reaching up to a 55%. Also, the leaching levels of metal are very low (less or equal to 0.3 ppm), which indicates that the active phase is stable in the reaction medium. It was also observed that the leaching levels in all the cases correspond approximately to the quantity of iron leached by the natural clay (which contributes approximately with 6% of Fe in all the solids) and therefore the iron introduced during the synthesis process should be fixed strongly to the support and contributes very little or nothing to the metallic lixiviation.

In both cases, in the phenol conversion as well as in the TOC conversion, the favorable effect of Ce is observed. The best activity and selectivity of the catalysts with Ce can be associated with textural improvement as a consequence of a better pillaring. Besides, we could think, even though our results do not allow us to confirm it yet, in other properties attributed to Ce and reported in literature for other catalytic systems [16,20]: the improvement of the dispersion and/or the improvement of the redox properties of the active phase (metallic oxide).

It was observed that the catalysts Al-Pilc and AlCe-Pilc, in which Fe is not introduced during the process of synthesis, showed a good catalytic activity. This is explained by the content of Fe in the natural clay, part of which could be found in the form of oxides or oxyhydroxides deposited on the sheets of the clay mineral as it is revealed by the transmission electron microscopy results (Fig. 3a). As it can be seen in this work, it is evident the catalytic activity of the iron species in the form of small ‘‘clusters’’, which depending on the size, could be located on the aluminum pillar or on the sheets of the clay. Therefore, once the clay has been pillared, iron oxides in the form of very small clusters present in the natural clay act as active sites due to the fact that the spacing between sheets are widened allowing thus the access of phenol molecules and other intermediate reaction compounds towards these sites. Once again it is evident the favorable effect of Ce in the catalyst AlCe-Pilc as compared with the catalyst Al-Pilc. Table 2, summarizes the conversion values of phenol and TOC for the different catalysts.

Table 2
Conversion of phenol and COT, and metallic leaching of the catalysts at 298 K, atmospheric pressure and pH 3.7 during 4 h of reaction

Catalyst	Phenol conversion (%)	COT conversion (%)	Metallic leaching (ppm Fe in solution)
Al-Fe (10%)	100	50	0.21
Al-Ce-Fe (10%)	100[a]	54	0.25
Al-Ce-Fe (5%)	100[a]	52	0.34
Al-Ce-Fe (1%)	100	55	0.27
Al-Ce-Pilc	100	51	0.21
Al-Pilc	100	39	0.20
Natural clay (scorched)	48	5	0.30

[a] Reached during the first hour of reaction.

4. Conclusions

The modification of the Colombian bentonite with polyhydroxicationic solutions of Al, Al-Fe or Al-Ce-Fe in moderate conditions of temperature and very short aging time leads, successfully, to the obtention of pillared solids with very good basal spacing.

The results obtained by elemental chemical analysis, EPR analysis and TEM reveal the formation of ‘‘nanoclusters’’ of iron species (probably oxides or oxyhydroxides) with no evidence of isomorphic substitution of Fe for Al. Although these results do not allow the confirmation of the existence of a mixed pillar, neither does it allow us to totally exclude such a possibility due to the possible existence of extremely small iron oxide nanoclusters located on the alumina pillar and which would be below the resolution of the microscopic technique applied.

The catalysts obtained by the pillaring of the Colombian bentonite with Al, Al-Fe or Al-Ce-Fe are highly efficient for the phenol oxidation reaction in diluted aqueous medium in very mild conditions of temperature and pressure (298 K and atmospheric pressure). The stability of the active phase in these catalysts is evident, showing extremely low metal leaching.

The addition of Ce during the synthesis of the catalysts show favorable results in the activity of these when dealing with the elimination of phenol and its intermediate compounds in the total oxidation reaction (conversion of TOC) thus ensuring the oxidation of great part of the content of this pollutants to CO_2 and H_2O.

Acknowledgements

The authors offer their gratitude to the international program ECOS-NORD COLCIENCIAS (99PFC17P07) and to the Dirección Nacional de Investigación de la Universidad Nacional de Colombia (DINAIN) for the financial support of project 20201005196.

References

[1] N. Maes, E.F. Vansant, Microporous Mater. 4 (1995) 43.
[2] L. Bergaoui, J.-F. Lambert, R. Franck, H. Suquet, J.-L. Robert, J. Chem. Soc., Faraday Trans. 91 (1995) 2229.
[3] J.M. Thomas, W.J. Thomas, Principles and Practice of Heterogeneous Catalysis, VCH Verlag, Weinheim, 1997.
[4] A. Gil, L. Gandia, M.A. Vicente, Catal. Rev.-Sci. Eng. 42 (2000) 145.
[5] F. Bergaya, N. Hassoun, L. Gatineau, J. Barrault, Prep. Catal. V (1991) 329.
[6] M. Lenarda, R. Ganzerla, L. Storaro, S. Enzo, R. Zanoni, J. Mol. Catal. 92 (1994) 201.
[7] M. Lenarda, R. Ganzerla, L. Storaro, S. Enzo, R. Zanoni, J. Mol. Catal. A 97 (1995) 139.
[8] W.Y. Lee, R. Raythatha, B. Tatarchuk, J. Catal. 115 (1989) 159.
[9] I. Pálinkó, K. Lázár, I. Kiricsi, J. Mol. Struct. 410 (1997) 547.

[10] C. Catrinescu, C. Teodosiu, M. Macoveanu, J. Miehe-Brendlé, R. Le Dred, Water Res. 37 (2003) 1154.
[11] A. Santos, P. Yustos, A. Quintanilla, S. Rodríguez, F. Garcia-Ochoa, Appl. Catal. B 39 (2002) 97.
[12] L. Chirchi, A. Ghorbel, Appl. Clay Sci. 21 (2002) 271.
[13] F. Banat, B. Al-Bashir, S. Al-Asheh, O. Hayajneh, Environ. Pollut. 107 (2000) 391.
[14] C.W. Jones, Application of Hydrogen Peroxide and Derivatives, Royal Society of Chemistry, Cambridge, 1999, pp. 41–45.
[15] R. Andreozzi, V. Caprio, A. Insola, R. Moratta, Catal. Today 53 (1999) 51.
[16] S.-K. Kim, S.-K. Ihm, Ind. Eng. Chem. Res. 41 (2002) 1967.
[17] M.J. Hernando, C. Pesquera, C. Blanco, F. González, Langmuir 18 (2002) 5633.
[18] M.J. Hernando, C. Pesquera, C. Blanco, F. González, Chem. Mater. 13 (2001) 2154.
[19] G. Fetter, P. Salas, L.A. Velázquez, P. Bosch, Ind. Eng. Chem. Res. 39 (2000) 1944.
[20] C. Leitenburg, D. Goi, A. Primavera, A. Trovarelli, G. Dolcetti, Appl. Catal. B 11 (1996) L29.
[21] E. Booij, J.T. Kloprogge, J.A.R. Van Veen, Appl. Clay Sci. 11 (1996) 155.
[22] B.A. Goodman, P.L. Hall, in: M.J. Wilson (Ed.), Clay Mineralogy: Spectroscopic and Chemical Determinative Methods, Chapman and Hall, London, 1994, p. 209.
[23] A. Montenero, K. Suzuki, T. Enoki, S. Vittorio, M. Dresselhaus, K. Koga, M. Endo, N. Shindo, Synthetic Met. 55 (1993) 3736.
[24] A. Kucherov, M. Shelef, J. Catal. 195 (2000) 106.
[25] D. Loveridge, S. Parke, Phys. Chem. Glasses 12 (1971) 19.
[26] E. Guélou, J. Barrault, J. Founier, J.-M. Tatibouët, Appl. Catal. B: Environ. 44 (2003) 1.