

# A comparison of Al-Fe and Zr-Fe pillared clays for catalytic wet peroxide oxidation

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## Abstract

Catalysts based on pillared clays with Al, Zr and Al-Fe and Zr-Fe have been synthesized from a commercial bentonite and tested for catalytic wet peroxide oxidation (CWPO) using phenol as target compound at 298 K. The Al-Fe pillared clay showed a higher activity than the Zr-Fe one for phenol oxidation, although the second was more active for H<sub>2</sub>O<sub>2</sub> decomposition. Fairly different values of apparent activation energy were obtained for this last reaction with these two types of catalysts, suggesting that the prevailing pathway in H<sub>2</sub>O<sub>2</sub> decomposition is different. The higher activity of the Al-Fe pillared clay for CWPO suggests that this catalyst favours the generation of OH<sup>•</sup> radicals, whereas with the Zr-Fe one H<sub>2</sub>O<sub>2</sub> decomposes predominantly to O<sub>2</sub> which has a low oxidation capacity at the mild operating conditions commonly used in Fenton oxidation. © 2006 Elsevier B.V. All rights reserved.

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## 1. Introduction

Industrial processes generate a wide diversity of wastewaters containing organic pollutants with negative impacts for ecosystems and humans. Such wastewaters have become a major social and economic problem as modern health-quality standards and environmental regulations are gradually being more restrictive. Among these pollutants an increased concern is directed towards organic refractory compounds which are difficult to remove by means of conventional wastewater treatment technologies. Phenol is one of the most important representative of this type of organic pollutants, because it is toxic even at low concentrations and its presence in natural waters can lead further to the formation of halogenated compounds during chlorine disinfection processes [1]. In the past 2 decades, wastewaters containing phenol and related compounds have received increased attention because of their toxicity and prevalence. In addition, phenol is considered to be an intermediate product in the oxidation pathway of higher molecular weight aromatic hydrocarbons and it can be considered as a model molecule, representative of the functionalised aromatic molecules class known for their toxicity [2].

Among the methods developed for the treatment of wastewaters with non or low biodegradable organic compounds, advanced oxidation processes (AOPs) will probably constitute the best option in the near future. AOPs have been defined as those aqueous phase oxidation processes which are based primarily on the intermediacy of the hydroxyl radical in the mechanism resulting in the destruction of the target pollutant or contaminant compound [3]. One of the more promising AOP's is based on the use of Fenton's reagent (H<sub>2</sub>O<sub>2</sub> + Fe<sup>+2</sup>). It is commonly carried out in homogeneous phase. The loss of iron, which has to be removed, making necessary the corresponding additional separation processes and sludge disposal, is a major drawback and limits in practice the application of the Fenton process. A solution to this problem can be the use of stable heterogeneous catalysts in the so-called catalytic wet peroxide oxidation (CWPO).

Different solids have been employed to catalyse the oxidation of organic compounds in wastewaters: transition-metal oxides and noble metals have been extensively used as active components. Transition metal exchanged zeolites [4] and Cu<sup>+2</sup> or Fe<sup>+3</sup>-montmorillonites have been proposed as active catalysts for organic compounds oxidation in aqueous phase [5].

Pillared clays have received increasing interest in the last 2 decades due to their textural and catalytic properties in different reactions [6,7]. They represent a new class of microporous materials that have potential applications as catalysts. In princi-

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ple, any metal oxide or salt forming polynuclear species upon hydrolysis can be inserted as a pillar [8,9]. Aluminium and Zirconium are found among the most popular cations used to constitute the pillars of the structure, yielding pillared clay materials with thermal and mechanical stability [10,11]. On the other hand, as indicated before, iron is the metallic ion used in Fenton's reagent. Thus, the intercalation of both pair of cations, Al-Fe or Zr-Fe, in the interlayer spacing of bentonites, should produce catalytically active materials for oxidation of organic compounds with hydrogen peroxide. In spite of the extensive literature reported about catalytic wet peroxide oxidation (CWPO) using pillared clays with Al-Fe [1,5], there are no works in which Zr-Fe pillared clays were used as catalysts for this reaction. This work presents a comparative study on the use of pillared clays with Al, Zr and Al-Fe and Zr-Fe mixtures as potentially active catalysts for CWPO, using phenol as target compound, at 298 K.

## 2. Experimental

### 2.1. Pillared clays preparation

The starting material used to prepare the pillared clays was a purified-grade bentonite supplied by Fisher Scientific Company (Loughborough, Oregon, USA). The chemical analysis (wt.%) of this bentonite was: SiO<sub>2</sub>, 52.22; Al<sub>2</sub>O<sub>3</sub>, 16.81; Fe<sub>2</sub>O<sub>3</sub>, 3.84; Na<sub>2</sub>O, 1.26; MgO, 0.88; CaO, 0.74; K<sub>2</sub>O, 0.80. The cation-exchange capacity (CEC) was 97 meq/100 g of clay.

The Al-pillared clays were synthesized by intercalating sodium clays with hydroxy-aluminum cations [12]. The pillaring solution was prepared by slow addition of a 0.2 M NaOH solution to a 0.1 M AlCl<sub>3</sub>, under constant stirring until a OH/Al ratio equal to 2 was reached. The stirring during the addition of NaOH was necessary to prevent local accumulation of hydroxyl ions, which invariably produced precipitation of Al(OH)<sub>3</sub> [13]. The oligomeric solution was aged for 3 h at 363 K and 2 h at 298 K. A suspension of 0.1 wt.% bentonite in deionized water was mixed with this oligomeric solution. A pillaring stoichiometry of 10 mmol Al/g clay was used. The interchange process was carried out at room temperature for 12 h under constant stirring. The resulting product was washed by centrifugation with deionized water until chloride free (conductivity lower than 10 μS). After air-drying, it was calcined for 2 h at 473 and 673 K. This sample is referred to *Al-PC*.

The pillaring solution employed in the synthesis of Zr-pillared clays was prepared by adding ZrOCl<sub>2</sub> to methanol, according to the method described elsewhere [14]. The pH value of the resulting solution, very low, was adjusted to 1.5 adding diluted Na<sub>2</sub>CO<sub>3</sub> in order to obtain the appropriate Zr species to form the pillars of the structure. The mixture obtained was stirred for 2 h at 298 K. The amount of methanol employed was 25 mL/g clay. This pillaring solution was slowly added to a suspension of bentonite (0.1 wt.%) in deionized water. A pillaring stoichiometry of 5 mmol Zr/g clay was used as in previous works [14]. The following steps were similar to the above described for the preparation of *Al-PC* samples. The resulting product is referred as *Zr-PC*.

The corresponding Al/Fe and Zr/Fe pillared clays were prepared by the same procedures described for *Al-PC* and *Zr-PC*, respectively, with the only difference of the pillaring solutions. In the case of the Al/Fe pillared clays this solution was prepared by slow addition of a 0.2 M NaOH to a mixture of AlCl<sub>3</sub> 0.1 M and FeCl<sub>3</sub> 0.1 M. A molar ratio Fe/(Al+Fe) of 0.1 was used. The resulting product was referred as *Al/Fe-PC*. The pillaring solution for Zr/Fe pillared clays consisted in a mixture of methanol with ZrOCl<sub>2</sub> and FeCl<sub>3</sub> 0.1 M solutions. The molar ratio Fe/(Zr+Fe) was 0.18 in order to maintain the same Fe amount in the two iron catalysts (1.11 mmol Fe/g clay). The resulting product is referred as *Zr/Fe-PC*.

### 2.2. Characterization methods

X-ray diffractograms of the pillared clays were obtained with a Siemens model D5000 diffractometer using Cu K $\alpha$  radiation. To maximize the (00 1) reflection intensity, oriented clay-aggregate specimens were prepared by drying clay suspensions on glass slides. BET surface area values were determined from 77 K N<sub>2</sub> adsorption in a Micromeritics Tristar 3000 apparatus. The samples were previously outgassed at 453 K and 5  $\times$  10<sup>-6</sup> T for 16 h.

### 2.3. CWPO experiments

The catalytic activity experiments for CWPO of phenol with the different pillared clays were performed in a 500 mL thermostated stirred glass batch reactor. The pH was continuously controlled within the range of 3–3.5, which has been reported as the optimal for Fenton oxidation [15] as well as for CWPO with Al-Fe pillared clays catalysts [16].

After stabilization of the temperature at 298 K, the desired amount of pillared clay was added to 125 mL of an aqueous phenol solution (2000 mg/L) and it was stirred for 15 min in order to allow phenol adsorption onto the catalyst. The amount adsorbed was always less than 5% of the initial phenol weight. Next, 125 mL of an aqueous H<sub>2</sub>O<sub>2</sub> solution (10,000 mg/L), which corresponds to the stoichiometric amount for complete oxidation of phenol up to CO<sub>2</sub> (molar ratio H<sub>2</sub>O<sub>2</sub>/phenol = 14/1) was added to the phenol solution and this was considered the initial time for the reaction. Samples from the reaction medium were withdrawn at initial time, 15 min, 30 min and each hour until completing 6 h of reaction. The catalyst in these samples was removed using a nylon filter of 0.2 μm pore size. The samples were stored in the freezer in order to stop the reaction. For the sake of checking, some samples were also analysed immediately after taken and no differences were found.

The oxidation process was followed from the evolution of TOC, phenol and H<sub>2</sub>O<sub>2</sub> concentrations. Phenol was analysed by HPLC (Varian Pro-Start 240) with a diode array detector (at 210 nm wavelength) using a C<sub>18</sub> 5 μm column (Microsorb-MV, 15 cm length and 4.6 mm diameter) and 1 mL/min of 4 mM aqueous H<sub>2</sub>SO<sub>4</sub> solution as mobile phase. The H<sub>2</sub>O<sub>2</sub> concentration was determined by a colorimetric titration method [17] based on the formation of a yellow coloured complex Ti(IV)-H<sub>2</sub>O<sub>2</sub>, using a UV-vis spectrophotometer at 410 nm.

Total organic carbon (TOC) was determined with a 1010 TOC Analyser. Residual Fe concentration in the reaction media was also analysed. A colorimetric method based on the formation of a reddish coloured complex of Fe with ortho-fenantroline and its analysis in an UV–vis spectrophotometer at 510 nm was used.

#### 2.4. Catalytic $H_2O_2$ decomposition experiments

Experiments were carried out to study the decomposition of  $H_2O_2$  using the catalysts investigated. These experiments were developed in stoppered Pyrex glass flasks (100 mL) containing definite amounts of the catalyst. The catalysts were used in powder form to avoid diffusion limitations [18]. These flasks were deposited into a thermostatic bath and were magnetically stirred along the experiment. For each flask a 500 mg/L  $H_2O_2$  solution was added quickly and the time was recorded. After a given time, an aliquot volume (2 mL) was taken from the flask and the catalyst removed by means of an Albet nylon filter of 0.2  $\mu\text{m}$  pore size. Analyses of  $H_2O_2$  were performed according to the above described method [17].

### 3. Results and discussion

#### 3.1. Characterization of the pillared clays

The oriented powder X-ray diffractograms of pillared clays are shown in Fig. 1. Quite sharp  $d_{001}$  peaks can be seen, indicating a relatively homogeneous pillaring process. However, the presence of a second peak at  $2\theta$  around  $9^\circ$ , which corresponds to the main peak found in the pattern of raw Fisher bentonite, seems to indicate the existence of a fraction of unpillared material. When the calcination temperature increased, the  $d_{001}$  peaks obtained became broader and their intensity lower, indicating

Table 1

Basal spacing ( $d_{001}$ ) and BET surface area values of the pillared clays synthesized

	$d_{001}$ (nm)		$S_{\text{BET}}^a$ ( $\text{m}^2/\text{g}$ )
	473 (K)	673 (K)	
Fisher bentonite	0.99	0.98	34
Al-PILC	1.77	1.73	174
Al/Fe-PILC	1.79	1.80	206
Zr-PILC	1.77	1.75	192
Zr/Fe-PILC	1.83	1.81	211

<sup>a</sup> Pillared clays calcined at 473 K.

a less uniform structure, although the differences are very small.

Table 1 reports the basal spacing  $d(001)$  and the surface area values of the pillared clays after calcination at 473 and 673 K. The corresponding values of the starting bentonite calcined at the same temperatures are also included for comparison. As can be seen, the basal spacing decreases when the calcination temperature is increased owing to the dehydroxylation of the pillars. It is known that the thickness of the natural bentonite layer is 0.96 nm. The pillaring process substantially increases both the basal spacing and BET surface area. Incorporation of Fe leads to a slight increase of  $d_{001}$  and a more significant one of surface area. All the following reaction experiments were carried out with the pillared clays calcined at 473 K.

#### 3.2. Activity of the pillared clays in CWPO of phenol

Fig. 2 shows the results obtained for phenol conversion,  $H_2O_2$  decomposition and TOC reduction. It is clearly seen that the inclusion of Fe in these pillared clays drastically increases their activity for phenol oxidation. The Al-pillared clays show a

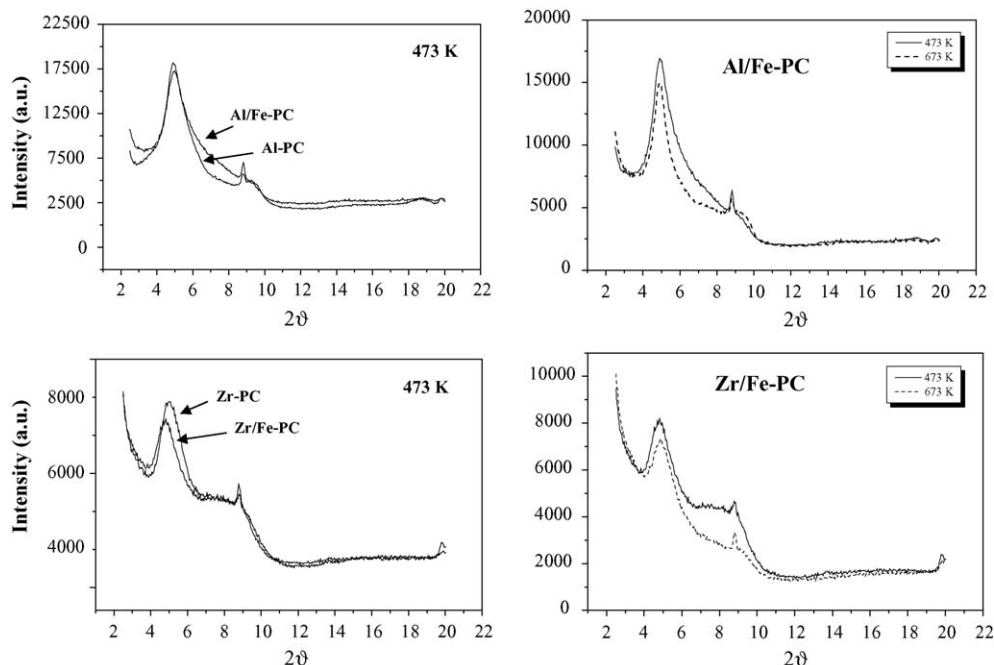


Fig. 1. X-ray diffractograms of the pillared clays at different calcination temperatures.

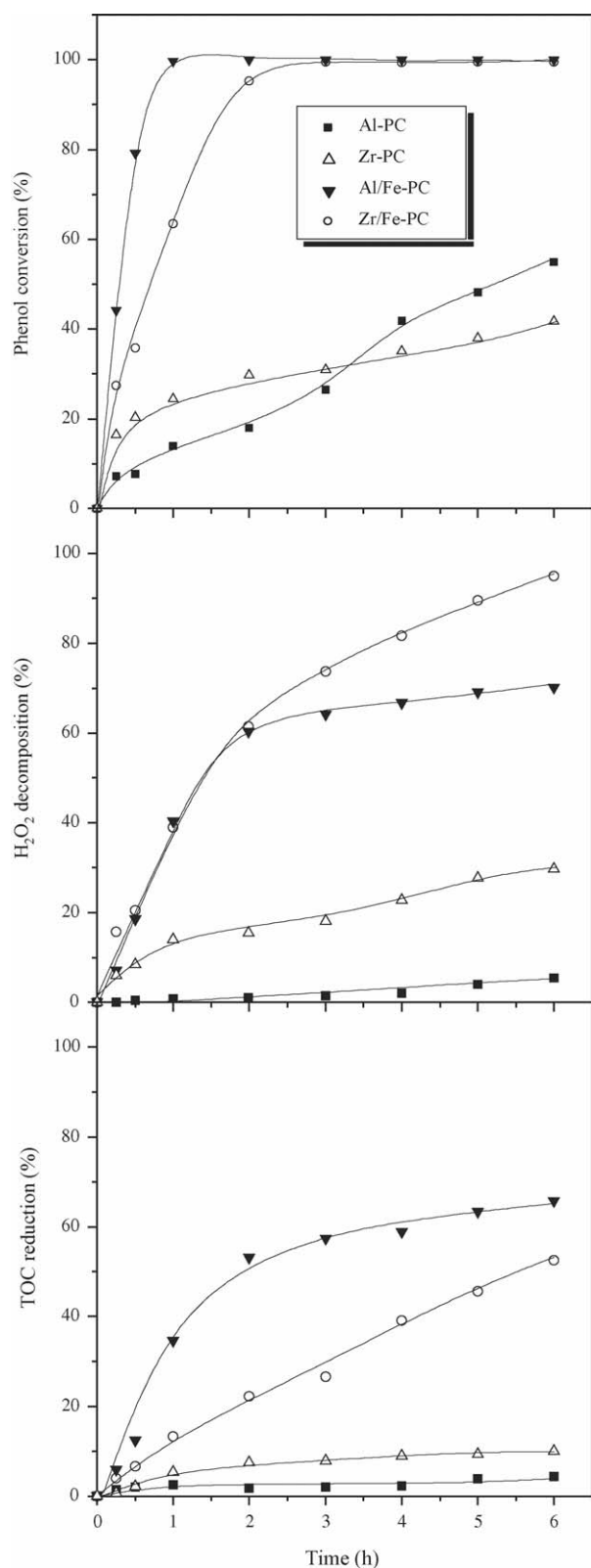


Fig. 2. Results obtained in CWPO of phenol.

higher activity than the corresponding Zr ones. With the Al/Fe-PC, almost complete phenol conversion (99%) is reached in 1 h whereas the Zr/Fe-PC leads to no more than 60% in the same time and complete conversion requires more than 3 h of

reaction. Nevertheless, the rate of H<sub>2</sub>O<sub>2</sub> decomposition appears fairly similar for both Al/Fe and Zr/Fe pillared clays during the first 2 h of reaction. This suggests that a different decomposition route is prevailing in both cases and whereas Al/Fe-PC promotes mainly the generation of OH radicals, in the case of Zr/Fe-PC a substantial percentage of H<sub>2</sub>O<sub>2</sub> must be giving rise to O<sub>2</sub>, with a low oxidation capacity at these mild operating conditions.

TOC reduction is, in all the cases, significantly lower than phenol conversion indicating that oxidation of phenol proceeds through the formation of different intermediates and the final result is far from complete mineralization, namely oxidation to CO<sub>2</sub> + H<sub>2</sub>O. The maximum TOC reduction reaches 65% after 6 h in the case of Al/Fe-PC and close to 50% for Zr/Fe-PC, which means that significant amounts of intermediates still remain in solution even at high reaction times.

Figs. 3 and 4 show the time-evolution curves of the intermediates identified. The former one, corresponding to aromatics, exhibits the typical pattern for a series reaction scheme. The main product among this group is catechol which shows a maximum concentration value significantly higher and at substantially lower time in the case of Al/Fe-PC in agreement with the higher rate observed for phenol conversion with this catalyst. Hydroquinone and *p*-benzoquinone are of particular relevance due to their high toxicities, much above that of phenol itself. Thus, it is important to reach a complete removal of these species, which requires a sufficiently high reaction time.

The aromatic intermediates evolve to carboxylic acids, the distribution of which can be seen in Fig. 4. Some important differences can be pointed out in this case among the two Fe-pillared clays. In the case of Al/Fe-PC, formic acid is the main product of this group of intermediates, showing a remarkable maximum concentration value and then a decrease due to mineralization. This trend is not observed in the case of Zr/Fe-PC, suggesting that whether mineralization is not taking place or it is balanced by acid formic formation from other carboxylic acids in the reaction pathway. The main carboxylic acid in the case of Zr/Fe-PC is oxalic which exhibits

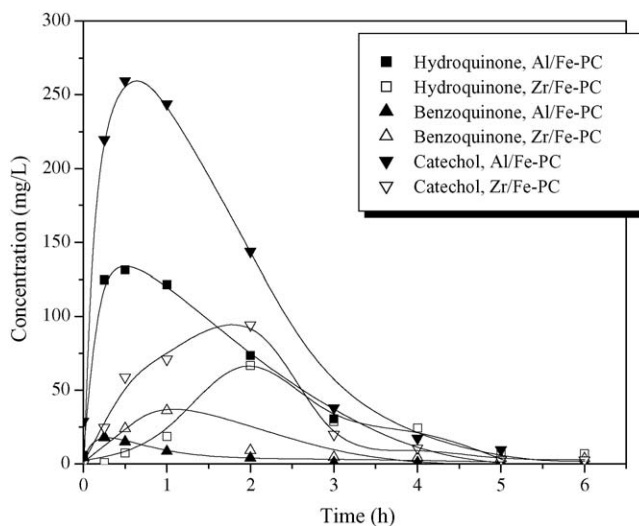
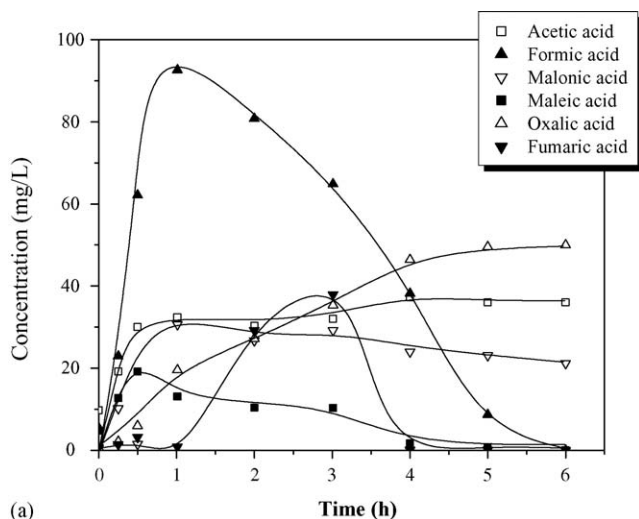
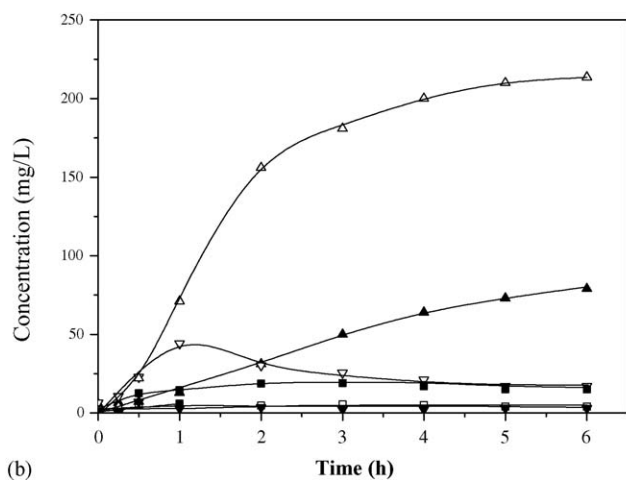


Fig. 3. Time-evolution curves of aromatic intermediates from CWPO of phenol with pillared clays.





(a)



(b)

Fig. 4. Time-evolution curves of carboxylic acids from CWPO of phenol with pillared clays: (a) Al/Fe-PC; (b) Zr/Fe-PC.

a refractory behaviour with both pillared clays, in agreement with the reported by other authors [19]. Another remarkable difference appears in the case of acetic acid which shows a substantially higher relative importance in the case of Al/Fe-PC. As in the case of oxalic, the time-evolution curves of acetic acid also suggest a refractory behaviour in the experiments carried out with the Al/Fe-PC catalyst.

Leaching of Fe was negligible within the reaction time required for a practically complete phenol conversion. As it can be seen in Fig. 5, it was 2 mg/L in the case of Al/Fe-PC and 5 mg/L in the case of Zr/Fe-PC, which corresponds to around 1 wt.% and 2 wt.%, respectively. Thus, it cannot explain the differences observed in the activity of both catalysts.

### 3.3. Hydrogen peroxide decomposition

As indicated in Section 3.2, the differences observed among the two Fe-pillared clays with regard to the oxidation process could be explained in terms of a different prevailing pathway in  $H_2O_2$  decomposition. To analyze this more in deep we have studied the kinetics of  $H_2O_2$  decomposition with each of these two catalysts in order to obtain the corresponding values of the

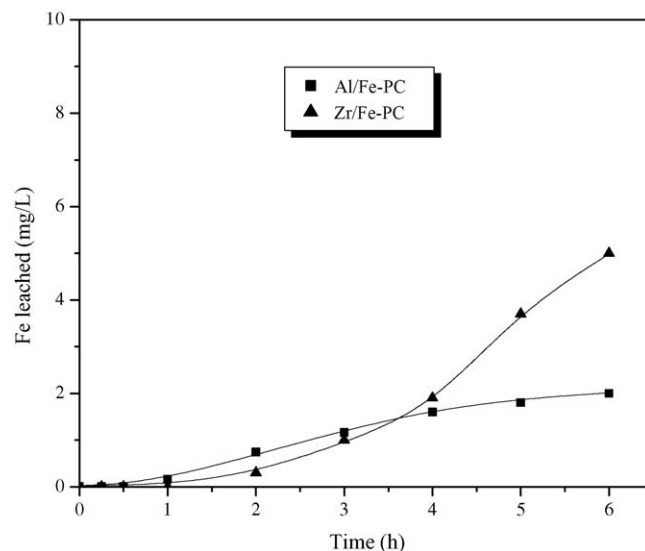


Fig. 5. Evolution of Fe leached from the catalysts during the oxidation runs.

apparent activation energy. In that sense we have obtained the time-evolution curves of  $H_2O_2$  in absence of phenol at three different temperatures within the 298–323 K temperature range.

Fig. 6 shows the results obtained. An initial  $H_2O_2$  concentration of 500 mg/L (14.7 mmol/L) and a dose of catalyst of

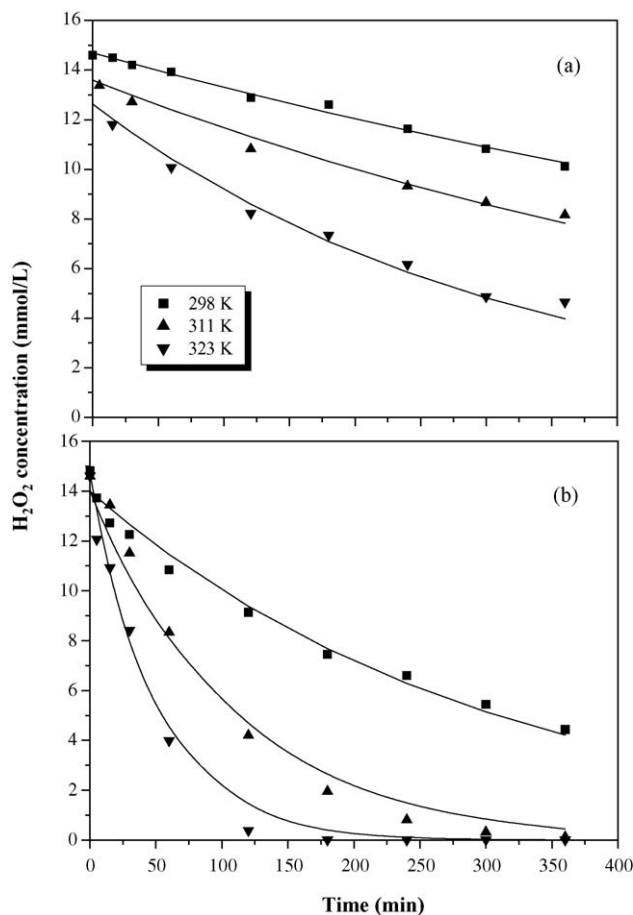


Fig. 6. Decomposition of  $H_2O_2$  with: (a) Al/Fe-PILC and (b) Zr/Fe-PILC at three different temperatures.

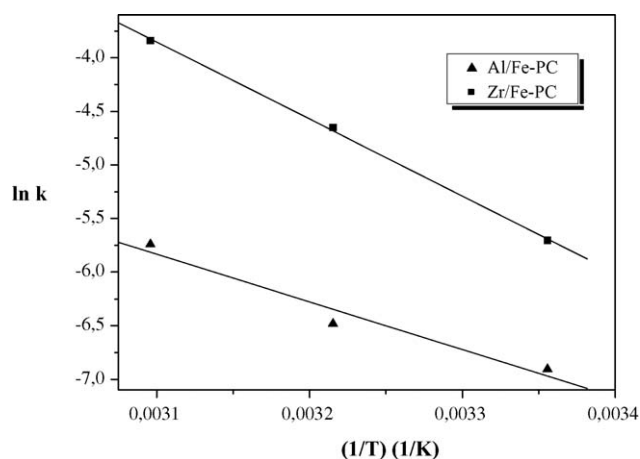


Fig. 7. Arrhenius plot of the apparent kinetic constant for  $\text{H}_2\text{O}_2$  decomposition with the two Fe-pillared clays.

2000 mg/L were used in all the experiments. As can be seen, the rate of decomposition is significantly higher with the Zr/Fe-PC catalyst. The experimental values of  $\text{H}_2\text{O}_2$  concentration versus time were adjusted to a first order kinetic equation and the curves resulting from this fitting are plotted in Fig. 6 together with the experimental points. It can be seen that this simple equation serves to describe fairly well the kinetics of  $\text{H}_2\text{O}_2$  decomposition with both catalysts at the three temperatures investigated.

The Arrhenius plot of the apparent kinetic constant values are presented in Fig. 7. The corresponding values of the apparent activation energy were 37 and 60 kJ/mol for Al/Fe-PC and Zr/Fe-PC, respectively. The literature reports values of the apparent activation energy for  $\text{H}_2\text{O}_2$  decomposition in the range of 55–71 kJ/mol with catalysts based on different ligands adsorbed on resins [20], 50–69 kJ/mol for transition metal complexes supported on silica-alumina [21], 32–40 kJ/mol for perovskites [22] and 31–43 kJ/mol for catalysts based on transition metal heterocyclic complexes [23].

The difference observed in our case in the values of apparent activation energy with the two Fe-pillared clays supports the hypothesis about a different prevailing mechanism for  $\text{H}_2\text{O}_2$  decomposition which was mentioned before to explain the results obtained for phenol oxidation with both catalysts.

#### 4. Conclusions

Pillared clays prepared from Al, Zr and Al-Fe and Zr-Fe mixtures with a commercial bentonite have been tested for phenol oxidation with hydrogen peroxide at 298 K. The catalysts based on pillared clays with Al-Fe showed a higher activity for phenol conversion and TOC removal, whereas the pillared clays with Zr-Fe decompose  $\text{H}_2\text{O}_2$  more rapidly. This can be explained from a different prevailing mechanism in  $\text{H}_2\text{O}_2$  decomposition, yielding predominantly  $\text{OH}^\bullet$  radicals in the case of Al/Fe-PC whereas with Zr/Fe-PC a higher contribution of decomposition to  $\text{O}_2$  must take place. This last species is much less active for oxidation in the mild conditions used. The significantly different values of apparent activation energy obtained for  $\text{H}_2\text{O}_2$  decomposition with both catalysts supports this conclusion. In spite of

the lower activity of the Zr-Fe pillared clay for CWPO, it showed a good behaviour with regard to Fe lixiviation which requires further research to establish the stability of both catalysts in a long-term basis. Moreover, the higher activity of the Zr-Fe pillared clay for  $\text{H}_2\text{O}_2$  decomposition can be of potential interest to remove residual concentrations of this species from aqueous effluents when needed.

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