Research Article

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Improved Fe_2O_3/Al_2O_3 as heterogeneous Fenton catalysts for the oxidation of phenol solutions in a continuous reactor

Carla di Luca,[a]* Paola Massa,[a] Rosa Fenoglio[a] and Francisco Medina Cabello[b]

Abstract

BACKGROUND: Improved Fe_2O_3/Al_2O_3 catalysts were studied for the catalytic oxidation of concentrated phenol solutions (5 g L^{-1}) with H_2O_2. To enhance catalyst stability, two strategies were investigated: the use of a high calcination temperature and a step of immersion into an organic acid solution. The reaction runs were performed in a continuous reactor at 70°C and atmospheric pressure.

RESULTS: For all the catalysts, almost complete phenol degradation was achieved. The mineralization levels were incomplete, reaching 60 and 50% for the catalysts treated with acetic and oxalic acid, respectively. The leaching levels were reduced from 25% (for the untreated catalyst) to 11% after the immersion in oxalic acid. In all cases, the formation of reversible carbonaceous deposits was observed during reaction and a progressive decay in phenol, TOC and H_2O_2 conversions was registered.

CONCLUSION: Catalyst resistance to leaching was significantly enhanced by combining both thermal and acidic treatments. These procedures did not affect the catalytic wet hydrogen peroxide oxidation (CWHPO) performance in terms of mineralization levels. The lixiviation levels were acceptable, taking into account the strong acidic reaction medium. Deactivation processes might be primarily associated with the formation of reversible carbonaceous deposits due to intermediates accumulation onto the catalyst surface.
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Supporting information may be found in the online version of this article.

Keywords: CWHPO; Fe_2O_3/alumina; Fenton-like reaction; phenol removal; fixed bed reactor

INTRODUCTION

Industrial effluents frequently contain toxic pollutants that are resistant to conventional treatments. Phenol and phenolic compounds are among the most important chemical contaminants from industry and are commonly used as model compounds for wastewaters studies.[1,2] Oxidation techniques have been applied for the abatement of these types of organics via complete breakdown into carbon dioxide and water or conversion to easily biodegradable products.[3,4] Advanced oxidation processes (AOPs) are considered to be interesting alternatives for water treatment at mild conditions of temperature and pressure.[5,6] These technologies are based on the potent action of hydroxyl radicals to destroy organic compounds. Among them, the so-called catalytic wet hydrogen peroxide oxidation (CWHPO)[7−9] appears to be a promising solution, most particularly in the case of heterogeneous Fenton oxidation. This process uses catalysts prepared by immobilizing transition metal cations (primarily iron, but not exclusively) over different supports that are further tested in CWHPO reactions,[2,10] using H_2O_2 as oxidizing agent. However, a major problem associated with these catalytic systems derives from the leaching of the active phase at low pH, producing strong deactivation of the catalyst and making it necessary to incorporate additional steps to separate the solubilized metal at the end of the process. In particular, some authors have reported that the presence of oxalic acid

as a by-product of phenol incomplete mineralization strongly contributes to increase the Fe leaching levels.[11]

Although the use of heterogeneous Fenton/Fenton-like systems has been the focus of extensive research,[2] most of the studies have been carried out in discontinuous reactors. Only a few have dealt with the treatment of organic pollutants by means of continuous processes using iron-based solid catalysts. The main results from these former contributions are reviewed in Table 1. It should be noted that the application of different catalytic systems requires specific conditions that need to be understood, especially those associated with deactivation mechanisms.

The objective of the present work was to reach higher degradation rates, minimizing the impact of leaching processes. For this purpose, pelletized Fe_2O_3/Al_2O_3 catalysts were prepared using different pre-treatments. Two combined strategies were explored in

* Correspondence to: Carla di Luca, INTEMA, CONICET-Universidad Nacional de Mar del Plata, Juan B. Justo 4302, Mar del Plata, Argentina. E-mail: cardiluca@fi.mdp.edu.ar

a INTEMA, CONICET-Universidad Nacional de Mar del Plata, Juan B. Justo 4302, Mar del Plata, Argentina

b ETSEQ, Universitat Rovira i Virgili, Av. Països Catalans 26 (43007), Tarragona, Spain

Table 1. Summary of CWHPO studies under continuous operation using iron heterogeneous catalysts*

Catalyst	Pollutant	Reactor	Conditions	Results	Ref.
7.7 wt% Fe/Al_2O_3 Ox. 450 °C powder	Catechol $TOC_0 = 36$ mg L^{-1}	UFBR	$T = RT$ $Q = 1.3$ mL min^{-1} $m_{cat} = 0.5$ g $R = 0.86$	TOC *not reported* Fe lix < 1%	12
Fe/GAC Fe from GAC impurities pellet (0.5–1 mm)	4-chlorophenol $TOC_0 = 560$ mg L^{-1}	FBR	$T = RT$ $Q = 0.06$ mL min^{-1} $m_{cat} = 2$ g $R = 1.54$	$X_{TOC} = 17\%$ *After saturation* Fe_{lix} *not calculated*	13
14 wt% Fe/SBA-15 ox. 650°C pellet (1.6–2 mm)	Phenol $TOC_0 = 766$ mg L^{-1}	UFBR	$T = 80°C$ $Q = 1$ mL min^{-1} $m_{cat} = 2.9$ g $R = 1$	$X_{TOC} = 66\%$ $Fe_{lix} = 1.7\%$	14,15
14 wt% Fe/SBA-15 ox. 550°C pellet (1–1.6 mm)	*Pharmaceutical effluent* $TOC_0 = 860$ mgL^{-1}	UFBR	$T = 80°C$ $Q = 0.5$ mL min^{-1} $m_{cat} = 2.9$ g $R = 2$	$X_{TOC} = 60\%$ Fe_{lix} *negligible*	16
4 wt% Fe/Al_2O_3 ox. 300°C powder	Phenol $TOC_0 = 77$ mg L^{-1}	CSTR	$T = 50°C$ $Q = 5$ mL min^{-1} $m_{cat} = 1.25$ g $R = 1$	$X_{TOC} = 50\%$ $Fe_{lix} = 5\%$	11
1 wt% Fe/AC ox. 800°C powder	Phenol $TOC_0 = 77$ mg L^{-1}	CSTR	$T = 50°C$ $Q = 5$ mL min^{-1} $m_{cat} = 5$ g $R = 1$	$X_{TOC} = 25\%$ *After saturation* $Fe_{lix} < 5\%$	17
7 wt% Fe/AC ox. 400°C pellet (1.4–1.7 mm)	Chicago Sky Blue $TOC_0 = 5$ mg L^{-1}	UFBR	$T = 50°C$ $Q = 2.5$ mL min^{-1} $m_{cat} = 10.25$ g $R = 2$	$X_{TOC} = 47\%$ *After saturation* $Fe_{lix} \sim 0.3$ mg/L	18
7 wt% Fe/AC ox. 300°C pellet (0.8–1.6 mm)	*Textile effluent* $TOC_0 = 175$ mg L^{-1}	UFBR	$T = 50°C$ $Q = 2$ mL min^{-1} $m_{cat} = 6.6$ g $r_{used} = 5.8$	$X_{TOC} = 74\%$ *After saturation* $Fe_{lix} = 0.36\%$	19
4 wt% Fe/Al_2O_3 ox. 300°C/red. 350°C powder	2,4,6-trichlorophenol $TOC_0 = 69$ mg L^{-1}	CSTR	$T = 50°C$ $Q = 2$ mL min^{-1} $m_{cat} = 0.5$ g $R = 1$	$X_{TOC} \sim 23\%$ $Fe_{lix} \sim 5\%$	20

*The reported values were chosen taking into consideration the best reaction results performed throughout the work.

The oxidant dose was reported as: $R = \frac{r_{used}}{r_{theorical}}$, where $r = \frac{[mg\ H_2O_2]}{[mg\ TOC_0]}$. For instance, R = 1 represents stoichiometric H_2O_2 dosage.

UFBR: Upflow fixed bed reactor.

CSTR: Continuous stirred tank reactor.

order to enhance catalyst stability: the use of a high calcination temperature and a step of immersion into an organic acid solution. From previous studies at *batch* scale, it was determined that a calcination treatment at 900°C could significantly enhance the catalytic stability by increasing iron-support interactions.[10] For the acid immersion pre-treatment, acetic and oxalic acid were chosen. Both of them are broadly known as main short-chain acid intermediates responsible for the residual organic content in the advanced steps of phenol oxidation and also for the lixiviation of active species (as was previously mentioned for oxalic acid). The CWHPO experiments were performed in a fixed bed reactor under continuous operation. In order to test the resistance of the iron species to solubilization, a relatively concentrated phenol initial charge (5 g L^{-1})

was selected, which imposes more demanding reaction conditions for the catalyst.

EXPERIMENTAL
Catalyst preparation
The $Fe_2O_3/\gamma-Al_2O_3$ catalyst was prepared by the incipient wetness impregnation method onto commercial alumina spheres (SASOL, $d_p = 2.5$ mm). The metal precursor salt chosen was Fe(III)-citrate (Sigma Aldrich) and the Fe load was adjusted to a nominal 4 wt%. In order to enhance the iron species dispersion onto the support, the impregnation procedure was carried out in two consecutive stages by adding half of the total iron amount each

step (a comparison of the different catalyst preparation procedures is provided as Supporting Information). After each impregnation, the sample was left for 12 h at room temperature and dried for 24 h at 150°C. Finally, the impregnated pellets were calcined at two different temperatures, 400 and 900°C, in a muffle furnace with integrated air circulation for 4 h (temperature ramp 10°C min⁻¹). The prepared samples resulted in bulk catalysts with a homogeneous metal dispersion inside the pellets. Based on the thermal treatment applied, the samples were labelled 4Fe400 and 4Fe900 for catalysts calcined at 400 and 900°C, respectively.

Two additional samples were prepared by treating catalyst 4Fe900 with different carboxylic acids, oxalic and acetic acid. These organic acids are recognized as phenol oxidation intermediates[11,21] and were chosen as a strategy to improve active phase stability by removing or re-dispersing labile iron species onto the catalyst surface. The acid treatment was performed by immersion of the pellets into an aqueous acid solution (1 mol L⁻¹) and the contact time was 24 h at room temperature. Afterwards, the catalysts were further washed with distilled water, dried at 150°C and re-calcined at 900°C for 2 h. The molar ratio between acid and Fe was set representing a supra-stoichiometric dose for Fe(III)-oxalate or Fe(III)-acetate formation. The treated samples were designed as 4Fe900ox and 4Fe900ac, corresponding to the oxalic and the acetic acid treatment.

Finally, an additional reduction stage was tested over the 4Fe900ac catalyst in order to develop a superficial distribution of Fe(II)/Fe(III) species. In a recent work, Muñoz and collaborators[20] reported an improved magnetic catalyst that significantly increased the decomposition of H_2O_2 leading to higher levels of degradation and mineralization of chlorophenols by comparison with a conventional Fe₂O₃/Al₂O₃ catalyst. Following their experimental procedure, the reduction treatment was carried out under H_2 atmosphere for 2 h at 350°C and the sample was labelled 4Fe900ac-R.

Catalyst characterization

Characteristics of the samples were determined by different conventional techniques. The surface area (BET method) and the porous structure was characterized from N_2-physisorption at −196°C using a Micromeritics ASAP 2000 surface analyzer; the samples were previously degassed overnight at 120°C.

The crystalline phases present in the catalysts were analyzed by X-ray diffraction (XRD) using a Siemens D5000 diffractometer with Cu Kα radiation (λ = 1.54056 Å). The angular 2θ diffraction range was between 10° and 70°. The crystalline phases were identified using the JCPDS files.

The surface of catalysts was investigated by scanning electron microscopy (SEM) using a JEOL JSM-6460LV electronic microscope. The elemental composition was determined by energy dispersive X-ray spectroscopy (EDAX) using an EDAX Genesis XM4-Sys60 equipment. Samples were metallized with Au-Pd in a sputtering device.

X-ray photoelectron spectroscopy (XPS) was employed for surface iron analysis using a multi-technique system (SPECS) equipped with a conventional dual Mg/Al X-ray source and a Phoibos 150 analyzer operating in the fixed analyzer transmission (FAT) mode. Spectra were recorded at a pressure below 2×10^{-8} mbar. Binding energies were referred to adventitious carbon at 285 eV. The data treatment was performed with the Casa XPS program.
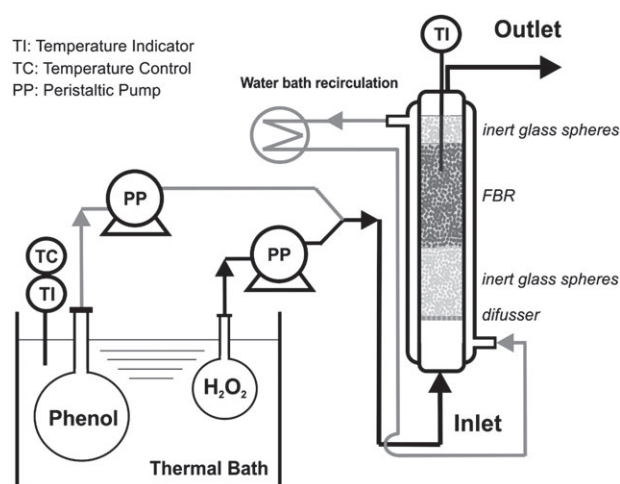

Figure 1. Experimental set-up of the upflow fixed bed reactor used for the CWHPO runs.

The organic matter removal of the used catalysts was determined by thermogravimetric analysis (TGA); measurements were carried out from 50 to 800°C under air current (20 mL min⁻¹; 10°C min⁻¹) using a Shimadzu TGA-50 apparatus.

The nature of carbonaceous deposits was explored by Fourier-transformed infrared spectroscopy (FTIR) with a Nicolet 6700 FTIR and recorded over the spectral range 4000–600 cm⁻¹. Solid samples were prepared by the KBr pellet method.

The iron content of fresh and used catalysts was determined by a standard colorimetric test (FerroVer® Iron Reagent, HACH), with previous nitric acid extraction of the solid samples. The total iron load of the 4Fe900 catalyst was determined before the calcination step. The final leaching levels were estimated by comparing the initial and final iron contents of the used catalysts. In order to ensure the reproducibility of the Fe contents determined, the reported values are the average of at least two different solid samples, each one measured in duplicate during the standard colorimetric method, with a coefficient of variation (Cv) below 5%.

CWHPO tests in an upflow fixed bed reactor

As previously mentioned, a relatively concentrated phenol initial charge (5 g L⁻¹) was selected in order to impose more demanding reaction conditions with the aim of testing the iron leaching resistance. This concentration represents the upper limit within the range of concentrations of phenolic compounds frequently found in industrial effluents.[2]

Figure 1 illustrates the experimental set-up employed for phenol abatement by means of CWHPO. The experiments were performed in a jacketed glass column with 2.3 cm internal diameter and 21 cm long, packed with 20 g (11.5 cm) of the catalyst pellets. Inert glass beads of the same size were placed above and below the catalyst packing, enabling a better distribution of the feed solution inside the catalyst bed. Both the phenol and hydrogen peroxide solutions were stored in separated reservoirs and pre-heated in a thermostatic bath. The reactor temperature was kept constant by the upstream circulation of hot water throughout the column jacket. The solutions were fed to the reactor in upflow mode using two peristaltic pumps. This scheme based on flooded packed-bed reactors ensures good catalyst wetting by the liquid phase and avoids air retention.

The fixed bed reactor (FBR) worked under atmospheric pressure. The temperature inside the reactor was measured on the top

Table 2. Summary of characterization results

Samples	BET surface area ($m^2\ g^{-1}$)	Pore volume ($m^3\ g^{-1}$)	Iron total content (%)	Phases detected by XRD
Al_2O_3	208	0.49	-	γ-Al_2O_3
Al_2O_3 (ox. 900°C)	138	0.46	-	γ-Al_2O_3
4Fe900	116	0.38	4.2	γ-Al_2O_3
4Fe900ac	135	0.43	3.8	γ-Al_2O_3
4Fe900ox	138	0.45	3.8	γ-Al_2O_3

section of the catalytic bed and maintained at 70 ± 2°C. It must be also noted that the beginning of the oxidation process is accompanied by a marked exotermia of about 10°C, controlled by means of the heating water. The phenol flow rate was set to 5 mL min^{-1} and the oxidant flow rate was adjusted to maintain a molar ratio [H_2O_2]/[phenol] of 10.5, which is 0.75 times the stoichiometric proportion (R = 0.75); the stoichiometric ratio for complete phenol oxidation is 14 (R = 1). For the reaction runs with the 4Fe900ac-R catalyst, this ratio was increased and kept at [H_2O_2]/[phenol] = 11.2 (R = 0.8) owing to the fact that this catalyst decomposes H_2O_2 more actively than 4Fe900 and the treated ones (4Fe900ac and 4Fe900ox). Thus, throughout this work the total flow rate was Q = 5.4 mL min^{-1}. The criterion for R adjustment was to make best use of the oxidant supplied, maximizing the efficiency of hydrogen peroxide.[10]

The residence time for the liquid phase in the packed bed reactor was 3.4 min and it was calculated following the procedure reported by Martinez and collaborators[14] using the flooded-bed simulator (Larachi and Grandjean (http://www.gch.ulaval.ca/)). This method takes into account the bed porosity (ϵ) and the liquid holdup (h_L) of the packed bed.

During the catalytic oxidation experiments, liquid samples were regularly taken out from the effluent at the top section of the column in order to evaluate phenol and total organic carbon (TOC) removal, hydrogen peroxide consumption and pH evolution. Phenol and hydrogen peroxide concentrations were determined by standard analytical techniques (colorimetric method and iodometric titration, respectively).[22] TOC contents were measured with a Shimadzu TOC-V CPN analyzer. The absorption spectrum of the effluent solution in the UV-visible region (600–200 nm) was also monitored with a Shimadzu UV-1800 spectrophotometer.

Finally, in order to confirm the repeatability of the CWHPO experiments carried out, a representative reaction run was performed in duplicate with the 4Fe900 catalyst obtaining a Cv < 4% for determined concentrations of phenol, TOC and H_2O_2 on analogous samples taken out at different selected reaction times.

RESULTS AND DISCUSSION

Characterization results

It was confirmed that the thermal treatment induced a reduction in the surface area and the pore volume of the alumina (Table 2). As a result of the calcination at 900°C, it was also observed that only a fraction of the total iron present in the catalyst could be extracted by nitric acid attack during the iron contents determinations. The thermal treatment might induce stronger iron–alumina interactions stabilizing the iron species onto the support. This was probably due to migration of Fe to inner or more defective regions of alumina. The formation of mixed oxides Fe–Al–O

(not detected through the characterization techniques employed) should not be completely discarded. However, it was reported that spinel-like phases are thermodynamically hindered at the pressure/temperature conditions selected for the catalysts preparation in the present study.[23,24] We have also calcined the catalytic system at 1400°C and performed XRD analysis. Even at this high temperature, no formation of large oxidic aggregates was observed, neither the presence of Fe–Al mixed phases; only alpha-alumina characteristic peaks were registered (XRD patterns are included as Supporting Information).

The iron contents of the different samples are summarized in Table 2. As expected, after immersion in the organic acid solutions, a fraction of the Fe species was removed: 9.5% of the initial iron loading was extracted after the treatment with oxalic or acetic acid. This extraction step would remove the most labile (or more superficial) iron species during the preparation of the catalyst, avoiding their further solubilization in the course of the CWHPO reaction process and minimizing the impact of secondary pollution. In turn, the acid treatment of the catalyst also induced a moderate increase of the surface area and pore volume of the catalysts, as reported in Table 2. The SEM image in Fig. 2 (4Fe900 catalyst) is representative of the surface morphology of the samples. The surface mapping of all the samples showed a regular distribution of iron species onto the catalyst. This is in agreement with XRD results that showed only gamma-alumina characteristic peaks (the XRD patterns are provided as Supporting Information). Due to the low concentration/good dispersion of Fe, no iron-containing phases were detected.

The nature of the superficial iron species were characterized by XPS. Fe 2p core level spectrum for 4Fe900ac catalyst is shown in Fig. 3. The XPS spectrum confirmed that the main iron species on the surface corresponds to Fe_2O_3, showing a well-defined peak at 711.4 eV and its doublet separated by 13.6 eV. Typical binding energy (BE) values for the Fe2p3/2 band oscillate in the range 710.7–711.4 eV (Naumkin *et al.* (http://srdata.nist.gov/xps)); the shift of this band to higher binding energies might suggest interactions between the iron and the alumina support. On the other hand, the ratio of the superficial (XPS) to the total Fe was 0.7, indicating that not all the iron loaded was available at the catalyst surface, probably due to diffusion of Fe species into the alumina matrix.

Reaction results

Figure 4 compares the CWHPO performance of 4Fe900, 4Fe900ac and 4Fe900ox catalysts. For all the catalytic runs, the oxidation started after approximately 2 h operation. At this point, a marked change in the colour of the solution was observed (from transparent to brown, due to the formation of quinone-like intermediate species) with a correlated increase in the oxidant consumption up to 100%. These high initial H_2O_2 conversion levels diminished progressively during the reaction time. A different behaviour was registered for the conversion of phenol, TOC and pH. Phenol conversion and TOC reduction remained practically constant during the first 7–8 h of CWHPO reaction and then gradually decreased; the pH values remained low and rather uniform throughout the process.

Regularly in advanced oxidation processes, complete mineralization is favoured at lower concentrations of the target pollutant. In our case, the relatively high initial phenol charge selected for the experiments led to higher concentration of intermediates accumulated in the reaction systems. It is broadly proposed that the phenol oxidation mechanism occurred through the formation of
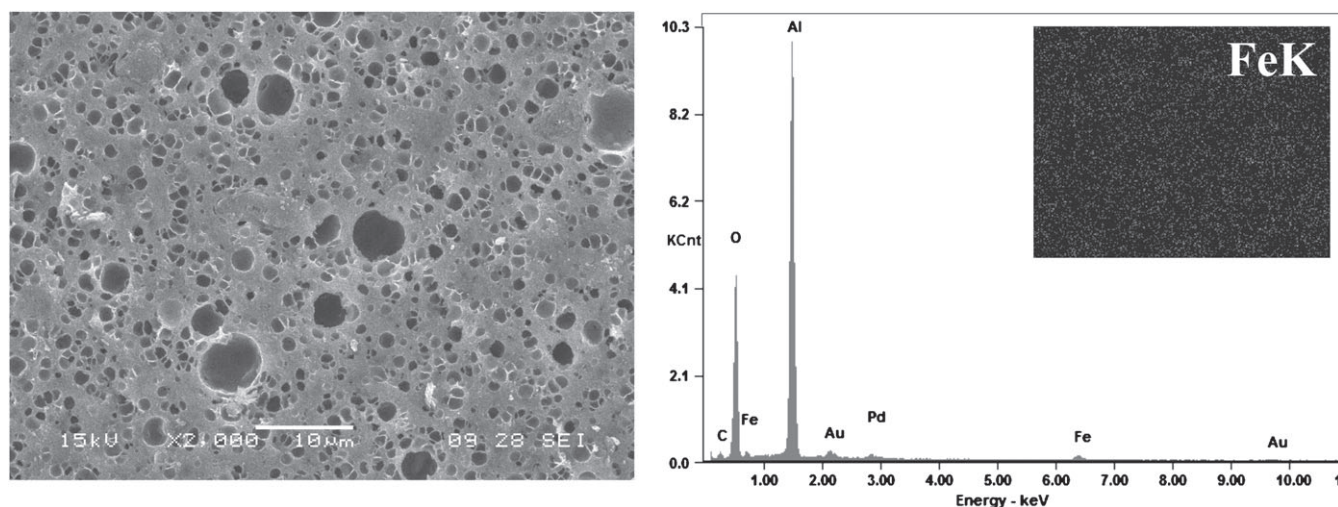
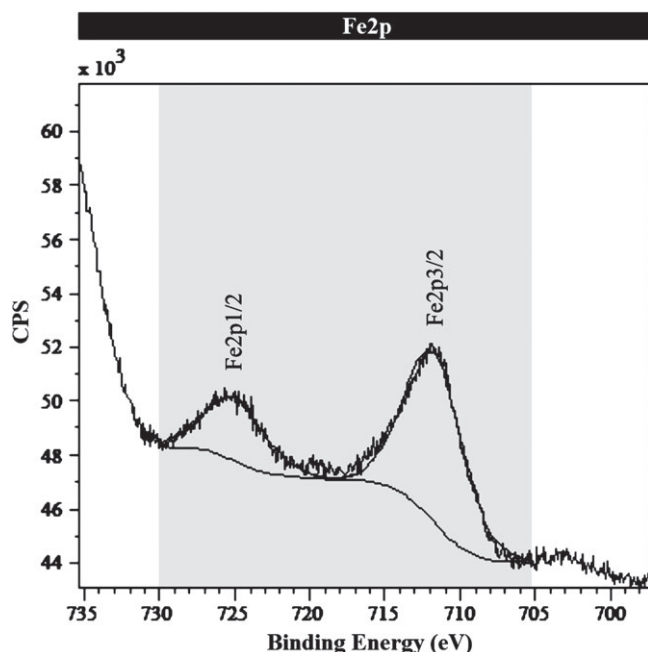**Figure 2.** SEM image (2000×), EDAX spectrum and surface mapping of 4Fe900 catalyst.

Figure 3. Deconvolution of Fe2p core level XPS spectrum for the 4Fe900ac catalyst.

quinone, hydroquinone and catechol that are progressively oxidized to short-chain organic acids (some of them, more refractory to CWHPO processes) and finally, to CO_2. The presence of the carboxylic acids would be responsible for the low pH of the reaction solution. At this strong acidic medium, the solubilization of iron is promoted (especially in the presence of certain species such as oxalic acid). Despite these reaction conditions, the iron leaching levels were markedly reduced, according to the results reported in Fig. 5. For the sake of comparison, Fig. 5 also includes the lixiviation percentage obtained for the catalyst calcined at 400°C (4Fe400).

The configuration of the fixed bed reactor might lead us to anticipate a lower incidence of the leaching processes, when compared with a stirred tank. However, for the experiments using the 4Fe400 catalyst, very high levels of metal stripping were reached (62%). The thermal treatment at 900°C had a significant impact on improving the resistance to leaching of the catalyst

(lixiviation was reduced up to 25%). For the treated catalysts 4Fe900ox and 4Fe900ac this effect was even more pronounced: leaching was reduced by about 80%.

As the metal leaching cannot be neglected, the iron species in solution could be also contributing to the overall degradation process. In order to evaluate this contribution, a series of *batch* experiments were carried out at 70°C, for 4 h (the experimental setup was similar to the reported elsewhere[10]). These *batch* tests were not representative of the continuous experiments, but served to estimate the catalytic activity of the leached Fe. First, we tested the catalytic activity of the outlet effluent of a typical FBR reaction run with 4Fe900 sample. Fresh phenol and H_2O_2 were added to the effluent solution in order to adjust the initial TOC to the same value as for the continuous runs ($TOC_0 = 3830$ ppm; $[H_2O_2]_0 = 0.67$ mol L^{-1}). Throughout the first 60 min of reaction time, a marked induction period was registered; afterwards, phenol and TOC conversions started to increase, achieving final levels of 78% and 40%, respectively. The lag phase could be explained by reduced iron activity due to the complexing effect of organic by-products. The formation of metal complexes could be hindering the reduction of Fe(III) to ferrous species that would be affecting the generation of hydroxyl radicals and the further progress of the oxidation reaction.[21] Also, homogeneous Fenton and Fenton-like tests were performed with $Fe(SO_4).7H_2O$ or $FeCl_3.6H_2O$ as catalysts (for the latter run the initial pH was set at 3, using H_2SO_4). The iron concentration employed was equivalent to the average Fe leached during the extended reaction test with the 4Fe900 catalyst (46 ppm). With both Fe(II) and Fe(III) species, the phenol conversion was practically complete after the first 10 min reaction time and no induction period was detected. The final TOC conversions were similar (47 and 48%, correspondingly); however, the initial mineralization rate was slower in the presence of ferric ions. It is noteworthy that these experiments overestimate the homogeneous contribution since the release of Fe ions is gradual throughout the reactor bed.

According to these results, the presence of an induction period at the beginning of the continuous runs might indicate that the reaction was started by a heterogeneous pathway. In spite of the Fe leaching levels registered, dissolved iron present in the outlet effluent could be forming metal complexes with refractory by-products from phenol incomplete oxidation, which exhibited poor catalytic activity. Thus, the influence of homogeneous iron as a secondary contribution for TOC mineralization might be strongly
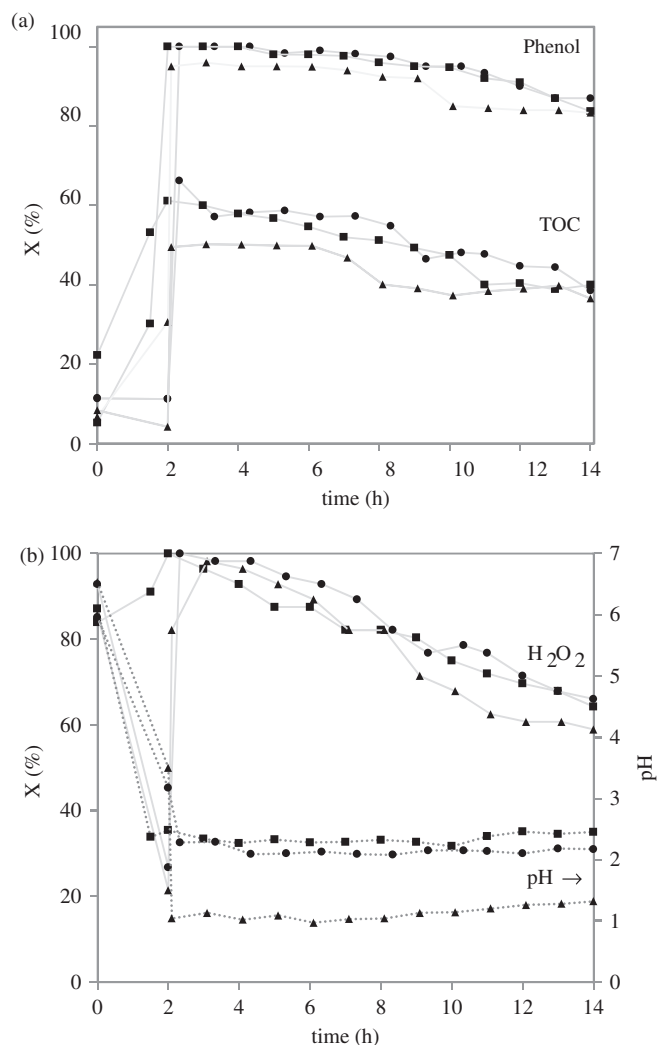
Figure 5. TOC conversion, efficiency of hydrogen peroxide consumption η_{H2O2} and final Fe leached (%) for the different catalysts tested: 4Fe400, 4Fe900, 4Fe900ac, 4Fe900ox and 4Fe900ac-R. (The TOC conversions and η_{H2O2} efficiencies were the average of the first 6 h reaction after the induction period.)

Equation (1):

$$\eta_{H_2O_2}(\%) = \frac{g\ TOC_{converted}/g\ TOC_{initial}}{g\ H_2O_{2\ converted}/g\ H_2O_{2\ initial}} \cdot \frac{100}{R} \qquad (1)$$

Both in terms of oxidant consumption efficiency and leaching levels, the differences between the two treated catalysts were not determinative. From the characterization of the samples, no distinguishable properties were inferred. However, the CWHPO performance of catalyst 4Fe900ox was slightly inferior. As shown in Fig. 4(a), the initial plateau of the TOC conversion was at a lower value (approximately 50%) and it dropped to near 40% at a shorter reaction time (it deactivated earlier). The pH of the outlet solution was also lower (Fig. 4(b)). All these observations are consistent with a less complete phenol oxidation process and a higher accumulation of intermediates. While the iron contents of both 4Fe900ac and 4Fe900ox were identical, the degree of interaction with the support could be rather different. The treatment with oxalic acid (pKa1 = 1.27; pKa2 = 4.27) is stronger than that with acetic acid (pKa = 4.76) and it could not only remove but also redisperse some of the iron present. This redispersion could explain the presence of more stabilized Fe species on the support that resulted in less catalytic activity for mineralization.

As a preliminary investigation, the catalyst treated with acetic acid was reduced at 350°C in order to obtain a Fe(II)/Fe(III) system onto the support. As mentioned above, the procedure was based on the recent work of Muñoz *et al.* that applied it to the preparation of a ferromagnetic Fe_3O_4/Al_2O_3 catalyst.[20] The behaviour of the reduced catalyst was different from the rest of the materials tested. The induction time practically disappeared and high TOC conversion (in the range of 65–70%) was reached during the first hour on stream. However, these levels began to decrease rapidly and the mineralization was near 45% after 8 h operation. The stability of the catalyst, in terms of resistance to leaching, was partly affected by the reduction treatment. Lixiviation levels for 4Fe900ac-R catalyst were higher than those obtained for the other treated catalysts 4Fe900ac and 4Fe900ox (Fig. 5). As Muñoz *et al.* reported,[20] the presence of ferrous species on the catalyst would increase the amount of leached Fe.

Figure 4. Extended tests for the CWHPO of phenol: (a) TOC and phenol conversions; (b) H_2O_2 conversion and pH evolution (● 4Fe900, ■ 4Fe900ac and ▲ 4Fe900ox).

limited. Furthermore, due to the short contact time in the catalytic bed during the continuous experiments, the overall activity of the catalyst could be mainly assigned to heterogeneous phenomena.

Another aspect to be considered is the oxidant dose. Under the present experimental conditions in which the oxidation is incomplete (due to the formation of refractory intermediates), the requirements of the H_2O_2 might be below the stoichiometric ratio. As Gogate and Pandit[25] reported, care should be taken while selecting the operating oxidant dosage. The loading of hydrogen peroxide should be adjusted in such a way that the entire amount is utilized and this can be decided based on the system in question. For these particular Fe_2O_3/Al_2O_3 catalysts, we registered that an excess of oxidant did not favour oxidation completion.[10] A compromise is then imposed between maximizing the oxidant consumption efficiency (i.e. avoiding unnecessary excess of H_2O_2) and maintaining the mineralization levels as high as possible (if the oxidant dosage is too low, the progression of oxidation could be halted). On this basis, a sub-stoichiometric $[H_2O_2]/[phenol]$ ratio of 10.5 was selected. Although the oxidant conversions were not complete, the catalysts showed elevated levels of efficiency in H_2O_2 consumption, in the order of 80% (Fig. 5). The percentage efficiency of oxidant consumption η_{H2O2} was defined according to
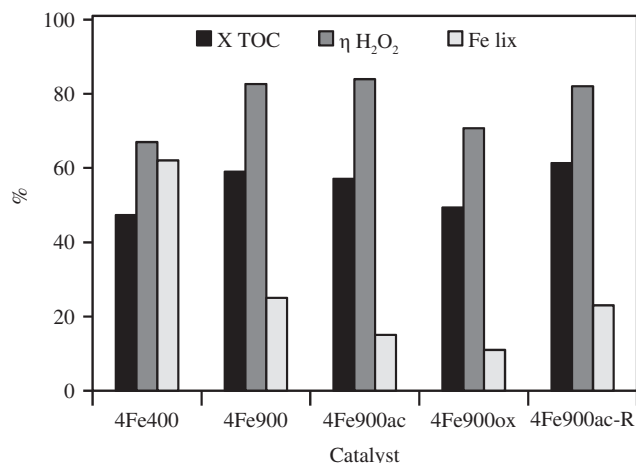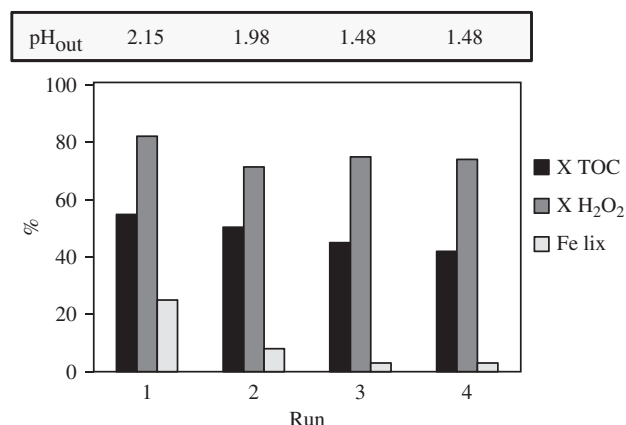
Figure 6. Life cycle tests with 4Fe900. TOC and hydrogen peroxide conversions after 9 h operation time and final Fe leached (%) of four consecutive tests under the same operating conditions, with a calcination step at 500°C after each run.

The decline in conversion levels was more pronounced in the case of the reduced catalyst. However, based on the conversions profiles of Fig. 4(a), the deactivation processes should not be dismissed in any of the catalysts studied. The lixiviation of the active phase would not be the only contribution to deactivation, as the formation of brown deposits on the catalyst surface was also detected. These would be most probably associated with the accumulation of reaction intermediates, presumably polymeric, that fouled the active sites of the catalyst. Other authors have reported the formation of solid by-products from phenol incomplete oxidation.[17] Again, the high phenol initial concentration would lead to the formation of a larger amount of these deposits. Thus, under the selected reaction conditions the contribution of fouling deactivation processes should be taken into account, even if a continuous reactor is used.

The nature of the carbonaceous deposits was analyzed by FTIR and it was observed that they were mainly compounded of quinone-like intermediates and carboxylic acids (the FTIR spectra are provided as Supporting Information). Thermogravimetric studies were also performed on the used samples. A mass loss of nearly 2.5% was registered (in the range 150–500°C) that would be compatible with the presence of reversible carbonaceous polymers. This would represent approximately 3% of the total amount of carbon fed to the reactor throughout the operating time. Therefore, the error of neglecting the fraction of TOC reduction produced by polymers formation (not by mineralization) would be minor.

After reaction, the catalysts were calcined at 500°C and reused for 9 h. Figure 6 summarizes the main reaction results after four consecutive runs (a total of 41 h on stream), using the 4Fe900 catalyst. It was registered that after calcination of the used samples, the mineralization levels of the fresh catalysts were recovered.

The iron content of the reused samples decreased; however, the lixiviation levels were progressively reduced (Fig. 6). The solubilization process could be minimized just by a plain decrease in the driving force as less metallic species are present on the catalyst or because the iron that remained after successive reaction runs was more stabilized onto the alumina support.

During these life cycle tests, the lower iron loading on the reactor had no appreciable effect on the maximum TOC conversion, which was maintained near 55%. The oxidant conversions were also unaffected after reusage. Thereby, the loss of iron from 4.2% to c. 2.8

wt% (for the fourth run) did not impact critically on the highest levels of mineralization and oxidant consumption efficiency achieved. However, some notable differences were registered. A more pronounced decrease in the TOC conversion levels with operating time was obtained after consecutive experiments, along with an extended induction period and more acidic outlet solutions. Lower amounts of Fe on the catalyst could change the distribution of the reaction products and led to a greater accumulation of intermediates (according to the pH and the colour of the outlet solution), leaving it more prone to deactivation due to formation of solid deposits.

On this basis, it would be relevant to advance in the development of catalytic materials with high iron contents, which can be more resistant to leaching. The ability to retain iron active species on the catalyst would play a key role to minimize other associated deactivation processes (such as fouling) that could affect the catalytic performance even more than leaching itself.

CONCLUSIONS

From these results it can be concluded that:

- after calcination at 900°C, the catalysts exhibited increased resistance to lixiviation; the iron leaching levels were satisfactory taking into consideration the strongly acidic reaction medium;

- pre-treatments with oxalic acid and acetic acid improved the stability of Fe$_2$O$_3$/Al$_2$O$_3$ catalysts, reducing the leaching by 56% for 4Fe900ox and 40% for 4Fe900ac with respect to the untreated 4Fe900. The effect of an additional reduction stage over 4Fe900ac was also explored; the impact of deactivation processes (fouling and Fe leaching) increased for 4Fe900ac-R catalyst;

- the 4Fe900ac and 4Fe900ox catalysts achieved complete phenol removal, mineralization levels above 50% and oxidant consumption efficiencies near 80% that were comparable with those of the untreated catalyst 4Fe900;

- under the studied reaction conditions, deactivation processes might be mainly associated to the formation of reversible carbonaceous deposits due to intermediates accumulation on the catalyst surface. These deposits were eliminated by means of calcination at 500°C and phenol, TOC and hydrogen peroxide conversion levels were recovered. However, the catalytic performance was affected by the lower initial iron content in used samples.

Supporting Information
Supporting information may be found in the online version of this article.

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