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Nanocomposite Fe_2O_3/SBA-15: An efficient and stable catalyst for the catalytic wet peroxidation of phenolic aqueous solutions

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Abstract

In this work, the catalytic wet peroxide oxidation of phenolic aqueous solutions over a novel Fe_2O_3/SBA-15 nanocomposite material was deeply studied. The catalytic performance was monitored in terms of aromatics and total organic carbon (TOC) removals. In order to reduce the major operation cost, significant operating reactions parameters that affect remarkably the overall catalytic performance of these processes, such as temperature and hydrogen peroxide concentration, were studied by means of a design of experiments. High temperature is necessary to obtain a fast and complete degradation of aromatic compounds. At 100 °C, moderate catalyst loading and hydrogen peroxide concentration (0.6 g/L and 75% of stoichiometric amount for phenol mineralization, respectively) were enough to achieve a total removal of aromatic compounds and remarkable TOC mineralization under non-controlled pH conditions. Resistance of iron species to be leached out into the aqueous solution has been also carefully examined with the purpose of elucidating the influence of different reaction parameters (temperature, oxidant concentration and pH). A schematic view of the heterogeneous catalytic peroxidation of phenol over this novel catalyst has been proposed. Finally, the stability of the catalyst has been established by recycling studies.

Keywords: Fenton; Heterogeneous catalyst; SBA-15; Phenol; CWHPO

1. Introduction

The degradation of aromatic pollutants present in wastewater streams generated by industrial processes has emerged as an important concern during last decade. The effective removal of these pollutants becomes a challenging task due to environmental laws and regulations are more restringing with time. Phenol and phenol-like compounds occupy a prominent position on the US EPA priority pollutants list due to the high toxicity for microorganisms, high chemical oxygen demand and poor biodegradability. By these reasons, advanced oxidation processes (AOPs) have emerged as interesting alternatives for the destruction of organic pollutants in industrial wastewater [1,2]. These processes involve the generation of non-selective and highly reactive hydroxyl radical ($OH^\bullet$), which is one of the most powerful oxidation agents, higher than others chemical oxidants commonly used in water treatments [3].

The reaction of H_2O_2 with ferrous salts (Fenton's reagent) or other low-valency transition metals (Fenton-like reactions) at room temperature is a well known source of hydroxyl radicals [4,5]. The oxidation of organic compounds by means of Fenton-like reactions has been studied in numerous works during last 15 years [6–8], in fact, this technology is used commercially to treat industrial wastewater [9–11]. However, this process presents two main drawbacks. Firstly, efficient hydroxyl radical generation mediated by Fenton-like reactions only occurs in a limited range of pH (2.5–3.5) and secondly, a final separation of soluble iron species from the treated water is needed. Neutralization or even flocculation units are usually necessary prior to recovery of the active iron species in form of iron sludge. These drawbacks have promoted the development of Fenton processes based on heterogeneous catalytic systems. In some cases, temperature of the process has been increased up to 80–120 °C leading to so-called catalytic wet hydrogen peroxide oxidation (CWHPO) processes. The use of this technology allows an easy separation and recovery of catalyst from the treated wastewater. Moreover, some researchers have reported that the presence of a solid catalyst may enhance the degradation rate due to mechanisms based on the reactivity of adsorbed organic compounds

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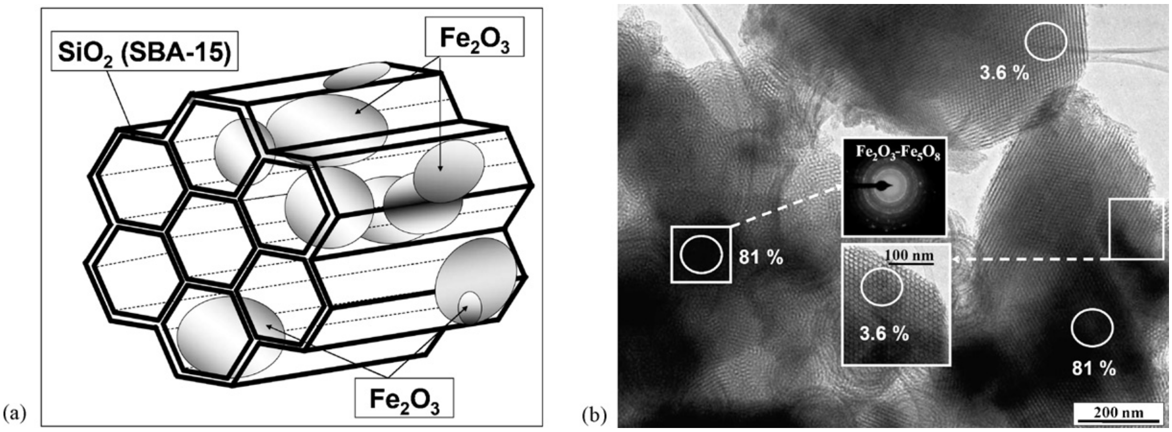

Fig. 1. (a) Model for the location of iron oxide particles and (b) TEM microphotographs, XRD of crystalline Fe_2O_3 particles and local iron content (wt.%) measured by EDX microanalysis.

with active oxygenated species coming from hydrogen peroxide decomposition over the catalyst surface [12]. An important issue in the design of heterogeneous Fenton-like catalysts is the stability of metallic species and their resistance to leaching, which is often related to the nature and environment of supported iron species [13–15]. The use of solid catalysts for CWHPO of phenolic aqueous solutions has been widely described in literatures [12–14,16–18]. However, the development of highly stable active materials which can work in a wide pH range is still a challenge for the oxidation of organic compounds in presence of hydrogen peroxide.

In this work, a nanocomposite solid catalyst consisted of a mixed of crystalline iron oxides supported over a silica SBA-15 matrix has been deeply studied for the peroxidation of phenolic solutions. This novel Fe–SBA-15 mesostructured material has been successfully used as an effective heterogeneous catalyst with a high catalytic activity and moderate iron leaching for the CWHPO and photo-assisted Fenton degradation of phenolic solutions [19,20]. Herein, a multivariate analysis, using factorial design of experiments, has been employed to assess the influence of main operating conditions (temperature and hydrogen peroxide concentration) on the activity and stability of the catalytic system. The effect of the aqueous solution pH has been also evaluated in order to make a more comprehensive understanding of the oxidation of the organic pollutants and its relationship with the iron leached-off from the catalyst. As result of this study, a reaction scheme for the catalytic wet peroxide oxidation of phenol over this novel heterogeneous catalyst has been proposed. Finally, the regeneration and reusability of the catalyst after reaction were also addressed.

2. Experimental

2.1. Catalyst preparation

Iron oxide supported into SBA-15 mesostructured material was prepared by co-condensation of iron ($FeCl_3 \cdot 6H_2O$; Aldrich) and silica (tetraethoxysilicate, TEOS; Aldrich) sources under acidic conditions and templated with Pluronic 123 as described elsewhere [21]. The procedure described in literature was slightly modified changing the pH of the reaction medium by addition of an appropriate amount of ammonia aqueous solution. The precipitation of non-soluble iron oxy-hydroxide particles was promoted during the ageing step of the resultant solution at 110 °C for 24 h under static conditions at a pH of 3.5 [15]. After this ageing step, the solid product was recovered by filtration and air dried at room temperature overnight. Transformation of hydrated iron species to oxidized particles and the template removal was accomplished by calcination in air at 550 °C for 5 h.

The resultant material is described as a composite material that contains different iron oxides particles (mainly crystalline hematite) embedded into a mesostructured SBA-15 support, although a little amount of ionic Fe^{3+} species isomorphously substituted within the silica framework has been also detected [15,19]. Iron oxide particles are present in a wide distribution of sizes (30–300 nm). The material exhibits a BET surface area of ca. 470 m^2/g lower than that usually found for pure SBA-15 silica (ca. 750 m^2/g), with a narrow pore diameter distribution centred at 72 Å and a total pore volume of 0.65 cm^3/g. The bulk iron content was around 16 wt.%. TEM images shown in Fig. 1 together with local XRD diffraction and EDX elemental microanalysis confirm areas with a good mesoscopic order and the presence of clusters of crystalline iron oxides particles. Fig. 1 also illustrates a schematic view of how the metal oxide particles may be located within the channels and/or on the external surface of SBA-15 support. The proposed model justifies the decreasing of surface area by the incorporation of iron oxide particles and it would be in agreement with observations reported by Vradman et al. for TiO_2/SBA-15 [22].

2.2. Oxidation reactions and analytical techniques

Catalytic wet peroxide oxidation experiments of phenol aqueous solution were carried out in a 100 mL glass autoclave reactor under continuous mechanical stirring (350 rpm) in contact with air. The appropriate amount of catalyst, suspended in water (0.6 g/L), is placed into the glass reactor. Afterwards, the system is pressurised up to 0.7 MPa with air and heated up to the selected temperature. Once the temperature was achieved, the required

Table 1
Experimental results of the factorial design for the CWHPO of phenolic aqueous solutions

Run	T (°C) (X)	[H_2O_2] (g/L) (Y)	$X_{TOC}^{10\,min}$ (%) (Z_1)		$X_{TOC}^{20\,min}$ (%) (Z_2)		$X_{TOC}^{40\,min}$ (%) (Z_3)		$X_{TOC}^{90\,min}$ (%) (Z_4)	
			Exp.[a]	Calc.[b]	Exp.[a]	Calc.[b]	Exp.[a]	Calc.[b]	Exp.[a]	Calc.[b]
1	−1 (60)	−1 (2.55)	18.0	20.5	20.0	24.7	30.8	33.0	46.3	48.1
2	−1 (60)	+1 (5.10)	37.3	36.0	39.4	40.2	46.6	50.3	54.4	56.1
3	+1 (100)	−1 (2.55)	43.4	42.1	45.4	46.2	45.4	49.1	46.0	47.8
4	+1 (100)	+1 (5.10)	55.1	57.7	57.0	61.7	64.3	66.4	73.6	75.3
5	0 (80)	−1 (2.55)	37.5	36.0	46.7	43.2	52.9	49.7	57.3	52.9
6	0 (80)	+1 (5.10)	43.7	42.2	50.9	43.2	56.9	49.7	64.3	60.7
7	−1 (60)	0 (3.82)	17.7	14.7	31.2	29.3	31.2	29.3	40.6	38.7
8	+1 (100)	0 (3.82)	66.4	63.4	67.8	66.0	72.0	70.1	77.0	75.0
9	0 (80)	0 (3.82)	32.6	39.1	44.0	47.6	47.4	49.7	52.0	56.8
10	0 (80)	0 (3.82)	32.9	39.1	38.7	47.6	44.2	49.7	51.6	56.8
11	0 (80)	0 (3.82)	27.4	39.1	44.0	47.6	48.7	49.7	53.7	56.8

$[Phenol]_0 = 1000$ ppm; pH_0 5.5; total air pressure = 0.7 MPa.

[a] Experimental values.

[b] Calculated values according to Eqs. (2)–(5).

amounts of phenol (1.0 g/L) and hydrogen peroxide were added into the reactor and this moment is set as zero-reaction time. Aliquots were withdrawn during the reaction course after 10, 20, 40 and 90 min and filtered by means of 0.22 μm nylon membranes before being analyzed.

Total organic carbon (TOC) content of the samples was analyzed using a combustion/non-dispersive infrared gas analyzer model TOC-V Shimadzu. Phenol and other by-products coming from the incomplete mineralization of phenol were measured by means of an HPLC chromatograph model Varian Prostar equipped with a Waters Spherisorb column and an UV detector at 215 nm. A buffer solution of $NaHPO_3/H_3PO_4$ at pH 2.6 was used as mobile phase. The contribution of different degradation products in the residual TOC in percentage of carbon was calculated as follows:

$$\text{Aromatics}\,(C^{A}) = \frac{\text{ppm of C coming from aromatic compounds measured by HPLC}}{\text{Residual TOC (ppm of C)}} \times 100$$

$$\text{Carboxylic acids}\,(C^{CA}) = \frac{\text{ppm of C coming from carboxylic acids measured by HPLC}}{\text{Residual TOC (ppm of C)}} \times 100$$

$$\text{Other by-products}\,(C^{BP}) = 100 - C^{A} - C^{CA}$$

Hydrogen peroxide concentration was measured by iodometric titration. Finally, iron content in the filtered solution after reaction was measured by ICP-AES analysis collected in a Varian Vista AX spectrometer in order to determinate the iron leaching degree from the catalyst within the aqueous solution.

3. Results and discussion

3.1. Design of experiments

Previous works have showed the outstanding activity and stability of the catalyst under study for the degradation of phenolic aqueous solutions through Fenton-like processes [19,20]. In this research, we have further assessed the influence of two significant variables (temperature and hydrogen peroxide concentration) on the activity and stability of this novel catalyst by means of an experimental design methodology. A complete 3^2 design of experiments [23] was carried out with temperature (X) and hydrogen peroxide concentration (Y) as independent variables. Low and high levels are denoted by −1 and +1, respectively, whereas the central point as 0. The temperature was ranged from 60 °C (−1) to 100 °C (+1), which are standard values reported in literature for CWHPO processes [13,14,16–18,20]. The hydrogen peroxide concentration was ranged from 5.1 g/L (+1) to 2.55 g/L (−1). Note that 5.1 g/L corresponds to the stoichiometric amount of oxidant that is necessary for the complete mineralization of 1 g/L phenol solution through reaction (1).

$$C_6H_6O + 14H_2O_2 \rightarrow 6CO_2 + 17H_2O \quad (1)$$

TOC conversion after 10 min (Z_1), 20 min (Z_2), 40 min (Z_3) and 90 min (Z_4) of reaction and iron lost from the catalyst at the end of the reaction (Z_5) were selected as response factors. Table 1 summarizes the factorial design of experiments, including experimental conditions of each run, the codified and real values of the independent variables, the experimental results for the response factors after performing the experiments and the predicted values calculated with the factorial design model. The catalytic run corresponding to the central point (80 °C and 3.82 g/L oxidant concentration) was repeated three times in order to check the reproducibility and the experimental error of the results obtained in the design of experiments.

The Levenberg–Marquardt algorithm for non-linear regression was used to obtain a polynomial expression that fits the

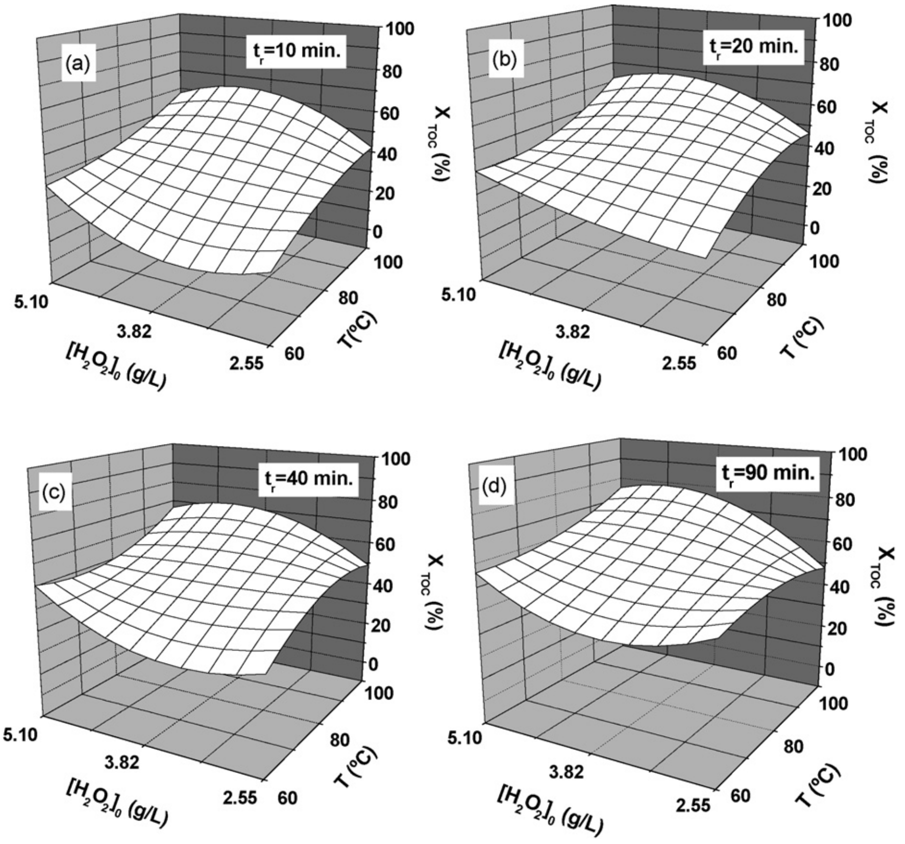

Fig. 2. 3D response surfaces for TOC conversions after 10 min (a), 20 min (b), 40 min (c) and 90 min (d) of reaction. $[\text{Phenol}]_0 = 1$ g/L; pH_0 5.5; total air pressure = 0.7 MPa.

experimental results. In this way, second-order polynomial expressions allow to predict the values of the response factors (Eqs. (2)–(5)). In the equations mentioned, terms of X and Y represent the temperature and hydrogen peroxide concentration, respectively, and parameters Z_1 to Z_4 correspond to TOC conversions after 10, 20, 40 and 90 min of reaction. Values in parenthesis describe the error associated to each coefficient of the equation. In those cases where the error was larger than the corresponding coefficient, the parameter was not considered in the polynomial model:

$$Z_1 = 39.1(\pm 1.2) + 24.4(\pm 1.5)X + 3.1(\pm 1.5)Y + 4.7(\pm 3.8)YX^2 - 13.5(\pm 3.8)XY^2 \tag{2}$$

$$Z_2 = 47.6(\pm 3.3) + 18.3(\pm 4.1)X - 4.4(\pm 3.9)Y^2 + 7.8(\pm 2.9)YX^2 - 7.6(\pm 4.9)XY^2 \tag{3}$$

$$Z_3 = 49.7(\pm 1.6) + 20.4(\pm 3.3)X + 8.7(\pm 2.3)YX^2 - 12.4(\pm 4.1)XY^2 \tag{4}$$

$$Z_4 = 56.8(\pm 1.5) + 18.2(\pm 3.1)X + 3.9(\pm 3.4)Y + 4.9(\pm 2.1)XY + 5.0(\pm 2.2)YX^2 - 13.4(\pm 3.7)XY^2 \tag{5}$$

Analysis of Eqs. (2)–(5) evidences relevant first-order effect associated with the temperature (X) in the TOC degradation for all the reaction times. In contrast, the hydrogen peroxide concentration exhibits an almost negligible contribution during the reaction. However, it is particularly remarkable the different sign of terms involving both oxidant concentration and temperature. Whereas there is a clear synergistic effect of the hydrogen peroxide concentration (Y) and high temperature (X^2), a negative effect is evidenced in the combination of temperature (X) and high initial amounts of hydrogen peroxide (Y^2), being this latter contribution more dominant. In this sense, an excess in the initial amount of oxidant, could have a negative effect in the TOC degradation. Nevertheless, coefficients of first-order temperature (X) show the critical influence of this reaction parameter on the phenol mineralization.

Fig. 2 shows the 3D response surfaces generated by Eqs. (2)–(5). Real numerical values for temperature and hydrogen peroxide concentration are used in the axis of the graphics. As it can be seen, there is a significant influence of the temperature, allowing a relevant increase of the TOC degradation regardless of the initial oxidant concentration. This enhancement is observed for all the reaction times although is probably more accentuated for initial times. Although the highest degradation rates and final TOC conversions are achieved at 100 °C, temperatures of operation higher than this were not considered in this work due to the non-efficient decomposition of hydrogen perox-

Table 2
Experimental results of the factorial design for the stability of the catalyst

Run	T (°C) (X)	$[H_2O_2]$ (g/L) (Y)	$\Delta Fe^{90\,min}$ (%) (Z_5)	
			Exp.[a]	Calc.[b]
1	−1 (60)	−1 (2.55)	3.23	3.22
2	−1 (60)	+1 (5.10)	3.78	3.77
3	+1 (100)	−1 (2.55)	6.15	6.14
4	+1 (100)	+1 (5.10)	5.15	5.14
5	0 (80)	−1 (2.55)	5.37	5.39
6	0 (80)	+1 (5.10)	4.88	4.90
7	−1 (60)	0 (3.82)	3.56	3.58
8	+1 (100)	0 (3.82)	4.66	4.68
9	0 (80)	0 (3.82)	4.76	4.71
10	0 (80)	0 (3.82)	3.94	4.71
11	0 (80)	0 (3.82)	4.61	4.71

$[Phenol]_0$ = 1000 ppm; pH_0 5.5; total air pressure = 0.7 MPa.
[a] Experimental values.
[b] Calculated values according to Eq. (7).

ide towards water and oxygen. In fact, thermal decomposition experiments carried out under different reaction temperatures with an initial hydrogen peroxide concentration of 5.1 g/L and absence of phenol have yielded oxidant conversions of 60% after 10 min at 120 °C as compared with values around 30% for 100 and 80 °C. These results clearly demonstrate that temperatures over 100 °C lead to the predominant peroxide decomposition to water and oxygen limiting the production of $OH^{\bullet}$ radicals available for oxidation. On the other hand, at 100 °C oxidant concentrations higher than 3.82 g/L leads to similar values of TOC conversion or even lower. The detrimental effect of more powerful oxidant conditions is explained due to the competition of oxidant and organic matter for the $OH^{\bullet}$ radicals through parallel reactions (6) [24]. Thus, an increase of hydrogen peroxide concentration will result in an increase in the rate of the radical scavenging which is favoured at high temperatures:

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \tag{6}$$

Although up to now, we have focused on the assessment of the process using the TOC conversion as main response factor; it is of great interest in this kind of processes to analyze the influence of operating conditions such as temperature and oxidant concentration on the stability of the catalyst. The effect of both variables was also studied following the same experimental factorial design used to evaluate the activity of the catalyst in terms of TOC conversion. In this case, the percentage of iron leached from the catalyst after 90 min of reaction (ΔFe) was selected as response variable (Z_5, Eq. (7)). Table 2 summarizes the real and codified values, the experimental results obtained in each experiment and the calculated values obtained from the polynomial fitted equation (Eq. (7)):

$$\begin{aligned} Z_5 = {} & 4.71(\pm 0.05) + 0.55(\pm 0.05)X - 0.25(\pm 0.05)Y \\ & -0.39(\pm 0.03)XY - 0.58(\pm 0.05)X^2 + 0.43(\pm 0.05)Y^2 \\ & +0.13(\pm 0.06)YX^2 + 0.52(\pm 0.06)XY^2 \end{aligned} \tag{7}$$

It can be seen in Fig. 3(a) that the values predicted by the second-order model agree perfectly with the experimental data. Fig. 3(b) depicts the 3D response surface obtained with Eq. (7). Iron leaching degree is shown mainly sensitive to the temperature. In contrast, the initial oxidant concentration displays a less important role. It is remarkable that results of leaching degree for all the catalytic runs used in this study are below 6.5% of the initial content within the catalyst, that evidences a remarkable stability of the iron-containing catalyst. Likewise, Mössbauer spectroscopic results of the catalyst after reaction have clearly shown that the leaching of iron species is mainly attributed to the ionic Fe^{3+} species rather than iron oxide particles [15].

Nowadays, two main hypotheses are commonly used to explain the instability of the iron species supported over Fenton-like catalysts. One of them is the acidic and oxidizing conditions in which the reaction takes place and the other one is related to the reactions occurring on the catalyst surface between the iron active sites and oxidizable organic compounds. Both of them are associated with extraction of iron ions from the catalyst to the aqueous solution [25,26].

In order to elucidate if there is any relationship between the iron leaching and the pH of the aqueous solution along the reaction, both variables were simultaneously monitorized. The results taken from the catalytic run carried out with initial hydrogen peroxide concentration of 3.82 g/L and temperature of

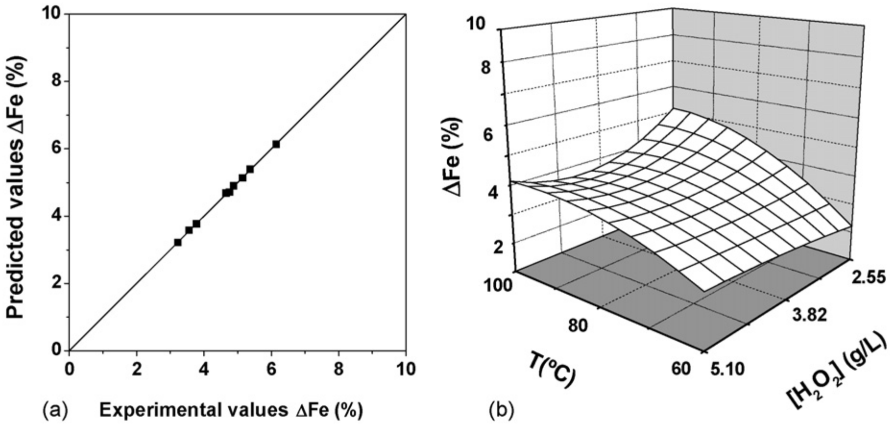

Fig. 3. (a) Accuracy of the predicted leaching values and (b) 3D response surface for the iron leaching degree after 90 min of reaction. $[Phenol]_0$ = 1 g/L; pH_0 5.5; total air pressure = 0.7 MPa.

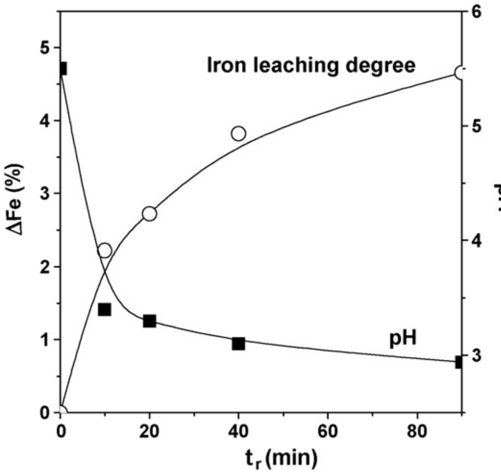

Fig. 4. pH and iron leaching degree profiles with reaction time. Reaction conditions: $[\text{Phenol}]_0 = 1$ g/L; $[H_2O_2]_0 = 3.82$ g/L; $T = 100$ °C; pH_0 5.5; total air pressure = 0.7 MPa.

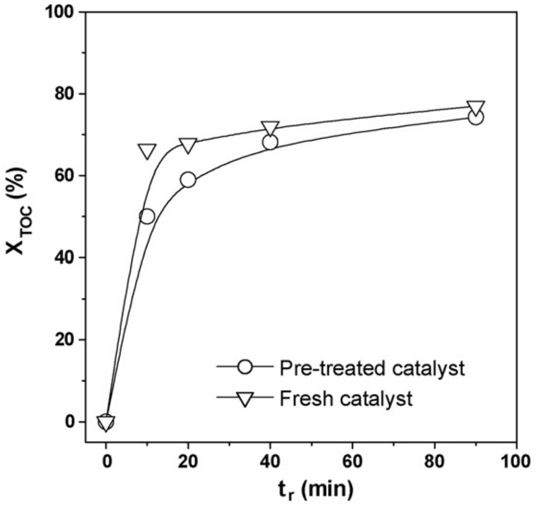

Fig. 5. TOC profiles of pre-treated and fresh catalyst in the CWHPO of phenolic aqueous solution. Reaction conditions: $[\text{Phenol}]_0 = 1$ g/L; $[H_2O_2]_0 = 3.82$ g/L; $T = 100$ °C; pH_0 5.5; total air pressure = 0.7 MPa.

100 °C (the most active conditions in this study) are depicted in Fig. 4. A marked decrease of the solution pH is observed for the first minutes of reaction. This fact is associated with the global generation of H^+ due to the production of hydroxyl radicals in the typical of Fenton-like reactions scheme (reactions (8)–(11)), and the formation of organic carboxylic acids as main by-products of the partial oxidation of phenolic compounds (12):

$$Fe^{3+} + H_2O_2 \Leftrightarrow Fe(OOH)^{2+} + H^+ \tag{8}$$

$$Fe(OOH)^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet} \tag{9}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\bullet} \tag{10}$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^+ + O_2 \tag{11}$$

$$\begin{aligned} RH + HO^{\bullet} \rightarrow H_2O + R^{\bullet} \rightarrow \cdots \rightarrow \text{oxygenated compounds} \\ + nH_2O + mCO_2 \end{aligned} \tag{12}$$

On the other hand, the initial decrease of the pH is accompanied with a noteworthy increase of the iron leaching degree, which keeps increasing along the reaction time. It should be remarked that the striking decrease of pH observed for the first 10 min of reaction is going together with a remarkable TOC removal and H_2O_2 conversion just in this period of time. Similar trends were observed in all the reaction conditions. For high reaction times, the pH almost reaches an asymptotic value as well as the leaching degree. The decrease of the iron leaching degree and the catalytic activity could be attributed to the formation of carbonaceous deposits over the catalyst surface as well as the dominant presence of refractory compounds under mild oxidizing conditions.

As it has been mentioned previously, another important aspect to be considered in the leaching of iron species is the oxidation–reduction reactions taking place on the catalyst surface by the adsorbed organic compounds [12]. The following experimental work was performed to determine this issue. The catalyst was hydrothermally treated under the same reaction conditions used in the CWHPO (0.7 MPa of air pressure, 100 °C, 0.6 g/L of catalyst, 3.82 g/L of hydrogen peroxide) but in absence of phenol and adding H_2SO_4 0.1N to reproduce an acid solution pH (ca. 2.9). Surprisingly, the iron leaching degree hardly reaches 1.1% after 90 min of treatment. After that, the catalyst was recovered by filtration and used in a new catalytic run, but this time in presence of phenol. Fig. 5 shows TOC profiles of catalytic runs carried out with pre-treated and fresh catalyst under reaction condition mentioned above. Similar TOC profiles were achieved and the iron leaching into the aqueous solution increases significantly up to the level detected by the fresh catalyst (ca. 4.5–4.7%). Therefore, there is no doubt that the presence of the organic substrate, or in other words, the reactivity of phenol or other intermediates on the catalyst surface, plays an important role on the leaching of the catalyst-supported iron. Nevertheless, the acidic and oxidizing conditions seem also to affect to the iron stability, even thought they are not the predominant responsible of the iron dissolution.

As the active species leached from the catalyst can contribute to the TOC removal by homogeneous Fenton reactions, two distinct experiments were carried out as follows. The first one consisted of an indirect test of the activity of the iron ions leached out into the aqueous solution. In this sense, a heterogeneous catalytic run was performed under given reaction conditions (100 °C and initial hydrogen peroxide concentration of 3.82 g/L) for 90 min. The resultant solution was filtered in hot conditions to remove the catalyst (note that ca. 5 ppm of iron species was detected in the aqueous solution). Thereafter, phenol and hydrogen peroxide were further added to set again initial concentrations of both of them in the filtered solution for running a new reaction. The second homogenous catalytic experiment was carried out using directly an iron(III) chloride salt as metallic source. The iron concentration dissolved into the aqueous solution was ca. 6 ppm, a little bit more of the typical concentration found in the heterogeneous experiment. The rest of reaction conditions were kept constant for this study.

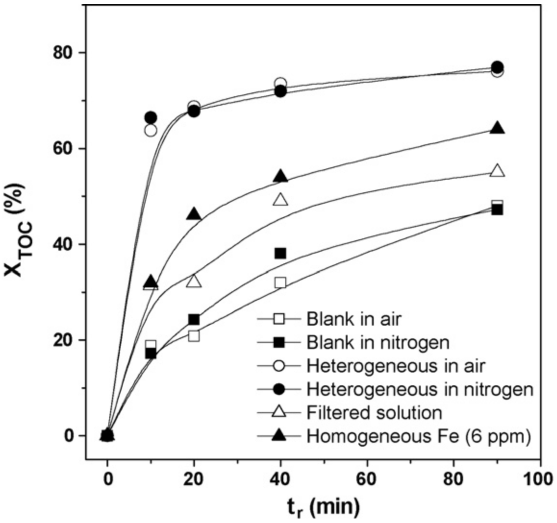

Fig. 6. Homogeneous catalytic tests for the degradation of phenolic aqueous solutions, blank experiments in absence of catalyst and reactions in nitrogen atmosphere. Reaction conditions: $[\text{Phenol}]_0 = 1$ g/L; $[H_2O_2]_0 = 3.82$ g/L; $T = 100\,^\circ$C; pH_0 5.5; total air pressure = 0.7 MPa (except experiments in nitrogen atmosphere).

Fig. 6 illustrates the TOC conversion of both types of homogeneous experiments together with a blank reaction (without catalyst) and the heterogeneous catalytic run. The evolution of TOC conversion for filtered solution evidenced a lower activity in comparison to that shown by the heterogeneous catalytic system, especially at the beginning of the reaction. Thus, after 10 min of reaction, TOC conversion of filtered solution was ca. 30% whereas this value increased up to 69% for the heterogeneous catalyst. Moreover, it must be noteworthy that the amount of iron species dissolved into the aqueous solution at this initial stage for the heterogeneous system is quite lower (less than 2 ppm) than that existing during the course of the filtered reaction (ca. 5 ppm). The minor activity of the iron species dissolved in the filtering solution may be accounted for the presence of stable iron organic complex with the residual carboxylic acids remained after the first reaction [12]. Nevertheless, the results obtained by Fe(III) chloride indicate a small increase of TOC conversion in comparison to the filtered homogeneous experiment but far from that of the heterogeneous system.

From these results, it can be demonstrated an important role of solid catalyst in the overall catalytic performance, in particular for initial reaction times, although the contribution of homogeneous iron species in the pollutant degradation cannot be completely ruled out. The benefits of homogeneous or heterogeneous catalytic systems are clearly evident from the comparison with the TOC conversion of the blank reaction.

Finally, in order to check the contribution of dissolved oxygen in the organic degradation, two additional experiments under nitrogen atmosphere has been performed in presence and absence of catalyst (Fig. 6). The additional reactions occurring in presence of oxygen can be summarized as follows:

$$R^\bullet + O_2 \rightarrow ROO^\bullet \qquad (13)$$

$$\text{Phenol} + ROO^\bullet \rightarrow R^\bullet + ROOH \qquad (14)$$

$$ROOH \rightarrow RO^\bullet + HO^\bullet \qquad (15)$$

The oxygen dissolved contributes to the formation of organic hydroperoxyl radicals ($ROO^\bullet$) from organic radicals ($R^\bullet$) (13), which were initially generated in Fenton-like reactions. Subsequent reactions of $ROO^\bullet$ radicals with phenol as represented in reaction (14) and other organic intermediates will lead to phenol depletion and consequent TOC reduction and an additional source of hydroxyl radicals (15). Note that oxygen should enhance the formation of radicals. However, catalytic results depicted in Fig. 6 indicate that the influence of air pressure on the rate of TOC removal is negligible under the reaction conditions studied and evidence the main role of hydrogen peroxide as oxidant and precursor of reactive radicals for phenol degradation and organic mineralization.

3.2. *Influence of pH on the catalytic performance*

It is well known that the optimum pH range for homogeneous Fenton processes is around 2.5–3.5. Therefore, this kind of processes requires acidification of the initial solution. As presented previously, the design of heterogeneous catalysts capable of working in a wide range of pH is currently an important challenge. Moreover, the effect of pH on the stability of the iron-containing catalyst has been previously discussed. In order to demonstrate the suitability of this heterogeneous catalytic system in a wide pH range, a new set of experiments were carried out at a different initial pH with and without any pH control during the reaction. The initial pH of the phenolic aqueous solution was modified up to values of 2.5 and 7.0 by additions of H_2SO_4 (1.0N) and NH_3 (2 wt.%) solutions, respectively. Fig. 7(a) shows TOC conversion profiles for these experiments, including the experiment carried out under the original pH of 1 g/L phenol aqueous solution (pH_0 5.5), whereas Fig. 7(b) collects the iron leaching degree and the solution pH after 90 min of reaction.

Interestingly, the catalyst shows similar profiles of TOC conversion regardless of the initial pH. Therefore, this novel composite material can be considered a pH tolerant catalyst. The final pH values are below 3.0 in all the cases, and a lower final pH seems to be associated with a higher iron leaching. With initial pH of 2.5, the final pH is about 2.4, and the leaching degree reaches up to 6.5%, whereas in the other cases, the final pH is about 2.9, with an iron leaching degree below 5.0%. These results suggest that a control of the pH of the media could prevent the leaching of the iron species. With the purpose of proving this theory, different KH_2PO_4/K_2HPO_4 buffer solutions were used to adjust and control the pH during the reaction. Phenolic aqueous solutions buffered at pH 3.9, 4.5 and 5.3 were studied. Fig. 8 illustrates the profiles of TOC conversion, pH and iron leaching degree as well as distribution of degradation products after 90 min of reaction.

The buffer solution limits the evolution of the pH in the reaction media, and it has an outstanding influence on the activity and stability of the catalyst. A high TOC conversion and complete degradation of aromatic compounds were achieved after 90 min of reaction when the solution pH was buffered between 3.9 and 3.4. Note that quite similar results were obtained by

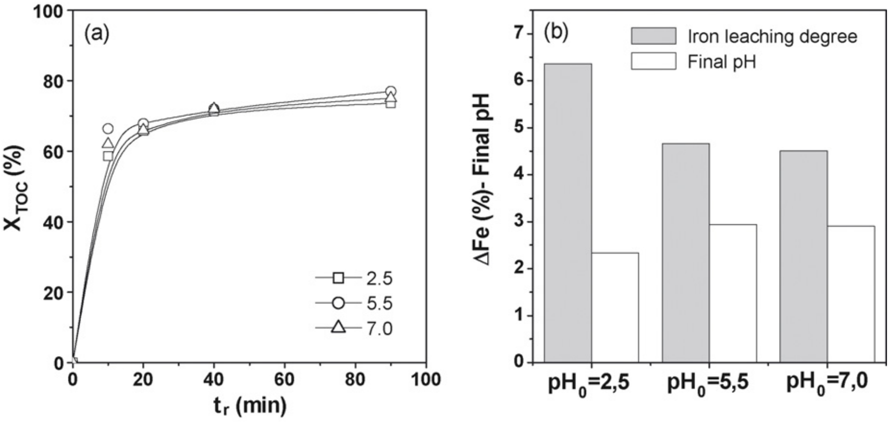

Fig. 7. Influence of the initial pH on (a) the TOC conversion and (b) the stability of the catalyst. Reaction conditions: $[\text{Phenol}]_0 = 1$ g/L; $[H_2O_2]_0 = 3.82$ g/L; $T = 100\,°C$; total air pressure = 0.7 MPa.

non-buffered catalytic experiment. In contrast, it is remarkable a lower degradation rate of TOC, with the presence of residual aromatic compounds in the aqueous medium after 90 min of reaction, when the pH was maintained around 4.4–4.2 or 5.3–5 (Fig. 8d). Looking at the stability of the catalyst, a strong reduction of the iron leaching for the experiments buffered at pH ranges higher than 4 is evidenced. The control of the pH above 4 is a good method for preventing the leaching of the iron species, but at the expense of a decrease of activity. All these results evidence a clear relationship between pH, TOC degradation and catalyst stability for CWHPO processes. A plausible hypothesis of the interaction of these terms could be explained taking into account that a high TOC degradation rate is achieved when the pH decrease up to values lower than 4.0. Likewise, as

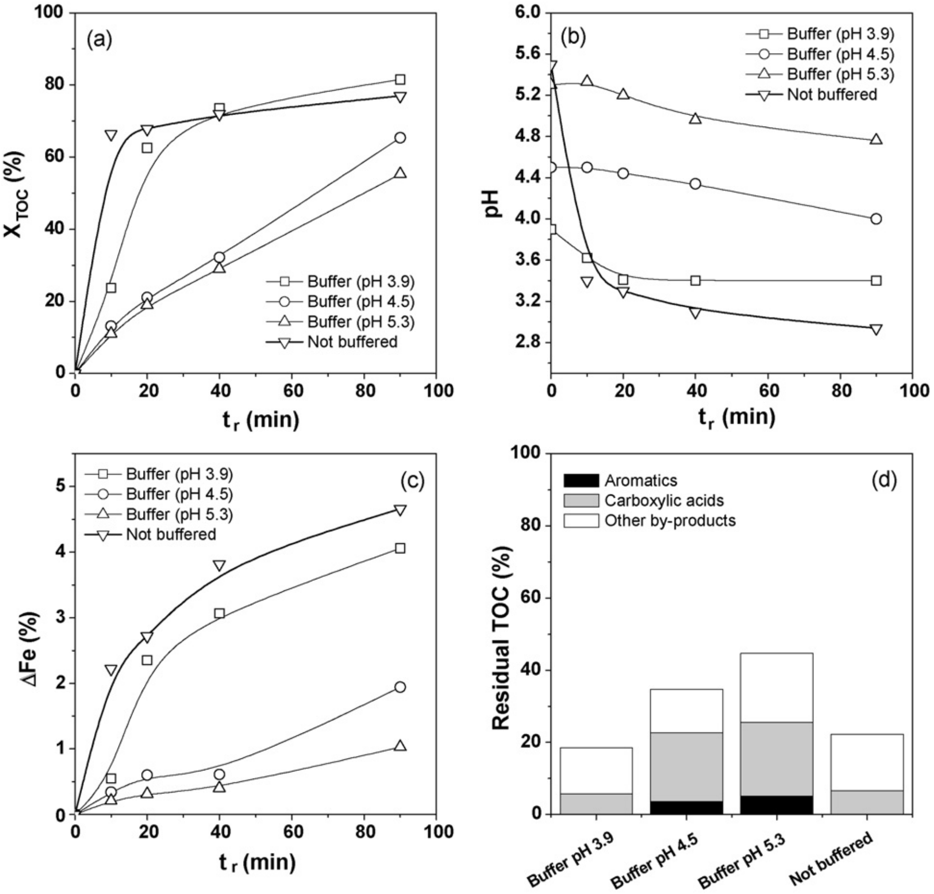

Fig. 8. Influence of the addition of different buffered solutions on: (a) and (d) the activity of the catalyst (b) evolution of the pH and (c) stability of the heterogeneous catalyst. Reaction conditions: $[\text{Phenol}]_0 = 1$ g/L; $[H_2O_2]_0 = 3.82$ g/L; $T = 100\,°C$; total air pressure = 0.7 MPa. Aromatics include phenol, cathecol and hydroquinone; carboxylic acids include oxalic, acetic and formic acids.

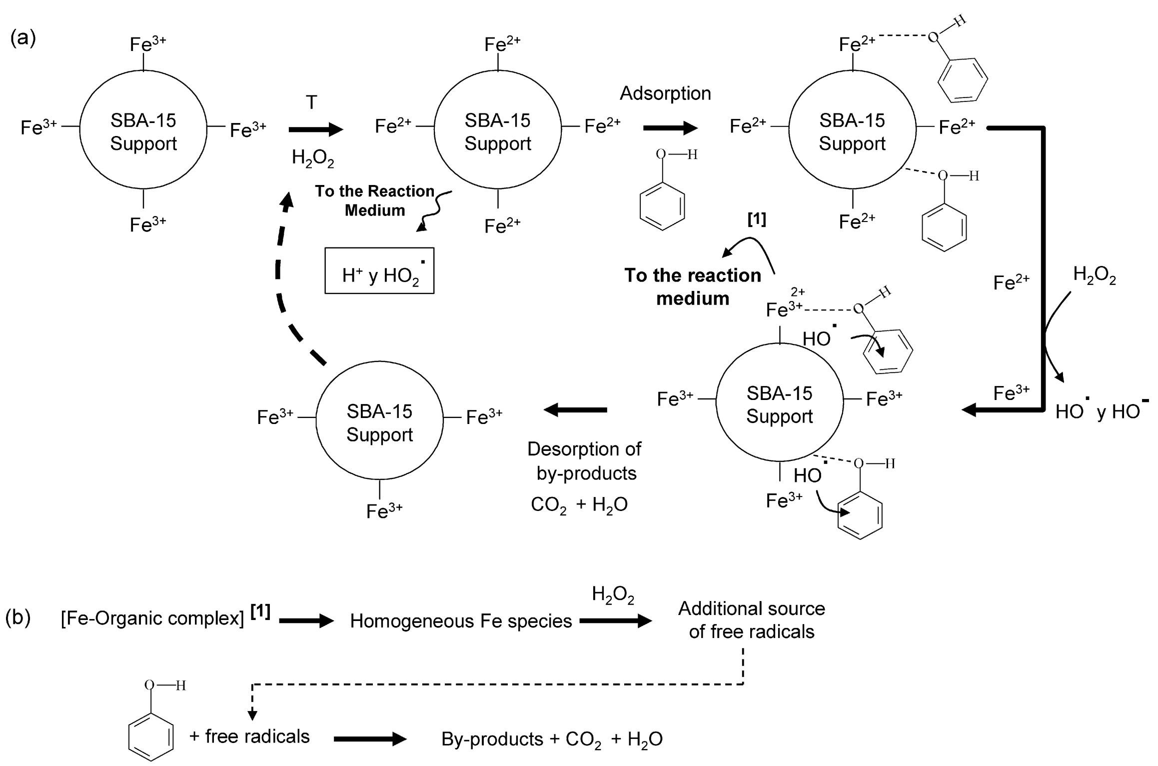

Fig. 9. General reaction scheme proposed for CWHPO of phenolic aqueous solutions over the nanocomposite Fe_2O_3/SBA-15 catalyst. (a) Reactions over the catalyst surface and (b) reactions in the bulk liquid phase.

result of a higher extension of the oxidation reactions of soluble organic molecules over the catalyst surface, an increase of the metal leaching could be expected.

3.3. Reaction scheme for the catalytic wet peroxidation of phenolic aqueous solutions over an heterogeneous Fe_2O_3/SBA-15 Fenton-like catalyst

From the results shown in this work, a reaction scheme for the heterogeneous Fenton-like oxidation process of a phenolic aqueous solution can be proposed. This reaction scheme involves several parallel processes (Fig. 9).

In a first step, reduction–oxidation reactions between Fe(III)/Fe(II) take place in presence of hydrogen peroxide, promoting the formation of reactive hydroxyl ($HO^{\bullet}$) and hydroperoxyl ($HO_2^{\bullet}$) radicals. In parallel, organic compounds such as phenol will be adsorbed over the catalyst surface, much more probably in the vicinity of iron active ions, although adsorption over other sites should not be ruled out. The hydroxyl radicals ($HO^{\bullet}$) generated by decomposition of hydrogen peroxide can oxidize either organic compounds adsorbed over the silica SBA-15 support or additionally soluble organic compounds in the surroundings of catalyst surface or even in the bulk liquid phase. It has been reported that other oxygenated species such as $HO_2^{\bullet}$, $O_2^{\bullet}$ or organic peroxyl radicals can be also involved in the degradation of organic compounds over the catalyst surface [12]. The degree of mineralization and chemical composition of by-products coming from the partial oxidation of phenol will depend on the reaction conditions. Finally, oxygenated intermediates can be desorbed into the aqueous solution.

Santos et al. have demonstrated that the composition of the reaction medium has a critical influence in the leaching of the metallic species supported over heterogeneous catalysts in wet air oxidation processes [26]. This is attributed to the formation of stable metallic organic complexes with the supported iron species. Some of them undergo their own extraction from the catalyst surface when oxidation by-products are desorbed. In this sense, in CWHPO processes, this mechanism is supposed to be responsible of the partial iron dissolution which can acts as homogeneous source of iron ions to enhance the overall catalytic performance.

In addition to the general proposed reaction scheme, parallel reduction–oxidation reactions of immobilized iron species can be responsible of part of the activity and stability of the heterogeneous catalyst, even in absence of hydrogen peroxide as it is depicted in Fig. 10. In fact, iron(III) ions have been reported to be effective oxidants for the direct degradation of phenol or intermediates of reaction [27]. These secondary reactions have been confirmed from the results obtained in a catalytic experiment carried out in absence of hydrogen peroxide at 100 °C (ca. 9% of TOC conversion).

3.4. Regenerability and reusability of the heterogeneous catalyst

Catalytic run over the used catalyst without any treatment (1 g/L of phenol, 3.82 g/L of H_2O_2, 100 °C, initial pH of 5 and total air pressure of 0.7 MPa) yielded a TOC conversion of just 12% after 10 min of reaction evidencing a remarkable lower degradation rate as compared with the fresh catalyst

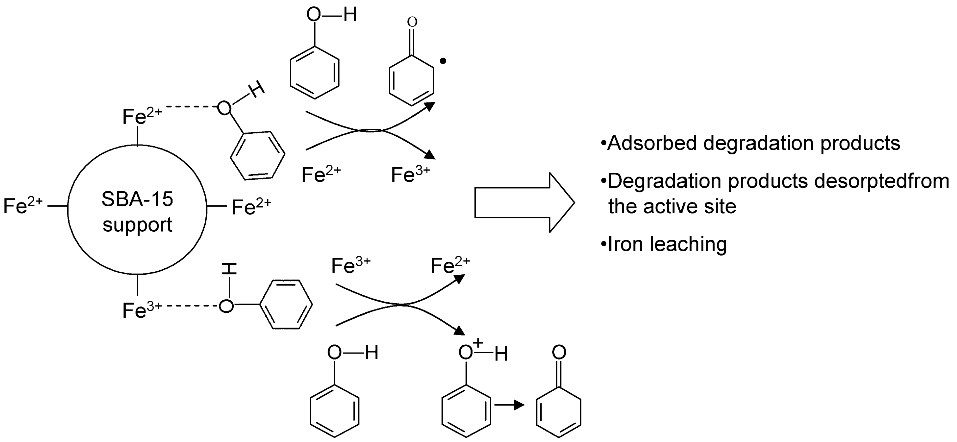

Fig. 10. Parallel reactions in absence of oxidant.

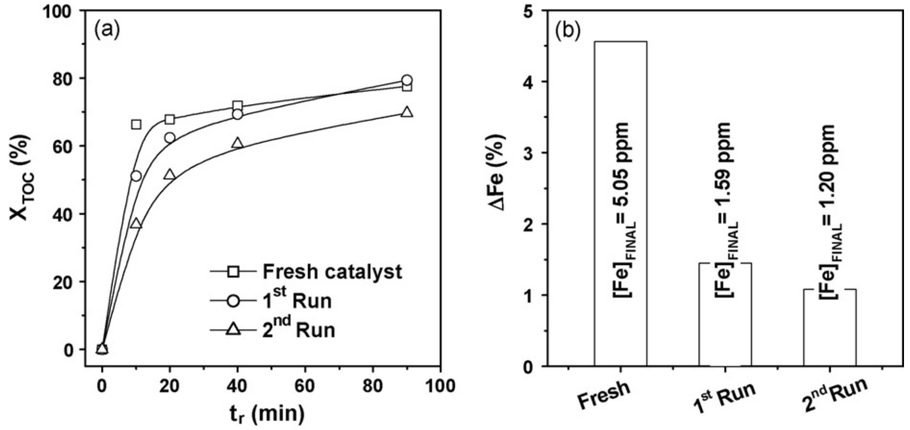

Fig. 11. (a) TOC degradation and (b) stability of iron species after subsequent reactions. Reaction conditions: $[\text{Phenol}]_0 = 1$ g/L; $[H_2O_2]_0 = 3.82$ g/L; $T = 100\,°C$; pH_0 5.5; total air pressure = 0.7 MPa.

(TOC conversion of ca. 65% after 10 min of reaction, Fig. 11). These catalytic results evidence that the presence of residual organic compounds adsorbed over the catalyst surface during the reaction has a negative effect in its reusability in subsequent reactions. However, when the catalyst was reused after an intermediate calcination step in air at 450 °C during 3 h (first run) the catalytic activity was almost restored, evidencing the most significant differences at the initial reaction times (Figs. 11(a) and 12). On the other hand, a remarkable decrease of the ion species leached out to the aqueous solution (Fig. 11(b)) is readily observed. This fact indicates that the most un-stable iron species (mainly Fe^{+3} ionic species) have been dissolved and lost during the first reaction. Further reuse of the catalyst in a second regeneration cycle (second run) has led to a lower catalytic activity as compared with the fresh and the first cycle catalyst. Note that all the catalysts yielded a similar TOC con-

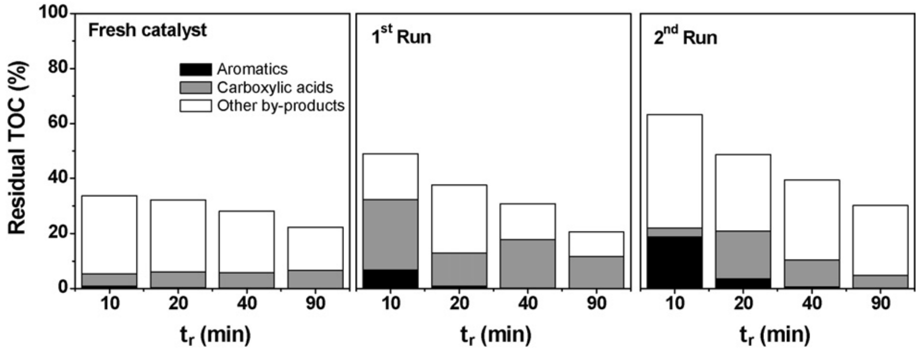

Fig. 12. Contribution of degradation products over the residual TOC in several recyclings of the catalyst. Reaction conditions: $[\text{Phenol}]_0 = 1$ g/L; $[H_2O_2]_0 = 3.82$ g/L; $T = 100\,°C$; total air pressure = 0.7 MPa. Aromatics include phenol, cathecol and hydroquinone; carboxylic acids include oxalic, acetic and formic acids.

version and the complete absence of aromatic compounds after 90 min of reaction.

A possible explanation of the loss of activity when the catalyst is reused after thermal regeneration could be attributed to different reasons. One of them is that physicochemical properties of mesoporous SBA-15 support could be affected by the successive regeneration cycles, producing changes in the adsorption capability for the organic compounds. In fact, textural properties of the catalyst after the first regeneration cycle kept similar to those of the fresh catalyst (BET surface area of 449 m^2/g and total pore volume of 0.61 cm^3/g), but the second regeneration cycle yielded a clear decrease of surface area and pore volume of the catalyst after thermal treatment (BET surface area of 259 m^2/g and total pore volume of 0.37 cm^3/g). Other important point is the iron concentration detected into the aqueous solution for each catalytic run. Although the role of heterogeneous catalyst has been clearly demonstrated in the previous part of the work, the contribution of homogeneous reactions was not ruled out. Thus, the decreasing of iron leaching for second and third run should influence on the overall catalytic performance undoubtedly. Finally, it must be remarked that oxidation-regeneration cycles of the catalyst can modify not only the textural properties of the mesostructured support but also the nature and environment of the iron active species.

4. Conclusions

A solid catalyst consisting of a crystalline Fe_2O_3/SBA-15 nanocomposite exhibits a high degradation rate for the mineralization of phenolic aqueous solutions in a wide range of pH and using moderate amounts of oxidant. A TOC degradation over ca. 75% has been achieved at 100 °C, hydrogen peroxide concentration of 3.8 g/L (75% of the stoichiometric amount necessary for the complete mineralization of the initial phenol concentration) and without any acidification of the reaction medium. This activity is accompanied with a remarkable stability of the iron oxides supported on the silica support. The reactivity of organic substrates with iron active sites over the catalyst surface seem to be the most important factor in the leaching of metal ions to the aqueous solution. The study of several operating variables in this process (temperature, initial hydrogen peroxide concentration and pH of the aqueous solutions) has allowed proposing a schematic view of the reactions involved in the CWHPO process. The role of the heterogeneous catalysts in the adsorption of the organic compounds and subsequent degradation over the solid surface has been demonstrated, leading to a remarkable enhancement of the overall catalytic performance as compared with homogeneous processes. Nevertheless, the contribution of homogeneous reactions due to the iron ions dissolved from the catalyst is also evidenced. Finally, the thermal regeneration of catalyst and successive reutilizations have led to final TOC conversions close to that obtained by the fresh catalyst and the complete removal of phenol. Further research is currently addressed for the application of this novel catalyst in a continuous fixed bed reactor.

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References

[1] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment. I. Oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 501–551.

[2] S. Esplugas, J. Gimenez, S. Contreras, E. Pascual, M. Rodriguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042.

[3] L. Plant, M. Jeff, Hydrogen peroxide: a potent force to destroy organics in wastewater, Chem. Eng. (1994) 16–20.

[4] C. Walling, Fenton’s reagent revisited, Acc. Chem. Res. 8 (1975) 125–131.

[5] E. Neyens, J. Baeyens, A review of classic Fenton’s peroxidation as an advanced oxidation technique, J. Hazard. Mater. 98 (2003) 33–50.

[6] J.J. Pignatello, Dark and photo-assisted Fe^{3+} catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environ. Sci. Technol. 26 (1992) 944–951.

[7] J. De Laat, H. Gallard, Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: mechanism and kinetic modelling, Environ. Sci. Technol. 33 (1999) 2726–2732.

[8] G. Centi, S. Perathoner, T. Torres, M.G. Verduna, Catalytic wet oxidation with H_2O_2 of carboxylic acids on homogeneous and heterogeneous Fenton-type catalysts, Catal. Today 55 (2000) 61–69.

[9] W. Luck, Wet air oxidation: past, present and future, Catal. Today 53 (1999) 81–91.

[10] R.M. Ramirez, M.T. Orta, A. Duran, An overview of Fenton’s reagent applications in Mexico as pre-treatment of industrial wastewaters for reuse, Water 21 (2004) 21.

[11] S.T. Kolaczkowski, P. Plucinski, F.J. Beltran, F.J. Rivas, D.B. McLurgh, Wet air oxidation: a review of process technologies and aspects in reactor design, Chem. Eng. J. 73 (1999) 143–160.

[12] S. Perathoner, G. Centi, Wet hydrogen peroxide catalytic oxidation (WHPCO) of organic waste in agro-food and industrial streams, Top. Catal. 33 (2005) 207–224.

[13] G. Ovejero, J.L. Sotelo, F. Martínez, J.A. Melero, L. Gordo, Wet peroxide oxidation of phenolic solutions over different iron containing zeolitic materials, Ind. Eng. Chem. Res. 40 (2001) 3921–3928.

[14] E. Guélou, J. Barrault, J. Fournier, J. Tatibouët, Active iron species in the catalytic wet peroxide oxidation of phenol over pillared clays containing iron, Appl. Catal. B: Environ. 44 (2003) 1–8.

[15] K. Lazar, G. Calleja, J.A. Melero, F. Martínez, R. Molina, Influence of synthesis route on the state of Fe species in SBA-15 mesoporous materials, Stud. Surf. Sci. Catal. 154 (2004) 805–812.

[16] C.B. Molina, J.A. Casas, J.A. Zazo, J.J. Rodriguez, A comparison of Al–Fe and Zr–Fe pillared clays for catalytic wet peroxide oxidation, Chem. Eng. J. 118 (2006) 29–35.

[17] N. Crowther, F. Larachi, Iron-containing silicalites for phenol catalytic wet peroxidation, Appl. Catal. B: Environ. 46 (2003) 293–305.

[18] J.L. Sotelo, G. Ovejero, F. Martínez, J.A. Melero, A. Milieni, Catalytic wet peroxide oxidation of phenolic solutions over a $LaTi_{1-x}Cu_xO_3$ perovskite catalyst, Appl. Catal. B: Environ. 47 (2004) 281–294.

[19] F. Martínez, G. Calleja, J.A. Melero, R. Molina, Heterogeneous photo-Fenton degradation of phenolic aqueous solutions over iron-containing SBA-15 catalyst, Appl. Catal. B: Environ. 60 (2005) 181–190.

[20] G. Calleja, J.A. Melero, F. Martínez, R. Molina, Activity and resistance of iron-containing amorphous, zeolitic and mesostructured materials for wet peroxide oxidation of phenol, Water Res. 39 (2005) 1741–1750.

[21] F. Martínez, Y. Jhan, G.D. Stucky, J.L. Sotelo, G. Ovejero, J.A. Melero, Synthesis and characterization of iron-containing SBA-15 mesoporous silica, Stud. Surf. Sci. Catal. 142 (2002) 1109–1116.

[22] L. Vradman, M.V. Landau, D. Kantorovich, Y. Koltypin, A. Gedaken, Evaluation of metal oxide phase assembling mode inside the nanotubular pores of mesostructured silica, Micropor. Mesopor. Mater. 79 (2005) 307–318.

[23] G.E.P. Box, W.G. Hunter, J.S. Hunter, Statistics for Experiments, an Introduction to Design, Data Analysis and Model Building, John Willey and Sons, New York, 1978.

[24] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constant for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($^{\bullet}$OH/O^{-}) in aqueous solutions, J. Phys. Chem. Ref. Data 17 (1988) 513–886.

[25] J. Feng, X. Hu, P.L. Yue, Effect of the initial solution pH on the degradation of Orange II using clay-based Fe nanocomposite as heterogeneous photo-Fenton catalyst, Water Res. 40 (2006) 641–646.

[26] A. Santos, P. Yustos, A. Quintanilla, G. Ruiz, F. Garcia-Ochoa, Study of the copper leaching in the wet oxidation of phenol with CuO-based catalyst: causes and effects, Appl. Catal. B: Environ. 61 (2005) 323–333.

[27] M. Papadaki, R.J. Emery, M.A. Abu-Hassan, A. Diaz-Bustos, I.S. Metcalfe, D. Mantzavinos, Sonocatalytic oxidation process for the removal of contaminants containing aromatic rings from aqueous effluents, Sep. Purif. Technol. 34 (2004) 35–42.