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Optimizing calcination temperature of Fe/activated carbon catalysts for CWPO

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ABSTRACT

The influence of the calcination temperature (within the temperature range 150–300 °C) on the chemical nature of the surface as well as on the activity of an own-made Fe/AC catalyst for catalytic wet peroxide oxidation (CWPO) has been studied. The catalyst surface was characterized by means of TG, TPD and N_2 adsorption/desorption analysis. The presence of iron promotes the oxidation of the activated carbon surface, increasing the amount of oxygen surface groups, mainly carboxylic acid, anhydride and lactone groups. On the other hand, the calcination step modifies the distribution of these groups, increasing the amount of lactone groups and reducing the pH_{slurry}. Within the temperature range studied, the calcination temperature does not affect to the porous structure. The changes observed in the catalyst surface led to an increase of the catalytic activity as a consequence of a higher H_2O_2 decomposition into $OH^{\bullet}$ radicals, probably due to a better dispersion of the active phase. Neither oxygen surface groups by themselves nor pH_{slurry} seemed to have influence on the catalytic activity.

1. Introduction

The development of efficient technologies able to treat industrial wastewater containing non-biodegradable compounds has focused considerable research efforts in the latest years [1]. In this sense, catalytic wet peroxide oxidation (CWPO) using solid catalysts, represents an interesting alternative to treat this kind of effluents. In this process, transition metals, mainly iron, are used to decompose catalytically hydrogen peroxide into $OH^{\bullet}$ radicals at mild conditions (atmospheric pressure and temperature around 50 °C). Alumina [2] mesostructured materials [3,4], zeolites [5–8], pillared clays [9–12], ion-exchange resin [13] and activated carbon [14] have been used as supports to prepare the catalysts. The use of activated carbon as support shows some advantages, for instance, the high surface area and porosity compared to other supports and the presence of oxygen surface groups which affect the catalytic activity [15]. These oxygen complexes are especially significant groups because they act as anchorage sites that interact with the metallic phase improving its dispersion [16–18]. Moreover, these groups can also influence the decomposition of H_2O_2. In this sense, the activated carbon surface is the main responsible of H_2O_2 decomposition into O_2 and H_2O (which is one of the main drawbacks of this support) whereas the presence of acidic oxygen surface groups retards that decomposition as it suppresses dissociation under those conditions [19].

The nature and the concentration of these groups may be modified through oxidation and/or thermal treatment under inert atmosphere. Oxidation can be used to increase the concentration of oxygen surface groups, whereas heating under inert atmosphere may be used to remove selectively some of these functional groups [20].

In a previous work [14] the suitability of an own-made Fe/AC catalyst for the CWPO process has already been demonstrated using phenol as target compound. The aim of this work is to learn on the effect of the temperature of calcination (in air atmosphere) on the chemical and textural properties of activated carbon-supported iron catalysts as well as their catalytic activity for CWPO.

2. Experimental

2.1. Catalyst preparation and characterization

Iron on activated carbon (Fe/AC) catalysts were prepared by incipient wetness impregnation of a commercial activated carbon (AC) with an aqueous solution of iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$). The volume of solution was 0.83 mL/g catalyst, which represents a 10% excess with respect to the pore volume of the active carbon. After impregnation, the solid was left 2 h at room temperature, dried during 12 h at 60 °C and finally heat-treated at different temperatures, in the range between 150 °C and 300 °C in air

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atmosphere for 4 h. All the catalysts had a similar nominal iron content (around 4 wt.%).

BET surface area and pore volume were obtained from 77 K N_2 adsorption–desorption isotherms using a Micromeritics ASAP 2010. Samples were outgassed at 250 °C to a residual pressure $<10^{-4}$ Pa. The micropore volume was obtained from the *t*-method [21]. Porosity studies were completed by mercury porosimetry using a CE Instruments Pascal 140/240. Total pore volume was evaluated combining both techniques. The total iron content of the catalysts was determined by means of inductively coupled plasma technique (ICP-AES) with a PerkinElmer Model Optima 3300DV. Temperature-programmed desorption (TPD) profiles in N_2 atmosphere were performed to asses the amount and nature of oxygen surface groups. A N_2 flow of 250 mL/min and a heating rate of 5 °C/min were always used and CO and CO_2 were analyzed by a Siemens Ultramat 23 infrared analyser. Thermal gravimetric (TG) analyse were accomplished with a TGA/SDTA 851e Module, Mettler Toledo in N_2 and air flow of 250 mL/min at a heating rate of 5 °C/min, from room temperature (rt) to 1000 °C. The pH_{slurry} were determined measuring, until constant value, the pH of an aqueous suspension of catalyst in distilled water (1 g/10 mL).

2.2. Activity tests

The activity of the catalysts was studied in batch using 100 mL stoppered glass bottles shaken in a thermostatic bath at an equivalent stirring velocity around 200 rpm. A volume of 50 mL of an aqueous solution containing 100 mg/L phenol and 500 mg/L H_2O_2 was used in all experiments. The dose of H_2O_2 corresponds to the stoichiometric amount for complete oxidation of phenol to CO_2 and H_2O. The starting solution was prepared by mixing aliquots of 200 mg/L phenol and 1000 mg/L H_2O_2, whose concentrations were previously analyzed. A dose of 500 mg/L of Fe/AC catalyst in powdered form (dp $<$ 100 μm) was always used. The experiments were carried out at 50 °C and the initial pH was adjusted, by using HCl, to 3, which is the optimum pH value for this treatment [6,10,14]. In addition to the activity experiments, phenol adsorption tests were carried out in the same conditions, but in absence of H_2O_2.

2.3. Identification of the oxidation products

The reaction samples were passed through fiber glass filters (Albet FV-C), and immediately analyzed. Phenol and aromatic intermediates were identified and quantified by means of HPLC (Varian Pro-Start 240) with a diode array detector (330 PDA). A Microsorb C_{18} 5 μm column (MV 110, 15 cm long, 4.6 mm diameter) was used as stationary phase and 1 mL/min of 4 mM aqueous sulfuric solution as mobile phase. Short-chain acids were measured using an Ion Chromatograph with chemical suppression (Metrohm 790 IC) and a conductivity detector. A Metrosep A supp 5-250 column (25 cm long, 4 mm diameter) was used as stationary phase and 0.7 mL/min of an aqueous solution of 3.2 mM Na_2CO_3 and 1 mM $NaHCO_3$ as mobile phase. TOC was quantified using a total organic carbon analyzer with infrared detector TOC-Vsch, Shimadzu. H_2O_2 and lixiviated Fe were determined by colorimetric titration with a Simadzu UV/Vis spectrophotometer using the titanium sulfate method [22] and the o-phenantroline method [23], respectively.

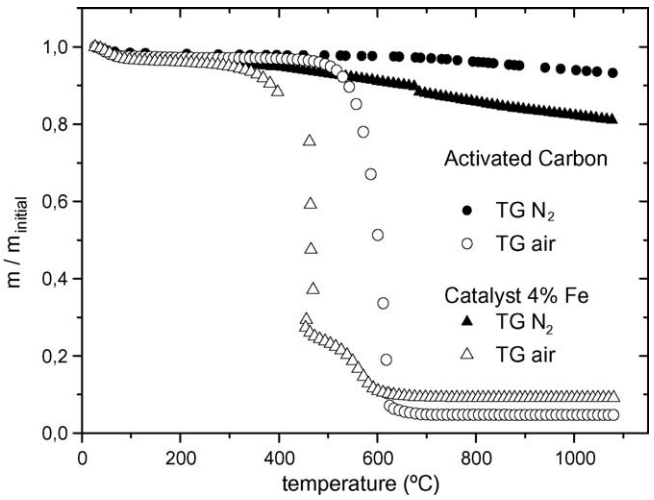

Fig. 1. TG curves of AC and Fe/AC under N_2 and air atmosphere.

3. Results and discussion

3.1. Catalysts characterization

In order to select the range of the calcination temperature to be investigated we obtained the TG curves in air atmosphere of both, the activated carbon support and the Fe/AC catalyst. In this case, the catalyst was prepared at the lower calcination temperature (150 °C). As can be seen in Fig. 1 the activated carbon is thermally stable up to 550 °C whereas the Fe/AC catalyst starts to burn-off around 350 °C. This difference is due to the promoting effect of Fe_2O_3, the predominant iron species in the catalyst [24], on the oxidation of the activated carbon. This also explains the higher weight loss observed for the Fe/AC catalyst with respect to the AC in N_2 atmosphere as a result of its higher content of oxygen surface groups. Another difference that can be appreciated is a small steep loss at around 700 °C that appears in the TG curve in N_2 atmosphere of the catalyst but not in activated carbon TG. From DTA it was determined that this weight loss is associated with an endothermic peak, most probably due to the reduction of Fe_2O_3 by activated carbon, which is oxidized to CO and CO_2.

According to the results of Fig. 1, a range of 150–300 °C was selected for the temperature of calcination in order to preclude the burn-off of the activated carbon. The characterization of the porous structure of the catalysts prepared at different calcination temperatures within that range is summarized in Table 1. A small but monotonical increase of the BET surface area is observed as the calcination temperature increase. The external or non-microporous area does not show any regular trend and fairly similar values were found at the four calcination temperatures. The evolution of micropore and mesopore volumes is consistent with those of BET and external surface area, respectively.

Table 1
Porous structure of the Fe/AC catalysts.

Calcination temperature (°C)	S_{BET} (m^2/g)	$A_{external}$ (m^2/g)	V_{micro} (cc/g)	V_{meso} (cc/g)	V_{Macro} (cc/g)	V_{Total} (cc/g)	Fe (%)
150	966	76	0.39	0.12	0.11	0.62	4.1
200	988	72	0.38	0.12	0.10	0.60	4.1
250	1037	82	0.42	0.13	0.11	0.66	4.2
300	1042	76	0.43	0.13	0.11	0.66	3.6

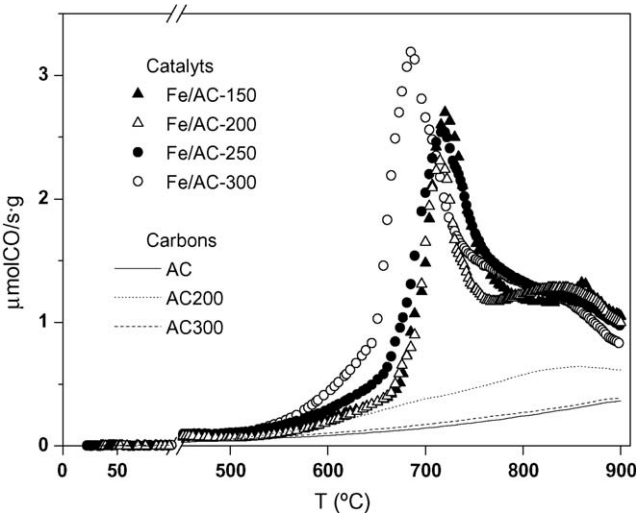

Fig. 2. CO profiles from TPD of the catalysts and the activated carbon support.

Figs. 2 and 3 show the CO and CO_2 profiles, respectively, obtained from TPD of the Fe/AC catalysts. For the sake of comparison we have included the corresponding curves for AC. The total amounts of CO and CO_2 released up to 900 °C are reported in Table 2. These results reveal a low content of oxygen-surface groups of the starting carbon even after heat-treatment at 200 °C and 300 °C in air atmosphere. On the contrary, the presence of iron increases significantly the amount of oxygen-surface groups in the resulting Fe/AC catalysts.

Table 2
Amounts of CO and CO_2 released from the catalysts and activated carbon by TPD (AC200, AC300 and AC-HNO_3 correspond to the activated carbon support calcined at 200 °C, 300 °C and treated with HNO_3, respectively).

Catalyst	µmol CO/g	µmol CO_2/g	pH_{slurry}
Fe/AC-150	2190	901	4.4
Fe/AC-200	2060	851	4.3
Fe/AC-250	2400	898	4.1
Fe/AC-300	2740	863	3.9
AC	430	70	7.5
AC200	500	100	7.3
AC300	887	58	6.9
AC-HNO_3	2090	865	3.1

Except in the lower temperature range, the amount of CO desorbed increases with the temperature of calcination. However the CO profile shows a peak centered at around 700 °C. This profile suggests that the CO desorbed comes in part from the aforementioned reaction between Fe_2O_3 and the activated carbon. This assumption can be roughly corroborated by estimating the amount of CO released by that reaction. For that, two simplifications were considered: (i) Fe_2O_3 is the only iron specie in the catalyst and (ii) the reaction between Fe_2O_3 and activated carbon is mainly addressed towards CO. Thereby, a 4% Fe content means 59.4 mg Fe_2O_3/g catalyst which would give rise to 1114 µmol CO/g catalyst as the highest amount of CO that could be released by that reaction in N_2 atmosphere. This amount is close to the average CO amount (≈930 µmol CO/g catalyst) associated to the peak appearing around 700 °C in the CO profiles from the TPD of the catalysts. With respect to CO_2, although the released amount hardly varies with the calcination temperature, there are significant differences in the

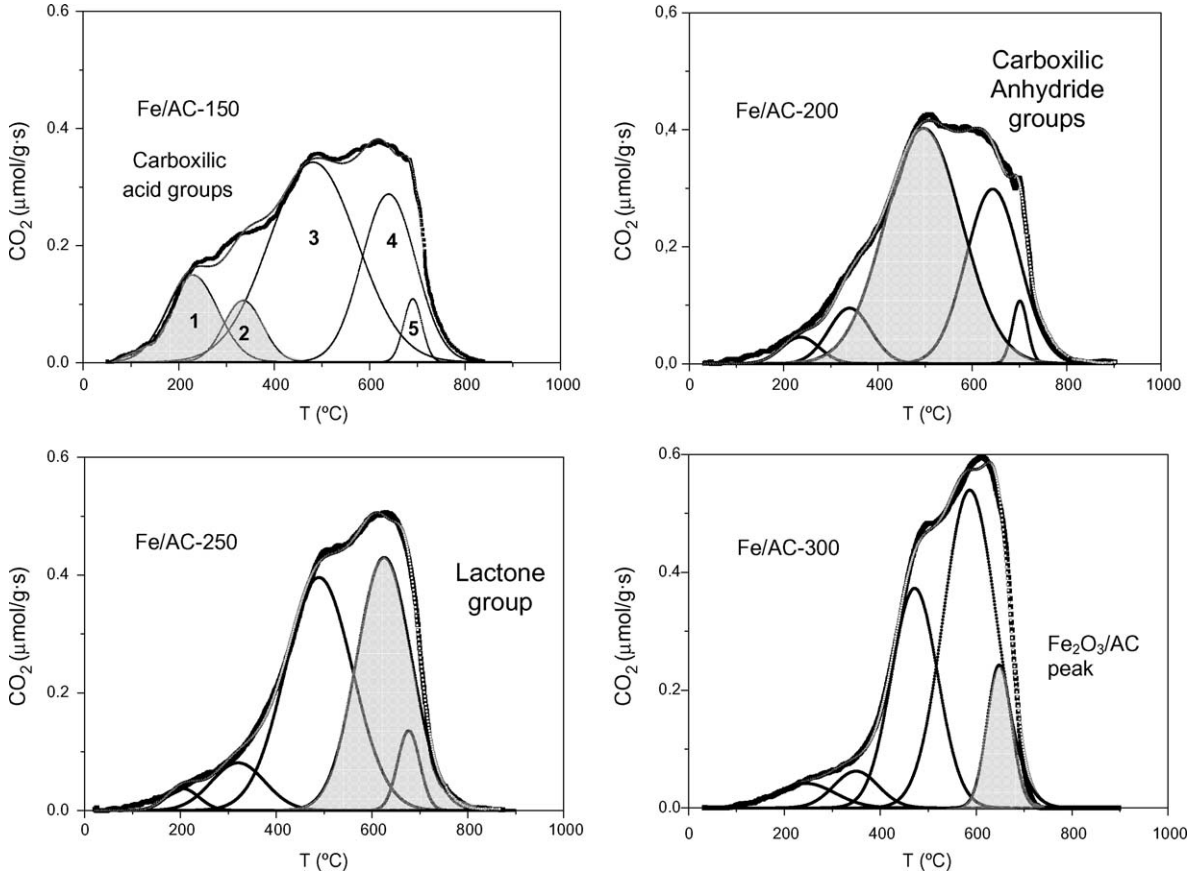

Fig. 3. Deconvolution of the CO_2 profiles from TPD of the Fe/AC catalysts. [·] Experimental data; [–] sum of individual peaks and [···] individual peaks [1,2]. Carboxylic acid groups; [3] carboxylic anhydride groups; [4] lactone groups; [5] Fe_2O_3 peak.

Table 3
Results of the deconvolution of CO_2 TPD spectra.

Peak	Fe/AC-150		Fe/AC-200		Fe/AC-250		Fe/AC-300		AC-HNO_3	
	%	μmol/g	%	μmol/g	%	μmol/g	%	μmol/g	%	μmol/g
Carb. acid(1)	12.7	115	3.1	27	2.1	18	4.3	37	23.3	202
Carb. acid(2)	6.9	62	7.3	62	7.4	66	4.9	42	22.9	198
Carb. anhydride(3)	50.9	458	56.9	485	45.4	407	30.3	261	46.0	398
Lactone(4)	26.2	236	29.6	252	40.1	360	50.2	433	7.8	67
Iron contribution (5)	3.3	30	2.9	25	5.1	46	10.4	90	–	–
Sum	901		851		897		863		865	

relative distribution of oxygen-surface groups, as it can be appreciated in Fig. 3, The CO_2 TPD curves have been deconvoluted considering the following contributions [20]: carboxylic acid (230 and 320 °C), carboxylic anhydride (480 °C) and lactone (650 °C) groups. Moreover, it was necessary to include another peak around 700 °C to match the TPD spectra. Again, this peak is most probably due in a great part to the reaction between Fe_2O_3 and the activated carbon. Nonetheless, the area under this peak was negligible compared with that of the peak appearing at the same temperature in the CO TPD curves. This also corroborates that the reaction between Fe_2O_3 and activated carbon in inert atmosphere is mainly headed towards CO. The deconvolution has been performed using PEAKFIT 4.11, selecting a multiple Gaussian function to fit each deconvolution peak of TPD spectra. The results are summarized in Table 3. According to them, the amount of carboxylic acid groups (peaks 1 and 2) is reduced when increasing the temperature of calcination because of either their decomposition or condensation with another carboxylic groups giving rise to anhydride groups [25]. This explains the maximum observed for the amount of carboxylic anhydride groups (peak 3) at a relatively low calcination temperature (200 °C). Beyond this temperature, these groups begin to decompose and their concentration decreases. The amount of lactone groups (peak 4) increases monotonically with calcination temperature, probably in part due to condensation of phenolic and carboxylic groups [25]. A similar trend is observed with peak 5. This peak is related to the reaction between Fe_2O_3 and activated carbon.

The surface acidity of the catalysts has been characterized by measuring the pH_{slurry} (Table 2). In aqueous media, anhydride and lactone groups undergo hydrolysis giving rise to carboxylic and alcohol groups, which explain the reduction of the pH_{slurry} value at increasing calcination temperature. In fact, there is a relationship between the amount of lactone groups in Fe/AC catalyst and the evolution of pH_{slurry}, as can be observed in Table 2. The Fe/AC catalysts show significantly lower pH_{slurry} than the corresponding AC support.

Thus, it can be concluded that iron promotes the oxidation of the activated carbon surface, increasing the amount of oxygen surface groups whereas the heat-treatment (calcination) modifies the distribution of these groups.

3.2. Catalytic activity

Fig. 4 shows the time–evolution curves for phenol and TOC upon CWPO with the Fe/AC catalysts. For the sake of discrimination between reaction and simply adsorption the results obtained in absence of H_2O_2 are also included. As can be seen a higher calcination temperature leads to a higher rate of phenol disappearance and the degree of mineralization, namely complete oxidation up to CO_2 and H_2O, is also increased. This enhancement of the oxidation process takes place in spite of the fact that the rate of H_2O_2 decomposition does not show any significant variation neither does adsorption. The effect of the heat treatment temperature is frankly important so that within the first 30 min

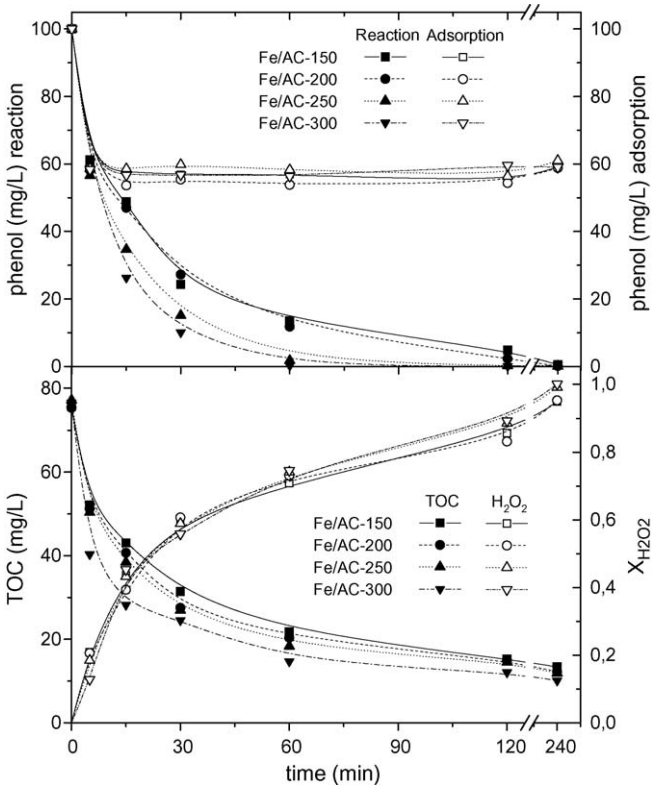

Fig. 4. Evolution of phenol, TOC and H_2O_2 upon CWPO of phenol with the Fe/AC catalysts.

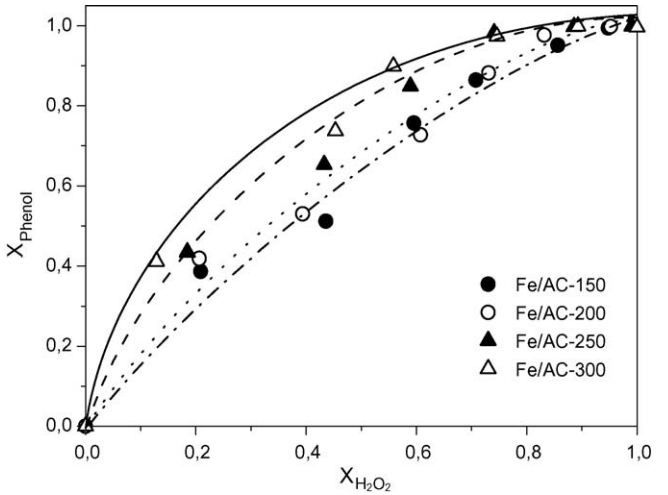

Fig. 5. Phenol conversion versus H_2O_2 conversion using Fe/AC catalysts (lines show trends).

of reaction, phenol conversion raised from 70% when the catalyst was calcined at 150 °C up to 90% when it was calcined at 300 °C. This was not related to any homogeneous contribution since the leaching of iron within the former 30 min was almost negligible (<0.5 mg/L) for all catalyst tested. It is noticeable the relation between phenol conversion and H_2O_2 decomposition. As can be seen in Fig. 5, the amount of phenol converted per unit of H_2O_2 decomposed increases markedly at increasing the calcination temperature. This indicates a more efficient use of H_2O_2, most probably due to a more selective decomposition of hydrogen peroxide into hydroxyl radicals instead of O_2 and H_2O. The second one is the main route of H_2O_2 decomposition by activated carbon in absence of iron [14]. Therefore, these results suggest a more homogeneous dispersion of iron over the catalyst surface (due to a higher concentration of oxygen-surface groups), favouring the reaction between H_2O_2 and iron rather than with the carbon surface, and/or an effect of the oxygen-surface groups (or some of them) addressing the H_2O_2 decomposition towards $OH^{\bullet}$ radicals.

To elucidate the role of these oxygen groups it was necessary to develop an activated carbon with an amount and distribution of these groups as close as possible to the Fe/AC catalyst. A first attempt was to leach the iron from the Fe/AC catalyst by treating with oxalic acid (100 mg/L) or HCl (1%) solution at 50 °C. In both cases, the complete leaching of iron was accompanied by a significant reduction of the CO_2-evolving oxygen groups (from 863 μmol CO_2/s g to 331 μmol CO_2/s g), in spite of the fact that these treatments did not show any significant effect over those oxygen groups when applied to the activated carbon support. This suggests a strong association of Fe and the oxygen of the surface groups. Another way to obtain an activated carbon with a large concentration of oxygen-surface groups comparable to that of the Fe/AC catalyst was intended by treating the starting AC support with HNO_3 (1 g of activated carbon + 10 mL of a 6 N solution for 20 min at boiling temperature [26]). The amount of oxygen-surface groups desorbing as CO_2 was quite similar (Table 2), although not their distribution (Table 3), being carboxylic acid the main group whereas the amount of lactone groups was lower than that of the catalyst calcined at 150 °C. Despite the large amount of oxygen-surface groups, this activated carbon did not show any catalytic activity, indicating that those functional groups by themselves do not promote the $OH^{\bullet}$ generation. Moreover, since the H_2O_2 decomposition is lower than that with the starting AC, the fact that the oxygen-surface groups hinder the H_2O_2 decomposition into O_2 and H_2O by activated carbon surface was also corroborated. Besides, as is shown in Table 2, the pH_{slurry} of AC-HNO_3 is lower than those measured in the case of Fe/AC catalyst, indicating the negligible relation between acidity and activity for this process.

Therefore, oxygen-surface groups must affect to iron dispersion. This is in agreement with others gathered in the reported in the bibliography, although for Pd on activated carbon catalyst [26] where, oxygen-surface groups enhance the dispersion of the active metallic phase on the surface of activated carbon. Moreover, the fact that acidic oxygen surface groups suppress H_2O_2 decomposition into H_2O and O_2 [19], increases the amount of H_2O_2 available for reacting with iron, leading to a higher $OH^{\bullet}$ generation.

The evolution of the oxidation intermediates is of crucial importance and much attention has to be paid to the aromatic byproducts, mainly hydroquinone and p-benzoquinone due to their toxicity [27]. Fig. 6 shows the concentration of all the identified intermediates upon reaction time. The analyses of the reaction samples matched always the TOC values with more than 90%. It can be seen that the rates of formation and disappearance of aromatic intermediates is increased with the catalysts prepared at the highest calcination temperatures (250 and 300 °C). For the last one the concentration of catechol reaches a significantly higher maximum value which may be explained as the consequence of an

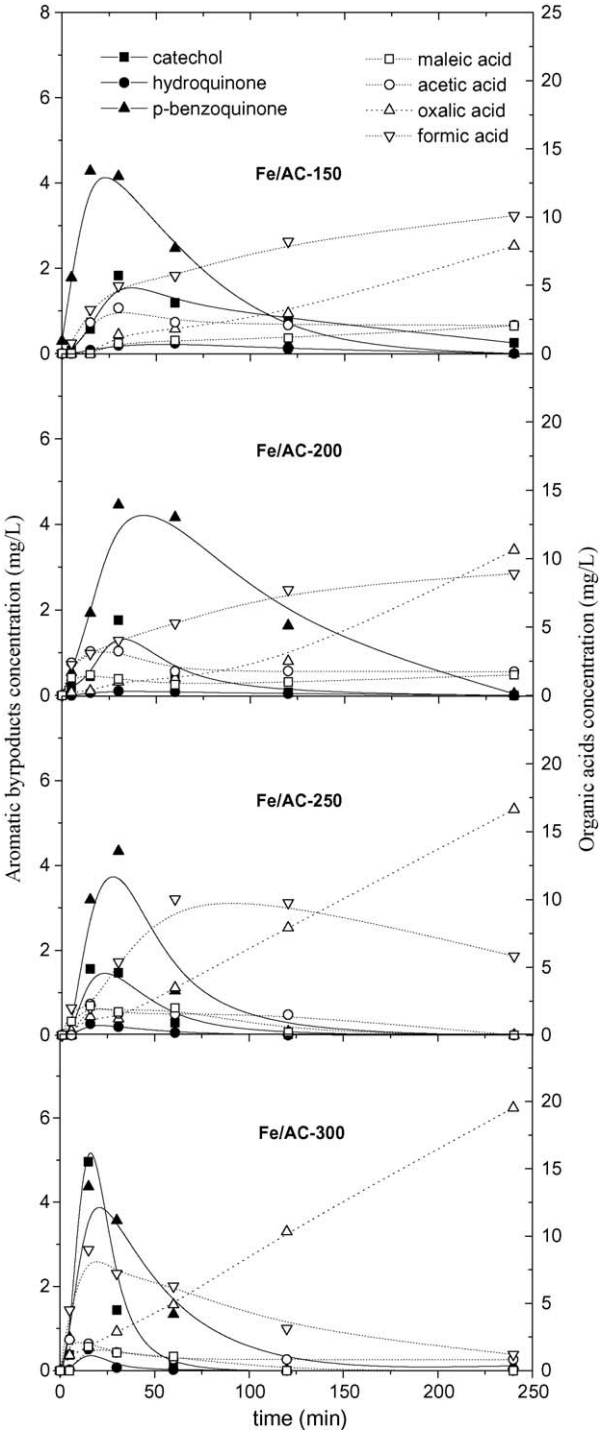

Fig. 6. Evolution of aromatic intermediates and organic acids upon CWPO of phenol using Fe/AC catalysts.

increasing of $OH^{\bullet}$ generation which favours ortho-hydroxylation of the aromatic ring with respect to the formation of oligomeric deposits over the catalyst surface. Moreover, the changes in the surface composition of the catalyst also reduced the extension of the oxidative-coupling reactions by both, reducing the amount of molecular O_2 (from decomposition of H_2O_2 into O_2 and H_2O) over the catalyst surface [28], and increasing the concentration of acidic surface oxygen groups [29].

On the other hand, the concentration of oxalic acid that can be considered as a final product since is quite refractory to CWPO, increases clearly at increasing calcination temperature, confirming

the increase of the catalytic activity. However, the higher oxalic acid concentration, the higher iron leaching from the catalyst. Both the trend and the ratio $Fe_{leached}$/oxalic acid were similar to the obtained in a previous work [14] where the calcination temperature was 200 °C. Therefore, we can conclude that the heat-treatment temperature has not a significant effect in improving the anchorage of iron to the activated carbon surface.

4. Conclusions

Own-made catalysts based on Fe supported on activated carbon have been successfully used in phenol oxidation with H_2O_2 at mild conditions. The temperature of calcination has shown an important effect on the activity of the catalysts. Both the oxidation rate and the overall TOC reduction were increased (without modifying adsorption capacity significantly) at increasing the calcination temperature (within 150–300 °C range). A TOC reduction higher than 80% was attained in all the cases, and the remaining TOC corresponds to low molecular weight organic acids. Thus, the toxicity was drastically reduced. The catalysts showed an acceptable stability, although some Fe leaching was observed, which has been related to the presence of oxalic acid.

This increase in catalytic activity can be explained as a result of the changes promoted by the heat-treatment over the amount and distribution of the oxygen-surface groups, mainly carboxylic acid, anhydride and lactone groups. Heat-treatment in air atmosphere increases the amount of lactone groups, in detriment of carboxylic and anhydrides groups. As a consequence of these changes, H_2O_2 decomposition into $OH^{\bullet}$ enhances, probably due to a better dispersion of the active phase.

Also, as a result of the heat-treatment, the pH_{slurry} is modified, being more acidic when using a higher calcination temperature within the range investigated. Nevertheless, neither pH_{slurry} nor oxygen-surface groups by themselves seems to be responsible of the catalytic activity.

Acknowledgements

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