

# OPTIMIZING CALCINATION TEMPERATURE OF Fe/ACTIVATED CARBON CATALYSTS FOR CWPO

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## Abstract

The influence of the thermal treatment temperature (during the catalyst preparation) on the activity of a Fe/activated carbon catalyst for catalytic wet peroxide oxidation (CWPO) has been studied using phenol as target compound. 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 heat-treatment step in the catalyst preparation modifies the distribution of these groups, increasing the amount of lactones. Within the temperature range 150-300 °C, calcination temperature does not affect to the porous structure. The changes observed in the oxygen-surface groups have shown a great influence on the catalytic activity. An increase of the calcination temperature up to 300°C leads to a higher catalyst activity in terms of phenol, intermediates and TOC removal, even though both, adsorption and the overall H<sub>2</sub>O<sub>2</sub> decomposition rate, hardly varied. Beyond that temperature, the activated carbon support starts burning-off and the catalytic activity decreases. The changes of the catalytic activity can be explained as a result of the increase of surface acidity, which enhances H<sub>2</sub>O<sub>2</sub> decomposition into OH· radicals instead of O<sub>2</sub> and H<sub>2</sub>O, therefore promoting a faster oxidation.

**Keywords:** calcination temperature, oxygen-surface groups, activated carbon, CWPO, Fe/AC.

## **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  $\text{OH}\cdot$  radicals at mild conditions (atmospheric pressure and temperature around  $50^\circ\text{C}$ ). 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  $\text{H}_2\text{O}_2$ . In this sense, the activated carbon surface is the main responsible of  $\text{H}_2\text{O}_2$  decomposition into  $\text{O}_2$  and  $\text{H}_2\text{O}$  (which is one of the main drawbacks of this support) whereas acidic oxygen surface groups hinder somehow that reaction [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.

## **Experimental**

### *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 ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ). All the samples were carefully dried at room temperature, and finally heat-treated at different temperatures, in the range between 150°C and 300°C, in air atmosphere. All the catalysts had a similar nominal iron content (around 4 wt. %).

BET surface area and pore volume were obtained from 77 K  $\text{N}_2$  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. 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 Perkin Elmer Model Optima 3300DV. Temperature-programmed desorption (TPD) profiles in  $\text{N}_2$  atmosphere were performed to assess the amount and nature of oxygen surface groups. A  $\text{N}_2$  flow of 250 mL/min and a heating rate of 5°C/min were always used and CO and  $\text{CO}_2$  were analysed by a Siemens Ultramat 23 infrared analyser. The pH slurry has been determined measuring, until constant value, the pH of an aqueous suspension of catalyst in distilled water (1g/10mL).

### *Activity tests*

The activity of the catalysts was studied in batch using 100mL stoppered glass bottles shaken in a thermostatic bath at an equivalent stirring velocity around 200 rpm. A volume of 50 mL of a 100 mg/L aqueous phenol solution was used in all experiments. The dose of hydrogen peroxide was 500 mg/L which corresponds to the stoichiometric amount for complete oxidation of phenol to CO<sub>2</sub> and H<sub>2</sub>O. 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 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<sub>2</sub>O<sub>2</sub>.

### *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<sub>18</sub> 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<sub>2</sub>CO<sub>3</sub> and 1 mM NaHCO<sub>3</sub> as mobile phase. TOC was quantified using a total organic carbon analyzer with infrared detector TOC-Vsch, Shimadzu. H<sub>2</sub>O<sub>2</sub> and lixiviated Fe were determined by colorimetric titration with a Simadzu UV/Vis spectrophotometer using the titanium sulfate method [21] and the o-phenantroline method [22], respectively.

## Results and discussion

### *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 Figure 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<sub>2</sub>O<sub>3</sub>, the predominant iron species in the catalyst [23], 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>O<sub>3</sub> by activated carbon, which is oxidized to CO and CO<sub>2</sub> [24].

According to the results of Figure 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.

Figure 2 and 3 show the CO and CO<sub>2</sub> 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<sub>2</sub> 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.

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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> is the only iron specie in the catalyst and ii) the reaction between Fe<sub>2</sub>O<sub>3</sub> and activated carbon is mainly addressed towards CO. Thereby, a 4% Fe content means 5.94 mg Fe<sub>2</sub>O<sub>3</sub>/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<sub>2</sub> 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<sub>2</sub>, although the released amount hardly varies with the calcination temperature, there are significant differences in the relative distribution of oxygen-surface groups, as it can be appreciated in Figure 3, The CO<sub>2</sub> TPD curves have been deconvoluted considering the following contributions [20]: carboxylic acid (230 and 320 °C), carboxylic anhydride (480 °C) and lactones (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<sub>2</sub>O<sub>3</sub> 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  $\text{Fe}_2\text{O}_3$  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  $\text{Fe}_2\text{O}_3$  and activated carbon.

The surface acidity of the catalysts has been characterized by measuring the  $\text{pH}_{\text{slurry}}$  (Table 2). In aqueous media, anhydride and lactone groups undergo hydrolysis giving rise to carboxylic and alcohol groups, which explain the reduction of the  $\text{pH}_{\text{slurry}}$  value at increasing calcination temperature. In fact, there is a relationship between the amount of lactone groups and the evolution of  $\text{pH}_{\text{slurry}}$ , as it can be observed in Figure 4. The Fe/AC catalysts show significantly lower  $\text{pH}_{\text{slurry}}$  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, with the result of an increase of the catalyst acidity.

### *Catalytic activity.*

Figure 5 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  $\text{H}_2\text{O}_2$  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  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , is also increased. This enhancement of the oxidation process takes place in spite of the fact that the rate of  $\text{H}_2\text{O}_2$  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 minutes of reaction, phenol conversion raised from 70% when the catalyst was calcined at  $150^\circ\text{C}$  up to 90% when it was calcined at  $300^\circ\text{C}$ . It is noticeable the relation between phenol conversion and  $\text{H}_2\text{O}_2$  decomposition. As can be seen in Figure 6, the amount of phenol converted per unit of  $\text{H}_2\text{O}_2$  decomposed increases markedly at increasing the calcination temperature. This indicates a more efficient use of  $\text{H}_2\text{O}_2$ , most probably due to a more selective decomposition of hydrogen peroxide into hydroxyl radicals instead of  $\text{O}_2$  and  $\text{H}_2\text{O}$ . The second one is the main route of  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  and iron rather than with the carbon surface, and/or an effect of the oxygen-surface groups (or some of them) addressing the  $\text{H}_2\text{O}_2$  decomposition towards  $\text{OH}\cdot$  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  $50^\circ\text{C}$ . In both cases, the complete leaching of iron was



accompanied by a significant reduction of the CO<sub>2</sub>-evolving oxygen groups (from 862.3 μmol CO<sub>2</sub>/s·g to 331 μmol CO<sub>2</sub>/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<sub>3</sub> (1 g of activated carbon + 10 mL of a 6N solution for 20 minutes at boiling temperature [26]). The amount of oxygen-surface groups desorbing as CO<sub>2</sub> 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· generation. Moreover, since the H<sub>2</sub>O<sub>2</sub> decomposition is lower than that with the starting AC, the fact that the oxygen-surface groups hinder the H<sub>2</sub>O<sub>2</sub> decomposition into O<sub>2</sub> and H<sub>2</sub>O by activated carbon surface was also corroborated.

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 hinder the reaction between H<sub>2</sub>O<sub>2</sub> and activated carbon surface [19], also favours the reaction between H<sub>2</sub>O<sub>2</sub> and Fe, leading to OH· 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]. Figure 7 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 increasing of OH-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<sub>2</sub> (from decomposition of H<sub>2</sub>O<sub>2</sub> into O<sub>2</sub> and H<sub>2</sub>O) 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<sub>leached</sub>/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.

## Conclusions

Own-made catalysts based on Fe supported on activated carbon have been successfully used in phenol oxidation with  $\text{H}_2\text{O}_2$  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°C-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 result of the heat-treatment, the pH slurry is also modified, being more acidic when using a higher calcination temperature within the range investigated. The higher catalytic acidity is a consequence of enhanced  $\text{H}_2\text{O}_2$  decomposition into  $\text{OH}\cdot$  radicals, probably due to a better dispersion of the active phase. Also, a higher concentration of acidic oxygen groups hinders  $\text{H}_2\text{O}_2$  decomposition to  $\text{O}_2$  by the activated carbon surface.

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## Figure captions.

**Figure 1.-** TG curves of AC and Fe/AC under N<sub>2</sub> and air atmosphere.

**Figure 2.-** CO profiles from TPD of the catalysts and the activated carbon support.

**Figure 3.-** Deconvolution of the CO<sub>2</sub> profiles from TPD of the Fe/AC catalysts.

[· ] experimental data; [-] sum of individual peaks and [...] individual peaks.

**Figure 4.-** Relation between pHslurry and the content of lactone groups in Fe/AC catalysts.

**Figure 5.-** Evolution of phenol, TOC and H<sub>2</sub>O<sub>2</sub> upon CWPO of phenol with the Fe/AC catalysts.

**Figure 6.-** Phenol conversion versus H<sub>2</sub>O<sub>2</sub> conversion using Fe/AC catalysts.

(Lines show trends)

**Figure 7.-** Evolution of aromatic intermediates and organic acids upon CWPO of phenol using Fe/AC catalysts.

## Tables.

**Table 1.** Porous structure of the Fe/AC catalysts.

**Table 2.** Amounts of CO and CO<sub>2</sub> released from the catalysts and activated carbon by TPD.

(AC200, AC300 and AC-HNO<sub>3</sub> correspond to the activated carbon support calcined at 200°C, 300°C and treated with HNO<sub>3</sub> respectively)

**Table 3.** Results of the deconvolution of CO<sub>2</sub> TPD spectra.

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**Table 1.** Porous structure of the Fe/AC catalysts.

<b>Calcination temperature (°C)</b>	<b>S<sub>BET</sub> (m<sup>2</sup>/g)</b>	<b>A<sub>external</sub> (m<sup>2</sup>/g)</b>	<b>V<sub>micro</sub> (cc/g)</b>	<b>V<sub>meso</sub> (cc/g)</b>	<b>V<sub>Macro</sub> (cc/g)</b>	<b>V<sub>Total</sub> (cc/g)</b>	<b>Fe (%)</b>
150	966	75.6	0.390	0.125	0.108	0.624	4.1
200	988	72.0	0.379	0.120	0.104	0.603	4.1
250	1037	81.7	0.416	0.133	0.114	0.660	4.2
300	1042	75.6	0.429	0.128	0.106	0.663	3.6

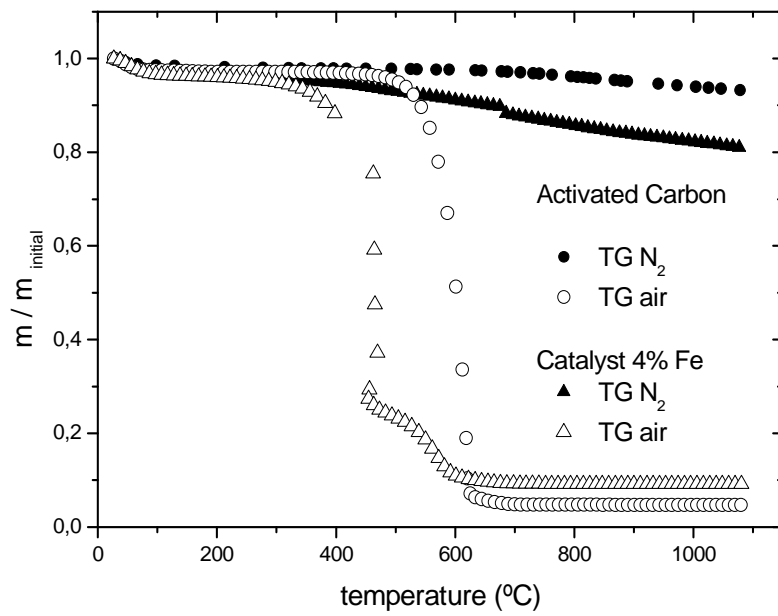
**Table 2.** Amounts of CO and CO<sub>2</sub> released from the catalysts and activated carbon by TPD. (AC200, AC300 and AC-HNO<sub>3</sub> correspond to the activated carbon support calcined at 200°C, 300°C and treated with HNO<sub>3</sub> respectively)

Catalyst	$\mu\text{mol CO/g}$	$\mu\text{mol CO}_2/\text{g}$	$\text{pH}_{\text{slurry}}$
Fe/AC-150	2187.1	901.2	4.41
Fe/AC-200	2058.2	851.5	4.27
Fe/AC-250	2402.9	898.3	4.11
Fe/AC-300	2736.4	862.6	3.95
AC	430.4	70.4	7.55
AC200	499.9	100.2	7.34
AC300	886.7	58.2	6.88
AC-HNO <sub>3</sub>	2095	865.1	3.15

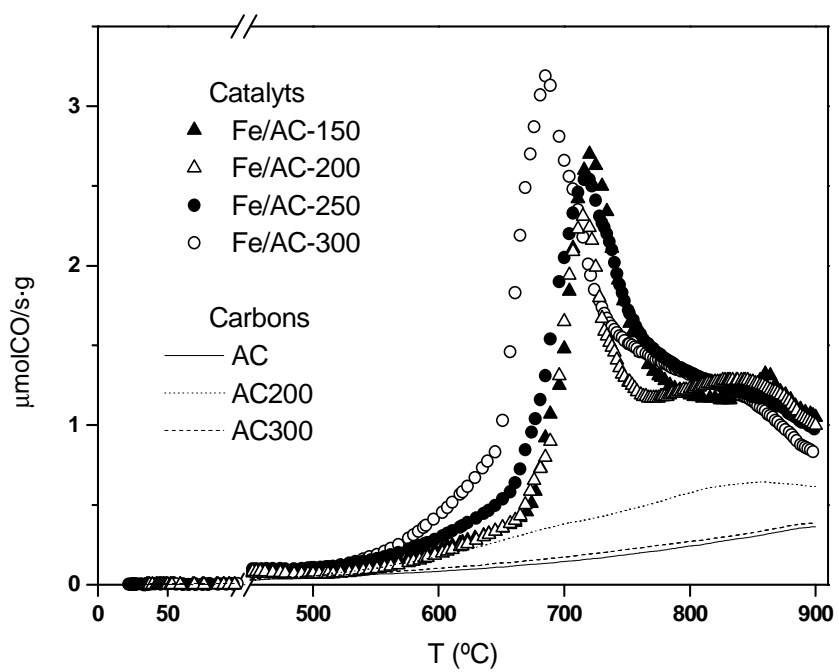


**Table 3.** Results of the deconvolution of CO<sub>2</sub> TPD spectra.

Peak	Fe/AC-150		Fe/AC-200		Fe/AC-250		Fe/AC-300		AC-HNO <sub>3</sub>	
	%	μmol/g	%	μmol/g	%	μmol/g	%	μmol/g	%	μmol/g
<b>Carb. acid(1)</b>	12.7	<b>114.8</b>	3.1	<b>26.7</b>	2.1	<b>18.5</b>	4.3	<b>36.8</b>	23.3	<b>201.6</b>
<b>Carb. acid(2)</b>	6.9	<b>62.1</b>	7.3	<b>62.5</b>	7.4	<b>66.2</b>	4.9	<b>41.9</b>	22.9	<b>198.1</b>
<b>Carb. Anhydride(3)</b>	50.9	<b>458.3</b>	56.9	<b>485.1</b>	45.4	<b>407.5</b>	30.3	<b>261.4</b>	46.0	<b>398.0</b>
<b>Lactone(4)</b>	26.2	<b>235.9</b>	29.6	<b>251.8</b>	40.1	<b>360.2</b>	50.2	<b>432.8</b>	7.8	<b>67.5</b>
<b>Iron contribution (5)</b>	3.3	<b>30.1</b>	2.9	<b>25.4</b>	5.1	<b>45.9</b>	10.4	<b>89.7</b>	-	-
<b>Sum</b>		<b>901.2</b>		<b>851.5</b>		<b>898.3</b>		<b>862.6</b>		<b>865.1</b>

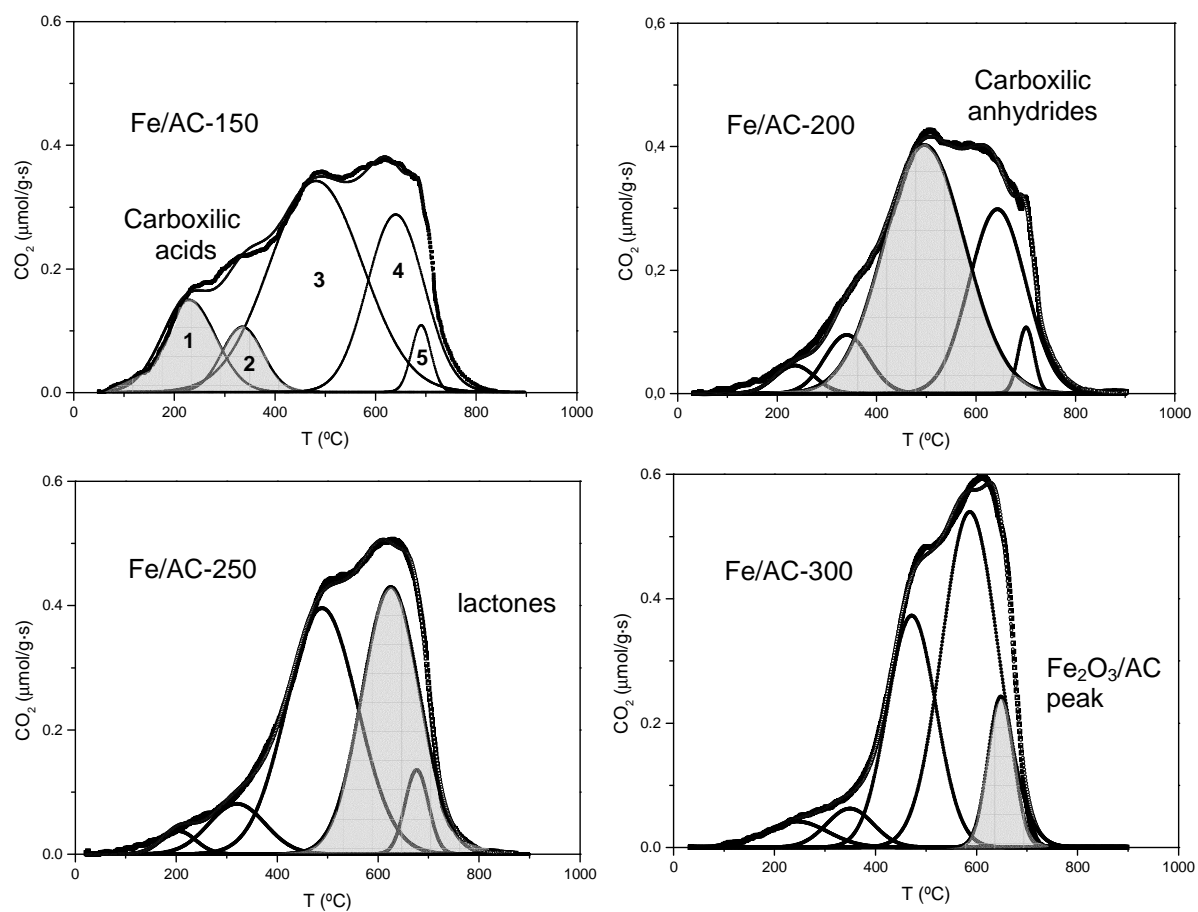


**Figure 1.-** TG curves of AC and Fe/AC under N<sub>2</sub> and air atmosphere.



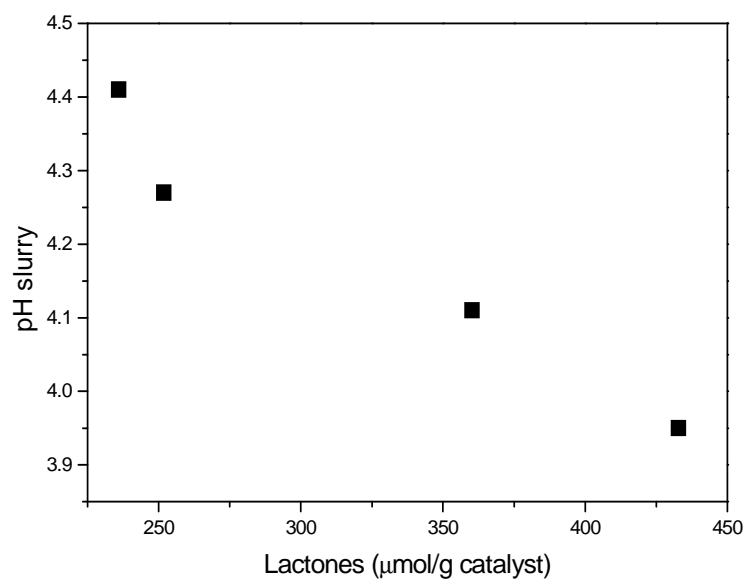
**Figure 2.-** CO profiles from TPD of the catalysts and the activated carbon support.

## 6. Figure

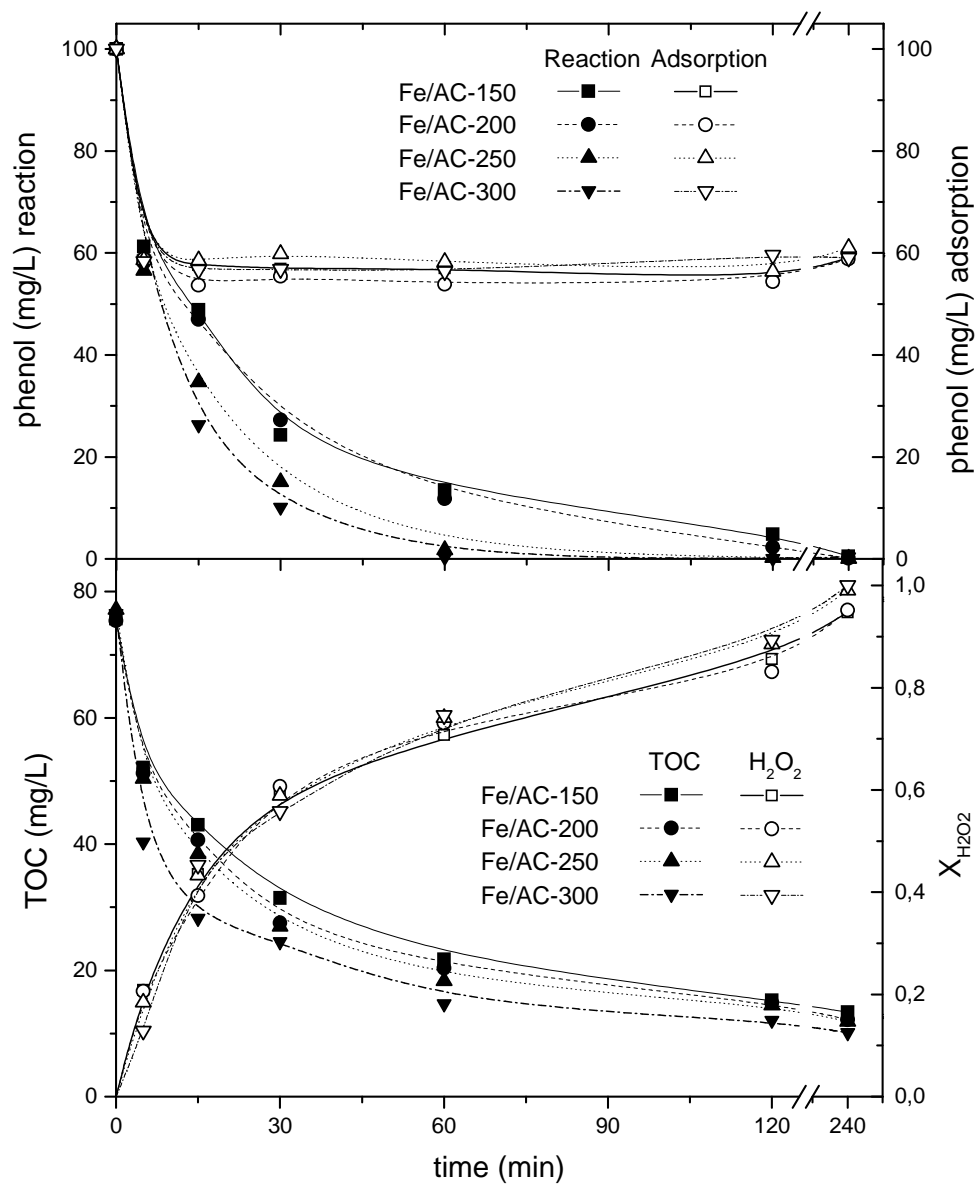


**Figure 3.-** Deconvolution of the CO<sub>2</sub> profiles from TPD of the Fe/AC catalysts.

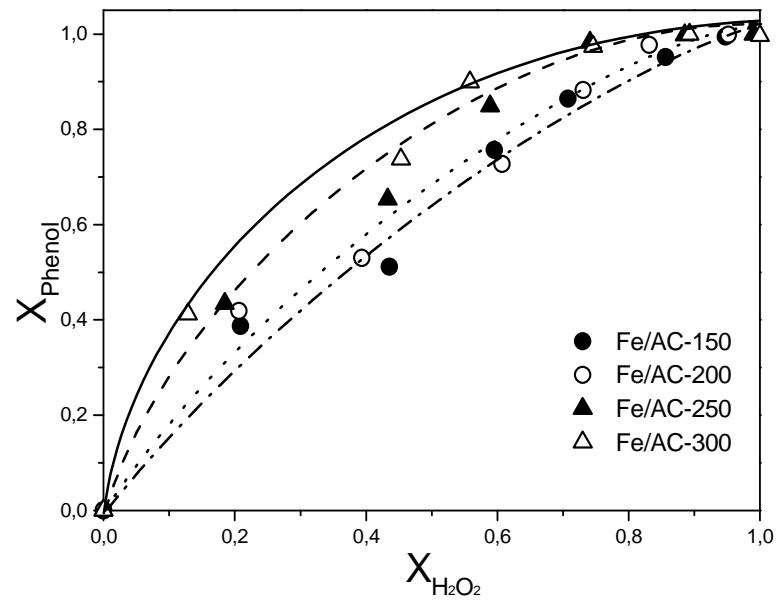
[•] experimental data; [-] sum of individual peaks and [···] individual peaks.



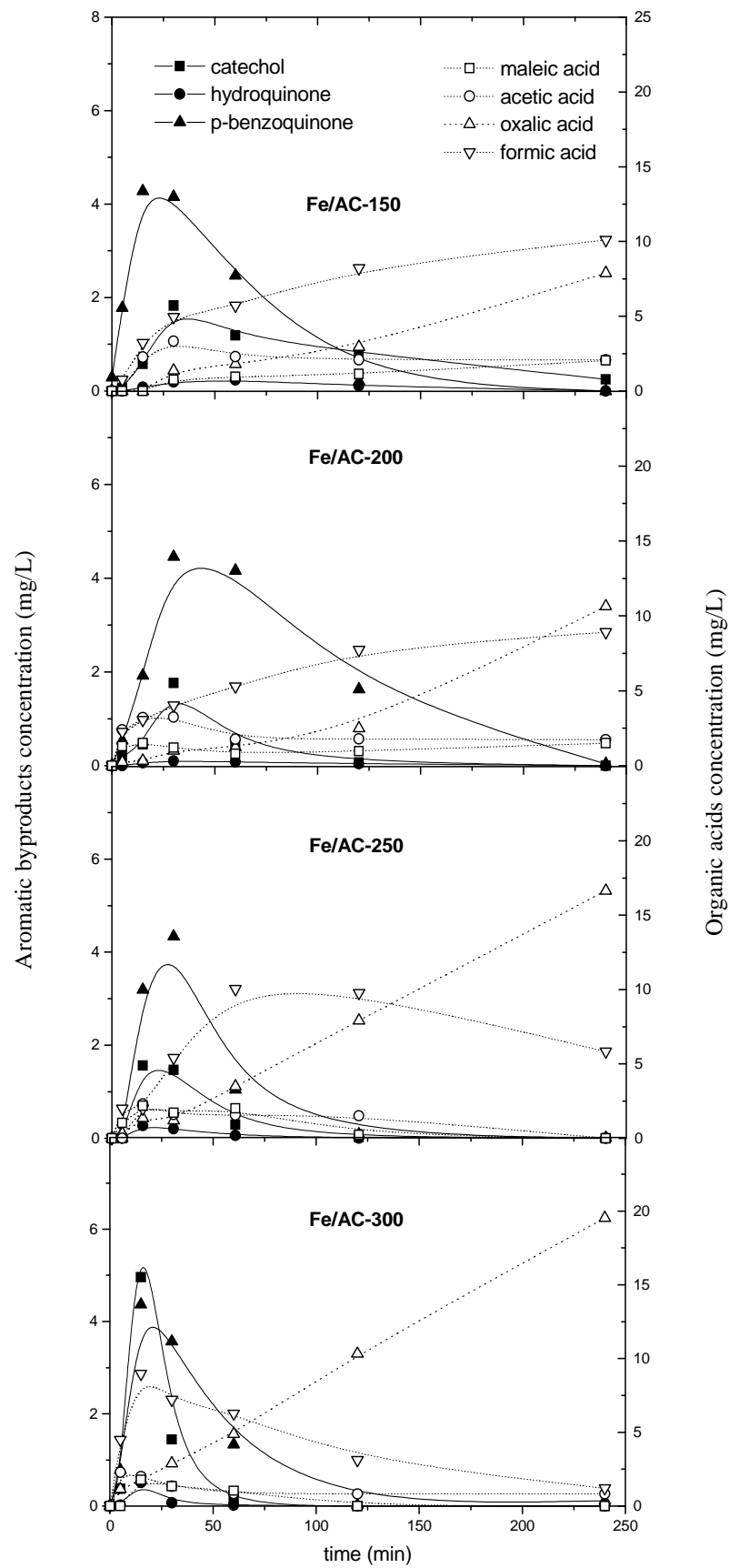
**Figure 4.-** Relation between  $\text{pH}_{\text{slurry}}$  and the content of lactone groups in Fe/AC catalysts.



**Figure 5.-** Evolution of phenol, TOC and  $H_2O_2$  upon CWPO of phenol with the Fe/AC catalysts.



**Figure 6.-** Phenol conversion *versus*  $\text{H}_2\text{O}_2$  conversion using Fe/AC catalysts. (Lines show trends)



**Figure 7.-** Evolution of aromatic intermediates and organic acids upon CWPO of phenol using Fe/AC catalysts.