

Modification of activated carbon hydrophobicity by pyrolysis of propene

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#### ABSTRACT

The chemical nature of the surface of a granular activated carbon has been modified by heat treatment under nitrogen at 1000°C followed by pyrolysis of propene in the 300-600°C temperature range. Cracking of propene produces deposits of coke on the more reactive sites of the carbon surface, those produced after the decomposition of the original oxygen surface groups along the previous heat treatment. The process leads to an initial reduction in the number of oxygen surface groups and in the capacity of the carbon to chemisorb oxygen. The further growth of the carbon deposit in the interior of the particle decreases the width of the micropore entrance, which is paralleled by the coating of the external surface of the particle. The reduction in the number of active sites of the carbon leads to a decrease in the enthalpy of immersion into polar liquids such as water and ethylenediamine, the carbon becoming more hydrophobic than the original.

*Keywords:* activated carbon, propene pyrolysis, immersion enthalpy, water adsorption.

## **1. Introduction**

Activated carbon is constituted by blocks of small size imperfect graphene layers randomly bound into a three-dimensional network, the free spaces within it constituting the pores [1,2]. The surface of the carbon is consequently rather hydrophobic since the interaction with water molecules is weak. However, activated carbon always contains small amounts of oxygen that increase the affinity towards water. This oxygen is bound to the unsaturated carbon atoms located on the edges of the graphene layers thus leading to a variety of oxygen surface groups. These surface groups are not distributed homogeneously on the surface of the carbon, but they are mainly concentrated on the sites where the blocks of graphene sheets crosslink.

Heat treatment of the activated carbon under nitrogen, hydrogen or vacuum [3-5] reduces the number of oxygen surface groups because their thermal stability is limited. For instance, a carboxylic group decomposes at 300°C to evolve as CO<sub>2</sub> and H<sub>2</sub>O, whereas a carbonyl group decomposes at 900°C with the evolution of CO [6]. The evolution of these molecules leaves behind unsaturated carbon atoms which, when in contact with air, chemisorb oxygen, thus leading to the formation of new oxygen surface groups. Consequently, the formation of these oxygen surface groups has to be reduced to a minimum in applications where the interaction of the carbon with polar molecules has to be reduced or in those in which an activated carbon with low affinity for water is a need because water can compete for the adsorption sites and reduce the

adsorption capacity for the molecules to be retained (e.g. adsorption of toxic gases on gas masks [7]). An approach that can be used would be to bind the unsaturated carbon atoms to other atoms or groups of atoms less electronegative than oxygen. In this particular work the radicals produced in the cracking of propene are used to stabilise the carbon sites produced along the decomposition of oxygen surface groups.

## **2. Experimental**

A low ash granular activated carbon, F, has been prepared following the method used for the preparation of carbon D-52 [8], carbonization of olive stones under nitrogen at 850°C and subsequent activation with carbon dioxide at 825°C until a burn off of 52% was reached. This carbon F has been heat treated under nitrogen until 1000°C (heating rate, 5°C/min) and cooled down to a temperature previously designed between 300 and 600°C, when the flow of nitrogen (100 mL/min) was changed to the equivalent flow of propene. After one hour under propene the sample was cooled down under a flow of nitrogen. A reference carbon, FN, was prepared under the same experimental conditions, but omitting the propene stage. Table 1 includes the nomenclature of the carbons prepared, where the temperature of propene treatment is indicated. The adsorption isotherms for nitrogen at -196°C and carbon dioxide at 0°C have been obtained in a home-built volumetric system equipped with two pressure transducers (0.0-1.1 kPa and 0.0-0.1 MPa). The carbons were outgassed at  $1 \times 10^{-4}$  Pa and 250°C for 4 hours. The volume of micropores has been determined applying the Dubinin-Radushkevich equation and the values obtained,  $V_0(\text{N}_2)$  and  $V_0(\text{CO}_2)$ , correspond to the volume of micropores with diameters smaller than approximately 2 nm and 0.7 nm, respectively [8,9].

Temperature Programmed Decomposition (TPD) was used to determine the profiles for CO<sub>2</sub> and CO. 100 mg of carbon were heat treated under a flow of helium (50 mL/min) using a heating rate of 10°C/min up to 1000°C, a mass spectrometer (Omnistar TM Baltazar) being used to monitor the CO<sub>2</sub> and CO evolved.

A Tian-Calvet immersion calorimeter (Setaram CD80) was used to determine the enthalpy of immersion of each carbon at 29°C into three liquids of different polarity: benzene, ethylenediamine and water. The experimental system used was described in a previous work [10].

The adsorption isotherms for water at 25°C have been determined in a volumetric automatic system (Omnisorb 100CX) thermostated at 41°C, the sample being placed in a bulb set at 25°C. Samples were previously outgassed at 150°C for 4 hours.

Table 1

### **3. Results and discussion**

Table 1 shows the increase in mass of the carbon samples along the treatment under propene. There is a loss of 6% in weight when carbon F is treated at 1000°C under nitrogen, as a consequence of the decomposition of oxygen surface groups. The resulting carbon, FN, is the one used as reference for this work.

There is a slight increase of weight in carbon FN when subjected at 300°C under propene, the increase being more noticeable for temperatures above 450°C. The amount of carbon deposited on carbon FN at 500°C is high enough

to cover the majority of the carbon particle, as shown in Figure 1; it is evident that the structure of the carbon deposit at 500°C is completely different to that produced at 300°C (since the deposit on FN300 is only 1 wt%, the structure is very similar to that of the starting FN carbon).

#### Figure 1

Carbon F is essentially microporous, the adsorption isotherm for nitrogen at -196°C being a clear type I. The heat treatment under propene does not produce large changes in the shape of the adsorption isotherm, except in the region of low relative pressures corresponding to small pores. For this reason the discussion is to be centred on the volume of micropores, the values of which have been plotted as a function of the temperature used in the propene treatment in Figure 2. The following aspects can be highlighted in this figure: i) the decrease observed from carbon F to FN (both in the volume axis) is small and it indicates that the loss of oxygen surface groups along the heat treatment at 1000°C does not affect much the porosity of the carbon; ii) no important changes in microporosity are observed up to 450°C and the micropore volumes for carbon FN300 and FN are very similar; iii) the carbon deposit produced along the pyrolysis of propene leads to a narrowing of the micropores since the differences among  $V_0(\text{N}_2)$  –volume of total microporosity- and  $V_0(\text{CO}_2)$  volume of narrow microporosity-becomes smaller.  $V_0(\text{CO}_2) \gg V_0(\text{N}_2)$  for 600°C because the entrance of the micropores become so narrow –near the molecular dimension of the adsorbate- that the diffusion of nitrogen is restricted due to the low temperature of adsorption, much lower than for the adsorption of  $\text{CO}_2$  [9].

## Figure 2

The micropore volume values in Figure 2 are on a weight basis. If one assumes that the deposited carbon is non-porous the mass increase in respect to carbon FN will decrease the actual volume of micropores. When the values of Figure 2 are expressed as  $\text{cm}^3/\text{g}$  of carbon free of deposit (using the values of  $\Delta m$  in Table 1) the differences in the  $V_0(\text{N}_2)$  values within the series become smaller, but there is still an abrupt decrease as from  $450^\circ\text{C}$ . However, the values of  $V_0(\text{CO}_2)$  are kept constant with the temperature of deposit. These results suggest that the carbon deposit is taking place mainly on the edges of the blocks of graphene layers defining the entrance of the micropores; the deposit decreases the size of the entrance of these micropores. However, the deposit is not taking place on the layers of graphene constituting the walls of the micropores, because this would reduce the width of the micropores and even close the narrow ones, thus decreasing  $V_0(\text{CO}_2)$  to a larger extent than  $V_0(\text{N}_2)$ . Consequently, the deposit from the propene pyrolysis can be used to control the microporosity of activated carbons and even to limit the access of molecules to the micropores, as it has been described for the pyrolysis of ethylene [11] and benzene, the latter leading to the production of carbon molecular sieves [12,13] since the carbon deposit produces a uniform narrowing of the micropore entrance.

Figure 3 includes the profiles for  $\text{CO}_2$  and  $\text{CO}$  evolved along the TPD experiments for carbons F and FNP300. Two peaks are seen for  $\text{CO}_2$ , one not well defined covering a wide range of temperatures ( $100\text{-}500^\circ\text{C}$ ) and a second one, large and better defined, with a maximum at around  $650^\circ\text{C}$  and attributed

to the decomposition of lactone groups [6]. There is only one asymmetric peak for CO, starting at 600°C and with a maximum at around 900°C. Most of the CO evolved is due to the decomposition of carbonyl and quinone groups. The heat treatment under propene does not change the shape of the profiles although the peaks are lower. In fact, no peaks for CO are detected at 500 and 600°C.

### Figure 3

The amount of groups decomposing to CO and CO<sub>2</sub> has been determined by calculating the area under the curves and the values have been plotted in Figure 4 as a function of the mass increase due to the propene pyrolysis.

Carbon F produces 200 μmol/g of CO<sub>2</sub> and 525 μmol/g of CO, values which are lower than those found in oxidised or chemically activated carbons [4,14]; this is not surprising since carbon F was prepared at a high temperature, 825°C, and the CO<sub>2</sub> groups and most of CO groups have been formed as a consequence of the chemisorption at atmospheric oxygen after the preparation. When the temperature is increased to 1000°C, carbon FN, the gas evolved decreases to 157 μmol/g for CO<sub>2</sub> and 362 μmol/g for CO. The decrease continues along the treatment under propene, more importantly for the CO groups. As from 450°C ( $\Delta m = 5\%$ ) the decrease is small and linear and it is mainly due to the mass gain of the carbon; if the value was referred to the weight of carbon free of deposit the amount of CO<sub>2</sub> or CO groups is the same for carbons treated between 450 and 600°C. This means that the oxygen content of the carbon decreases up to 450°C and is kept constant at higher temperatures, even although the amount of carbon deposited is much larger. This is a confirmation

of the deposit of carbon on the sites where the unsaturated carbon atoms are formed upon decomposition of the oxygen surface groups at 1000°C, before the carbon is in contact with propene. A small amount of carbon is enough to saturate the bonds with the active carbon atoms of the surface. Thus, saturation occurs at around 450°C, when the amount of oxygen surface groups decreases to around 100  $\mu\text{mol/g}$ . This value is mainly due to the oxygen taken up by the new carbon deposit, which has a lower capacity to chemisorb oxygen than the original carbon.

#### Figure 4

It has been described that the pyrolysis, when using a flow of pure propene and temperatures below 600°C, is occurring through cracking and polymerization reactions, thus producing hydrogen, methane, ethene and polymeric carbon [15]. The mechanism involved, through a chain of free radicals, starts by cracking propene to the radicals allyl ( $\text{C}_3\text{H}_5\cdot$ ) and hydrogen ( $\text{H}\cdot$ ) and propagates through reaction of propene and the radical allyl to produce a growing polymer and radicals  $\text{H}\cdot$ . At the same time, the radical  $\text{H}\cdot$  may react with propene to produce propyl ( $\text{C}_3\text{H}_7\cdot$ ), a radical that decomposes to ethene ( $\text{C}_2\text{H}_4$ ) and methyl ( $\text{CH}_3\cdot$ ). Any of these radicals, from  $\text{H}\cdot$  to the polymeric ones, may react with the carbon atoms left on the carbon surface after the decomposition of the original oxygen surface groups, which then become stabilised, thus avoiding the chemisorption of oxygen when in contact with air and, consequently, inhibiting the formation of new surface groups.



These cracking and polymerisation reactions occur both in gas phase and on the carbon surface [16]. There is first diffusion and then chemisorption of the reactive species on the active sites of the carbon, mainly placed at the edges of the basal planes and the coke carbon grows there. Pyrolysis in gas phase leads to the formation of large aromatic polycyclic hydrocarbons as intermediates of the carbon formation, which are adsorbed and act as growing nuclei on the surface of the solid. At low temperature, 300°C in this case, the concentration of radicals is so low that the diffusion to the interior of the carbon particle and reaction on active sites predominated, but at 500°C the reactions in gas phase are much faster and the growth of the deposit on active sites is complemented by the formation of polyaromatic hydrocarbons in gas phase that are physically adsorbed on the external surface of the particle.

Carbons F, FNP300 and FNP500 have been treated for 4 h at 300°C under a flow (100 mL/min) of air, this producing an increase in mass of 2.8, 0.7 and 0.5 wt%, respectively, due to the chemisorption of oxygen. Since the more important differences are found for carbons F and FNP300, one can deduce that the small amount of carbon deposited (1wt%) is enough to stabilise the active sites of the carbon. Consequently, the oxidation of the propene-treated carbon must occur through the chemisorption of oxygen on the new carbon material since the values for FNP300 and FNP500 are very similar.

The TPD profiles for the carbons treated in air  $F_{(a)}$  and  $FNP300_{(a)}$  have been included in Figure 3. Oxidation of carbon F produces some modification in the shape of the profiles, but the more important change is the increase in the amount of groups, especially those evolving as CO. This affinity for oxygen decreases when the carbon is treated under propene since the increase from

FNP300 to FNP300<sub>(a)</sub> is small in respect to the differences between F and F<sub>(a)</sub>. One may conclude that the treatment with propene prevents the chemisorption of oxygen (and, very probably, slows down the aging of the carbon) and that the groups evolving as CO are mainly those stabilised by propene pyrolysis, as shown in Figure 4.

In order to test the decrease in the interaction between polar molecules and the surface of the carbon produced by the reduction in the amount of oxygen surface groups, the enthalpy of immersion of the carbons into three liquids with different polarity (benzene, ethylenediamine and water) has been determined and the values are provided in Table 1. Carbon FNP600 has not been considered because the values of enthalpy are very much influenced by the access of the three molecules into the porosity, which is restricted very differently. The tendency of immersion enthalpy into benzene with the temperature of propene treatment is similar to that described for V<sub>0</sub>(N<sub>2</sub>): small change when comparing F and FN and a clear decrease when the temperature is above 450°C. Something similar occurs for the immersion into ethylenediamine and water, except that the decrease observed when comparing F and FN is not so significant.

#### Figure 5

To be able to separate the effect of porosity and chemical nature of the carbons surface, the values of enthalpy in Table 1 have been normalised by the BET surface area (N<sub>2</sub> at -196°C) and this areal enthalpy has been plotted in Figure 5 as a function of the amount of oxygen surface groups. The values for benzene

do not change with the number of groups, thus indicating that the decrease seen in Table 1 is due to the decrease produced in the volume of micropores and surface area. Consequently, the results confirm that the chemical nature of the carbon does not affect the interactions with a non-polar molecule such as benzene, this not being the case for ethylenediamine or water[17-19]. There is in both cases a decrease of the order of 15%, which is mainly due to the decrease in groups evolving as CO, those affecting to a larger extent the enthalpy of immersion in water [17].

## Figure 6

Figure 6 includes, as typical examples, the adsorption isotherms of water at 25°C on three activated carbons, F, FNP300 and FNP500. The isotherms are of type V and they are similar to those published for activated carbons containing a certain amount of oxygen surface groups [20,21]: the uptake of water at low relative pressures is almost nil and a significant uptake occurs only at relative pressure above 0.5. As it is well known [20-22] the adsorption of water is initiated on active sites (the so-called primary active centres) and it proceeds through the formation of water clusters which coalesce by hydrogen bonding to fill the porosity of the adsorbent at high relative pressures. Consequently, the decrease observed in the amount of water adsorbed between F and FNP500 is due to the porosity whereas the one observed at low relative pressures (see the insert in Figure 5) is due to the lower number of primary active centres of adsorption in the propene-treated carbon. Carbon FNP300 exhibits a lower capacity than carbon F to retain humidity at low relative pressures, but the

differences above  $P/P_0 > 0.5$  are negligible because the porosity is being filled, the volume of which is similar in both carbons.

A way to quantify the differences in uptake at low relative pressures is to determine the number of primary active adsorption centres,  $a_0$ ; such values can be obtained from the application of the Dubinin-Serpinsky equation to the adsorption isotherm of water [23]. The values of  $a_0$  (Table 1) decrease with the intensity of the treatment in propene since this produces larger amount of deposit carbon, with a structure different to that of the original carbon (F or FN), this leading to a different adsorption of water [16]. This effect is more clearly seen in FNP500, for which an increase in weight of 13wt% of the new carbon material produces a decrease in  $a_0$  near 58% in respect to carbon F. However, the more important changes occur in the first carbons of the series, where the loss of oxygen is more important. Thus, only 1% of carbon deposit on FNP300 is enough to produce a decrease of 35% in the primary centres of adsorption, without appreciable decrease in the volume of micropores.

#### **4. Conclusions**

The thermal treatment of a granular activated carbon under propene (300-600°C) produces deposits of carbon material in both the interior and exterior surface of the carbon particle. This carbon goes to the active sites in the interior of the particle, thus reducing the number of oxygen surface groups, especially those decomposing to CO. These active sites are located at the entrance of the micropores and the growing of the deposit progressively narrows the microporosity. Best results were obtained at 300°C since a small amount of carbon deposit decreases to half the number of oxygen surface groups, without appreciable changes in the volume of micropores. Furthermore, the active sites

become stabilised since the capacity for the chemisorption of oxygen is reduced. The decrease in the amount of oxygen surface groups weakens the interaction of the carbon surface with polar molecules, a decrease in the enthalpy of adsorption in water and ethylenediamine being observed, without a change in the enthalpy into benzene, a non-polar liquid. The hydrophobicity of the carbon also increases and a treatment under propene at 300°C reduces appreciably the amount of water adsorbed at relative pressure below 0.5.

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## Figure captions

Figure 1. SEM micrographs of activated carbons. a) FNP300; b) FNP500.

Figure 2. Total,  $V_0(\text{N}_2)$  and narrow,  $V_0(\text{CO}_2)$  micropore volume of carbons as a function of the temperature of propene pyrolysis.

Figure 3. TPD profiles for a)  $\text{CO}_2$  and b)  $\text{CO}$  evolved from some activated carbons.

Figure 4. Evolution of oxygen surface groups decomposed as  $\text{CO}_2$  and  $\text{CO}$  as a function of with the mass increase due to propene pyrolysis.

Figure 5. Relationship between the areal immersion enthalpy and oxygen surface groups.

Figure 6. Water adsorption isotherms for some activated carbons.

## **Table captions**

Table 1. Some characteristics of activated carbons

Table 1. Some characteristics of activated carbons

Activated Carbon	$\Delta m$ (%)	$\Delta H_i$ (J/g)			$a_0$ ( $\mu\text{mole/g}$ )
		$\text{C}_6\text{H}_6$	$\text{C}_2\text{H}_8\text{N}_2$	$\text{H}_2\text{O}$	
F	-	152	222	41	216
FN	0	153	206	37	177
FNP300	1	149	196	35	140
FNP400	3	139	182	32	135
FNP450	5	130	170	28	125
FNP475	9	116	145	24	105
FNP500	13	100	117	22	90
FNP600	29	-	-	-	-

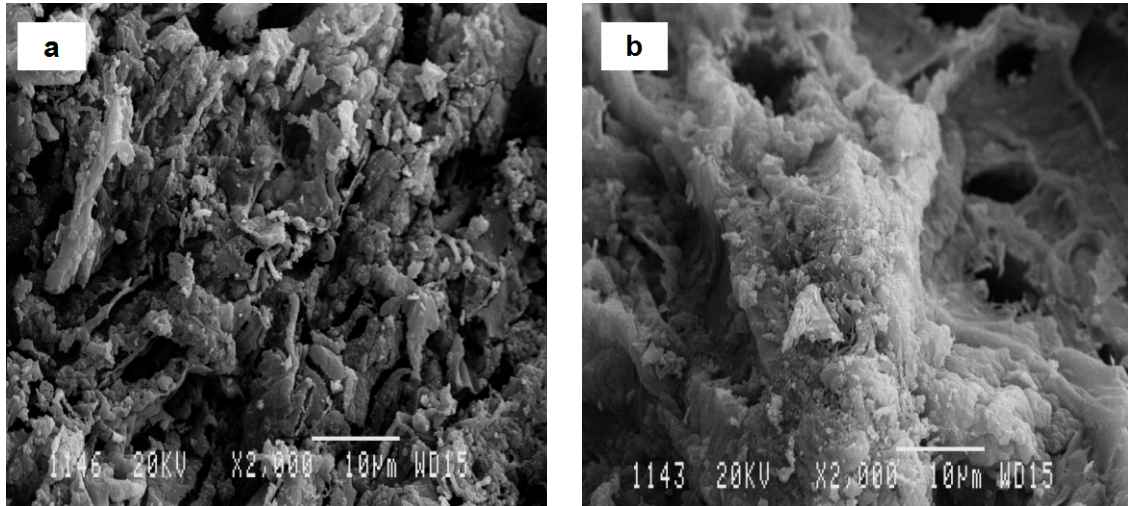


Figure 1

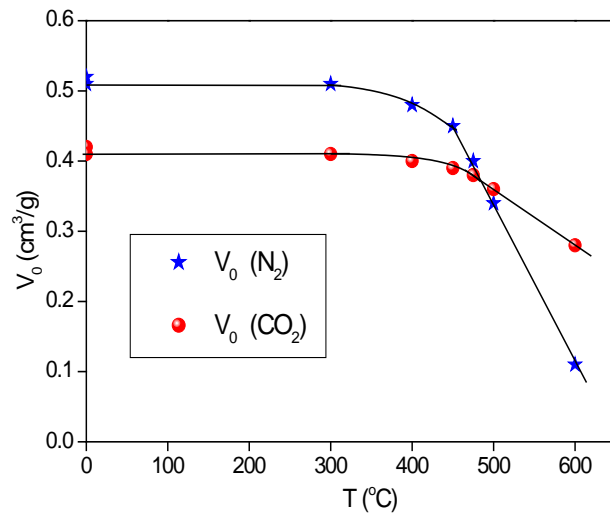


Figure 2.

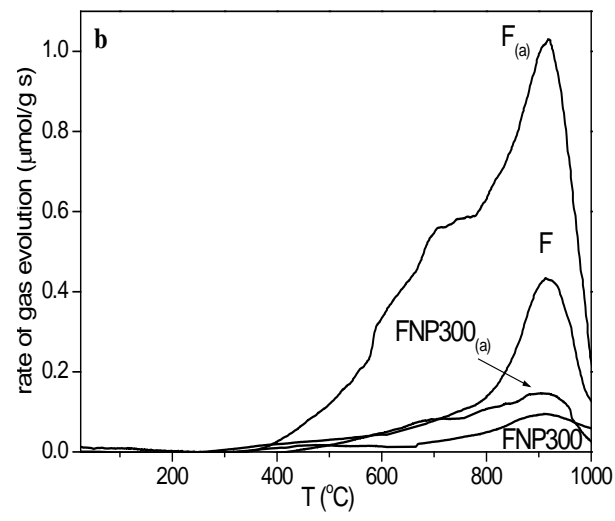
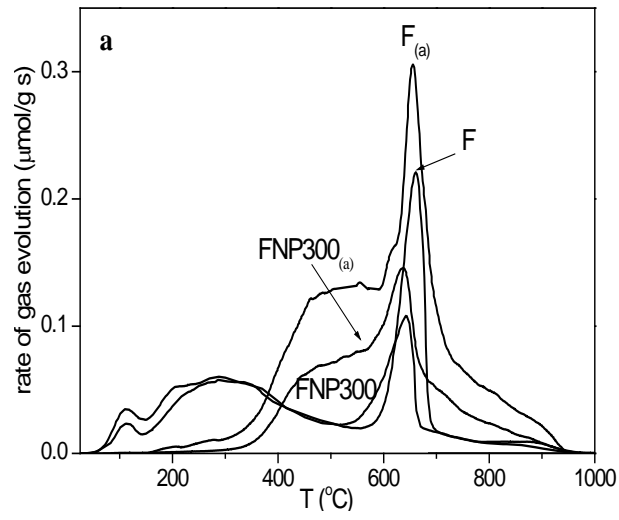


Figure 3.

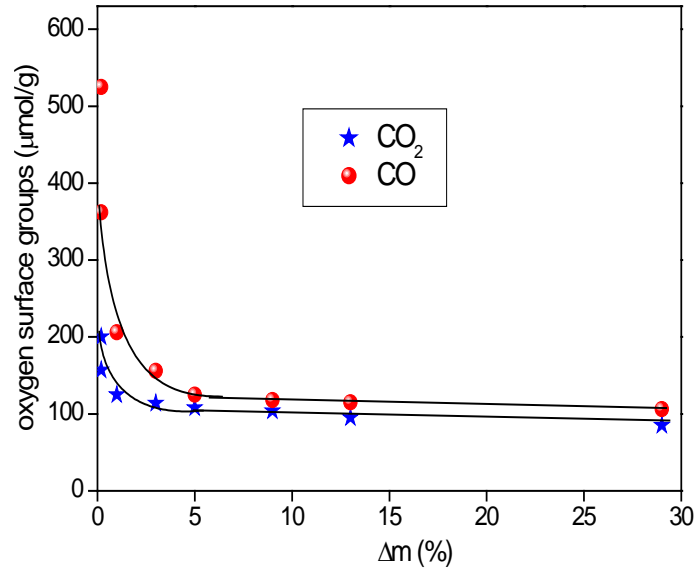


Figure 4.

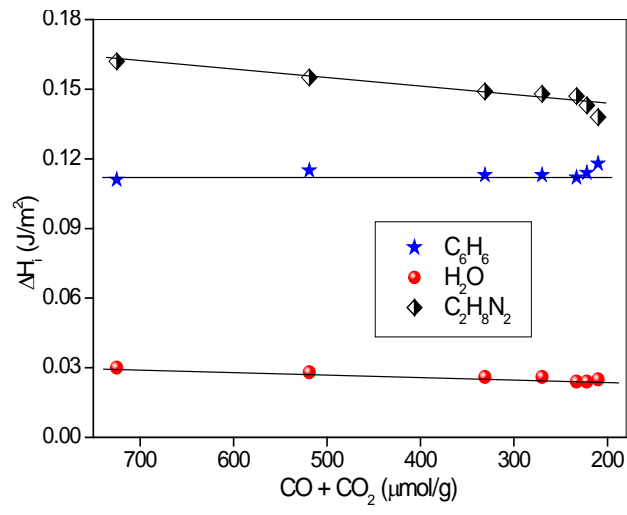


Figure 5.



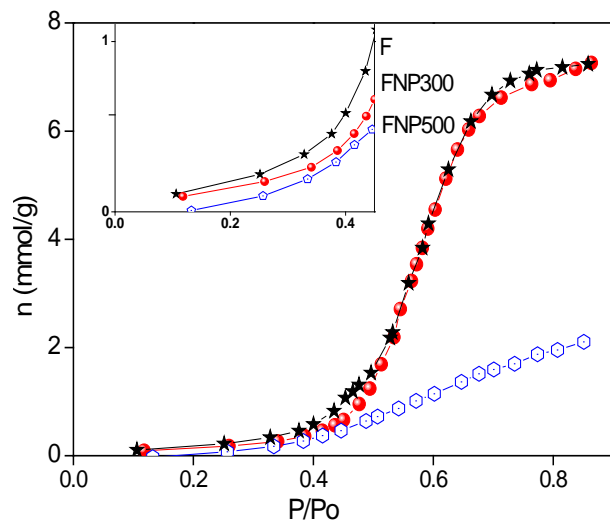


Figure 6.