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Surface acid functionalization of activated carbons and its influence in the copper-support interactions.†

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Abstract: Two sets of commercial activated carbon (AC) were surface functionalized by an acid treatment using a) strong acid HNO_3 (AC80 y AC90) and b) a weak acid $C_6H_8O_7$ (ACC). The effect of the functionalization on the surface chemistry and structure of the AC samples was studied by means of TGA-DSC, XRD, FT-IR, N_2 adsorption, TPD and tested in the decomposition of isopropanol. The catalysts were synthesized by the deposition of copper using a recirculation impregnation method. Metal dispersion, average size of metallic domains and metal-support interactions were correlated with the surface functionalization by using XRD, S_{BET}, SEM-EDS, AAS, N_2O. The acid treatments showed no effect on the crystal structure, however, increments in the acid/basic site concentration and the surface oxygen-containing functional groups (OFGs) content were observed, mainly in the AC80 and AC90 samples. BET surface measurements show a small decrease due to OFG and/or copper incorporation. Copper distribution was uniform and its content shows a direct correlation with the OFG concentration. XRD reveals the presence of Cu° and Cu_2O in the Cu/AC80 and Cu/AC90 samples, possibly associated with an auto-reduction process assisted by the OFGs near the metallic centers. Cu/AC and Cu/ACC XRD patterns show no evidence of copper phases, due to low content and high dispersion. The HNO_3 treated supports showed the higher dispersions and the smallest metallic domain sizes (30% - 3.3 nm Cu/AC80 and 22% - 4.5 nm Cu/AC90) while Cu/ACC showed a 17% dispersion and an average metallic domain size of 5.8 nm. The presence of surface OFGs promotes: selective adsorption of Cu, increase in the metal dispersion, decrease of domain size and the presence of alternative copper-derived phases, showing an increased metal-support interactions.

Keywords: Activated Carbon; Acid functionalization; Copper; Metal-support interaction.

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1. Introduction

Metals have been deposited in several supports (i.e. Carbon materials, metallic oxides and polymeric supports, among others) Specially, carbon supports have been frequently used in the catalysis field due to its specific properties like acid and basic media resistance, thermal stability, metal recovery by combustion, low cost, and high flexibility in the pore structure and surface chemistry modification regarding the requirements of diverse catalytic chemical reactions.

The nature and concentration of surface functional groups is a relevant topic since it can strongly influence the anchoring of synthetic precursors or active phases in the synthesis of supported catalysts, or in a direct manner, they can act as active sites for catalytic reactions. Oxygenated Functional groups (OFGs) like carboxylate, carbonyl, phenol and lactone are the most relevant ones, since they can be spontaneously obtained by air exposure and its concentration can be modified by thermal and oxidative treatments [1]. An increase in the surface OFGs amount can be induced by the treatment with oxidizing agents like HNO_3, H_2O_2, H_2SO_4 and citric acid. Among them, HNO_3 shows the best performances, probably associated with its strong acid nature and high oxidizing potential. The degree of functionalization depends on the acid used, temperature, acid concentration and treatment time [2].

One of the actual goals in the catalysis field is the design of selective-low cost catalysts. In the particular case of partial oxidation reactions, noble-metal based systems have shown the best results [3]. However, their high cost has focus the attention on transition metals and transition metal oxides based systems, such Cu and Ni ones, with no appreciable conversion decreases [4]. Particularly, copper has been applied to C-H breaking chemical reactions, like partial or selective oxidation reactions.

In this paper, monometallic Cu/ACx catalysts have been synthesized and characterized in order to get information and a better understanding on the effect of the OFGs presence and nature in the content and dispersion of surface copper species over AC and ACx samples. Moreover, the structural and surface chemical properties of the ACx samples were studied and correlated with the operational parameters of the functionalization process.

2. Experimental

2.1. Supports and Catalysts Preparation

Commercial AC were treated by two different methods: a) using HNO_3 (60 %) at T = 80 °C(AC80) and 90 °C (AC90) and b) citric acid (20%) at T = 60 °C (ACC). The AC were suspended in acid solutions with magnetic stirring; after 2 h of reaction, the ACs were washed with distilled water and dried in a conventional oven at 60 °C for 45 minutes. Copper was surface deposited by a recirculation impregnation method of half saturation point $Cu(NO_3)_2.3H_2O$/ethanol solution. The impregnated supports were washed several times with ethanol and distilled water, then dried at 60 °C for 45 minutes and finally calcined at 450 °C for 3 hours in flowing Argon.

2.2. Supports and Catalysts Characterization

The AC was studied by using TGA/DSC, and the supports and catalysts by means of XRD, SEM, S_{BET}, FT-IR, isopropanol decomposition test, TPD, AAS and N_2O dissociative chemisorption.

3. Results and discussion

Since carbonous materials tend to decompose, in presence of oxygen, at different temperatures depending on its crystal structure, and taking into account subsequent synthesis steps (decomposition of metallic precursors), thermal stability was tested in flowing air by TGA-DSC. TGA-DSC curves showed a first weight loss of 5% between 38-70 °C associated with surface water evaporation, and a second exothermic event between 460-665 °C corresponding to the thermal decomposition of AC (90 % of the initial weight loss) [5]. A limit temperature of 600 °C was selected for thermal treatments in non-oxidizing atmosphere and to carry out the catalysts synthesis.

Surface functionalization was carried out using acids of different strengths. Two temperatures were tested for HNO_3 (80 and 90 °C) and one temperature for citric acid (60 °C), in order to study the degree of functionalization and the distribution of the different OFG surface species. Both effects may induce changes in structure and surface properties of the AC, particularly specific surface area (S_{BET}) and surface acid-base properties.

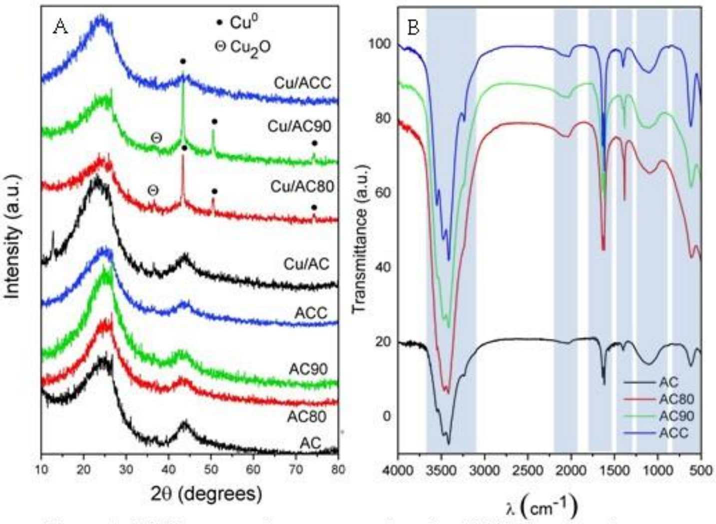

Figure 1. A- XRD patterns for supports and catalyst. B- FT-IR spectra of supports.

XRD patterns of the samples are shown in Figure 1A, with no appreciable changes in the structure of the AC support after functionalization. Acid-treated samples show a drop in the specific surface area (S_{BET}) of a 20.6 % for AC80, 16.3 % for AC90 and a 4.8 % for ACC. These drops seem to be related with the possible formation of OFGs species at the pore opening region, blocking the access to N_2 molecules [6]. The S_{BET} decrease shows a direct correlation with the strength of the acid and the functionalization temperature.

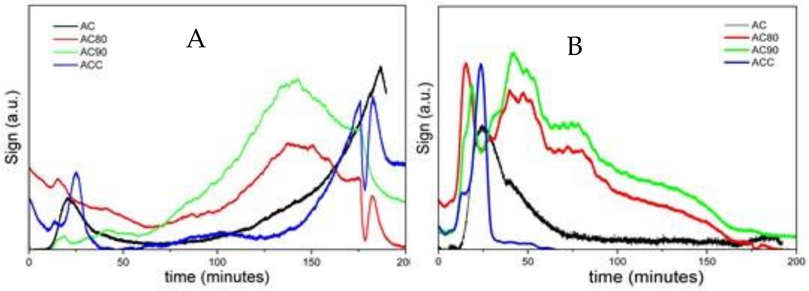

Figure 2. TPD-MS profiles of (A) CO and (B) CO_2 from supports

Figure 1B shows the FT-IR spectra collected for the supports. A preliminary analysis suggests the presence of similar surface OFG species with some intensity discrepancies. The spectra show a band between 3100-3500 cm^{-1} associated with the O-H stretching mode in hydroxyl, carboxyl and phenol groups; the bands located at 1636 cm^{-1} and 1398-1100 cm^{-1} could be assigned to the C=O and C-O stretching modes, respectively, of carboxyl, lactone, anhydrides and esters OFGs. Finally the signals observed at 670 cm^{-1} were associated with C-OH torsion modes [7]. All this information demonstrates the actual occurrence of the surface functionalization at different extents, depending on the conditions of the treatment.

Support TPD measurements can be qualitatively and semi-quantitatively correlated with the surface OFGs composition. For the case of the carbonous supports, Figure 2 shows the evolution of evolved CO and CO_2 signals associated with the thermal decomposition of the OFGs [8]. CO-signal evolutions are shown in Figure 3A and are mainly associated with the high temperature decomposition of phenol, anhydride, quinone, and carbonyl surface groups, while figure 3B shows two different group of CO_2 release-signals, the low temperature ones associated with the decomposition of carboxylic and anhydride groups and the high temperature ones with lactone decompositions. It has been reported that decomposition of anhydride and carboxylic groups tend to generate both CO and CO_2 signals while phenol, ether, carbonyl and quinone groups decomposition presents only CO signals of markedly higher intensities than the CO_2 ones observed for the other OFGs [7].

In order to study semi-quantitatively the OFGs surface contents the obtained signals showed at Figure 3 were integrated after normalization considering the surface area of each sample (see Table I). The OFGs amount increases with the strength of the acid treatment and temperature, showing the order AC<ACC<AC80<AC90. The analysis of the integrated intensities calculated for the CO and CO_2 signals gives information about the OFGs nature. By this hand, AC surface seems to be mainly composed by carboxyl and anhydride groups, while the HNO_3-treated samples showed a markedly higher CO signal intensity, suggesting a preferential functionalization to phenol, ester, carbonyl, and quinone OFGs. For the ACC sample, the observed CO_2/CO signal ratio shows a tendency to the generation of Carboxyl and anhydride OFGs when citric acid is used [7].

Table 1. TPD signal of the supports.

Support	**Sign [Scan Quad/m^2]**				
	T (°C)	**CO_2**	**T (°C)**	**CO**	**Total**
AC	75	8 x10^{-10}	700	5.66 x10^{-10}	1.36 x10^{-9}
AC80	78-173	1.7 x10^{-9}	69-545-728	3.22 x10^{-9}	4.92 x10^{-9}
AC90	86-177- 323	1.95 x10^{-9}	88- 605	1.17 x10^{-8}	1.37 x10^{-8}
ACC	93	2.93 x10^{-9}	73- 747- 761	8.1 x10^{-10}	3.74 x10^{-9}

FTIR and TPD results probe the effective surface functionalization of the commercial AC and a clear dependency of this process with the acid strength and temperature. The presence of different OFG groups at the surface of the samples could affect the acid-base surface properties. In order to study this effect, the model reaction of dissociative adsorption of isopropanol (2-POH) was tested for the supports. This reaction allows the identification and quantification of different surface acid and basic sites, where depending on the nature of the surface sites the reaction can occur via two different paths: Dehydration or dehydrogenation of 2-POH [9]. The first one occurs at the acid sites of the surface via an E1 and/or E2 mechanisms rendering Propylene (P) and/or di-isopropyl-ether (DIE); while the second reaction occurs over basic and/or redox sites, rendering Acetone (A) as a final product. So, the analysis of the obtained products provides helpful information about the density, strength and amount of the sites at the surface [10]. Figure 3 shows the results obtained for the 2-POH model reaction, where the AC support results show only a small amount of strong acid Lewis sites or strong basic Bronsted sites. The oxidative treatment modifies the acid and/or basic sites distribution. AC80 and AC90 show high basic sites content, being smaller in the case of AC90; moreover, the acid sites show a similar increase with respect to AC. In the case of ACC, the surface sites distribution changes, displaying a high acid sites content (similar to the observed for AC80 and AC90) and a minimum amount of basic ones, manifesting the weak character of citric acid. From this analysis, the surface functionalization of the commercial AC is clear, generating different kind and contents of surface OFG, which can be traduced in a modified metal-support interaction.

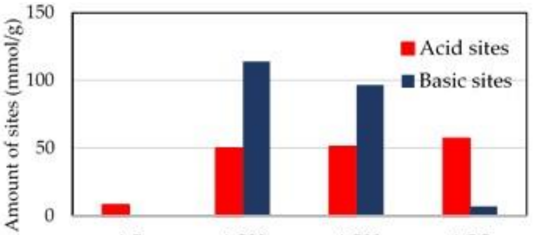

Figure 3. Distribution of acid and basic sites on the supports.

Figure 1A displays the XRD patterns collected for the supports and catalysts. Two broad peaks centered at $2\theta = 23$ and 43 ° are due to the carbon support material. New thin peaks are observed at $2\theta = 43.3$, 50.5 y 74.3° for Cu/AC80 and Cu/AC90 corresponding to main reflections of metallic copper (PDF: 96-901-3015), while a tiny reflection due to the presence of small amount of Cu_2O is observed at $2\theta = 36.4°$ (PDF: 96-900-5770) [11]. Previously, it has been reported the presence of reduced copper species in functionalized carbons due to OFG-mediated chemical reduction in the region next to copper oxide in inert atmospheres and high temperature [11}. On the other side, AC and ACC shows no evidence of reduced copper species at the XRD patterns, possibly related with the high dispersion and low percentage of the surface metal compounds.

The copper content of the catalysts was measured by AA spectroscopy and the results showed a 0.78%, 1.71%, 2.41% and 1.84 % for Cu/AC, Cu/AC80, Cu/AC90 and Cu/ACC, respectively. From these data, a direct correlation between copper and surface OFG contents can be proposed, where Cu/AC sample showed the smallest OFG and copper contents while AC90 displayed the highest OFG and copper contents. Regarding ACC and AC80, both show intermediate content of copper and OFG (TPD data from Table 1). Taking into account the measured data for XRD and AAS, no intense XRD reflections should be expected in the four patterns. Cu/AC and Cu/ACC respect this statement showing no intense peaks associated to copper phases, however, both AC80 and AC90 displayed sharp reduced copper-related reflections. The intensity of this reflections (related with Cu°) are not related with a high copper content, but probably related with the amount and kind of surface OFG composition, which at inert atmosphere treatments, may reduce the Cu(II) species rendering Cu° and Cu(I) ones. The small observed value of FWHM (0.22 °) calculated for the peaks associated to Cu° and the coincidence of the d values (2.07 Å) measured for the (002) and (111) reflections of Carbon and Cu°, respectively, suggests the possibility of an epitaxial growth of the metal on the (002) surface lattice plane of carbon, generating, by this way, “highly crystalline” reflections, even still its concentration is less than 2%. In fact a comparison of the inter-atomic distances of Cu° and Carbon at the above-mentioned crystal directions matches very well, supporting the epitaxial growth of Cu nanocrystals hypothesis. The presence of OFG facilitates this metal growth, so interactions between copper and the OFG seems to be of great importance in these systems. If this fact could be confirmed, more information about the location of OFGs at the carbon surface and its interactions with copper species could be obtained, but at the moment this issue continues under debate.

SEM-EDS analysis showed and homogeneous distribution of copper species at the supports surface (Figure 4) with no evidence of Cu-agglomerates for the Cu/AC80 and Cu/AC90 samples, supporting the hypothesis of the preferential orientation.

Finally, metallic dispersion and average metallic particle diameter where determined from Selective N_2O chemisorption experiments, as reported elsewhere [12]. The calculated dispersion and average particle diameter for the catalysts were

30% (3.3 nm), 22% (4.5 nm) and 17% (5.8 nm) for Cu/AC80, Cu/AC90 and Cu/ACC, respectively.

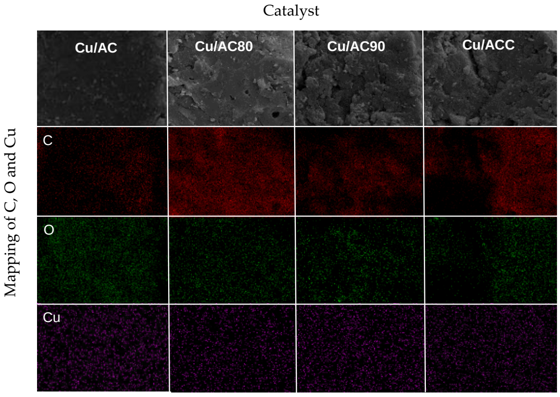

Figura 4. Mapping of C, O and Cu for catalyst

A narrow metallic particle diameter distribution is obtained indicating a disperse disposition of metallic nanoparticles on the surfaces, possibly showing different degrees of metal-support interactions taking into account the different surface OFG composition.

At the moment the catalysts Cu/ACx are being analyzed by XPS in order to determine the surface copper distribution, oxidation state and metal support interaction. Furthermore, the ratio Cu^{2+}/Cu^{+} and preferential copper environments are under study by EPR. In a next step, all these samples will be tested in the glycerol selective oxidation reaction.

3. Conclusions

The oxidative treatments applied to the AC samples induced interesting surface modifications, but no effect on the support crystal structure was observed. The observed functionalization of the samples showed a marked dependence on the strength of the acids and temperature, generating diverse contents of surface oxygenated functional groups (OFGs), being AC90 the sample showing the highest degree of surface modification. The presence of OFG induced changes in the amount and nature of the acid-base sites of the support, increasing its amount in comparison with commercial AC. The content and kind of OFG showed a direct relation with the deposited copper content and nature, supporting the selective copper adsorption hypothesis. Furthermore, in the particular case of the supports treated with HNO_3, the OFGs induced the reduction of Cu(II) species, identifying Cu° and Cu_2O at the AC80 and AC90 surfaces. In fact, these two catalysts showed the smallest average metallic particles diameters and the largest dispersions.

From all these data, it can be concluded that a highly functionalized surface allows selective Cu-adsorption/deposition, rendering small copper nanoparticles with different metal-support interaction degrees. The control of the parameters related with the acid surface treatments and the metal deposition allowed the design of catalysts with defined surface acid-base properties and a narrow distribution of metallic particle size, depending on the target catalytic reactions.

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