HYDROGEN ADSORPTION BY ACTIVATED CARBONS CONTAINING IRON OR CUPPER

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Introduction

The incorporation of metals into activated carbon is an alternative that is being studied to improve the adsorption capacity and hydrogen storage [1,2].

To achieve a high metal dispersion and good distribution, and a highly developed micropore volume in the carbon, which are very important in the adsorption of H_2, a preparation method based in loading the metal precursor into the carbon precursor, rather than the more usual method of preparation consisting in the impregnation of the activated carbon, was developed by our group [3]. Since the metals are introduced in the early stages of preparation, they condition the dispersion and distribution, and also affect the microporosity developed during the activation process. In this work, activated carbons with high micropore volume have been obtained from mesophase pitch containing the metal precursor by chemical activation with KOH The pitches were obtained by pyrolysis of a petroleum residue, to which compounds of iron or copper were added.

Experimental

The activated carbons were prepared by chemical activation with KOH at 800 ºC (KOH / pitch 3:1) of metal containing mesophase pitches in an atmosphere of N_2 (flow 100ml/min). The pitches were prepared by co-pyrolysis of a petroleum residue and ferrocene in the case of iron or copper (II) acetylacetonate in the case of copper, at 713K for 4 hours, at a pressure of 1MPa (Fig. 1)
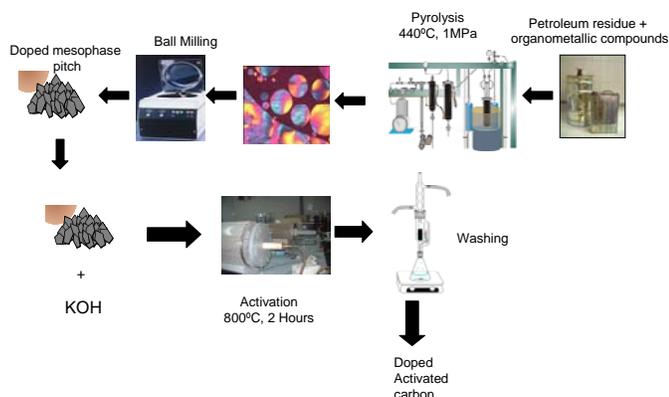

Figure 1. Scheme of the preparation of doped activated carbons

The initial concentration of iron or copper in the mixture of pyrolysis ranged from 1 to 10 wt%. To compare the effect of iron or copper addition, an activated carbon without metal (PA) was also prepared using the same experimental conditions.

The porosity of the samples was determined from the N_2 adsorption isotherms at 77K and CO_2 adsorption isotherms at 273K. The dispersion of the metal in the carbonaceous matrix was determined by scanning electron microscopy (SEM). Hydrogen adsorption isotherms were performed up to 10 MPA at 298K. Previously, the samples were subjected to a reduction process of 2 hours at 473K and 0.5 MPa H_2 to ensure the reduction of metal in the activated carbon.

Results and Discussion

Five different doped pitches have been prepared, one without metal, three with copper using mixtures with the petroleum residue of 1, 2 and 10 wt% and one with iron using a mixture of 2wt% Fe. Thus, five different activated carbon were obtained form these pitches. Table 1 show the results for H_2 adsorption isotherms at 298K and 10 MPa and the textural characterization of the activated carbons obtained by N_2 adsorption isotherms at 77K, CO_2 isotherms at 273K.

Table 1. Activated carbon characterization properties

Sample	Metal content (XRF)(wt%)	S_{BET} (m^2/g)	$V_0(N_2)$ (cm^3/g)	V_{TOTAL} (N_2) (cm^3/g)	$V_0(CO_2)$ (cm^3/g)	H_2 wt%	*$V_{ads\,H2}$ / $V_0(CO_2)$
PA	0	2825	0,99	1,34	0,71	0,68	107
PCu1A	--	2621	0,98	1,23	0,64	0,65	114
PCu2A	24	2343	0,81	1,14	0,58	0,67	130
PCu10A	50	1754	0,61	0,91	0,36	0,63	194
PFe2A	7	2743	0,98	1,32	0,69	1,09	177

*$V_{ads\,H2}$ obtained from H_2 isotherm at 298K and 10 MPa

It can be observed that there is a decrease in the BET surface area when increasing the metal content, although for the mixtures with 1 or 2% the decrease in the surface is not very large and all the samples have areas larger than 2300m^2/g. On the contrary when the addition of copper is 10wt% there is a larger surface area decrease caused by the presence of the metal. It seems that the pore size distribution is similar in all samples, except PCu10A, in which the narrow microporosity, $V_0(CO_2)$, has a higher decrease than the total microporosity, $V_0(N_2)$, the closure of narrow micropores being caused by the metal particles.

Figure 2 presents some SEM images that show the metal particles on the surface. It can be observed that in the case of sample PCu10A metal particles are in form of aggregates of 1-2 µm particle size, although there is still a large amount of metal in sub-micron particles which cannot be observed by SEM. In the case of iron, particle size seems to be of lower size and more submicron particles are present in this sample. It seems there is an increase of particle size with the increase of metal concentration in the mixture of the petroleum residue with the organometallic compound.
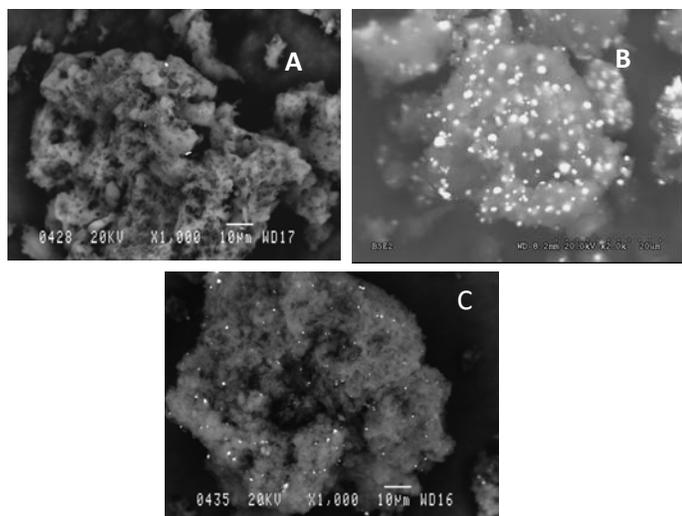
**Figure 2. SEM images of activated carbons:
a) PA; b) PCu10A; c) PFe2A**

The amount of hydrogen absorbed at 298K and 10 MPa of the five samples is presented in Table 1. The sample without metal, PA, adsorbs a larger amount of hydrogen than all the samples containing copper, although the differences are not large. However, the sample with iron, PFeA adsorbs a larger amount of hydrogen than all other samples, including PA.
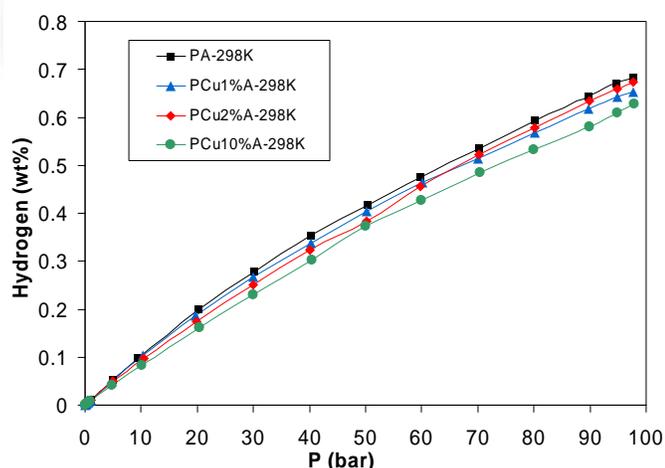
Figure 3. Hydrogen isotherms at 298K and 10 MPa of the activated carbons containing copper.

When analyzing the hydrogen isotherms at 298K, Fig. 3, there is a great similarity in the shape of the isotherms, the uptake decreasing with the amount of copper loading. This is what it should be expected taking into account the decrease in surface area and micropore volume due to the presence of metal. However, when representing the data of hydrogen adsorbed (wt%) versus the narrow microporosity (Fig. 4) it seems that the percentage of adsorbed hydrogen versus the volume of narrow microposity is higher for the samples

containing metals, specially for the sample containing iron, PFeA, and the samples containing the largest amount of copper.
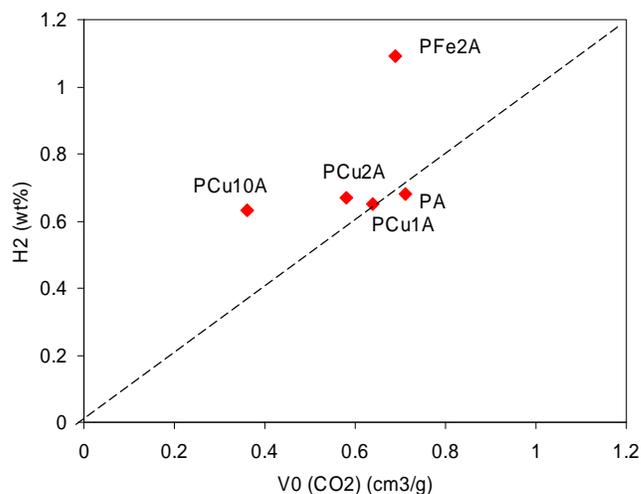
Figure 4. Amount of hydrogen adsorbed (wt%) vs volume of narrow microporosity ($V_0 (CO_2)$)

This is more clearly observed when calculating the ratio of the hydrogen adsorbed (volume) at 10 MPa versus the CO_2 adsorbed volume at 273K presented in Table 1. This parameter increases with metal content, being also much higher in the case of iron. Thus, it seems that the presence of metal contributes to the hydrogen adsorption, the sample adsorbing higher amounts of hydrogen than the one expected according to their surface area and micropore volume.

Conclusions

The method of copyrolysis of petroleum pitches with metal organometallic compounds allows producing activated carbons with high surface area and good metal distribution. The particle size of the metal increases with the metal content, being always lower than 2-3 microns. The presence of metal particles decreases surface area and microporosity. However, the amount of hydrogen adsorbed does not decrease much in the case of copper and even increases in the case of iron. It seems that the presence of the metal is enhancing the amount of hydrogen adsorbed.

References

[1] Strobel, R, Garche, J, Moseley, PT, Jorissen, L, Wolf, G. J. Power Sources 2006; 159(2):781-801.

[2] Thomas, K M. Catal. Today 2007; 120(3/4):389-398.

[3] Monteiro de Castro, M., Martínez-Escandell, M, Molina-Sabio, M, Rodríguez-Reinoso, F. Carbon 2010 48(3):636-644.