

N-DOPED ACTIVATED CARBONS AND ACTIVATED CARBON FIBRES FOR SO₂ REMOVAL FROM FLUE GASES. INFLUENCE OF THE N-FUNCTIONAL GROUPS

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Introduction

Carbon materials, such as activated carbons (AC) and activated carbon fibres (ACF) are efficient for low-temperature removal of SO₂ from combustion gases [1-4]. Due to their physical and chemical characteristics, they possess, in addition to a considerable adsorption capacity for various gases, catalytic activity for SO₂ to H₂SO₄ oxidation in the presence of oxygen and H₂O. The preparation of carbon materials with tailored porous texture and surface chemistry is, in most of cases, essential to achieve the best performance [1,2].

Previous studies have demonstrated that N functional groups are very active sites for the adsorption and oxidation of SO₂ [4], although it has not been established up to now the nature of the N groups which have the higher activity. In this sense, the objective of the present work is to analyse the effect of the N content as well as the role of the different N-containing functional groups on the catalytic activity for SO₂ oxidation. For this purpose, in this study a number of AC and ACF doped with different kinds of N species have been prepared by different experimental methods and deeply characterised.

Experimental

The samples used in this study are carbonaceous materials in which N has been incorporated into their structure by two methods: i) reaction in an autoclave of already activated carbon samples (i.e., AC KUA16 and Aox and ACF A20) with different nitrogenated reagents (NH₃, Urea, Dicyanodiamine –DCD-) using N,N-dimethylformamide –DMF- as solvent and ii) by blending a nitrogenated resin with a low softening point pitch at the first step of the ACF manufacture, followed by the spinning, stabilisation, carbonisation and activation to a 30 and 70% B.O. (i.e., samples N3F30 and N3F70, respectively). For comparison purposes, commercial ACF derived from PAN (FE-400) and non doped samples, such as the commercial ACF A10 and A20, and ACF obtained by CO₂ (CFC series) or steam (CFS series) activation, have also been used.

Table 1 presents the characterisation of all the materials, including the porous texture obtained applying the D-R equation to the isotherms of CO₂ at 273 K and N₂ at 77 K, the percentage of N and the chemical nature of N species obtained by XPS after a heat treatment of the samples up to 1173 K.

The catalytic activity for SO₂ oxidation was determined for the samples heat treated up to 1173 K, using a discontinuous reactor in liquid phase at 303 K and a conductivity detector [5].

Results and Discussion

Table 1 shows that the two experimental procedures are effective for doping the AC and ACF to a considerable amount. Thus, in certain samples, a N content as high as 4.6 wt% can be reached, which surpasses the value of the commercial ACF derived from PAN (sample FE-400). The nitrogenated species that can be detected by XPS after the heat treatment of the materials up to 1173 K, are presented in Figure 1. In all the cases the N-containing functionalities more abundant are pyridinic and quaternary-like N (Table 1).

The introduction of N into the structure of the AC and ACF analysed can produce important changes in the porosity of the materials. This evaluation of this effect is very important considering the influence of the porous texture on the catalytic activity for SO₂ oxidation [1,2]; thus, in general, the lower the micropore volume, the lower the catalytic activity. Table 1 indicates that the doping of the carbon samples by reaction in an autoclave produces modifications into the porous texture, which are especially important in those materials having a narrow micropore size distribution (i.e., sample KUA16 and Aox). In all the cases, the reaction with urea results in the strongest decrease of the micropore volume.

Taking into account the effect of the micropore volume on the catalytic activity, samples with similar porosity should be compared to analyse the influence of the N species. In this sense, Table 1 shows that, when the catalytic activity for SO₂ oxidation for samples containing or not nitrogen is compared (i.e., samples A10 vs. FE-400 and N3F30 or A20 vs. A20/DCD and N3F70), the N-doped materials present higher activity. Additionally, there exists a correlation between the basic character of these samples and the activity, that is the activity increases with the basicity of the carbon surface.

In order to generalise the comparison between the materials studied, the specific catalytic activity of the AC and ACF has been calculated using the surface area determined from gas adsorption. In this way, it should be possible to account for the different surface area of the materials and, then, to compare the effect of the N content and nature of N species.

Figure 2 plots the specific catalytic activity versus the N content of the AC and ACF. The figure shows that the specific catalytic increases with the N percentage for all the N-doped samples, indicating the catalytic effect of the heteroatom. However, two different trends are found.

These trends can be explained from the XPS characterisation. In this sense, if we observe the XPS spectra of the N1s region for these materials (Figure 3), it can be observed that the samples which fit to the same trend in Figure 2, have a similar distribution of nitrogenated species at their surfaces. Thus, the FE-400 fibres and the N-containing samples prepared from ACF A20, AC KUA16, have a comparable amount of pyridinic and quaternary N (binding energies of 398.5 and 401.2 eV, respectively) meanwhile samples from AC Aox and ACF N3F, which are those with the higher catalytic activity, present a higher proportion of pyridinic N. Additionally, we have also observed that the pyridinic species have a larger basic character than the quaternary N.

These results indicate that the nitrogenated species that are favouring in a higher extent the catalytic activity for the removal of SO₂ are the pyridine-like ones, because they contribute more to increase the basicity of the carbon samples. In this sense, Figure 4 shows the variation of the specific activity versus the content of pyridinic N in the carbon materials. It can be clearly observed that in this plot, all the N-containing materials fit into the same trend. It is remarkable that the behaviour of materials with different origins, porosity and preparation methods, is nicely explained in this figure.

Table 1.- Characterisation and activity of the materials

Sample	V _{N₂} cm ³ /g	V _{CO₂} cm ³ /g	Activity μmol/g.min	%N	Main N-species
A10	0.47	0.40	18.9	-	-
A20	0.70	0.47	29.6	-	-
A20/DMF	0.70	0.52	25.7	0.4	
A20/NH ₃	0.73	0.46	38.1	0.8	~35% pyridines
A20/DCD	0.74	0.49	61	1.3	~40% quaternary
A20/Urea	0.55	0.45	72	3.0	
N3F30	0.42	0.37	60.5	1.7	~46% pyridines
N3F70	0.68	0.55	87.6	1.8	~20% quaternary
FE-400	0.48	0.38	45	1.8	~36% pyridines ~55% quaternary
CFC29	0.44	0.43	21.3	-	-
CFC42	0.71	0.54	25	-	-
CFS22	0.31	0.32	3.9	-	-
KUA16	0.60	0.55	48.8	-	-
KUA16/DMF	0.47	0.57	20.1	0.8	~41% pyridines
KUA16/NH ₃	0.56	0.46	25.2	0.8	~36% quaternary
KUA16/Urea	0.35	0.39	36.5	2.2	
Aox	0.33	0.32	34.9	-	-
Aox/DMF	0.30	0.29	53	1.9	
Aox/NH ₃	0.39	0.32	-	2.3	~50% pyridines
Aox/DCD	0.20	0.18	10.7	4.6	~15% quaternary
Aox/Urea	0.23	0.16	11.5	3.4	

Conclusions

The presence of N heteroatoms at the surface of AC and ACF favours the catalytic activity towards SO₂ oxidation reaction because the basic character of the material is increased. The nitrogenated functionalities most active for SO₂ oxidation are the pyridinic species which are placed at the edges of the graphene layers.

Acknowledgements

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References

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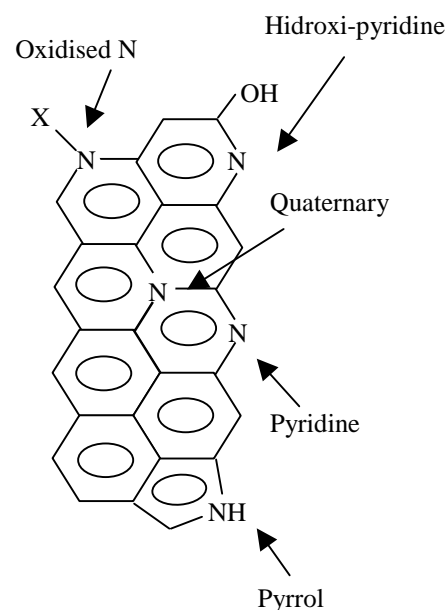


Figure 1.- N functionalities

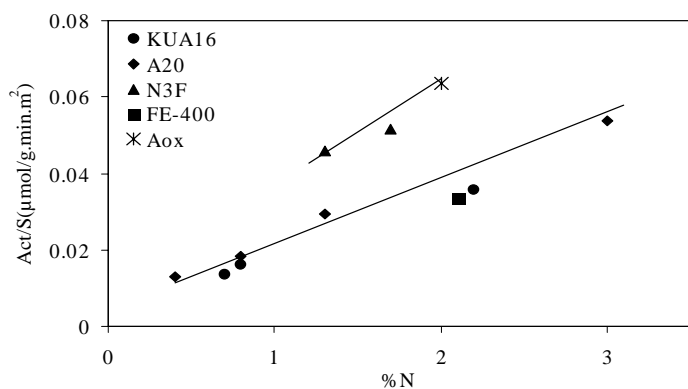


Figure 2.- Specific catalytic activity versus N percentage

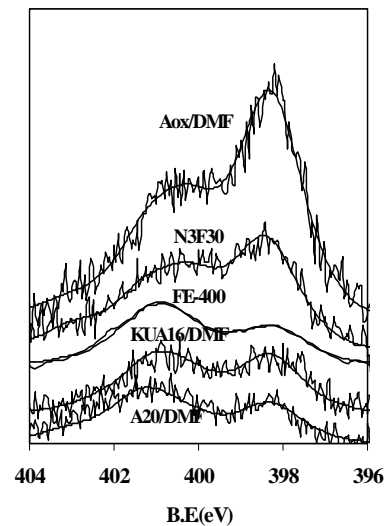


Figure 3.- N1s XPS spectra

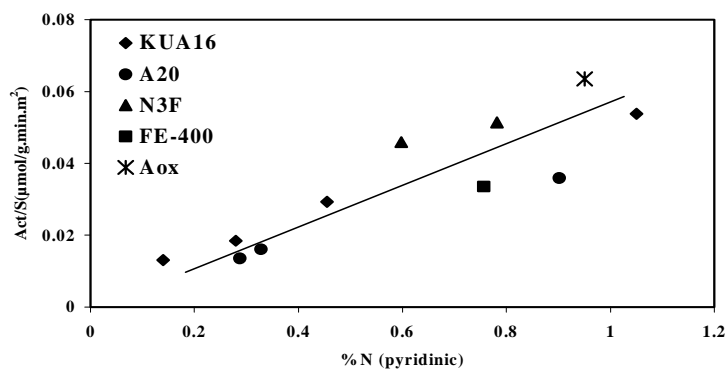


Figure 4.- Specific catalytic activity versus pyridinic N percentage