A NOVEL APPROACH FOR CHARACTERIZING CARBON CATALYSTS BY TAP EXPERIMENTS

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Two samples were used in this study: a coal based carbon obtained by carbonisation and a gas-phase oxidized sample from the raw carbon. These samples were extensively characterized and their NO removal capacity was also determined.
TAP-2 (Temporal Analysis of Products) reactor was used to obtain adsorption parameters and diffusion coefficients of the system NO-carbon catalyst. The diffusivity of NO as well as the enthalpy of adsorption does not change after increasing the number of functional groups by an oxidative pretreatment of the carbon.

INTRODUCTION

Combustion of fossil fuels in power plants contributes to acid rain and photochemical smog due to NO emissions [1].

The selective catalytic reduction (SCR) is the only flue gas denitrification technique so far that has proven to be very effective. It has been extensively studied, successfully commercialised and applied on a large scale [2]. Carbon can be used as catalyst in the SCR unit at lower temperatures than those used with conventional SCR catalysts.

The adsorbent and catalytic properties of carbons are usually dependent on the physicochemical features such as surface areas, pore size distributions and surface chemistry. Especially, surface oxygen functional groups are closely related to the catalytic activity of carbons. These groups are expected to change the interaction between the carbon surface and the reactants through a variation of adsorption and reaction characteristics [3]. Besides traditional characterization techniques (temperature programmed desorption, acid-base titration, gas physisorption) transient experimental techniques are a powerful tool in the investigation of adsorption and catalytic reaction mechanisms [4]. Thus, the measurement of the concentrations of reacting species in transient conditions gives direct information on the surface processes. Moreover, modelling of the transient responses allows extraction of the adsorption parameters and the diffusion coefficients in the micropores.

This work shows the ability of the temporal analysis of products technique to obtain the transport and sorption parameters for the NO-carbon system. These parameters are directly related to the nature and number of functional groups on the carbon.

EXPERIMENTAL

Preparation and characterization of carbons

Carbon labelled SC900 was obtained from carbonisation of a low rank coal from NW of Spain in inert atmosphere at 900ºC of temperature. Experimental installation for preparation of carbons is described elsewhere [5].

Sample SC900 was treated with a flow containing 1000 ppmv SO_2, 6% v/v O_2, 10% v/v H_2O and N_2 to obtain an amount of 400 mg sulphuric acid equivalent that is removed thereafter by heating up to 400ºC and maintained at this temperature until SO_2 evolution is negligible. Sample thus obtained was labelled as SC900R. Both samples were sieved to a particle size 0.2-0.3 mm.

Elemental analysis of the samples was carried out in a Carlo Erba CHNSO 1108 apparatus. Ash content was determined according to ASTM standards for coal and coke.

Surface areas were determined with N_2 (BET equation) and CO_2 (DR equation) physisorption at 77K and 273K, respectively, in an Autosorb-1 apparatus from Quantachrome. Outgassing conditions were a temperature of 250ºC and a pressure of 10^{-6} mm Hg.

Temperature programmed desorption (TPD) experiments were carried out to determine the relative amounts of CO and CO_2 evolving from each sample. An amount of 0.6 g of sample was placed in a quartz tube under a stream of argon flowing at a rate of 30 ml min^{-1}. Gas evolved was analysed by gas chromatography.

Boehm's procedure [6] was used to titrate carboxyls, lactones, phenols and carbonyls functional surface groups.

NO removal

The NO removal capacity of the carbons was determined by passing a flow of 0.5 l/min containing 1000 ppmv of NO, 6% O_2, 1000 ppmv NH_3 and nitrogen as a balance through a fixed bed of 15 g of carbon at 150ºC. The NO concentration was measured before starting an experiment by bypassing the reactor. The effluent concentration was monitored continuously during the reaction. More details of the experimental installation and the operational procedure is described elsewhere [7].

TAP experiments

The TAP-2 reactor system [4] was used to perform transient response experiments under vacuum and at temperatures ranging from 300 to 400ºC. A carbon loading of 100 mg was placed between two layers of quartz particles (0.2-0.3 mm particle size). Neon was used as an internal standard for calibration and as a reference for diffusion. Nitric oxide and neon were introduced by pulses in the microreactor (25.4 mm in length and 4 mm in diameter) in a volume ratio of 1:1. The reactor was continuously evacuated and the response of the pulses as a function of time was analysed on –line by a quadrupole mass spectrometer.

RESULTS AND DISCUSION

Table 1 reports the elemental analysis and the ash content of the samples studied. The ash content is high for each sample due to the low grade coal precursor.

Table 1 also reports surface areas of both samples. There is an increase of surface area and pore volume after treatment of raw sample. This fact can be explained in terms of the following reaction:

$$2H_2SO_4 + C \rightarrow 2SO_2 + CO_2 + 2H_2O$$

Table 1. Elemental analysis, ash content and surface areas of the studied samples.

	SC900	SC900R
Ash, %	32	32
Carbon, %[a]	94.8	95.0
Hydrogen, %	0.7	0.7
Nitrogen, %	0.3	0.3
Total sulphur, %	4.1	4.1
S_{BET} (N_2), m^2/g	52	112
Pore volume (HK), cm^3/g	0.025	0.055
Pore volume (BJH), cm^3/g	0.061	0.082
S_{DR} (CO_2), m^2/g	389	350
Pore volume (DR), cm^3/g	0.170	0.156

[a] dry and ash free basis

The treatment with a flow containing SO_2+H_2O+O_2 gives an amount of 400 mg of sulphuric acid. Heating up this sample, sulphuric acid is removed from the surface by reduction that leads to carbon consumption. This mild gasification can produce either an opening of the microporosity to mesoporosity and/or the creation of new microporosity. This can be followed by the increase of pore volume calculated by Horvath-Kawazoe (HK, for micropores) and Barret-Joyner-Halenda (BJH, for mesopores) methods.

The treatment of the raw sample produces an increase in oxygen functionalities as can be deduced from Table 2 where amounts of CO and CO_2 evolved during a TPD experiment are reported. The surface chemical structures that evolve CO_2 are less stable and are related to carboxylic, anhydride or lactonic functions. The evolution of CO is attributable to fairly stable structures and could be postulated as phenols, quinones, ethers and carbonyls (3, 8). CO is more abundant than CO_2 during decomposition of surface oxides for both samples, indicating the presence of more stable groups on the samples surface. Moreover, sample SC900R was heated up to 400ºC after chemical treatment, so an important part of CO_2-evolving structures had disappeared before TPD experiments.

Table 2. Total amount of CO and CO_2 evolved from TPD experiments and Boehm's [6] titration.

	SC900	SC900R
CO_2, mmol/g	0.36	0.65
CO, mmol/g	0.49	1.03
O, %[a]	1.94	3.73
Carboxyls, meq/g	0.102	0.153
Lactones, meq/g	0.111	0.152
Phenols, meq/g	0.042	0.048
Carbonyls, meq/g	0.320	0.855

[a] from the amount of CO and CO_2

Figure 1 shows TPD profiles for both samples. The TPD patterns indicate that surface groups yielding oxygen evolved almost completely below 1100ºC. The CO profiles for sample SC900 show a single and quite symmetric peak centered at about 800ºC, probably due to carbonyl and/or quinone-like groups that are thermally more stable than phenolic or hydroquinone groups. The chemical treatment does not shift this peak meaning that surface functional groups introduced are of the same type that exist on the raw sample. This can be confirmed with the results obtained by Boehm's titration. The most important change is observed for the carbonyl groups, increasing its value almost three times.

The CO_2 profile exhibits a peak at about 400ºC and 700ºC for sample SC900R, indicating the presence of two different surface functionalities with different thermal stability. The first peak is attributable to carboxyl groups that are present on the sample SC900 in a low extent. This can be confirmed by the results from Boehm's titration shown in Table 2.

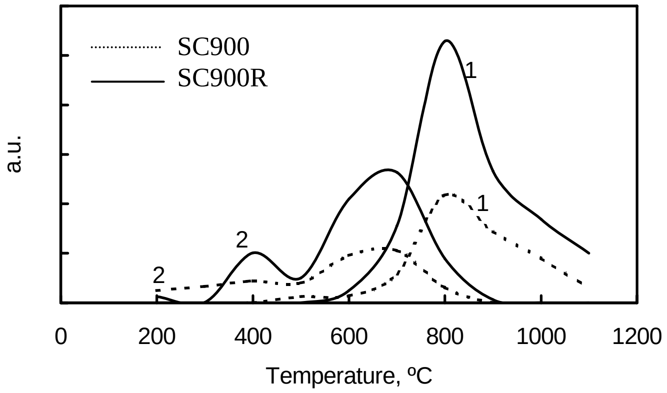

Figure 1. Profiles of CO (1) and CO_2 (2) evolution during a TPD experiment.

Once the samples were characterized by conventional methods, the NO removal capacity was tested. The curves corresponding to NO conversion and amount of NO removed versus time are shown in Figure 2.

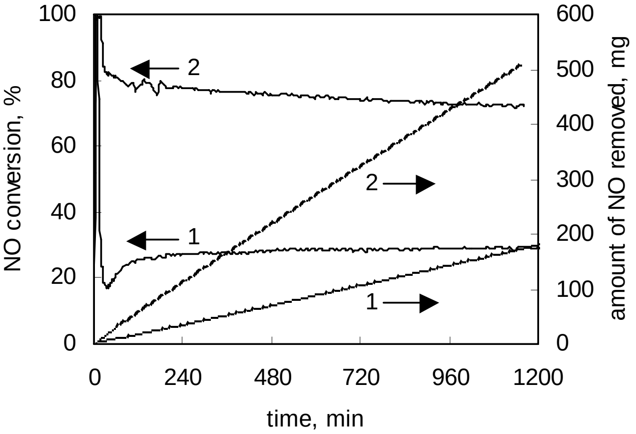

Figure 2. NO removal capacity of samples SC900 and SC900R versus time.

The breakthrough of NO does not occur before 10 min, and it needs more than 10 h until the steady state is reached. The fact that the breakthrough of the gas occurs so late indicates that he surface reaction takes place between species adsorbed in a large amount in a preceding step.

The gas-phase treatment enhances the catalytic activity of the carbon. However, it is difficult to attribute this enhancement to only one feature of the treated carbon, i.e., chemical or physical characteristics. The activation of the raw sample leads to an increase in surface area and pore volume as well as to an increase in the surface functionalities. The literature shows no consensus on the correlation between the NO conversion and the carbon surface area [8, 9]. In this case, the surface area of sample SC900R is about twice as large as that of sample SC900 but the NO conversion increases approximately four times. The contradictory findings in the literature and the results showed here lead to believe that the chemical characteristics of the functional groups are an important element for the NO removal performance of the carbons.

The enhanced reduction of NO due to the introduction of new oxygen functional groups can be understood in terms of the production of active sites. In the present case, the structures that increase to a larger extent after the treatment are the carbonyls. The creation of stable C-O complexes was found beneficial as also reported in the literature [10, 11] and an optimum for the amount of active sites was found.

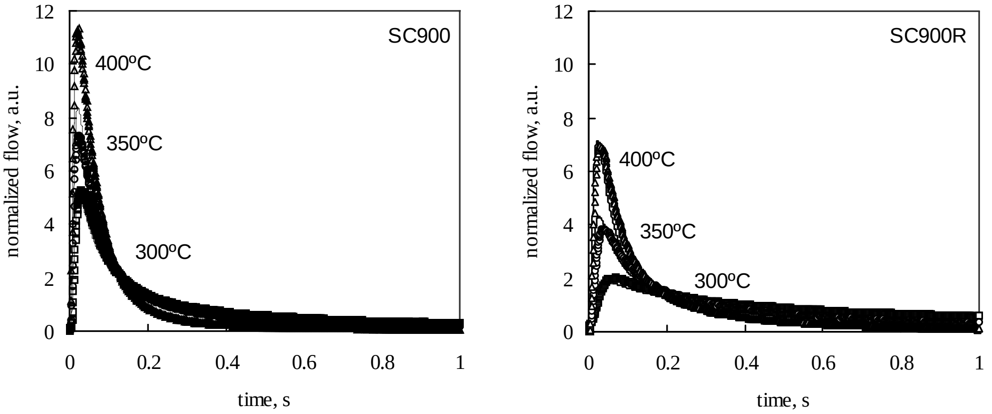

Figure 3. Experimental (points) and model (lines) responses from TAP-2 experiments.

The adsorption characteristics of the samples SC900 and SC900R were studied with transient adsorption experiments using NO as adsorbate. Figure 3 shows the experimental (points) and model (lines) responses from TAP-2 experiments for samples SC900 and SC900R at 300, 350 and 400ºC of temperature. The results of the nitric oxide pulse experiments demonstrate that NO removal occurs in a bigger extent over the gas-phase oxidized sample, where the surface area as well as the number of surface functional groups have increased as reported in Tables 1 and 2.

The model fits adequately the experimental data allowing the extraction of the adsorption parameters and the diffusion coefficients for the transport inside the micropores. Table 3 reports these parameters for both samples. Similar diffusion parameters were found for both samples. Despite the difference in volume of the micropores as calculated by the HK method (Table 1), a big difference between S_{BET} and S_{DR} for each sample is found indicating problems of accessibility for nitrogen molecules at the low temperature at which the adsorption process is carried out (77 K). The micropore volume according to the DR method gives similar values for both samples (Table 1) The values of the diffusion parameters found by modelling of the transient responses for both samples are very close.

Adsorption enthalpies are also very similar but quite different pre-exponential factors are obtained. This indicates that the same sites are involved for the adsorption of NO but their number has increased. The increase of the number of active sites can be confirmed by TPD experiments obtaining that the total amount of CO and CO_2 increased considerably after treatment of the raw sample (Table 2). On the other hand, the amount of different type of surface groups varies in a low extent after treatment of the raw sample, except for the carbonyls that increases in concentration by approximately a factor of three. So, these structures could be the responsible of the enhancement of the NO conversion once determined that diffusion coefficients are similar for both samples.

Table 3. Estimated parameters for NO on carbon samples.

Sample	D^o m^2s^{-1}	Ediff kJ mol^{-1}	H^o	$-\Delta H$ kJ mol^{-1}
SC900	$3.4\ 10^{-9}$	15	$2.4\ 10^{-5}$	72±3
SC900R	$2.8\ 10^{-9}$	15	$8.5\ 10^{-5}$	73±3

In conclusion, the transient technique TAP has been shown to be a powerful tool for the fast characterization of carbon catalysts and the results are in accordance with those inferred by conventional methods and also allowed to obtain assess the transport and sorption parameters for the NO-carbon system. Further research will be carried out to gain more understanding on the catalytic reduction of NO over carbon catalysts.

REFERENCES

1. I. Smith. Nitrogen oxides from coal combustion-environmental effects, IEA Coal Research, London, 1990.
2. I. Aarna, E.M. Suuberg. Fuel 76(1997)475.
3. F. Rodriguez-Reinoso in: H. Marsh, E.A. Heintz, F. Rodríguez-Reinoso (Eds.) Introduction to Carbon Technologies. Univ. of Alicante, 1997 p. 35.
4. J.T. Gleaves, G.S. Yablonskii, P. Phanawadee, Y. Shuurman. Appl. Catal. A: General 60(1997)55.
5. R. Moliner, J.V. Ibarra, M.J. Lazaro. Fuel 73 (1994)1214.
6. H.P. Boehm. Carbon 32(1994)759.
7. M.T. Izquierdo, B. Rubio. Environ. Sci Technol. 32(1998)4017.
8. M.J. Illan-Gomez, A. Linares-Solano, C. Salinas-Martinez de Lecea, J.M. Calo. Energy Fuels 7(1993)146.
9. S.N. Ahmed, J.M. Stencel, F.J. Derbyshire, R.M. Baldwin. Fuel Proc. Technol. 34(1993)123.
10. M.T. Izquierdo, B. Rubio, C. Mayoral, J.M. Andres. Appl. Catal. B: Environ. 33(2001)315.
11. L. Singoredjo, F. Kapteijn, J.A. Mouljin, J.M. Martin-Martinez, H.P. Boehm. Carbon 31(1993)213.