Denitrification of Stack Gases in the Presence of Low-Rank Coal-Based Carbons Activated with Steam

M. T. Izquierdo,^{*,†} B. Rubio,[†] M. C. Mayoral,[‡] M. T. Bona,[‡] and J. M. Andres[‡]

Department of Energy and Environment and Department of Chemical Processes, Instituto de Carboquímica (CSIC), C/ Miguel Luesma Castán, 4, 50018 Zaragoza, Spain

Received November 8, 2006. Revised Manuscript Received March 20, 2007

The effect of the steam activation of low-rank coal-based carbons under different conditions on catalytic NO reduction is examined. Oxygen surface functional groups are closely related to this catalytic activity. Because factors such as surface area make interpretation of the results difficult, it is necessary to study the role of the surface chemistry using samples with different chemical properties but of the same origin and with similar Brunauer–Emmett–Teller surface areas. Such materials, obtained by varying steam activation conditions over the same precursor, were tested in low-temperature selective catalytic reduction of NO with NH₃ in order to study the influence of the presence of oxygen groups on the catalytic activity, avoiding as far as possible the effect of porosity.

1. Introduction

The modern manufacturing processes of activated carbons basically involved the following steps: raw material preparation, low-temperature carbonization, and activation.¹ The activation step is crucial for tailoring the pore size distribution, and the conditions are carefully controlled to achieve the desired pore structure. The influence of the activation process conditions on the microporous structure of activated carbons has been widely discussed by Rodríguez-Reinoso and Linares-Solano.²

It is well-known that the porous structure of activated carbons plays an important role in gas adsorption. In addition, surface chemistry can affect the behavior of activated carbons when they are used as adsorbents or as catalysts, especially surface oxygen complexes.^{3–6} However, the influence of operational conditions during the steam activation step on the final surface chemistry state of carbons remains still unanswered.

There exist in the literature a number of studies showing that the catalytic activity of activated carbons for NO conversion increases with the oxygen concentration on the carbon surface.^{7–11}

It is currently assumed that surface functional groups containing oxygen change the interaction between the carbon surface and the reactants through a variation of adsorption and reaction characteristics. However, it is difficult to study the effect of surface chemistry because surface area also affects the catalytic activity. Therefore, to avoid difficulties in the interpretation of the obtained results, it seems necessary to study the role of surface chemistry using samples with different chemical properties but of the same origin and with a similar Brunauer–Emmett–Teller (BET) surface area.

In this work, activated carbons containing different oxygen functionalities but similar surface area obtained under varying activation conditions over the same precursor were tested in the low-temperature selective catalytic reduction (SCR) of NO with NH₃ in order to study separately the influence of the presence of oxygen groups on the catalytic activity of carbons avoiding as much as possible the effect of a porous system of them.

2. Experimental Section

2.1. Preparation and Characterization of Carbons. The research reported in this paper was conducted on four different carbons (S750A20, S750A40, S750A75, and S750A100) obtained from the same precursor. This precursor was obtained from the pyrolysis of a Spanish low-rank coal at 750 °C in a N₂ atmosphere and named S750. Samples S750A20, S750A40, S750A75, and S750A100 were obtained from the steam activation of sample S750 at 720 °C over 2 h at percentages of steam in N₂ of 20, 40, 75, and 100%, respectively. The ash content and elemental analysis of the samples are given in Table 1.

Samples were characterized by acid–base titration, infrared spectroscopy (FTIR), temperature-programmed desorption (TPD), and N₂ and CO₂ adsorption.

Boehm's procedure¹² was used to titrate carboxyls', lactones', phenols', and carbonyls' functional surface groups by using bases of different strengths: NaOH, Na₂CO₃, NaHCO₃, and NaOC₂O₅.

(11) Ku, B. J.; Lee, J. K.; Park, D.; Rhee, H. K. *Ind. Eng. Chem. Res.* **1994**, *33*, 2868–2874.

(12) Boehm, H. P. *Carbon* **1994**, *32*, 759–769.

* Corresponding author. Fax: +34 976 733318. E-mail: mizq@icb.csic.es.

[†] Department of Energy and Environment.

[‡] Department of Chemical Processes.

(1) Yang, R. T. *Adsorbents: Fundamentals and Applications*; Wiley: Hoboken, NJ, 2003; pp 79–123.

(2) Rodríguez-Reinoso, F. J.; Linares-Solano, A. Microporous Structure of Activated Carbons as Revealed by Adsorption Methods. *Chemistry and Physics of Carbon*; Marcel Dekker: New York, 1989; pp 1–146.

(3) Bansal, R. C.; Donnet, J. B.; Stoeckli, F. *Active Carbon*; Marcel Dekker: New York, 1988; pp 27–119.

(4) Solar, J. M.; Leon y Leon, C. A.; Oseo-Assare, K.; Radovic, L. R. *Carbon* **1990**, *28*, 369–377.

(5) Leon y Leon, C. A.; Radovic, L. R. Interfacial Chemistry and Electrochemistry of Carbon Surfaces. *Chemistry and Physics of Carbon*; Marcel Dekker: New York, 1994; pp 213–310.

(6) Izquierdo, M. T.; Rubio, B.; Mayoral, C.; Andres, J. M. *Appl. Catal., B* **2001**, *33*, 315–324.

(7) Ahmed, S. N.; Baldwin, R. M.; Derbyshire, F. J.; McEnaney, B.; Stencil, J. *Fuel Process. Technol.* **1993**, *34*, 123–136.

(8) Singoredjo, S.; Kapteijn, F.; Moulijn, J. A.; Martin-Martinez, J. M.; Boehm, H. P. *Carbon* **1993**, *31*, 213–222.

(9) Teng, H.; Hsu, Y. F.; Tu, Y. T. *Appl. Catal., B* **1999**, *23*, 145–154.

(10) Muñiz, J.; Marban, G.; Fuertes, B. *Appl. Catal., B* **2000**, *27*, 27–36.

Figure 1. Experimental installation for NO removal capacity testing.

Table 1. Elemental Analysis and Ash Content of Carbons (%)

	S750A20	S750A40	S750A75	S750A100
ash	25.0	25.8	26.7	28.4
carbon	71.0	70.1	69.4	68.7
hydrogen	1.1	0.9	0.7	0.5
nitrogen	0.5	0.4	0.4	0.3
sulfur	3.9	4.0	4.2	4.2
oxygen ^a	23.5	24.6	25.3	26.3

^a By difference.

Approximately 0.5 g of each sample was mixed with 50 mL of a 0.1 N solution of each base. The suspension was shaken for 24 h at room temperature. After that time, the solution was filtered, and an aliquot of this liquid was titrated with 0.1 N HCl.

FTIR spectra of the solid samples were run in KBr pellets (120 mg, 1 wt %). Spectra were recorded by coadding 64 scans at a resolution of 2 cm⁻¹ with a Nicolet Magna 550 spectrometer. Spectra were scaled to 1 mg sample/cm². The selected zone of the FTIR spectra (1800–900 cm⁻¹) was studied carefully, and the position of the bands was established from the second derivatives of the corresponding spectra.

The TPD profiles were obtained with a custom-built setup, consisting of a tubular quartz reactor placed inside an electric furnace. TPD experiments were carried out by heating the samples up to 1100 °C in an Ar flow at a heating rate of 10 °C/min, recording the amounts of CO and CO₂ evolved at each temperature with a quadrupole mass spectrometer from Balzers. The calibrations for CO and CO₂ were carried out by standards diluted in Ar. In a typical run, 0.6 g of carbon was placed in a vertical quartz tube reactor under a stream of 30 mL/min of Ar.

Surface areas were determined with N₂ at 77 K and CO₂ at 273 K. The BET equation was applied to N₂ adsorption isotherms and the Dubinin Radushkevich (DR) equation to CO₂ adsorption data. Prior to each analysis, samples were outgassed at 150 °C and up to a vacuum less than 10⁻⁵ mmHg. The volume of macro- and mesopores was obtained using the Barret, Joyner, and Halenda method (BJH) applied to the desorption branch of the N₂ isotherm.

2.2. NO Abatement Experiments. An experimental installation (Figure 1) was used to test the NO removal capacity of carbons. It consists of a fixed-bed reactor and devices for the preparation of gas mixtures, temperature control, and online analysis of the concentration of the gas stream. A flow of 0.5 L/min of gas containing 1000 ppmv NO, 6% (v/v) O₂, 1200 ppmv NH₃, and N₂ as the balance is passed through a bed of 15 g of carbon at a temperature of 150 °C. The reactor was provided with a bypass which allows the measurement of the NO concentration before each experiment. The NO analyzer is a nondispersive infrared photometer.

The reaction results are described in terms of NO conversion as %NO conversion = [(NO_{in} - NO_{out})/NO_{in}].

More details of the experimental procedure are given in ref 13.

3. Results and Discussion

3.1. Characterization of Carbons. Table 1 shows the ash content and elemental analysis of the samples. The ash content

Table 2. Data from N₂ and CO₂ Adsorption of Carbons

	S750A20	S750A40	S750A75	S750A100
S _{BET} , m ² /g	305	315	316	319
V _{macro+meso} (BJH), cm ³ /g	0.16	0.12	0.13	0.14
S _{DR} , m ² /g	394	333	298	232
V _{micro} (DR), cm ³ /g	0.17	0.14	0.12	0.10

Table 3. Total Amount of CO and CO₂ from TPD Experiments (mmol/g)

	precursor	S750A20	S750A40	S750A75	S750A100
CO	0.21	0.69	0.98	1.07	1.12
CO ₂	0.07	0.22	0.23	0.21	0.19
CO/CO ₂	3.16	3.14	4.26	5.09	5.92

Table 4. Surface Oxygen Groups by Boehm's Method (mmol/g)

	precursor	S750A20	S750A40	S750A75	S750A100
carboxyls	0.611	1.124	1.295	1.286	1.253
lactones	0.158	0.708	0.688	0.683	0.678
phenols	0.068	0.019	0.048	0.039	0.028
carbonyls	0.028	0.018	0.039	0.047	0.048
total acidity	0.865	1.869	2.070	2.055	2.007

as well as oxygen content increase as water vapor percentages increase in the activating gas stream. The chemical analysis of the ash did not differ between samples. The temperature of activation was the same in the preparation of the samples, and this is the main parameter that could affect the composition of the ash.

Data from N₂ and CO₂ adsorption are given in Table 2. The surface area obtained from the adsorption of CO₂ at 273 K is higher than that obtained from N₂ at 77 K for sample S750A20, which corresponds to the less-activated carbon. This difference is indicative of pore constrictions at the entrance of the micropores, indicating activated diffusion for nitrogen due to its narrow microporosity.¹⁴

BET surface area data corresponding to samples S750A40, S750A75, and S750A100 indicate that these carbons have a highly developed porous system corresponding to their high activation level. However, sample S750A100 exhibits a lower surface area measured in CO₂ than that measured in N₂. The extent of the activation has been too high, and a part of the porous system created at a lower burnoff has been destroyed. The micropore volume measured in CO₂ decreases for this sample, as can be observed in Table 2.

The activation conditions used in this work change the amount and type of surface oxygen functional groups of carbons, as can be observed from Tables 3 and 4 and Figures 2 and 3.

The profiles of CO and CO₂ evolution during a TPD experiment are shown in Figure 3. The total amount of CO and CO₂ evolved up to 1000 °C in a TPD run for each carbon is reported in Table 3.

The amounts desorbed and the temperatures at which these gases were released have been found to be characteristic of various oxygen complexes. In general, it is agreed that each type of oxygen surface group decomposes to a defined product. It has been proposed that CO₂ derives from complexes like carboxylic acids, anhydrides, and lactones and CO derives from complexes like phenolic and quinonic groups. The complexes yielding CO₂ have been shown to decompose typically over a range of temperatures of 150–600 °C and complexes yielding CO at temperatures in the range of 600–1000 °C.³

(13) Izquierdo, M. T.; Rubio, B. *Environ. Sci. Technol.* **1998**, *32*, 4017–4022.

(14) Illan, M. J.; Linares-Solano, A.; Salinas-Martinez de Lecea, C. *Energy Fuels* **1993**, *7*, 146–154.

Figure 2. CO₂ (1) and CO (2) profiles in TPD runs (y axis in arbitrary units): (a) S750A20, (b) S750A40, (c) S750A75, and (d) S750A100.

Figure 3. FTIR spectra: (1) S750A20, (2) S750A40, (3) S750A75, and (4) S750A100.

The activation with steam led to a change in TPD spectra not only in the amount evolved but also in the shape of CO₂ and CO peaks.

Samples show asymmetric peaks for both CO₂ and CO profiles. The CO₂ profile of S750A20 shows a shoulder at 620 °C and a peak at about 750 °C. The first peak can be assigned to lactones and the second one to thermally stable anhydrides. Anhydrides evolved as well as CO, and a peak of CO can be found at 750 °C. A higher-temperature CO peak

can be attributed to carbonyl and/or quinonic groups, which are thermally more stable than phenolic and etheric structures. This pattern is similar to those found in TPD spectra from samples S750A40, S750A75, and S750A100. However, CO₂ and CO peaks are shifted at higher temperatures, because of the increase of the stability of surface complexes due to the increase in the severity of activation conditions.

The total number of surface complexes measured as total CO and CO₂ evolved in TPD experiments increases at an increasing activation degree, as can be seen in Table 3. This result agrees with the oxygen contents given in Table 1. The introduction of surface groups that yield CO increases with the activation degree. However, the amount of CO₂ yielding groups is similar when a different concentration of steam is used as the activating agent. The creation of these types of groups by steam activation competes with their destruction because of the temperature of activation.

The selective base neutralization method gives more information on the oxygen surface functionality of the carbons studied. The results of the base neutralization are given in Table 4.

The acidity enhancement is evidently due to the activation of the samples because there is a saturation of dangling bonds with oxygen. As a result, the total acidity of the activated carbons is 2 times higher than that of the precursor. Less-stable surface oxygen complexes, such as carboxyls and lactones, remain almost constant at an increasing severity of activating conditions. However, the increase in the amount of phenol and carbonyl groups can be observed only in samples S750A40, S750A75, and S750A100. These groups are thermally more stable than carboxyls and lactones, and these results are in agreement with those obtained from TPD.

The FTIR spectra of carbon samples are shown in Figure 3. The broad bands observed in the spectra are expected because the functional groups within exist in a wide range of different electronic environments.

Figure 4. Reaction profiles of NO conversion: (a) S750A20, (b) S750A40, (c) S750A75, and (d) S750A100.

An inspection of Figure 3 shows that there are three bands of interest in the regions of 3500, 1550, and 1100 cm^{-1} . The IR assignments of functional groups on carbon surfaces have been carried out following refs 15–17.

The band at 3500 cm^{-1} can be assigned to the O–H stretching mode of hydroxyl functional groups that can be attributed to carboxyl groups. The intensity of this band does not change appreciably, indicating the presence of similar amounts of those groups in the samples, confirming results from Boehm titration. The band at 1550 cm^{-1} is associated with quinone and ceto-enol groups. This band is shifted from 1620 cm^{-1} (sample S750A20) to 1530 cm^{-1} (samples S750A40, S750A75, and S750A100). This fact can be explained in terms of the higher contribution of quinone groups and agrees with results from Boehm titration and TPD experiments. Moreover, the intensity of this band increases with the severity of the activation conditions. Samples have a broad band that extends from 1000 to 1300 cm^{-1} . This has been assigned to C–O stretching and O–H bonding modes of alcoholic, phenolic, and carboxylic groups. For sample S750A20, the band is sharper, and it is shifted to 1070 cm^{-1} , which could indicate a higher contribution of phenolic and ether groups. Samples S750A40, S750A75, and S750A100 exhibit this band at 1140 cm^{-1} , indicating greater participation of the carboxylic –OH group. Arguments in favor of this assignment can be obtained from the results presented in Table 4.

3.2. Catalytic Activity. The NO conversion curves versus time for samples S750A20, S750A40, S750A75, and S750A100 are shown in Figure 4.

Previous experiments with varying flow rates at constant contact times showed that the reaction was not limited by outer mass transfer. Similarly, no pore diffusion limitation occurred above 120 °C. Experimental error on the conversion values was observed within 3%.

The conversion of NO on the samples decreased from nearly 90% to different levels of conversion after an initial period of time. The rapid decrease in NO conversion observed during the initial period of the reactions suggests that NO was removed by adsorption as well as catalytic reduction. After this initial period, a constant value of conversion is achieved, indicating that a steady state has been reached. This constant value of conversion is maintained for 20 h afterward. Table 5 shows the conversion values at a steady state as well as the amount of NO removed after 15 h of experimentation.

Selectivity of the reaction to N_2 was 100% in all of the experiments performed at the experimental conditions used.

High de-NO_x activities are achieved by activated carbons, increasing conversions at the steady state at an increasing degree of burnoff.

Table 5. NO Conversion at Steady State and Amount of NO Removed after 15 h of Reaction (in mg NO Removed/g of Sample)

	S750A20	S750A40	S750A75	S750A100
conversion, %	56	64	80	87
amount removed (mg/g)	21.8	23.9	29.3	31.8

The NO removal capacity of the carbons studied directly correlate neither with the BET surface area nor with the total number of oxygen surface groups, as can be deduced from Tables 2–5.

Conversion levels reached by the carbons studied follow an increasing trend with activation levels and BET surface areas. However, there is not a direct correlation, as can be deduced from Table 2 and Figure 4. An increase of 25% of the conversion level from samples S750A20 and S750A100 cannot be explained from the small differences between both BET surface areas.

It is currently assumed that the SCR reaction of nitrogen oxide with ammonia over carbon catalysts in the presence of oxygen occurs according to the mechanism which was first proposed by Mochida et al.¹⁸ They concluded that the adsorption of ammonia and nitrogen oxide occurs on adjacent acidic and basic surface oxides, resulting in the formation of NH_4^+ ions and NO_2^- like species, respectively. Then, the adsorbed species react to produce water and nitrogen.

Previous studies on activated carbons obtained from low-rank coal as a precursor showed that the introduction of new functional groups enhanced the carbon activities for NO removal.^{6,13} Moreover, an optimum range in the amount of oxygen functional groups where the de-NO_x activity was markedly enhanced was found.⁶ However, those research works were carried out on carbons that have different surface areas, and the surface chemistry made it difficult to separately study the influence of each one on the performance of the carbons.

In the present case, activated carbons exhibit similar surface areas, but the activation has led to a different extent in the number of oxygen functional groups. Here, the study of the effect of the surface chemistry of carbons on NO removal can be carried out “discarding” the influence of BET surface areas.

A study using transient techniques over two samples of low-rank coal-based carbons showed that CO-yielding groups in TPD experiments were the most important oxygen functional groups in determining high NO removal activities.¹⁹ Among these groups, carbonyls seemed to be the appropriate group to enhance the performance of carbons for NO removal. However, in that paper, the influence of surface area could not be obviated.

Table 2 shows that surface areas of samples are in the same range, but a large difference in NO conversion can be found. On the other hand, the most activated samples, S750A75 and S750A100, exhibit the highest amount of CO-yielding groups in a TPD experiment (Table 3) and CO/CO₂ ratio as well as surface area. In this case, both samples have comparable NO removal activities. Moreover, comparing titration results from Boehm’s procedure in Table 4, one can infer that the most important difference among surface groups is due to carbonyls, the contribution of carboxyls being similar for the three samples.

(15) Zawadzki, J. *Infrared Spectroscopy in Surface Chemistry of Carbons. Chemistry and Physics of Carbon*; Marcel Dekker: New York, 1989; pp 147–380.

(16) Starsinic, M.; Taylor, R. L.; Walker, P. L., Jr.; Painter, P. C. *Carbon* **1983**, *21*, 69–74.

(17) Fanning, P. E.; Vannice, M. A. *Carbon* **1993**, *31*, 721–730.

(18) Mochida, I.; Ogaki, M.; Fujitsu, H.; Komatsubara, Y.; Ida, S. *Nippon Kagaku Kaishi* **1985**, *4*, 680–684.

(19) Fierro, V.; Izquierdo, M. T.; Schuurman, Y.; Rubio, B.; Mirodatos, C. *Stud. Surf. Sci. Catal.* **2002**, *144*, 255–260.

This fact can be the object of controversy, because one can find in the literature studies postulating that surface and/or phenolic groups play the role of catalytically active acidic sites in the mechanism of the SCR reaction of NO with ammonia.^{20,21} In marked contrast, it is reported that the heat treatment of a pitch-based activated carbon fiber (ACF) of very large surface area provided much higher de-NO_x activity.^{22,23}

This latter result could be in agreement with the results presented in this paper. A heat treatment up to temperatures not exceeding 500 °C would remove carboxyls but not carbonyls, which appear to be responsible for the catalytic enhancement of carbons, as it was reported previously¹⁹ and seemed to be confirmed in this paper.

A work is in progress using transient techniques, following the procedure reported in ref 19, that will allow the in situ heat

treatment of the samples in order to study the influence of the removal of selected oxygen surface groups on the NO removal capacity of carbons.

4. Conclusions

This study has demonstrated that the activity of carbon catalysts in catalytic NO reduction with ammonia does not correlate with BET surface area. However, for similar surface areas, the volume of macro- and mesopores increases with the severity of activation conditions and the volume of micropores decreases. This result suggests that surfaces in carbon micropores are not fully utilized in the reaction.

The activity of activated carbons increases with the amount of CO evolved during TPD experiments. The main change in surface oxygen groups corresponds to carbonyls, this result being supported by FTIR and Boehm titration.

EF060557L

(20) Teng, H.; Tu, T.; Lai, Y. C.; Lin, C. C. *Carbon* **2001**, 39, 575–582.

(21) Teng, H.; Ho, J. A.; Hsu, Y. F. *Carbon* **1997**, 35, 275–283.

(22) Mochida, I.; Kawano, S.; Kismori, S.; Fujitsu, H.; Maeda, T. *Carbon* **1994**, 32, 175–177.

(23) Mochida, I.; Kawano, S.; Yatsunami, S.; Yoshikawa, M. *Energy Fuels* **1995**, 9, 659–664.