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SELECTIVE CATALYTIC REDUCTION OF NO WITH NH_3 OVER ACTIVATED CARBONS. I: EFFECT OF ORIGIN AND ACTIVATION PROCEDURE ON ACTIVITY

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Abstract—The activity for the selective catalytic reduction of NO with NH_3 (SCR) of a suite of different activated carbons has been studied in the temperature range 373–550 K. The effect of origin (bituminous coal, peat, plum stones, and olive pits), activation agent (steam, CO_2), and degree of activation was investigated by activity measurements. In general, the SCR activity, which is relatively high at 373 K, decreases with increasing temperature, and for some carbons increases again above 450 K. Two types of SCR processes are operative. In the lower temperature range, the narrow microporosity affects the rate by increased adsorption of NO, resulting in higher local concentrations. In the higher temperature range, oxygen functional groups determine the SCR activity level. Precursors yielding narrow microporous carbons result in better activities below 450 K. Steam-activated carbons gave higher SCR activity above 450 K than CO_2-activated carbons.

Key Words—Activated carbon, microporosity, selective catalytic reduction of NO with NH_3, surface oxygen groups

1. INTRODUCTION

Activated carbons are common adsorbents for gases, vapours, and solutes from aqueous solution[1]. However, carbonaceous materials can also be used as catalysts and catalyst supports[2]. In fact, activated carbons have been used for years for clean-up of industrial process gases and off-gases, such as H_2S, SO_2, and NO_x[3]. Operating temperatures below 470 K are generally required to avoid carbon gasification by oxygen. The subject of this paper is the removal of NO—a typical contaminant mainly produced in industries and electricity generation plants—by using activated carbons as catalysts. Carbons obtained by different preparation procedures, from different raw materials, and of different porous texture were used.

Several catalysts and reactions have been suggested in the literature[4,5] for the removal of NO_x, mainly via selective catalytic reduction with ammonia (SCR), where a high NO_x removal efficiency (>80%) is obtained, viz.,

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O. \quad (1)$$

Most of the proposed catalysts[6–8] are active at temperatures above 573 K, but the use of low-temperature catalysts could be desirable when the SCR reactor has to be placed as an add-on unit at the end of the flue gas system ($T < 500$ K), and especially when carbon is the catalyst support in order to avoid gasification reactions[9].

There are a few papers in the literature[3,10–15] dealing with the use of activated carbons as catalysts in the SCR reaction at these low temperatures, but still above 363 K, to avoid the formation of ammonium nitrate.

In general, the properties of activated carbons depend on several factors, such as preparation procedure (raw material, activating agent, etc), porous texture, and surface chemistry[16,17]. These factors strongly influence the transport phenomena in the carbon, adsorption and chemisorption characteristics, and the activation of molecules in catalytic reactions. The role of a catalyst is twofold: (a) to concentrate reacting molecules locally, and (b) to activate these species selectively for the desired reaction, typically via adsorption of the reactants. Especially for exhaust gas catalysis, the first aspect is important in view of the low concentrations that must be treated. In a previous study[18] it was found that in low-temperature SCR over modified carbons, adsorption phenomena affect the rate considerably. The origin of the carbon has been demonstrated to

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be important for SCR activity and stability of the carbon catalyst[19]. The presence of heteroatoms like oxygen and nitrogen also influences SCR activity[14,18,20]. Even a crude linear correlation has been reported[21] between the active surface area (ASA) and SCR activity of some high-temperature carbon samples prepared from oxidized bituminous carbon, although no conclusive relationship was found. From these studies, no clear-cut picture arises of what causes the SCR activity of carbonaceous materials. This is mainly due to the large diversity of precursors and the various methods and degrees of activation. In this paper at attempt has been made to explore the effect of origin and the method and degree of activation on the SCR activity.

2. EXPERIMENTAL

2.1 *Activated carbons*

Several carbonized materials and activated carbons were selected for the SCR process: polymers, lignocellulosic materials, subbituminous coals, and peat. These carbons were activated in carbon dioxide and steam. Some of these carbons (series P and D) were prepared in the Department of Inorganic Chemistry of the University of Alicante (Spain), and others were provided by DMT—formerly Bergbau Forschung (series B)—(Essen, Germany) and Norit (series N) (Amersfoort, The Netherlands). Table 1 summarizes the preparation conditions for the samples. It is noted that the samples of the same origin were produced simultaneously, and differ only in the degree of activation. Prior to their characterization and use for SCR, all carbons were crushed and sieved to a particle size between 0.20–0.25 mm.

2.2 *Determination of the porous texture of the carbons*

N_2/77 K and CO_2/273 K adsorption-desorption isotherms of the activated carbons were determined in a Carlo Erba Sorptomatic 1800 system. Samples of 100–200 mg carbon were outgassed in vacuum (10^{-3} torr) at 473 K for three hours. Adsorption equilibration time was one hour for the first experimental measurement and 20 min for the others. Each desorption step required 30 min. Apparent surface areas (S) of the carbons were calculated by applying the BET method[22]. Cross-sectional areas of 0.162 nm^2 for each N_2 molecule adsorbed at 77 K, and 0.187 nm^2 for CO_2 at 273 K were assumed. The micropore volumes of the carbons were calculated from the Dubinin-Radushkevich (DR) equation[23]. Liquid densities of 0.808 g/cm^3 for N_2/77 K and 1.023 g/cm^3 for CO_2/273 K were used[18].

Meso- (pore size greater than 3.8 nm) and macroporosity of the carbons have been obtained using mercury porosimetry (Porosimeter 4000, Carlo Erba).

2.3 *Temperature Programmed Desorption*

Temperature Programmed Desorption (TPD) experiments were carried out for most carbon samples in a thermobalance (Setaram TG 85). Carbon samples (60 mg) were heated in Ar at a rate of 10 K min^{-1} to 1673 K, followed by an isothermal step at 1673 K. The evolved gases were analyzed by gas chromatography for CO, CO_2, and CH_4.

2.4 *SCR reaction*

Catalytic activity for NO reduction was tested in an apparatus described elsewhere[9]. In this system, six catalyst samples can be tested simultaneously by means of six parallel reactors placed in one oven.

Table 1. Some characteristics of the activated carbons

Carbon	Manufacturer	Raw material	Activation procedure
D55/2	BF[a]	Subbituminous	Steam
D45/2	BF	Subbituminous	Steam
A35/2	BF	Subbituminous	Steam
A59%	BF	Subbituminous	Steam
A3985	Norit	Peat	Steam
A3984	Norit	Peat	Steam
A3983	Norit	Peat	Steam
RX1-extra	Norit	Peat	Steam
SX-plus	Norit	Peat	Steam
X	IC[b]	Plum stones	CO_2
Y	IC	Plum stones	CO_2
Z	IC	Plum stones	CO_2
D8	IC	Olive pits	CO_2
D19	IC	Olive pits	CO_2
Z1	IC	Almond shell	$ZnCl_2$
CA1	Norit	Saw dust	H_3PO_4
P	IC	Olive pits	H_3PO_4

[a] DMT, former Bergbau Forschung, Essen, Germany.
[b] Inorganic Chemistry Department, University of Alicante, Alicante, Spain.

Table 2. Standard conditions of the activity measurements

NO	500 ppm
NH_3	550 ppm
O_2	2 volume %
He	Balance
Temperature	373–548 K
Pressure	1 atm
Flow rate	25 cm^3 (STP)/min
Carbon sample	300 mg
Volume hourly space velocity (VHSV)	5000 h^{-1}

One of the reactors was always used as an empty blank or reference. Gases leaving the system were analyzed with a computer-controlled mass spectrometer. Standard conditions of the activity measurements are presented in Table 2. The carbon samples were initially outgassed in a 100 ml/min nitrogen flow at 573 K for 30 min, to remove any adsorbed water. The temperature was then decreased to 423 K, and the reaction mixture was kept flowing for 12 hours until steady-state conditions were attained. Screening tests of the carbon catalysts started at 373 K; the temperature was then increased stepwise to 383, 398, 423, 448, 473, 498, 523, and 548 K. At all temperatures the catalyst activity was monitored for at least two hours. In order to find if any catalyst deactivation occurred during the SCR reaction, the activity of some activated carbons was determined in consecutive increasing-decreasing temperature cycles.

3. RESULTS

As a typical example, Fig. 1 presents the concentration of evolved NO, NH_3, and N_2 as a function of the temperature for carbon D55/2. Up to 500 K, NO and NH_3 react in a 1 : 1 ratio according to eqn (1). Above 500 K, NH_3 oxidation occurs, resulting in a higher consumption rate than NO. Also the formation of CO_2 is then observed (m/e = 44). From experiments with $^{15}NH_3$, the formation of N_2O could be excluded, according to previous studies[24]. Therefore, for safe operation the reaction temperature should be kept below 450 K. Furthermore, the N_2 evolution pattern shows a minimum around 440 K; at higher and lower temperatures, N_2 formation by SCR is greater[24].

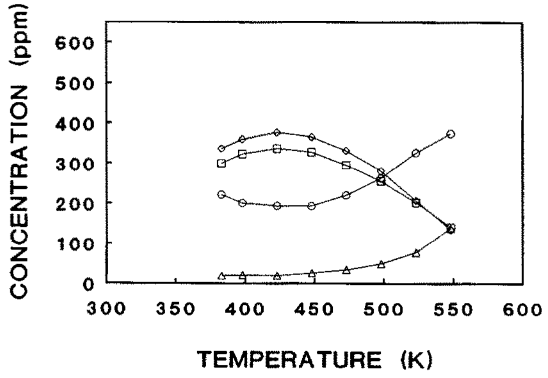

Fig. 1. Concentration profiles of NO, NH_3, and N_2 as a function of the temperature. Sample: Carbon D55/2. (□) NO; (◇) NH_3; (○) N_2; (△) m/e = 44.

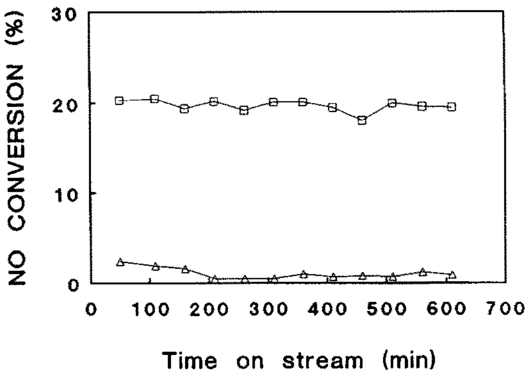

Fig. 2. Influence of oxygen in the SCR reaction. Carbon catalyst A3985. T = 423 K: (△) without; (□) with 2% volume O_2.

As indicated in eqn (1), the presence of oxygen is essential for SCR, in agreement with Richter *et al.*[3,25]. Figure 2 shows the degree of NO removal efficiency reached with the carbon catalyst A3985 with and without oxygen in the reaction mixture. In the range of temperature considered and in the absence of oxygen, the activity is low, and a noticeable decrease in NO reduction after 200 min of time on stream is observed. A much higher and constant NO conversion is achieved in the presence of oxygen. From the product analysis it could be verified that the reaction stoichiometry of eqn (1) is satisfied in the latter case.

Several factors may affect the efficiency of NO removal with activated carbons. In this work the raw precursor (peat, subbituminous coals, plum stones, olive pits), the activation agent (steam, CO_2), and the carbon burn-off were considered. Figures 3a and b show NO conversion as a function of temperature for the steam-activated carbons, and Figures 3c and d the corresponding activities for CO_2-activated carbons. Steam-activated carbons from Bergbau Forschung (series B) initially show a decrease in NO conversion up to 450 K, which thereafter either remains unchanged (carbon A59%), or increases at higher temperatures in the order: A35/2 < D45/2 < D55/2 (see Fig. 3a). As shown subsequently, the behaviour of carbon A59% is the most representative of the carbons tested in this work. In fact, all steam-activated carbons from Norit (series N) tested show the same variation of NO conversion as a function of temperature as carbon A59% (Fig. 3b). NO removal efficiency decreases in the order: A3985 > A3984 = A3983 = RX1-extra.

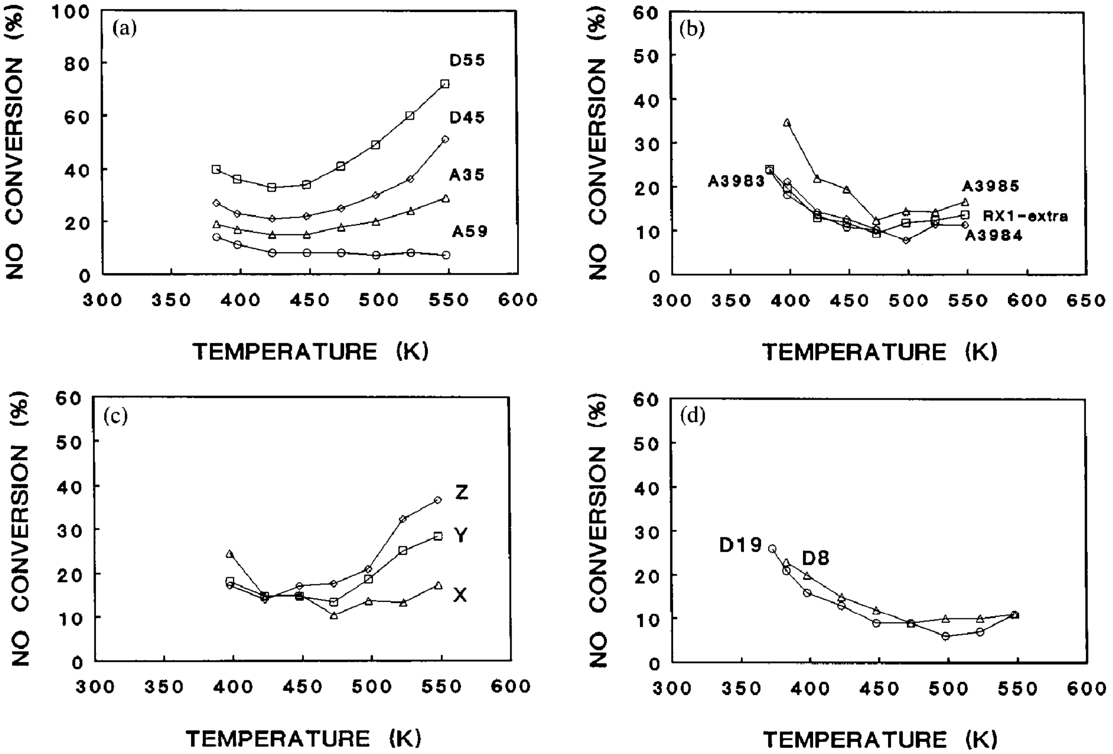

Fig. 3. NO conversion as a function of reaction temperature for steam- and CO_2-activated carbons. Steam-activated carbons: (a) Series B: (□) D55/2, (◇) D45/2, (△) A35/2, (○) A59%. (b) Series N: (△) A3985, (◇) A3984, (○) A3983, (□) RX1-extra. CO_2-activated carbons: (c) Series P: (△) X, (□) Y, (◇) Z. (d) Series D: (△) D8, (○) D19.

CO_2-activated carbons D8, D19 (series D), and X (Figs. 3c and d) follow the same trend as carbon A3985 with increasing reaction temperature, but the NO reduction level never exceeds 25%. Additionally, there is no difference in the percentage of NO removed at low temperatures in carbons with a wide micropore size distribution (Y and Z). Therefore, the raw material, the degree of burn-off, and the activating agent all influence SCR behaviour for the activated carbons used in this work, with steam seeming more efficient than carbon dioxide.

Some repetitive runs were carried out for all the carbon samples to determine their activity behaviour with time and temperature. No decrease of NO conversion was noted for any of the carbons, in contrast with the behaviour of chemically activated carbons (which were also studied, although they have not been included here), where a noticeable decrease in activity was always found after the first run.

Figures 4a and b show the N_2(77 K) adsorption isotherms for series B and N, respectively. The cor-

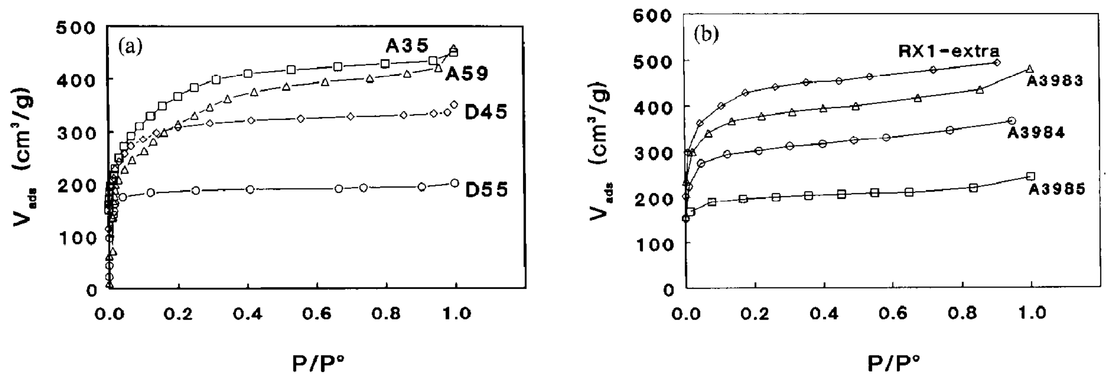

Fig. 4. N_2/77 K adsorption isotherms of steam-activated carbons. (a) Series B: (○) D55/2, (◇) D45/2, (□) A35/2, (△) A59%. (b) Series N: (□) A3985, (○) A3984, (△) A3983, (◇) RX1-extra.

Table 3. Characterization data of steam-activated carbons

	N_2/77 K-BET		V_0 (cm^3/g)-DR		V_p[a]	Hg poros. (cm^3/g)	
Carbon	S (m^2/g)	C	N_2	CO_2	(cm^3/g)	Meso	Macro
D55/2	809	247	0.30	0.28	0.30	0.05	0.29
D45/2	1142	316	0.40	0.35	0.52	0.16	0.37
A35/2	1348	112	0.42	0.33	0.67	0.32	0.45
A59%	1155	84	0.43	0.31	0.65	0.32	0.11
A3985	766	2402	0.31	0.29	0.34	0.07	0.29
A3983	1172	768	0.48	0.32	0.57	0.14	0.40
A3984	1398	845	0.55	0.34	0.68	0.19	0.44
RX1-extra	1542	390	0.65	0.45	0.77	0.15	0.45
SX-plus	1089	978	0.42	0.29	0.73	—	—

[a] Pore volume filled at $P/P^o = 0.95$ in the N_2 adsorption isotherm.

responding N_2(77 K) adsorption isotherms of the CO_2-activated carbons (series P and D) have been published elsewhere[26,27]. Tables 3 and 4 include the apparent surface areas and micropore volumes of these carbons. The shapes of the adsorption isotherms are consistent with essentially microporous materials. Carbon D55/2 has the smallest apparent surface area and pore volume of series B, its N_2 adsorption isotherm showing the presence of a narrow microporosity in the carbon. The agreement between N_2 and CO_2 micropore volumes (DR) also confirms the existence of such a narrow and uniform microporosity[18]. Carbons D45/2 and A35/2 (series B) have a more developed porous texture, since they are of an increasing degree of activation. Carbon A59% has a much wider pore size distribution (there is a noticeable knee in the N_2 adsorption isotherm for relative pressures below 0.2), a higher adsorption capacity, and larger pore volume than carbon D55/2. On the other hand, the adsorption isotherms of series N exhibit the same features as those of series B. Carbon A3985 has the smallest pore volume and the narrowest micropore size distribution (Table 3), whereas the N_2 adsorption isotherm of carbon RX1-extra shows a much wider and developed porous texture. With respect to CO_2-activated carbons, those with a burn-off below 25% (D8, D19, X) present a narrow pore size distribution and apparent surface areas below 1000 m^2/g; thus, these carbons have a porous texture quite similar to carbons D55/2 and A3985. Higher degrees of activation (increase of the burn-off) produced an enlargement of the porous texture of the carbons (Y and Z), mainly of the microporosity (Table 4).

According to Figures 3 and 4, the least porous carbons having a narrow micropore size distribution are the most efficient catalysts for SCR, and thus, the existence of a developed porosity in the carbon does not favour NO conversion. As in the case of the series B carbons, a narrow micropore size distribution in series N favours NO reduction, but there is no such increase in activity at high reaction temperatures. Thus, the type of precursor can also influence SCR activity, which is, in general, lower for series N. The same is valid for CO_2-activated carbons, although lower NO conversions than steam-activated carbons are obtained.

Efficiency of carbons as catalysts may be influenced not only by their porosity, but also by their surface chemistry (mainly oxygen complexes). An indirect measurement of the oxygen complexes can be obtained from the TPD profiles of the carbons. Figures 5a and b show the TPD profiles in Ar corresponding to the evolution of CO and CO_2 as a function of the temperature from carbons D55/2 and A59%, those having the highest and lowest NO conversion, respectively, in the series B of steam-activated carbons. As expected, the evolution of CO_2 is produced at lower temperatures than CO, and always the amount of CO is larger than that of CO_2 (0.9 wt% CO_2 and 3.3 wt% CO for carbon D55/2, compared to only 0.3 wt% CO_2 and 1.8 wt% CO for

Table 4. Characterization data of CO_2-activated carbons

		N_2/77 K-BET		V_0 (cm^3/g)-DR		V_p[a]	Hg poros. (cm^3/g)	
Carbon	% burn off	S (m^2/g)	C	N_2	CO_2	(cm^3/g)	Meso	Macro
D8	8	647	2805	0.26	0.26	0.27	0.10	0.10
D19	19	797	1908	0.31	0.30	0.34	0.10	0.23
X	23	812	453	0.35	0.32	0.36	0.06	0.45
Y	52	1627	273	0.68	0.45	0.73	0.20	0.56
Z	71	2365	106	1.08	0.49	1.18	0.28	0.45

[a] Pore volume filled at $P/P^o = 0.95$ in the N_2 adsorption isotherm.

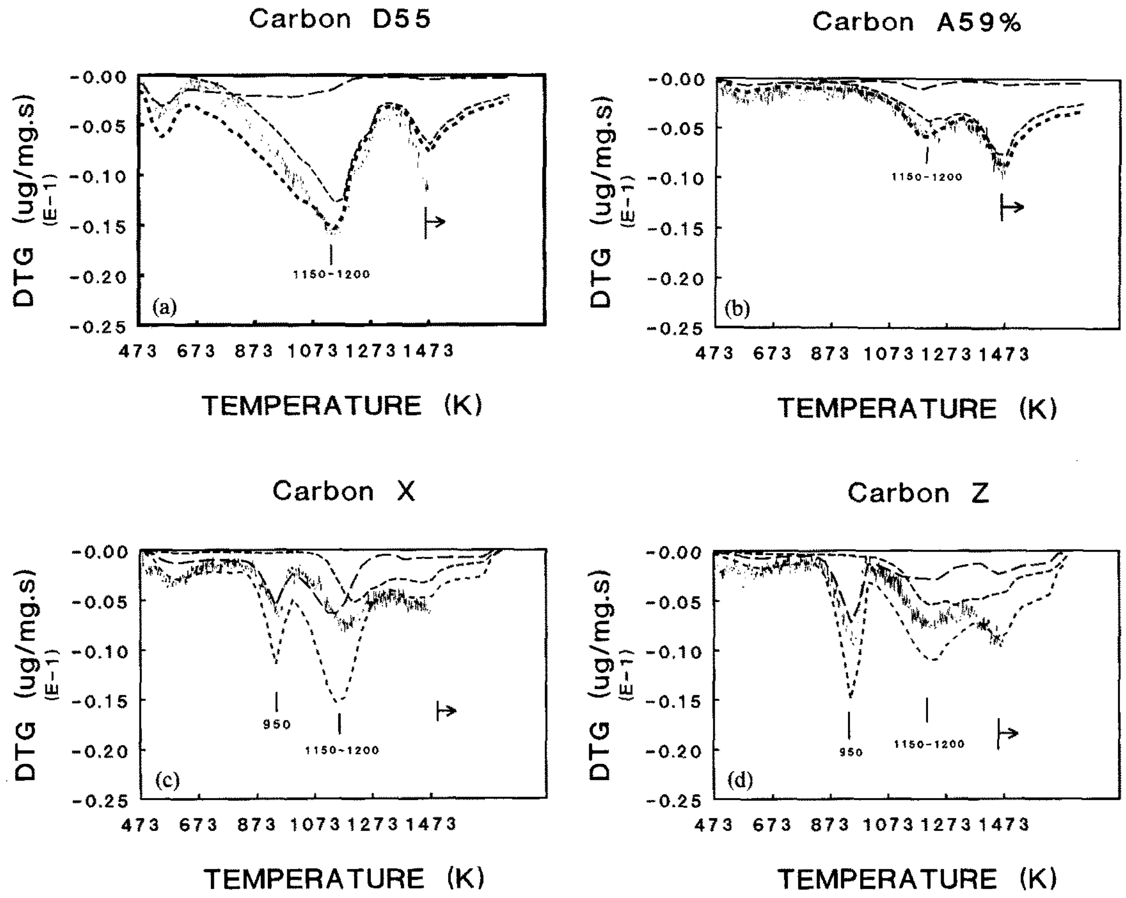

Fig. 5. Weight loss rate as a function of the temperature during a TPD experiment in Ar of carbons. (———) mass loss, (· · · ·) CO + 2CO$_2$, (——— ———) CO$_2$, (– – –) CO. Steam-activated carbons: (a) D55/2, (b) A59%. CO$_2$-activated carbons: (c) X, (d) Z.

carbon A59%). The major peak appears between 1150–1200 K, which corresponds to CO; even above 1473 K, a noticeable CO loss is observed. Carbons with burn-offs between those of D55/2 and A59% yield intermediate results. Therefore, SCR activity of series B of activated carbons at high temperature can be determined by the adsorption effect in the narrow micropores and the surface chemistry of the carbon.

With respect to CO$_2$-activated carbons, TPD profiles of carbons X and Z (Figs. 5c and d), having a narrow and a wide micropore size distribution, respectively, exhibit a slight difference in weight loss around 950 K due to the release of CO$_2$. This CO$_2$ evolution might be due to a decomposition of CaCO$_3$ produced from calcium oxide in the mineral matter of plum stones, which readily forms calcium carbonate upon cooling from activation in CO$_2$. Furthermore, in the CO$_2$-activated carbons the weight loss between 1150–1200 K and above 1473 K (due to CO release) also occurs in the steam-activated carbons. For those carbons the amounts of CO and CO$_2$ increase with the burn-off and thus, SCR activity is enhanced in the carbons with the highest degree of activation.

Comparing the results for the series B and P of carbons, it may be concluded that the narrow microporosity enhances SCR activity below 450 K, whereas the narrow microporosity and/or the oxygen functionality of the surfaces may determine the activity above 450 K (the highest CO and CO$_2$ evolution, the greater SCR activity).

4. DISCUSSION

The selective catalytic reduction of NO by activated carbons is most effective at temperatures below 450 K in order to maintain an NO and NH$_3$ reaction stoichiometry 1 : 1. At higher temperatures, NH$_3$ oxidation occurs and CO$_2$ is produced, resulting in degradation of the carbons. O$_2$ is always needed for the reaction, and the activity level of the physically activated carbons is maintained after several runs.

It is clear from the results that the nature of the carbons (raw material, activation procedure, degree of burn-off) determines their catalytic behaviour in the SCR process. The most striking result is that the least activated samples (i.e., those with the narrowest microporosity) within one series exhibit the

Table 5. Characterization data of carbons prepared by chemical activation

Carbon	S_{BET} (m^2/g)	V_0 (cm^3/g)-DR N$_2$	V_0 (cm^3/g)-DR CO$_2$	V_p[a] (cm^3/g)
Z1	729	0.32	0.19	0.34
CA1	1257	0.51	0.29	0.93
P	1409	0.57	0.32	0.94

[a] Pore volume filled at $P/P^o = 0.95$ in the N_2 adsorption isotherm.

highest activity in most cases at 373 K (carbons D55, A3985, X). Increasing degree of activation lowers the activity to a certain level (series N, series P), irrespective of porosity. At the highest temperatures, series B with order of activity D55/2 > D45/2 > A35/2 > A59%, and series P with Z > Y > X do not only correlate with the type of porous texture (just opposite for these series), but with the CO and CO_2 amounts evolved in the TPD diagrams of the activated carbons. It is suggested that the adsorption effect in the narrow micropores combined with the surface oxygen groups are probably the factors responsible for SCR activities of activated carbons above 450 K. For the activated carbons studied, there is apparently a relationship between the number of oxygen complexes in the carbon and SCR activity.

On the other hand, the series activated in steam exhibit higher activity than the CO_2-activated carbon series, indicating that additional factors than the narrow microporosity and the amount of oxygen functionalities on the carbon surface may determine SCR activity in carbons. More experimental work is currently being carried out to substantiate this hypothesis.

The initial decrease of activity vs temperature for some carbons (Fig. 3) can be explained by considering that at low temperature (373 K), NO and/or NH_3 can be strongly retained in the carbons, due to the adsorption potential of the micropores. Due to this adsorption, the concentration and residence time of the reactants in the pores will be longer, and the reduction of NO will be more efficient. According to the literature[28,29], NO molecules can dimerize in the narrow micropores of carbons due to the high intrapore pressure. Thus, a higher concentration of NO can exist in the narrow micropores, leading to a higher degree of NO conversion to N_2.

However, the degree of adsorption and the existence of $(NO)_2$ decreases the temperature (373–450 K), leading to a reduction of No conversion; apparently the highest activity is obtained at 373 K. This implies that the heats of adsorption of NO with NH_3 involved are larger than the activation energy of the (unknown) rate-determining step, resulting in an observed overall negative activation energy[24]. Apparent negative activation energies have been found more with reactions in which NO is involved, like the oxidation of NO to NO_2[30,31], the reaction between NO_2 and NH_3[32], and reactions between NO or NO_2 with the NH_2 radical[33–36], all in the temperature range of this study. The oxygen pressure dependence of the SCR reaction over carbon[24] suggests that the NO oxidation or the oxidative abstraction of hydrogen from NH_3 is an important step, but the present data are insufficient to allow more conclusions. Another possible explanation of the slightly negative activation energies (<10 kJ mole^{-1}) might be the participation of the NO dimer in a rate-determining step in microporous carbons with narrow porosity at low temperature.

Summarizing the results, it appears that two types of reaction mechanisms are operative in SCR over activated carbons: (a) At low temperature the activity is controlled by the narrow microporosity of the carbon. (b) At high temperature the activity is governed by the narrow microporosity and/or oxygen functionalities. Both types of activity depend on the method of activation and precursor. For intermediate temperatures there is a contribution of both types of activity.

Correlation with narrow microporosity implies that adsorption phenomena play a role in the SCR process. Adsorption increases the local concentration of reactants, which leads to higher reaction rates and very probably favours the formation of NO dimers in the micropores due to the high effective intrapore pressure.

On the other hand, the positive role of oxygen functionalities on the carbons in the SCR process at high temperature may be ascribed to the activation of NH_3 (perhaps by hydrogen abstraction) and/or the chemisorption of NO in nitrate or nitrite complexes where carbon acts as a catalyst. In this way, the carbon also acts as an activator of the reactants. However, the role and the type of these oxygen groups should be investigated in more detail.

The precursor and the activation procedure of the carbon determines SCR activity. Narrow microporosity-forming precursors (e.g., subbituminous coals) are favourable for low-temperature activity. The introduction of oxygen functionalities works positively, especially at the higher temperature region, although depending on the carbon, this may extend to the low-temperature region, resulting in composite activity.

5. CONCLUSIONS

1. Activated carbons can be used as catalysts to reduce NO with NH_3 at temperatures as low as 373 K. Generally, one observes an activity decrease from 373 to 450 K, whereas for higher temperatures there is an increase for some carbons. The relatively high activity at 373 K can be explained as a favoured adsorption of reactants in the narrow micropores of the catalyst, enhancing the reaction rate by the

increased local concentration of NO, which favours the formation of NO dimer.

2. Oxygen surface complexes on the carbon (determined as CO and CO_2 evolved in TPD diagrams) contribute to the activity in the SCR process above 450 K.

3. Steam-activated carbons show higher SCR activity than CO_2-activated carbons.

4. The method of activation, the raw material, and the degree of activation together determine the final catalytic activity, depending on the development of the narrow microporosity and on the introduction of stable surface oxygen complexes in the sample.

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