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Influence of nitrogen surface functionalities on the catalytic activity of activated carbon in low temperature SCR of NO_x with NH_3

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Abstract

The reduction of nitrogen oxide with ammonia was studied using carbon catalysts with chemically modified surfaces. Carbon samples with different surface chemistry were obtained from commercial activated carbon D43/1 (CarboTech, Essen, Germany) by chemical modification involving oxidation with conc. nitric acid (DOx) (i), high temperature treatment (~1000 K) under vacuum (DHT) (ii) or in ammonia (DHTN, DOxN) (iii). Additionally, a portion of the DOx sample was promoted with iron(III) ions (DOxFe). The catalytic tests were performed in a microreactor at a temperature range of 413–573 K. The carbon sample annealed under vacuum (DHT) showed the lowest activity. The formation of surface acidic surface oxides by nitric acid treatment (DOx) enhanced the catalytic activity only slightly. However, as can be expected, subsequent promotion of the DOx sample with iron(III) ions increased drastically its catalytic activity. However, this was accompanied by some loss of selectivity, i.e. formation of N_2O as side product. This effect can be avoided using ammonia-treated carbons which demonstrated reasonable activity with simultaneous high selectivity. The most active and selective among them was the sample that was first oxidized with nitric acid and then heated in an ammonia stream (DOxN). A correlation between catalytic activity and surface nitrogen content was observed. Surface nitrogen species seem to play an important role in catalytic selective reduction of nitrogen oxide with ammonia, possibly facilitating NO_2 formation (a reaction intermediate) as a result of easier chemisorption of oxygen and nitrogen oxide.

Keywords: Activated carbon; Oxidation; Ammonia treatment; Nitrogen oxide; SCR; Catalytic properties

1. Introduction

All literature studies unanimously show that the catalytic activity of active carbons for NO conversion increases with the oxygen concentration on the carbon surface [1–12]. It is currently assumed that surface functional groups containing oxygen change the interaction between the carbon surface and the reactants through variation of adsorption and reaction characteristics [1–14]. However, there are still several unanswered questions concerning the effect of surface chemistry because of the complex influence of additional variables such as the physical characteristics (e.g. porosity, electronic properties, crystallographic structure) or presence of other hetero-atoms in the studied carbon catalysts [4,15]. Therefore, to avoid difficulties in the interpretation of the obtained results, it seems necessary to study the role of the surface chemistry, using samples with different chemical properties but of the same origin and with identical or similar porous structure.

Some reports indicate that incorporation of nitrogen into the carbon structures enhances the SCR activity [3,6,9–11,14]. However, the explicit role of the incorporated nitrogen is not entirely clear [4,6]. Thus the effect of surface nitrogen species on the catalytic behavior of activated carbons in the SCR reaction requires studies in more detail. In this work, the results of catalytic tests for carbon samples containing various amounts of different surface nitrogen and/or oxygen functionalities but with similar porous structure, obtained by appreciable modification of activated carbon D43/1 are reported.

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Table 1
Structural parameters obtained by the DFT method for the modified activated carbons [16]

Modified carbon	Mesopore surface area, S_{N_2} (m^2/g)	Macropore surface area, S_{N_2} (m^2/g)	Specific surface area, S_{N_2} (m^2/g)	Micropore volume, V_{mic} (cm^3/g)	Mesopore volume, V_{mes} (cm^3/g)	Total pore volume, V_{tot} (cm^3/g)
DHT	28	5	897	0.356	0.052	0.408
DHTN	31	4	883	0.346	0.042	0.389
DOx	20	4	798	0.335	0.026	0.361
DOxN	28	0	924	0.360	0.033	0.395
DOxFe	20	4	739	0.314	0.027	0.341

2. Experimental

2.1. Carbon modification and characterization

Four samples of de-ashed and chemically modified commercial activated carbon D43/1 (CarboTech, Essen, Germany) were studied: annealed in vacuum at 1023 K for 3 h (DHT sample), oxidized with concentrated nitric acid at 353 K for 3 h (DOx sample), as well as DHT and DOx carbons heated in ammonia at 1173 K for 2 h (DHTN, DOxN). Additionally, a portion of the DOx sample was promoted with iron(III) ions by ion-exchange with 0.05 M $Fe(NO_3)_3$ solution for 48 h. All prepared samples were stored in ambient air. The details of the modification of the studied carbons, as well as their physicochemical characteristics (FTIR, XPS, acid–base properties and porous texture) are given elsewhere [15–18].

In addition, the surface chemistry of the investigated carbons was characterized by temperature-programmed desorption (TPD-QMS) of decomposition products. The TPD-QMS experiments were carried out using a Netzsch STA409C apparatus equipped with a quadrupole mass spectrometer. The TPD-QMS technique was also applied to determine the acidic properties of the catalysts by performing thermal desorption of ammonia from the carbon samples preliminary treated with ammonia. The details of TPD experiments are given elsewhere [19–20].

2.2. Catalytic tests

Activity and selectivity in the SCR of NO with NH_3 were measured in a fixed-bed microreactor over a temperature range 413–573 K under the following conditions—gas velocity: 100 ml min^{-1}, mass of catalyst: 400 mg, gas pressure: 1 bar, gas composition: 800 ppm NO and NH_3, 3% O_2 and the rest helium. Educts and/or products (NO, N_2O, CO_2) were analyzed with a NDIR analyzer (Hartmann and Braun) on line at steady state.

3. Results and discussion

3.1. Characterization of carbon catalysts

All the modified carbons possess a well-developed, nearly the same porous structure, as described before (Table 1) [16]. Only in the case of the oxidized carbon (DOx) a small decrease in micro- and mesoporosity was observed. This is believed to be a consequence of the fixation of a part of surface oxygen complexes at the entrance of the pores which increases their constriction [15,17]. The presence of such functionalities narrows pore entrances or even may block them. After annealing in ammonia (DOxN), the restitution of the lost porosity occurred due to the removal of the mentioned groups [15]. The subsequent promotion of the DOx sample with Fe(III) ions by ion-exchange with nitrate solution decreased the microporosity further.

The oxidation enhances acidic properties, whereas annealing at high temperatures in ammonia (DHTN, DOxN) enhanced the basic properties of carbons at the expense of their acidic properties (Table 2). Our previous investigations [15,17] showed that the acidic properties of the investigated carbons resulted from the presence of carboxylic, phenolic and carbonyl structures in different chemical environments, whereas the basic properties originate from the presence of such oxygen functionalities, as pyrone structures or

Table 2
Acid–base properties of the modified carbons [15,16]

Carbon	NH_3[a] (×10^8 a.u.)	Concentration[b] (meq/g)					
		Acidic groups					Basic sites
		Total	–COOH	–COO–	>C–OH	>C=O	
DHT	1.63	0.223	0	0.01	0.124	0.089	0.420
DHTN	1.07	0.317	0	0.025	0.075	0.217	0.632
DOx	9.14	2.054	0.725	0.382	0.556	0.391	0.131
DOxN	–	0.357	0	0.04	0.068	0.213	0.722

[a] Amount of chemisorbed NH_3 from TPAD measurements (peak area).

[b] The results of the Boehm titration.

Table 3
Chemical surface composition (at.%) of the modified carbons obtained by XPS, disregarding hydrogen [15,18]

Carbon	Surface concentration (at.%)						
	C	O	N	Fe	O/C	N/C	O/N
DHT	97.24	2.30	0.46	–	0.024	0.005	5.000
DHTN	95.61	1.73	2.66	–	0.018	0.027	0.650
DOx	90.08	9.2	0.72	–	0.102	0.008	12.777
DOxN	94.26	1.35	4.39	–	0.014	0.047	0.308
DOxFe	54.48	35.50	0.82	9.20	0.652	0.015	43.293

molecularly adsorbed oxygen in the form of superoxide ions O_2^-, as well as nitrogen containing groups. In addition, carbon surfaces also contained basic sites which are thought to be oxygen-free Lewis sites located at regions rich in π electrons within the basal planes [18]. For all the investigated carbons the basicity increased with decreasing O/C and O/N ratio (Tables 2 and 3).

The N 1s spectra reveal the presence of several different nitrogen species. The nitrogen functionalities in high temperature carbons ($T > 1000$ K) are attributed to pyridinic nitrogen located at the edges of graphene structures (N-6, BE $\sim$ 398.5 eV) and to nitrogen incorporated in these structures, replacing a carbon atom and thereby becoming more positively charged resulting in a shift to higher binding energies (quaternary nitrogen, N-Q, BE $\sim$ 401.5 eV) [15,21–23]. In addition, due to the exposure to either air or nitric acid, the chars were oxidized and some pyridones (BE $\sim$ 400.5 eV), pyridine N-oxides as well as nitrogen oxides or nitro structures (BE $\sim$ 403–404 eV) were also present (N-X) (Table 4) [14,15,21–23]. The more pronounced basic properties of ammonia-treated carbons result from the presence of additional basic groups like pyridinic structures at the edges of graphene structures (N-6) (Tables 2 and 4). It may be therefore concluded that, for annealed carbons, the higher nitrogen content (especially, in the pyridinic form (N-6)), the higher the basicity.

The TPD results showed considerable amounts of decomposition products (e.g. CO, CO_2, H_2O and NO) for DOx carbon, whereas only traces of such products were recorded for samples annealed in vacuum (Fig. 1). The treatment in NH_3 also led to a decrease of these products. According to Jansen and van Bekkum the nitrogen functionalities are stable up to 1200 K [24].

Table 4
Distribution of nitrogen functional groups of the modified carbons determined from deconvolution of XP N 1s spectra [15,18]

Carbon	Functional group distribution (%)			
	N-6	N-5	N-Q	N-X
DHT	25.6	35.1	25.2	14.1
DHTN	31.8	46.6	15.6	5.9
DOx	20.8	34.0	30.9	14.4
DOxN	42.9	37.9	13.1	6.2
DOxFe	21.2	45.8	20.7	12.4

During thermal decomposition of surface oxygen containing groups CO_2 is produced from carboxylic acid at low temperatures, and from anhydrides, lactones or lactols at higher temperatures; CO results from phenols, ethers and carbonyls (and quinones). Carboxylic anhydrides give rise to both a CO and a CO_2 peak [17]. The CO_2 desorption profile of the DOx carbon shows two broad overlapping peaks located at about 553 and 680 K. The former peak is tentatively assigned to carboxyl groups, whereas the latter to anhydrides, lactones or lactols [17]. The CO desorption profile of DOx shows a very broad peak with the maximum at about 950 K and small badly resolved peaks at 550 and 680 K, respectively. At this temperature nitrogen oxide also evolves owing to the decomposition of surface nitro groups formed during nitric acid treatment [17,25].

The performed TPAD measurements reveal that ammonia chemisorbed on the investigated carbons (Fig. 2). The highest amounts of ammonia was chemisorbed on the oxidized carbon DOx and desorption was completed below about 800 K. There are three overlapping peaks with maxima at ca. 413, 560 and 693 K, respectively. The latter two peaks appear at the same temperature as the peaks on CO_2-profile assigned to carboxylic structures. This indicates that part of chemisorbed ammonia exists in the form of ammonium carboxylates which is in good agreement with earlier IR experiments concerning ammonia adsorption on oxidized carbons [25]. However, the presence of the most pronounced peak at 413 K reveals that the majority of ammonia is chemisorbed on the carbon surface more weakly. Possibly, as in the case of acidic catalysts like zeolites [26], the most acidic groups act as primary adsorption centers on which other ammonia molecules are associated through hydrogen bonds. In the case of annealed carbons, the amount of chemisorbed ammonia was considerably lower (Table 2), in good agreement with lower acidity for DHT. However, similarly as for the DOx sample, some ammonia is retained up to 800 K.

3.2. Catalytic activity

The modified carbons promote selective catalytic reduction (SCR) of NO with NH_3 to nitrogen and water. Traces of N_2O were observed only at higher temperatures, for the DHTN sample (Fig. 4). The carbon sample annealed under vacuum (DHT) showed the lowest SCR activity (Fig. 3). The formation of surface acidic oxides by nitric acid treatment enhanced the catalytic activity only slightly (DOx). Similarly as observed before for carbon catalysts [27,28] and other acidic SCR catalysts, such as zeolites or molecular sieves [30,31], the promotion of the DOx sample with Fe^{3+} ions enhanced SCR activity drastically, and the DOxFe sample became the most active catalyst (Fig. 3). However, this high activity is accompanied by some decrease in selectivity—N_2O appeared as a side product (Fig. 4). The ammonia-treated carbons DHTN and DOxN demonstrated high selectivity and reasonable activity. The sample first oxidized with nitric acid and then heated in an ammonia

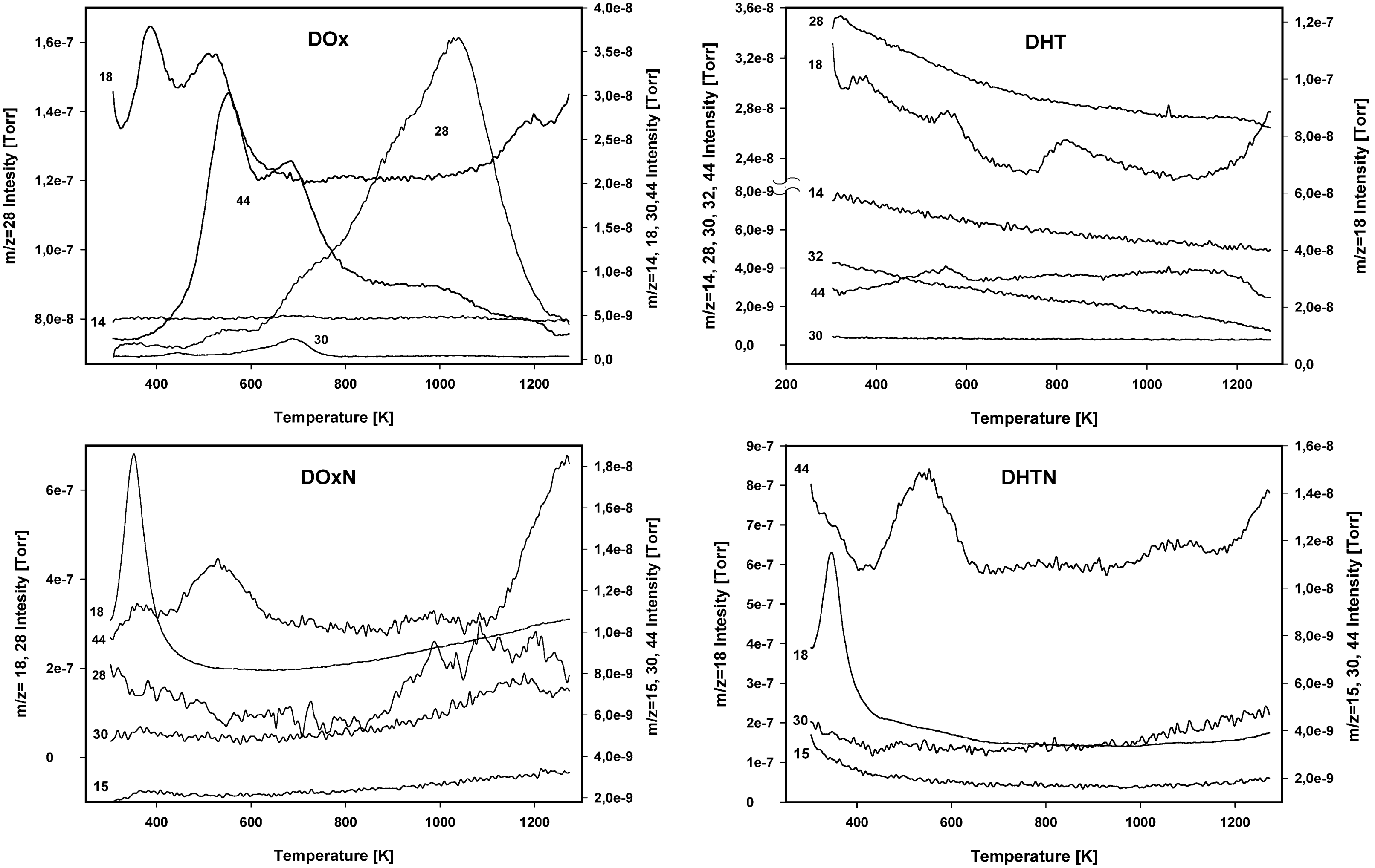

Fig. 1. TPD profiles for the DOx, DOxN, DHT and DHTN carbons: CO (28), CO_2 (44), H_2O (18), NO (30) and NH_3 (15).

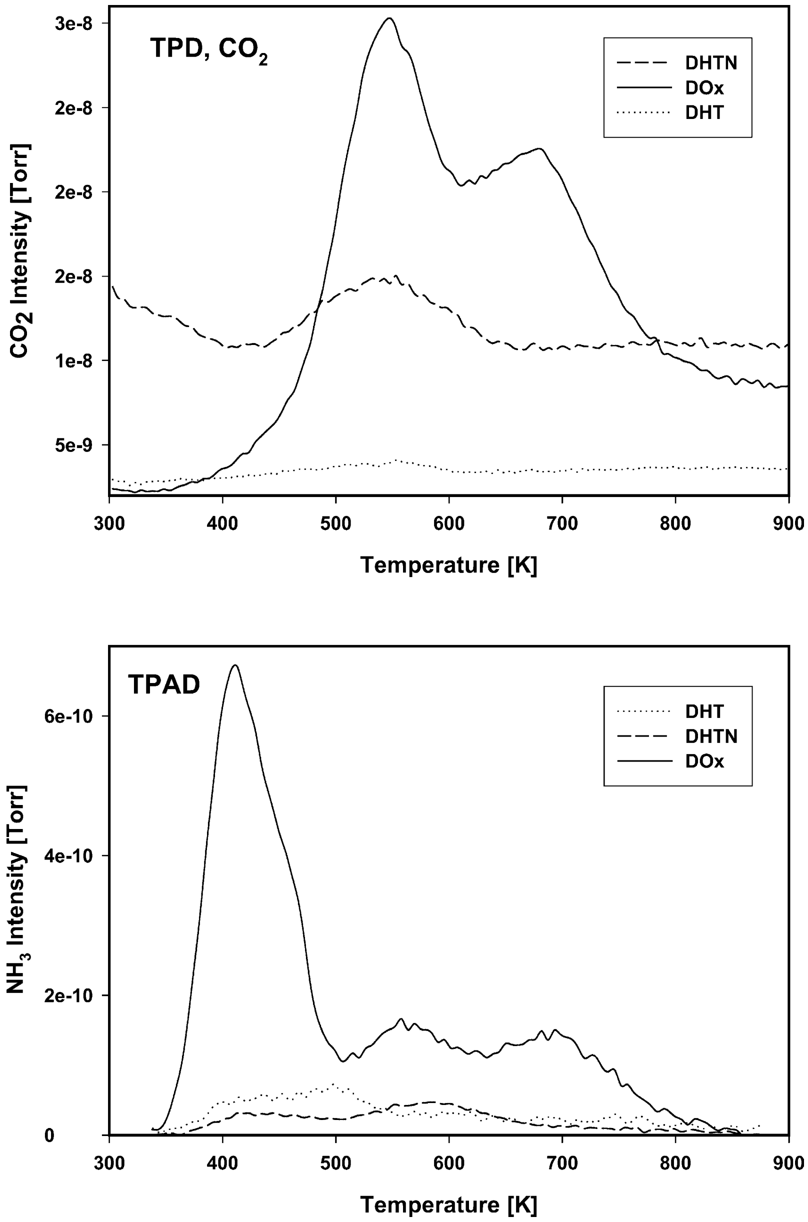

Fig. 2. TPAD spectra of the catalysts studied.

stream (DOxN) showed activity and selectivity higher than DHT and DOx.

A weak maximum in NO conversion was observed for the oxidized sample (DOx) and its ion-exchanged form (DOxFe) at ca. 493 K. The samples heated both in vacuum and ammonia exhibited at weak minimum at ca. 453 K. Such contradictory effects depending on different modification were also reported by other researchers [1,4–6,9,10,14,27,28]. The existence of the above mentioned minimum was also reported earlier by other researchers for various carbons [1,4–6,9,10,14,27–29].

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. [12]. They concluded that 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. This mechanism is also supported by the latest results obtained by Teng et al. [7,8]. They postulate that surface carboxylic and/or phenolic groups play the role of catalytically active acidic sites while the basic sites are pyrone-like structures.

The observed maximum at 493 K in NO conversion for the oxidized sample (DOx) and its ion-exchanged form (DOxFe) (Fig. 3) as well as the lower catalytic activity of the DOx sample in catalytic tests performed in cooling mode rather than in rising temperature mode (Fig. 5) can be explained by a partial decomposition of catalytically active surface oxides during the reaction at higher temperatures. The temperature

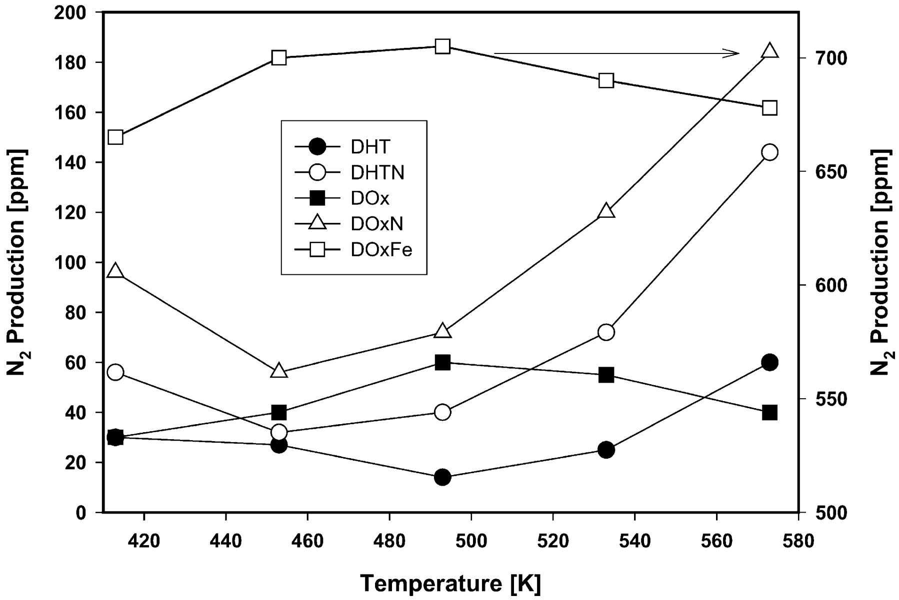

Fig. 3. Activity of the modified carbons in SCR of NO with ammonia.

of maximum catalytic activity corresponds to the maximum temperature of the first peak on the CO_2 evolution curve and the second peak on the H_2O evolution curve which are usually assigned to decomposition of single carboxylic groups or dehydration of two adjacent carboxylic groups, respectively [17]. This supports previous statements of Teng et al. [7,8] that these groups are one of the active sites responsible for the catalytic activity of the oxidized carbon (DOx) and explains the lowest catalytic activity of the sample annealed under vacuum (DHT) in which only traces of CO_2 in evolved gases during TPD experiments were observed (Fig. 1).

It must be observed, however, that catalytic activity of the oxidized sample (DOx) was only slightly higher than for the sample heated in vacuum (DHT), in spite of the high surface oxides concentration. This suggests that either some catalytically active sites may be formed on the surface of the DHT carbon during the reaction as a result of oxidation with oxygen and/or the SCR reaction requires additionally the presence of other active sites which are probably responsible for NO oxidation to NO_2-like species.

For all annealed carbons a correlation between the degree of NO conversion and carbon basicity was observed in the

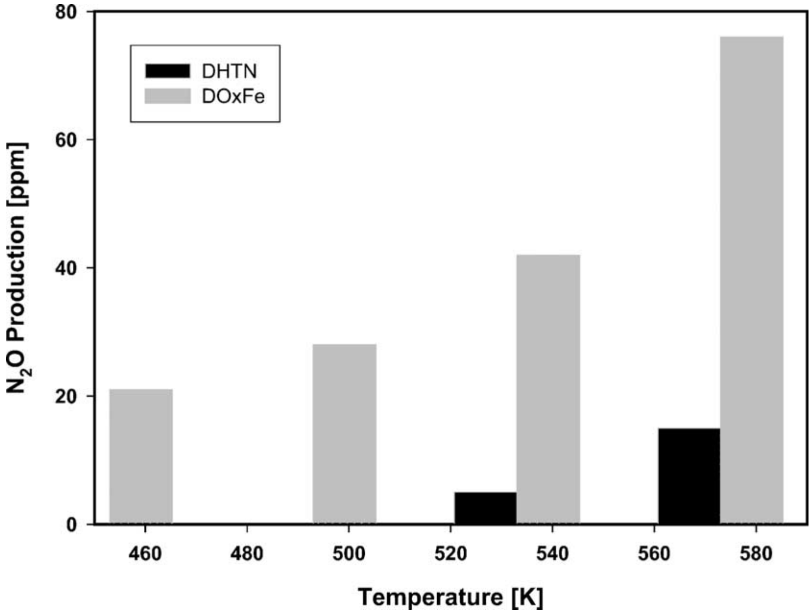

Fig. 4. N_2O production of the studied catalysts.

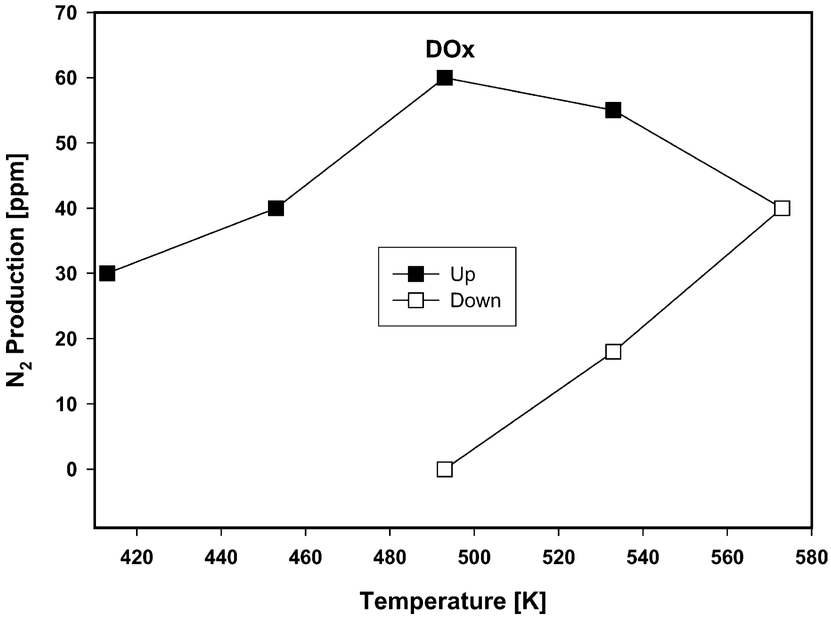

Fig. 5. NO conversion for the studied catalysts in SCR process carried out over a cycle of increasing (up)/decreasing (down) temperature.

whole studied temperature range. An increase in carbon basicity enhances NO conversion. As stated above the higher the nitrogen content, especially in the pyridinic form (N-6), the higher the basicity (Tables 2 and 4). Similar effects of nitrogen content on carbon basicity and SCR activity were observed also by Huang and Teng for other nitrogen-containing carbons [14].

Pyridinic nitrogen due to its basic nature should have affinity towards weakly acidic molecules like NO. The presence of nitrogen in the carbon matrix was reported to enhance adsorption of NO [14,32,33]. The increased adsorption for higher nitrogen content may be associated with an electron transfer from the carbon surface to the NO molecules [38]. Stöhr et al. found that the ammonia treatment of the carbon surface facilitated chemisorption of molecular oxygen [34]. According to them when nitrogen atoms were substituted for carbon atoms within the graphene layers, the extra electrons tended to be delocalized and could be easily transferred to the adsorbed species forming reactive surface intermediates. This was also supported by the results of quantum chemical calculation conducted by Strelko et al. [35].

The latest IR and TPD investigations of NO oxidation on various carbon materials indicate that NO is oxidized to NO_2-like species by chemisorbed oxygen [13,36]. The chemisorbed oxygen species can be ascribed to ion-radical surface compounds [25,36] or superoxo ions O_2^- [34].

It has been established for various carbon materials that the catalytic reduction of NO by NH_3 was controlled by two consecutive steps: the strong adsorption of NH_3 on active sites, followed by the addition of NO or NO_2 in the neighborhood of $C(NH_3)$ complexes [4,6–12].

The performed TPAD measurements indicate that even ammonia-treated carbons have, beside basic sites, also some acidic sites capable of strong chemisorption of ammonia (Fig. 2). This can explain the lack of NO removal dependence on ammonia concentration, observed by Huang et al. for other nitrogen-containing carbons [14]. Therefore it is reasonable to assume that NO removal over nitrogen-containing carbons occurs in the same way as for other carbons. Thus, the higher SCR activity of the ammonia-treated carbons can be explained by a more facile NO_2 formation due to easier chemisorption of oxygen and NO.

The presence of the minimum in NO conversion for the annealed carbons (DHT, DHTN and DOxN) in the temperature range 413–493 K is commonly ascribed to the existence of two different reduction mechanisms for low and high temperatures [1,4–6,8–10,14]. Thus, at low temperatures, carbons act as a concentrating medium for reactant species (NO and NH_3) instead of being a true catalyst, and as a consequence, the initial decrease in NO conversion with temperature is due to a decreased adsorption degree as temperature increases. At higher temperatures, chemisorption of reactant species takes over physical adsorption and carbon acts as a true catalyst in the SCR reaction [1,4–6,8–10,14]. In this sense, it is expected that nitrogen species incorporated in carbon matrix act as adsorption sites at low temperatures ($<$473 K) and as catalytic active sites at high temperatures (473–573 K). Previous studies showed that the NH_3 adsorption on carbon surface is an important step affecting the rate of catalytic reduction of NO [4–6,12]. Consequently, the larger amount of NO adsorbed at low temperatures due to higher basic sites concentration would possibly retard the process of NH_3 adsorption on active sites, leading to the decrease in NO reduction rate with NO concentration at low temperatures.

The more facile formation of NO_2 can be also responsible for the drastic increase of SCR activity of the oxidized sample after promotion with iron(III) ions. According to the literature data the improvement of the SCR activity for Fe^{3+}-containing zeolites and molecular sieves is related to the formation of NO_2 by oxidation of NO on Fe^{3+} sites by O_2 [29–31,37]. For such catalysts active forms of adsorbed diatomic oxygen are present as superoxide ions O_2^- or peroxo groups [37–39]. The interaction of such species with NO_x results in NO_2 formation [30–31,36]. During the SCR reaction, gaseous NH_3 molecules are adsorbed onto the Brønsted acid sites to form NH_4^+ ions, and then the formed molecules of NO_2 react with adjacent NH_4^+ ions to produce N_2 and H_2O [30–31]. NO oxidation to NO_2 is probably the rate-determining step for SCR reaction on such catalysts [31]. The same shape of catalytic activity curve for the DOxFe sample as well as for the DOx carbon (Fig. 2), in spite of very different activity, may support above suggestion that also in this case the introduced iron species act as additional active sites for NO oxidation. Thus the simultaneous presence of high concentration of acidic groups, capable of adsorbing ammonia, as well as sites for NO_2 formation due to molecular oxygen activation, can be responsible for the observed drastic increase in SCR activity. The XPS results indicate that the introduced iron species of different valence can be present in various surroundings (e.g. FeOOH, Fe_xO) [40].

4. Conclusions

Catalytic tests showed that chemical modification of the surface of the commercial carbon D43/1 led to a change in catalytic activity. All the modified carbon samples selectively catalyze reduction of NO to nitrogen and water. The generation of surface acidic oxides by nitric acid treatment enhanced the catalytic activity to some extent (DOx). However, the highest activity was demonstrated by the samples heated in ammonia. For all the annealed carbons, a decrease in catalytic activity between 413 and 493 K was observed. This somewhat unusual temperature dependence is typical for carbon catalysts. Probably at low temperatures, carbons act as a concentrating medium for reactant species (NO and NH_3) instead of being a true catalyst [1,4–6,8–10,14].

It has been proposed on the basis of this study that catalytic activity is determined not only by the presence of acidic surface oxides (e.g. carboxylic and lactonic groups) but also other sites which are probably responsible for NO oxidation to NO_2-like species. The observed correlation between the nitrogen content, especially in the pyridinic form (N-6), and the catalytic activity suggests that the incorporated nitrogen species may act as such sites. Their extra electrons tend to be delocalized and can be easily transferred to the adsorbed species forming reactive surface intermediates. In addition, the nitrogen functionalities due to their basic properties can act as adsorption sites for nitrogen oxides. The improvement of SCR activity for the DOxFe sample can be ascribed to more facile formation of NO_2 as an effect of easier molecular oxygen activation on introduced iron species [29–31,37].

It is commonly assumed that porosity also plays an important role, especially at low reaction temperatures; thus the controversy reported in the literature [3–4,6,9,10] about the role of nitrogen functionalities in the SCR reaction may result from very different porous structures in the carbon materials applied. Most probably, the overall activity behavior of the carbon catalysts is comprised of a combination of several factors like porosity, surface chemistry (e.g. oxygen and nitrogen functionalities) and interaction of oxygen with the carbon.

References

[1] S.N. Ahmed, R.M. Baldwin, F. Derbyshire, B. McEnaney, J. Stencel, Fuel 72 (1993) 287.
[2] E. Richter, J. Schmidt, H.-G. Schecker, Chem. Eng. Technol. 13 (1990) 332.
[3] H. Jüntgen, in: P. Thrower (Ed.), Chemistry and Physics of Carbon, vol. 22, Marcel Dekker, New York, 1989, p. 145.
[4] S.N. Ahmed, J.M. Stencel, F.F.J. Derbyshire, R.M. Baldwin, Fuel Process. Technol. 34 (1993) 123.
[5] J.M. Martin-Martinez, S. Singoredjo, M. Mittelmrijer-Hazeleger, F. Kapteijn, J.A. Moulijn, Carbon 32 (1994) 897.
[6] S. Singoredjo, F. Kapteijn, J.A. Moulijn, J.M. Martin-Martinez, H.P. Boehm, Carbon 31 (1993) 213.
[7] H. Teng, T. Tu, Y.-C. Lai, C.-C. Lin, Carbon 39 (2001) 575.
[8] H. Teng, Y.-F. Hsu, Y.-T. Tu, Appl. Catal. B: Environ. 20 (1999) 145.
[9] J. Muñiz, G. Marbán, A.B. Fuertes, Appl. Catal. B: Environ. 23 (1999) 25.
[10] J. Muñiz, G. Marbán, A.B. Fuertes, Appl. Catal. B: Environ. 27 (2000) 27.
[11] B.J. Ku, J.K. Lee, D. Park, H-K. Rhee, Ind. Eng. Chem. Res. 33 (1994) 2869.
[12] I. Mochida, M. Ogaki, H. Fujitsu, Y. Komatsubara, S. Ida, Nippon Kagaku Kaishi 4 (1985) 680.
[13] Z. Zhu, Z. Liu, S. Liu, H. Niu, Fuel 79 (2000) 651.
[14] M.-C. Huang, H. Teng, Carbon 41 (2003) 951.
[15] S. Biniak, G.S. Szymański, J. Siedlewski, A. Świątkowski, Carbon 35 (1997) 1799.
[16] G.S. Szymański, Pol. J. Environ. Stud. 10 (Suppl. II) (2001) 67.
[17] G.S. Szymański, Z. Karpiński, S. Biniak, A. Świątkowski, Carbon 40 (2002) 2617.
[18] G.S. Szymański, S. Biniak, G. Rychlicki, Fuel Process. Technol. 79 (2002) 217.
[19] T. Grzybek, J. Klinik, M. Rogóż, H. Papp, J. Chem. Soc. Faraday Trans. 94 (1998) 2843.
[20] T. Grzybek, J. Pasel, H. Papp, Phys. Chem. Chem. Phys. 1 (1999) 341.
[21] A. Cuesta, A. Martinez-Alonso, J.M.D. Tascon, R.H. Bradley, Carbon 35 (1997) 967.
[22] F. Kapteijn, J.A. Moulijn, S. Matzner, H.-P. Boehm, Carbon 37 (1999) 1143.
[23] E. Raymundo-Piñero, D. Cazarola-Amoros, A. Linares-Solano, J. Find, U. Wild, R. Schlögl, Carbon 40 (2002) 597.
[24] R.J.J. Jansen, H. van Bekkum, Carbon 32 (1994) 1507.
[25] J. Zawadzki, in: P. Thrower (Ed.), Chemistry and Physics of Carbon, vol. 21, Marcel Dekker, New York, 1988, p. 147.
[26] F. Lónyi, J. Valyon, Micropor. Mesopor. Mater. 47 (2001) 293.
[27] T. Grzybek, H. Papp, Appl. Catal. B: Environ. 1 (1992) 271.

[28] J. Pasel, P. Kässner, B. Montanari, M. Gazzano, A. Vaccari, W. Makowski, T. Lojewski, R. Dziembaj, H. Papp, Appl. Catal. B: Environ. 18 (1998) 199.
[29] G. Morban, A.B. Fuertes, Catal. Lett. 84 (2002) 13.
[30] R.Q. Long, R.T. Yang, J. Catal. 207 (2002) 274.
[31] H.Y. Huang, R.Q. Long, R.T. Yang, Appl. Catal. A: Gen. 235 (2002) 241.
[32] S. Matzner, H.P. Boehm, Carbon 36 (1998) 1697.
[33] C.-M. Yang, K. Kaneko, J. Colloid Interf. Sci. 255 (2002) 236.
[34] B. Stöhr, H.P. Boehm, R. Schlögl, Carbon 29 (1991) 707.
[35] V.V. Strelko, V.S. Kuts, P.A. Thrower, Carbon 38 (2000) 1499.
[36] J. Zawadzki, M. Wiśniewski, K. Skowrońska, Carbon 41 (2003) 235.
[37] Z.-X. Gao, Q. Sun, W.M.H. Sachtler, Appl. Catal. B: Environ. 33 (2001) 9.
[38] L.J. Lobree, I.-C. Hwang, J.A. Reimer, A.T. Bell, Catal. Lett. 63 (1999) 233.
[39] H.-Y. Chen, El-M. El-Maki, X. Wang, R.A. van Santen, W.M.H. Sachtler, J. Mol. Catal. A: Chem. 162 (2000) 159.
[40] S. Biniak, G.S. Szymański, A. Świątkowski, in: Proceedings of ICCS'97, Essen, 7–12 September 1997, 1835.