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The interaction of NO with active carbons promoted with transition metal oxides/hydroxides

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Abstract

The interaction of NO with active carbons promoted with transition metal oxides (Mn, Cr, Co, Ni) was studied. Activity in reduction by carbon increased from ca. 573–653 K in comparison to unpromoted active carbon. The extent of increase in activity, as well as selectivity to N_2, depended on the type of active material. Product distribution (N_2, N_2O) showed similarities with SCR by ammonia which suggests that some steps are in common for both reactions. TPD experiments indicate that undissociated NO molecule adsorbed on the surface may be the source of N_2O.

Keywords: NO reduction; Active carbon; TPD

1. Introduction

Air pollution abatement is one of the most important problems facing modern catalysis. Nitrogen oxides which are formed during energy production play an important role in the formation of acid rains and ozone depletion. The only method used now on industrial scale to remove NO_x from stationary sources is selective catalytic reduction of NO with ammonia. The most often used catalyst is V_2O_5–WO_3–TiO_2. However, its maximum activity is observed at a medium temperature region (from ca. 250 °C) and low temperature catalysts active at ca. 150 °C are still searched for. Active carbons were proposed for SCR for low temperature region and are, though not so often, used also on industrial scale. Although their activity is rather low it may be increased by the addition of transition metal oxides/hydroxides [1–4]. Active carbons are additionally interesting, because when used as supports, they form more active low temperature catalysts than similarly promoted ones based on Al_2O_3 or SiO_2 [5,6]. Lately, much interest has been paid to carbon fibres [6–8]. They are reported to form even more active systems. Yoshikawa et al. [6] showed that low temperature activity for manganese promoted carbonaceous materials as compared to Mn/Al_2O_3 or V_2O_5/TiO_2 formed a sequence: Mn/carbon fibre > Mn/active carbon > V_2O_5/TiO_2 > Mn/Al_2O_3. Carbonaceous materials were also studied for non-selective NO reduction (NCR) with CO [9–11] or direct reduction by carbon [12–22]. The latter reaction, apart from the possibilities of the studies of NO interaction in relation to SCR or NCR, may also give some valuable information concerning the possibility of simultaneous reduction of NO and soot from Diesel engines [24–26]. Although several aspects of direct reduction of NO with promoted active carbons have been described in literature (different active materials: Ni [12–14,18], Cu [12–14,22], Fe [13,19], Co [13–15], Cr [14], Ca [12,19] or K [20,21]; the role of oxygen [12,13,18]; pretreatment of carbonaceous catalyst [15], etc.), there are still many open questions, arising from the fact that the experiments were carried out on different active carbons, in some cases not fully characterised, and/or under differing reaction conditions.

Several mechanistic considerations have been discussed as well, both in case of direct NO reduction by active carbons and reactions of soot with NO, in the presence or absence of oxygen. Generally, the following facts seem to be agreed upon: the presence of the catalyst (e.g. $CuFe_2O_4$ [23])

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activates both reactants—carbon and oxygen—leading to the formation of oxygen-containing active intermediates; in the absence of a catalyst the overall oxygen surface coverage is connected mainly with the formation of stable C–O complexes [22]; other activation procedures e.g. sulphuric acid pretreatment may also activate NO reduction [27]; the plausible role of O_2 is the formation of NO_2 either in the gas phase [23] or perhaps on the surface [28]; a certain ignition temperature is necessary to start the NO reduction with carbon while at low temperatures NO is only sorbed on the surface e.g. [29,30].

Most mechanisms, however, are not very clear about differences introduced by varying the active materials and in most cases they do not address the origin of N_2O in the presence of oxygen. In contrast, origin of N_2 seems to be agreed upon. Nevertheless, the formation of N_2O is not a minor problem, as N_2O forms sometimes a considerable portion of the products, e.g. ca. 25% shown for $CuFe_2O_4$ catalyst [23]. Okuhara and Tanaka [29] and Kakuta et al. [30] studied N_2O formation in the absence of oxygen and concluded from labelling and TPD experiments that N_2O was formed on the surface of K-promoted or K + Cu or Zn, Mn, Sn, Ni, Fe promoted active carbons. NO transformed on such a surface to several adsorbed species, such as $N_2O(a)$, $NO_2(a)$ or $(NO)_2(a)$. N_2O desorbed from the surface below 403 K, $(NO)_2(a)$ decomposed directly around 473 K to N_2 and N_2O and $NO_2(a)$ reacted with carbon to form NO, N_2 and CO_2 above 553 K.

The presented work focused on the interaction of NO with carbonaceous materials with different inorganic additions, and especially the role of ash and the influence of the type of active material in the presence of oxygen in the reaction mixture, with special stress laid on the formation of N_2O.

2. Experimental

Catalysts studied were: (i) unpromoted active carbons with different ash content (N, B, D and N-ox = N oxidised with a mixture of HNO_3 and H_3PO_4); ash content and composition are given in Table 1; (ii) N promoted with oxides/hydroxides of Mn, Co, Ni or Cr. Details of preparation are fully described elsewhere [31].

Table 1
Ash content and composition for the studied active carbons [31]

	Catalyst			
	N	B	D	N-ox
Ash content (wt.%)	22.3 (a)	4.9 (b)	0.2 (c)	5.6 (d)
SBET (m^2/g)	794	861	1094	1049

a, b, c: composition of ash obtained by incineration of active carbon at 1123 K [ppm]—(a) 85 500 (Al), 464 (Cu), 81 650 (Fe), 1390 (Mn), 222 (Ni), 815 (Sr), 19 600 (Mg), 74 000 (Ca); other elements B, Ba, Be, Cd, Co, Cr, Pb, Zn <150. (b) 5333 (Al), 11 385 (Fe), 64 (Mn), 520 (Mg), 1692 (Ca). (c) 23 947 (Al), 34 529 (Fe), 5969 (Mn), 15 091 (Mg), 24 100 (Ca). (d) Not measured.

In order to characterise the catalysts the following methods were used:

- Low temperature sorption (Ar or N_2) in order to determine the texture. Before experiments samples were outgassed at 393 K.
- Temperature programmed desorption, TPD, to determine surface oxides under the following conditions: a sample underwent reaction in the microreactor at 413 K for 2 h with a mixture of 800 ppm NO and 3% O_2 in helium, then it was removed to TPD equipment (NETZSCH STA 409C) where desorption was carried out for 50 mg of the sample from room temperature to 1273 K with a heating rate 10 K/min and an analysis of products by mass spectrometer for mass numbers $m/e = 17$, 18 (H_2O), 28 (CO), 30 (NO), 44 ($CO_2 + N_2O$).
- X-ray photoelectron spectroscopy to determine chemical state and distribution of active material. The spectra were recorded with a Leybold AG spectrometer equipped with a Mg Kα source and a multichannel plate analyser working in FAT mode ($\Delta E = \text{const.}$) at a pass energy of 29.6 eV. The samples were studied in the form of pellets loosely packed onto the sample holder. The pressure in the main chamber was better than 3×10^{-8} mbar. The spectra were smoothed, a non-linear background was subtracted and the fitting was carried out with a 50/50 convolution of Lorentz and Gauss curves. The main C 1s peak at a binding energy of 284.6 eV was used as a calibration standard. The composition of the samples was calculated using the areas of the appropriate peaks and the sensitivity factors of Wagner et al. [32].

The interaction with NO was studied under the following conditions: a fixed-bed microreactor; reaction mixture: 800 ppm NO in helium with or without the addition of 3% O_2; mass of catalyst: 400 mg; flow: 100 ml/min; products analysis: gas chromatography (N_2, N_2O, CO_2). Three types of catalytic experiments were carried out:

(i) Type I: first the sample was calcined at 523 K for 2 h in a 5% O_2–helium mixture and then after cooling in helium to 453 K, a mixture of NO + O_2 + helium was introduced. Reduction products were measured after 30, 70 and 110 min on-line. After 120 min temperature was raised by 40 K, and the measurement was repeated. The whole experimental cycle contained measurements every 40 K starting from 453 to 693 K. No steady state was attained during this time due to substantial loss of carbon, different for each catalyst, except for unpromoted active carbon at lower experimental temperatures. Three experimental points for each temperature shown later represent the extent of conversion loss.

(ii) In order to compare all samples under the same conditions, NO reduction was additionally carried out for fresh samples at 613 K (experiments of type II). The choice of temperature was connected with the possibility of comparing all the samples (very active and less active) under the same conditions in the same temperature. Other experimental conditions: time and temperature of calcination previous to reaction, reaction mixture composition and flow as well as mass of catalyst were the same as stated for the experiments of type I.

(iii) The literature suggests that NO is sorbed on carbonaceous materials at lower temperatures than those necessitating the direct reduction by carbon. In order to gain some insight into this process, the experiments of type I were repeated under identical conditions using IR analyser (Hartmann and Braun) instead of gas chromatograph which enabled the determination of $NO + NO_2$ (as a sum, in the form of NO) and N_2O in the products (experiments of type III).

3. Results and discussion

3.1. The influence of ash content on NO reduction

Table 2 compares NO conversion for active carbons with different ash content (N, B, D) and samples with different surface chemistry—N and N-ox, containing different amount of oxygen-containing surface groups. Only active carbon N containing very high ash content showed considerable NO conversion at temperatures from ca. 613 K. B and D with lower ash content were inactive. The oxidation process resulted in partial demineralisation of sample N and a change in surface chemistry—the formation of oxygen-containing surface groups (decomposing to CO and CO_2 in TPD) and an increase in acidity of active carbon N-ox in comparison to N [33]. As N lost its activity upon oxidation, it may be derived that ash plays a much more important role in NO reduction than the formation of oxygen-containing surface functionalities [31]. Similar observations were made by Pasel et al. [34] for SCR of NO with ammonia. The most probable explanation is connected with the presence of catalytically active ash components—oxides of iron, copper, manganese and/or calcium. Their additions to active carbons was reported to increase activity of NO reduction by carbon [12–14,19]. Additionally, it must be mentioned that the producer of active carbon N declared the presence of considerable amounts of potassium in N [35] which, as declared in literature [20,21], may also add to high activity. Our ash analysis could not show this due to high volatility of K compounds under conditions used in the procedure to obtain ash.

Table 2
NO conversion[a] (%) at different temperatures for active carbons with different ash content

	T (K)						
	453	493	533	573	613	653	693
N	0	0	1	8	26	80	100
N-ox, B, D	0	0	0	0	0	0	0

[a] After 60 min on stream at each temperature.

3.2. The influence of promotion with transition metal oxides

3.2.1. Characterisation of catalysts

Table 3 summarises binding energies of the introduced active material and surface composition of the studied samples.

Table 3 shows: (i) the binding energy of Mn 2p as well as Mn 3s splitting indicate that Mn is present as Mn_3O_4 [36]; (ii) binding energies of cobalt, nickel and chromium are shifted towards higher binding energies in comparison to those observed for bulk oxides, possibly due to chemical shift. An attempt to calibrate the position of Co 2p fixing the position of O 1s at literature value of either CoO or $Co(OH)_2$ as suggested by Grzybek et al. [37] shows that cobalt is present as either CoO, CoOOH or $Co(OH)_2$ or their mixture. Similar results were obtained for N–Ni where no differentiation between NiO and $Ni(OH)_2$ was possible. However, for N–Cr the above-mentioned procedure suggests the presence of Cr_2O_3; (iii) for N–Mn very high surface

Table 3
XPS data for the studied promoted active carbons: binding energies (calibrated to C 1s at 284.6 eV) and surface composition

Sample	Binding energy (eV)		Composition (at.% or at.%/at.%)				
	Active material	O 1s	Me	O	C	Me/C	O/C
N–Mn	Mn $2p_{3/2}$, 642.0[a]	529.8 531.0 532.0	15.2	42.8	42.0	0.362	1.019
N–Co	Co $2p_{3/2}$, 783.1	532.8 534.0 535.3	2.2	44.6	53.2	0.041	0.838
N–Ni	Ni $2p_{3/2}$, 857.0	533.1 535.2	2.9	46.6	50.6	0.057	0.920
N–Cr	Cr $2p_{3/2}$, 578.3	531.3 532.6 534.6	4.1	31.4	64.5	0.064	0.487

[a] Mn 3s splitting = 5.5 eV.

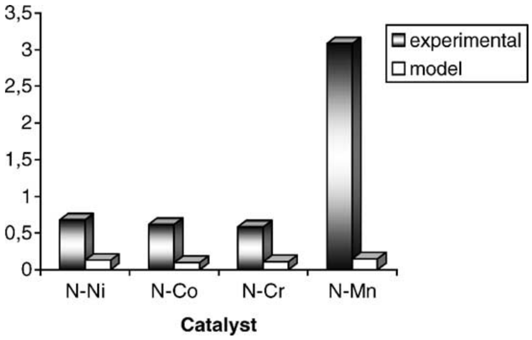

Fig. 1. The comparison of I_{Me}/I_C values obtained from XPS experiment and calculated from Kerkhof and Moulijn model.

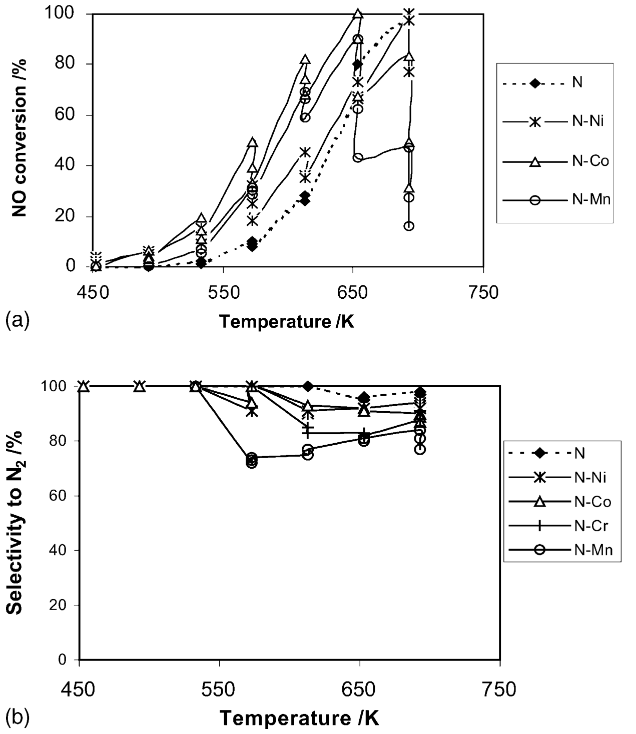

Fig. 2. NO conversion (a) and selectivity to N_2 (b) for the studied catalysts. Reaction conditions—reaction mixture: 800 ppm NO, 3% O_2, in helium; mass of catalyst: 400 mg; flow: 100 ml/min (three points at each temperature correspond to 30, 70 and 110 min on-line and thus give information about deactivation).

amounts of Mn were registered which, as already described before [33], indicates uneven distribution with manganese oxide present preferentially on the outer surface of grains of the support; (iv) surface Me/C ratios for N–Ni, N–Co and N–Cr indicate somewhat more even distribution. Fig. 1 compares intensity ratios of active material (Me 2p) to C 1s as obtained from XPS experiment and calculated from the model of Kerkhof and Moulijn [38] for a monolayer distribution. As it may be seen from the picture, also in these cases, there is the preferential deposition of active material on the outer surface of the grains of the support, although the difference between experimental and calculated values is much smaller than for N–Mn, indicating that more active material found its way into porous system. The fact that specific surface areas are still high (ca. 800 m^2/g) and the used support is mainly microporous allows a conclusion that Ni, Co or Cr oxides/hydroxides present inside the porous system form small crystallites, clusters and/or perhaps even individual cations. This hypothesis could explain the unusual shift of binding energies for these materials because it was observed before that small clusters of metallic atoms (Ni, Pt, etc.) led to such shifts [39,40].

TPD spectra of fresh and calcined samples were described in detail elsewhere [41]. They show that fresh samples exhibit some rest nitrates of active materials which are decomposed upon calcination.

3.2.2. Catalytic performance

Fig. 2a and b shows NO conversion and selectivity to N_2 for the studied samples. From Fig. 2 it may be derived that: (i) while the reaction starts for unpromoted active carbon N at ca. 573 K, the addition of Ni, Co or Mn shifts the onset of reaction to lower temperatures by ca. 40 K; (ii) at medium temperatures (573, 613 and 653 K) the addition of Co, Ni or Mn considerably increased NO conversion but with the increase in temperature the gain became smaller. At 613 K the catalysts formed a sequence: N–Co > N–Mn > N–Ni > N. For 693 K NO conversion for active carbon was higher than for promoted samples due to carbon loss which was caused by gasification at lower temperatures. This process was promoted to a higher extent by transition metal oxides than carbon alone; (iii) at medium temperatures, selectivity to N_2 falls into two groups: high for N, N–Ni and N–Co (ca. 90–95%) and N–Mn and N–Cr (ca. 70–80%). These results show similar trends as those obtained for the same catalysts for selective catalytic reduction of NO with ammonia (cp. Fig. 3 for N–Ni, N–Co and N–Cr and literature data for N–Mn [45]). When reaction temperatures of ca. 533 and 573 K (which was studied for both reactions) are compared, the amount of N_2O in the products is low for N–Ni and N–Co and considerable for N–Mn and N–Cr [41,45]. Possibly in both cases the same intermediate formed on active material plays an important role. It could be either partially dissociative and partially associative adsorption of NO, thus enabling the reaction $N_{ads} + NO_{ads} \rightarrow N_2O$. The proof of such mechanism as a possible reason for N_2O formation is discussed later, in connection to TPD results. The second possibility would be oxidation of part of N_2 with active oxygen species. The presence of such species on e.g. chromium oxides leading to high selectivity to N_2O during SCR (NH_3) was postulated by Curry-Hide et al. [43].

The reaction of NO reduction was accompanied by CO_2 formation due to carbon gasification with oxygen, as illustrated in Fig. 4. The addition of Co or Mn oxides increased CO_2 amount at lower temperatures in comparison to unpromoted active carbon while Ni oxides did not influence the process to a greater extent.

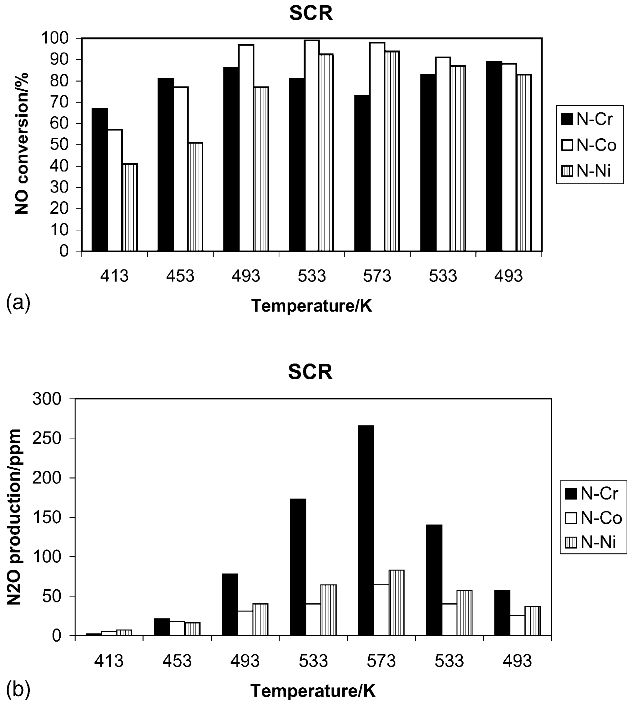

Fig. 3. NO conversion and N_2O production in selective catalytic reduction of NO with ammonia (SCR) for N–Ni, N–Co and N–Cr (reaction conditions—reaction mixture: 800 ppm NO, 800 ppm NH_3, 3% O_2 in helium; mass of catalyst: 500 mg; flow: 100 ml/min) [42].

NO conversions measured for fresh samples at 613 K are compared in Fig. 5. As it may be seen from the figure, activity forms a sequence: N $\approx$ N–Cr $<$ N–Mn $\approx$ N–Ni $<$ N–Co. The deactivation behaviour differs for the studied samples: active carbon does not seem to deactivate, while N–Co deactivates very quickly. This is in good agreement with the considerable increase in the produced amount of CO_2 for the latter sample in comparison with the former and thus in case of N–Co deactivation must be primarily due to carbon loss. The mechanism of N–Ni deactivation does not necessarily come from gasification alone. Its total extent is similar to that of N–Co, but the behaviour of the sample is different for longer times on stream: the former deactivates steadily with time on stream while for the latter after a first short period of considerable loss of NO conversion, deactivation slows down. Additionally the comparison with Fig. 4 indicates that CO_2 production for N–Ni is almost the same as for N. Thus different mechanism seems to play an important role for N–Ni, possibly connected with the chemical state or distribution of active material.

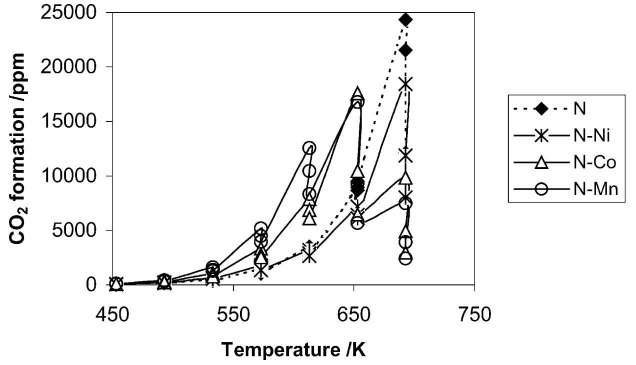

Fig. 4. CO_2 formation for the studied catalysts. Reaction conditions as given in Fig. 2.

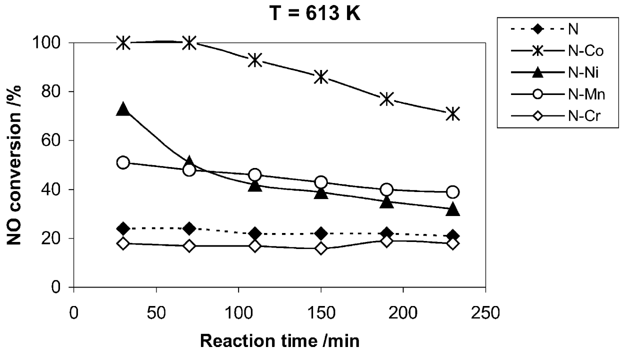

Fig. 5. NO conversion as a function of time for the studied catalysts at 613 K.

The total extent of deactivation through the loss of carbon is reflected by elemental composition (C, H, N) (Table 4) determined after a whole experimental series of type I ($T = 453, 493, 533, 573, 613, 653, 693$ K). From Table 4 it may be seen that there was a considerable carbon loss for the promoted samples in comparison to active carbon N. Taking into account Fig. 2, it may be speculated that N–Cr and N–Ni deactivate more quickly at higher temperatures (653 and 693 K) while N–Co deactivates steadily from 613 K.

3.2.3. *The influence of oxygen*

The influence of oxygen on NO conversion is illustrated in Fig. 6 for N and N–Mn. Oxygen considerably increases reaction rate but its lack does not totally stop the reaction. N–Mn is only slightly more active than N in the absence of oxygen, indicating that both oxygen-containing surface groups and oxygen bound to active material play some role in NO reduction. It must be mentioned additionally that gasification ceases when O_2 is removed from reaction mixture for both N and N–Mn which is reflected by very low CO_2 amounts in the products.

Table 4
Elemental composition of the studied catalysts after NO reduction series (sequentially at 453, 493, 533, 573, 613, 653 and 693 K for 120 min at each temperature)

Sample	Elemental composition (wt.%)		
	C	H	N
N	70.4	1.47	0.45
N–Ni	59.8	1.33	1.47
N–Co	40.3	1.38	0.93
N–Cr	46.5	0.84	0.79

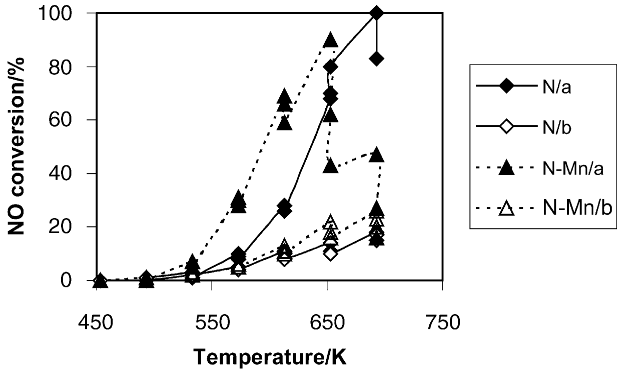

Fig. 6. NO conversion for active carbon N or manganese promoted active carbon N–Mn for a reaction mixture containing: (a) 800 ppm NO, 3% O_2, rest He; (b) 800 ppm NO in He. Three experimental points in each temperature—cp. explanation to Fig. 2.

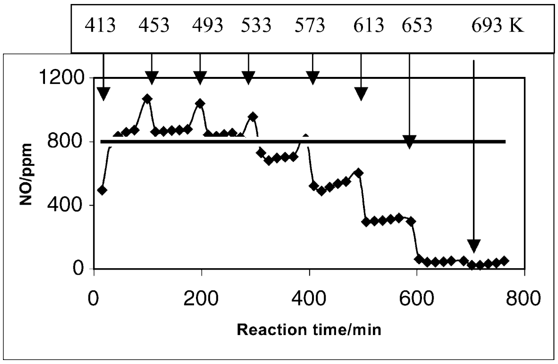

Fig. 7. The amount of NO at the outlet of the reactor for N–Ni ([41]—reprinted with the permission of the editor).

3.2.4. Low temperature versus high temperature behaviour of promoted active carbons

Active carbons were considered in literature as catalysts for NO oxidation to NO_2 or reduction to N_2. Fig. 2 illustrates the latter behaviour but no information on the former is possible from the experiments of type I where only the content of N_2 and N_2O in the products was studied. Fig. 7 [41] illustrates the amount of NO at the reactor outlet for N–Ni. It may be seen that up to ca. 533 K the amount of NO in the products is for a certain temperature (453, 493, 533 K) for short times on stream somewhat higher or much higher than at the inlet to the reactor and decreases with time on stream. For 573 K or higher temperatures, the amount of NO is considerably reduced. Other samples (N–Co, N–Mn) show similar tendency, with the exception that deactivation discussed above causes that the total reduction of NO at higher temperatures is not as high as for N–Ni. This behaviour may be rationalised only if two different mechanisms of NO interaction with promoted active carbons may be assumed: low temperature mechanism of adsorption (possibly in the form of NO_2) and desorption (either as NO or NO_2) and high temperature mechanism of NO reduction with carbon. This is in good agreement with literature discussion of the mechanism. The sequence of reaction steps in each (low and high temperature) mechanism must be different (thus leading to different products) but they undoubtedly start with NO sorption. The proof of such assumption is delivered by TPD experimental results [41]. In order to discuss the surface species formed during reaction, TPD spectra were measured for fresh samples as well as those which were flushed with a mixture containing 800 ppm NO, 3% O_2 and helium at 453 K for 2 h. Fig. 8 shows the desorbed amounts for $m/e = 30$ (NO) for the studied catalysts [41]. The desorption profile—temperature of maximum desorption and the area of the peaks differed considerably for unpromoted N and promoted samples. Active carbon N showed two types

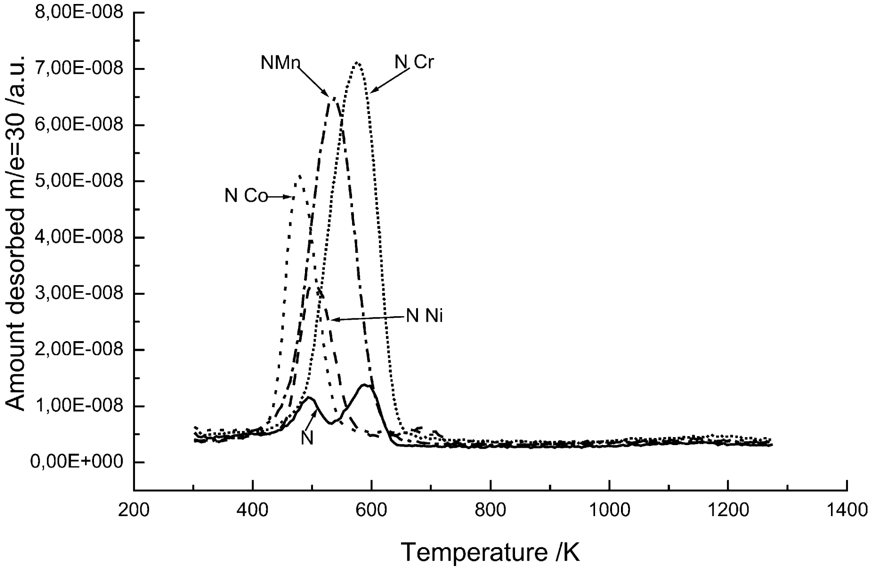

Fig. 8. TPD profiles for mass no. $m/e = 30$ (NO) for the studied catalysts after reaction (reaction conditions—reaction mixture: 800 ppm NH_3, 3% O_2 in helium; temperature: 353 K; mass of catalyst: 400 mg; flow: 100 ml/min; time: 120 min) ([41]—reprinted with the permission of the editor).

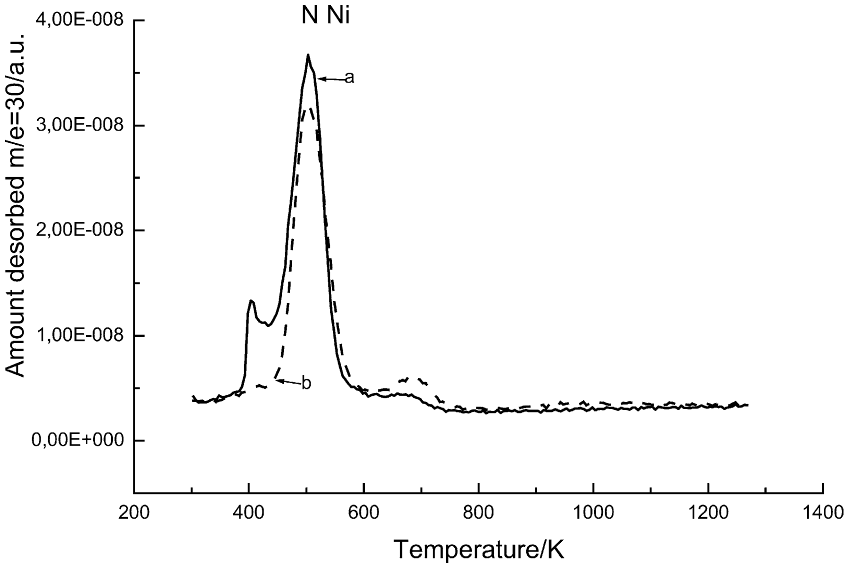

Fig. 9. TPD profiles of mass no. 30 (NO) for fresh N–Ni (a) and the sample after reaction (b) (conditions as for Fig. 8) ([41]—reprinted with the permission of the editor).

of sites while all promoted carbons showed only one. The comparison of fresh samples which contained nitrates of active materials and those after NO sorption is shown as an example in Fig. 9 for N–Ni [41]. Other samples gave similar spectra. Fresh samples showed two TPD peaks while after reaction only one was observed. The positions of the second peak before NO interaction and the one observed after reaction were identical but their area differed. In order to exclude rest nitrate originating from the fresh catalysts, calcined samples were measured additionally. No $m/e = 30$ spectrum was found in the discussed region. This may suggest that the species formed on contact with $NO + O_2$ mixture are rather of nitrate type than pure NO(ads). Possibly, nitrosyl species, which are known to be formed on such materials are short-lived intermediates leading to more stable forms found in our TPD spectra. It is, however, impossible to answer if they are –O–NO or $–O–NO_2$ species.

The peak area (which is proportional to the number of sorption sites) forms a sequence: N $<$ N–Ni $<$ N–Co $<$ N–Mn $<$ N–Cr. Thus undoubtedly the promotion with transition metal oxides increased the number of sorption sites. However, there was no direct correlation with NO reduction activity (cp. Fig. 2).

The maximum of the peak reflected that for some samples NO sorption was stronger than for others and formed a sequence: N–Co (ca. 480 K) $<$ N (ca. 490 K, 1st maximum) $<$ N–Ni (ca. 500 K) $<$ N–Mn (ca. 530 K) $<$ N–Cr (ca. 580 K) $<$ N (ca. 590 K, 2nd maximum). NO desorption ceased at ca. 500 K (N–Co), 550 K (N–Ni), 650 K (N–Mn) and 700 K (N–Cr). It is characteristic that both promoted samples which gave considerable amounts of N_2O as a side product (N–Mn and N–Cr) showed considerably stronger NO sorption in the high temperature region where NO interaction with the surface results in its reduction while for N–Co and N–Ni the NO desorption peaks were shifted towards much lower temperatures. Thus it may be assumed that in the high temperature region (over ca. 533 K) the mechanism of N_2O formation for promoted active carbons includes the following steps:

1. $NO_g \rightarrow NO_{ads}$
2. $NO_{ads} \rightarrow$ O–NO or $O–NO_2$
3. O–NO or $O–NO_2 \rightarrow N_{ads}$
4. $N_{ads} + NO_{ads} \rightarrow N_2O_{ads}$

The third step is tentative but well agreed upon by several other authors.

The presence of active material leads additionally to the changes in $m/e = 28$ (CO) and $m/e = 44$ (CO_2, N_2O) profiles, as described in detail by Grzybek et al. [41]. The amount of produced oxygen-containing groups differ depending on the active material. The comparison with fresh samples, however, e.g. profiles of $m/e = 28$ and 44 for N–Ni proves that no new type of sites result from the reaction. However, Yamashita and Tomita [22] showed that stable oxygen-containing complexes play smaller role in NO reduction in contrast to active intermediates which could not be registered under the conditions used in this work.

The mechanistic role of oxygen in this model is still uncertain. There may be several possibilities. One of them may be that not NO but NO_2 or –O–NO is a reaction intermediate as reported on active carbons [28,44]. It seems to be backed up by the discussed similarity between TPD for $m/e = 30$ for fresh samples containing nitrates and samples after reaction. Similar assumptions were made for SCR catalysts and it should be born in mind that e.g. at 573 K direct reduction of NO reported here gives similar products as SCR (NH_3) for the studied catalysts—N–Mn and N–Cr produce considerable amounts of N_2O in addition to N_2, while almost no

N_2O was found for N–Co and N–Ni [42]. The other possibility may be connected with reduction-oxidation cycles of active materials, assuming that only certain forms with appropriate structure are able to split N–O bond and/or sorb NO molecule undissociatively. This, however, needs some more experimental data.

4. Conclusions

Active carbons promoted with transition metal oxides (Mn, Cr, Co, Ni) show high activity in NO reduction by carbon from ca. 573 to 653 K. The reaction onset is by ca. 40 K lower than for unpromoted support. For higher temperatures deactivation due to the added active materials surpasses the gain in activity. The extent of increase in activity depends on the type of active material. Their choice influences also selectivity to N_2 and stability. Mn or Cr promoted active carbons, apart from the main product N_2, form considerable amounts of N_2O while selectivity to N_2 is much higher for N–Ni and N–Co.

Products distribution (N_2, N_2O) for 573 K shows similarities between direct NO reduction by carbon and SCR by ammonia which suggests that some steps are in common for both mechanisms. TPD experiments suggest that NO sorbed on the surface is not present as an undissociated molecule for N–Ni and N–Co at temperatures of ca. 573 K where high reduction activity is observed for these systems while it is present for N–Mn and N–Cr. Thus undissociated NO molecule sorbed on the surface may be the source of N_2O.

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