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Nitrogen-promoted active carbons as catalytic supports 2. The influence of Mn promotion on the structure and catalytic properties in SCR

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Abstract

Catalytic properties of active carbons treated with N-compounds and promoted with manganese oxides were studied in selective catalytic reduction of NO with ammonia. The following elements of the preparation had a beneficial effect on activity and selectivity of the catalysts: pre-oxidation of active carbon prior to the introduction of N-species, the choice of N-compound, together with the post-treatment procedure, and the optimisation of the amount of active material. Apart from the introduction of N-surface groups, it was important to control the amount of acidic surface species which in turn determined the distribution of MeO_x and reducibility of the samples, thus influencing the formation of undesired by-product (N_2O).

Keywords: $DeNO_x$; Ammonia; Active carbon; N-functionalities; Manganese oxides

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1. Introduction

Selective catalytic reduction of NO_x with ammonia is a widely used method for the removal of nitrogen oxides from outgases from stationary sources. The most often applied catalyst ($V_2O_5/WO_3/TiO_2$/monolith), however, does not show satisfactory activity at low-temperature region (below 250 °C). Carbonaceous materials are promising catalysts for this region and they may be modified in several ways leading to a considerable increase in activity. The most important types of modification are: (i) textural, obtained by tailoring preparation (mainly activation conditions [e.g. 1]), (ii) promotion with transition metal oxides/hydroxides or (iii) the introduction of surface functionalities (containing oxygen or nitrogen).

Promotion with oxides/hydroxides or salts of Mn, Fe, Ni, Co, Cr, Cu or V [2–8] turns them into efficient catalysts, in many cases more active or active at lower temperatures than the same materials based on the traditional supports (SiO_2 or Al_2O_3) [e.g. 9].

Surface groups play a dual role in the increase of activity of carbonaceous materials. Firstly, they may lead to higher NO conversion. Komatsubara and co-workers proved that for active carbons prepared from coal or polyacrylonitryl oxidized with sulphuric acid [10,11]. Teng et al. [12] compared the effect of oxidation by H_2SO_4 and HNO_3 and related that it was different depending on the presence or absence of oxygen in the reaction mixture. In the former case NO conversion formed a sequence: AC modified with HNO_3 (ACN) > AC > AC modified with H_2SO_4 (ACS), while in the latter it was ACN > ACS > AC. These results could be correlated to the amount and type of the formed oxygen-containing surface species, as studied by TPD. In the presence of oxygen there was a correlation with species desorbing to CO and in the absence of O_2 with those decomposing to CO_2. On this basis, the mechanism was proposed. In both cases, the first step was assumed to be adsorption of NH_3 on Broensted sites with the formation of NH_4^+. In the absence of O_2, the site was OH part of carboxyl group and in the presence of oxygen, phenol group. The subsequent step was NO adsorption in the form of –ONO complex—in the former case on C=O part of carboxyl group and in the latter on a neighbouring C=O surface species.

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The increase in activity obtained by the introduction of oxygen-surface species is, however, low in comparison to the promotion with transition metal oxides/hydroxides. In order to exclude the possible effect of ash, Hsu and Teng [13] studied ash-free active carbons and showed that the increase in NO conversion caused by the oxidative pre-treatment with HNO_3 was under 10% while the addition of transition metal oxides (Cu or Fe) resulted in the increase of NO conversion of ca. 30–95% in the temperature range of 110–200 °C.

Apart from the direct effect on SCR activity which was observed for unpromoted samples, surface groups play a very important role in the distribution of active material on carbonaceous supports. There are numerous examples described in literature for Cu, Fe, Mn, Ni, V etc. promoted carbonaceous materials. E.g. Marban and Fuertes [2] pre-treated carbon–carbon composites with HNO_3, H_2SO_4 and H_2O_2 solutions before introducing active material (MnO_x). The pre-treatment influenced activity and selectivity in SCR. Similarly, Galvez et al. [14] observed that for V-promoted carbonaceous catalyst, initial oxidation of carbon support by HNO_3 or H_2O_2 led to the formation of more active catalyst. The effect was discussed thoroughly by Zhu et al. [15] who concluded that oxidative treatment resulted in the increase of negative surface charge, thus improving adsorption of active material on carbonaceous surface during impregnation. Thus the combination of oxidation of carbon materials and their promotion with transition metal oxides/hydroxides gives better SCR catalysts than each of these procedures alone.

Apart from oxygen-containing functionalities, the introduction of nitrogen-containing surface groups was also investigated as a possible way to increase SCR activity. Such groups may be obtained on carbonaceous materials either by carbonisation and activation of nitrogen-containing polymers, or carbon precursors (e.g. coal) treated with N-containing molecules [e.g. 16–18], or post-treatment of already formed active carbons (or carbon fibers) with such molecules [19,20]. Some articles [19,20] suggest that the introduction of oxygen-containing surface species before N-groups formation on the surface also leads to better results than the treatment of carbonaceous materials without pre-oxidation.

There are no systematic studies, however, on the combination of N-species introduction and promotion with metal oxides/hydroxides and thus the main subject of this work was the systematic study of the application of both procedures, with an additional (optional) use of the third mentioned treatment, i.e. pre-oxidation.

2. Experimental

Carbonaceous supports containing nitrogen species were prepared by modification of commercial active carbon N produced by Gryfskand, Hajnówka (further designated C) with ammonia or urea, as shown in Fig. 1. Active carbons containing nitrogen-surface species were prepared using either NH_3 (route 1) or urea (route 2) as the source of N according to the scheme: *route 1*: active carbon (designation C) → optional oxidation in concentrated HNO_3 at 90 °C for 1 h (designation C90) → treatment with NH_3 at 800 °C for 2 h followed by cooling in NH_3 to 100 °C (designation C/N/800/N or C90/N800/N); *route 2*: active carbon (designation C) → optional oxidation (C90) → promotion with aqueous solution of urea (C/90 or C90/U) → curing in air at 350 °C (designation C/U/350 Air or C90/U/350 Air). So obtained materials were treated as supports and promoted with 5 wt.% Mn by incipient wetness technique from aqueous solution of $Mn(NO_3)_2$. Additionally, one sample was promoted with 2 wt.% Mn (designation C90/U/350 Air/Mn2). Although it has been found before that isoelectric point increased after amoxidation or amination [21] still manganese nitrate was chosen, assuming that cations will not anchor preferentially on basic sites and eliminate (cover) them. On the other hand, if nitrate groups were adsorbed on N-sites, it was assumed that they could be removed by calcination.

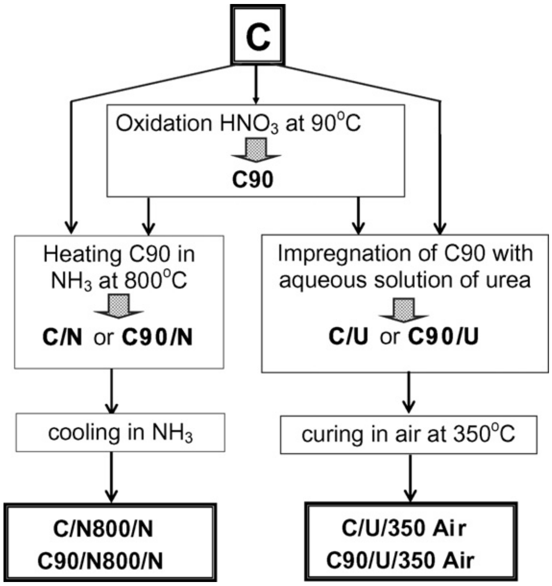

Fig. 1. The scheme of modification of active carbons with N-compounds.

Catalysts were characterized by: (i) temperature-programmed reduction in order to determine the type and amount of labile oxygen. TPR was carried out using an AMI-100 (Altamira Instruments) under the following conditions: first the samples were pre-treated similarly as during SCR reaction ($T = 250$ °C, 2 h, helium flow), then reduced with 5% H_2 in argon from 50 to ca. 730 °C with the temperature increase of 10 °C/min and kept at the end temperature for additional 5 min, (ii) temperature-programmed desorption of ammonia TPAD in order to determine the type/amount of acidic sites. The experiments were carried out as follows: first samples were pre-treated under identical conditions as for TPR. Then ammonia was sorbed at 60 °C, and the system was flushed with helium (25 ml/min) for 1 h in order to remove physically sorbed species. Afterwards desorption was carried out from 60 to 600 °C with a heating rate of 10 °C/min and mass number *m*/*e* 15(NH_3) was registered and (iii) X-ray photoelectron spectroscopy XPS in order to determine surface composition using Hemispherical Energy Analyzer PHOIBOS 150 MCD (SPECS GmbH). The main C 1s peak at 284.6 eV was used as an internal standard to calibrate binding energies. The areas of main peaks Mn $2p_{3/2}$, C 1s, N 1s, O 1s and sensitivity factors of Scofield were used to calculate surface composition.

Catalytic reduction of NO with ammonia was studied under the following conditions: mass of catalyst 400 mg; reaction mixture: 800 ppm NO, 800 ppm NH_3, 3% O_2, He; flow: 100 ml/min; before reaction supports and catalysts were heated at 250 °C for 2 h in helium (flow100 ml/min).

3. Results and discussion

3.1. Temperature-programmed reduction TPR

Fig. 2 depicts TPR profiles for the studied supports and catalysts. N-promoted carbonaceous materials (supports) exhibit a peak with a maximum over ca. 530 °C. Its area depends on the modification procedure: it is small for carbonaceous material modified with ammonia at high temperature (C/N800/N), and much higher for active carbons treated with urea (C/U/350 Air or C90/U/350 Air), confirming that some oxygen-containing species are formed on the surface during the curing process in air at 350 °C. C90 and C90/U/350 Air show different reduction profiles—the main peak was shifted by ca. 50 °C towards lower temperature for the latter sample and the amount of labile oxygen increased.

TPR profiles of N-containing carbonaceous materials changed after promotion with Mn—more labile oxygen was detected, as shown by the formation of new peaks with a maximum at ca. 360 °C and a weakly marked shoulder at ca. 300 °C. Additionally, the high-temperature peak shifted to temperature lower by ca. 100 °C. The introduction of lower amounts of manganese species onto the surface (sample C90/U/350 Air/Mn2) led to the increase in overall number of sites in the low-temperature region but no separate peaks were discernible.

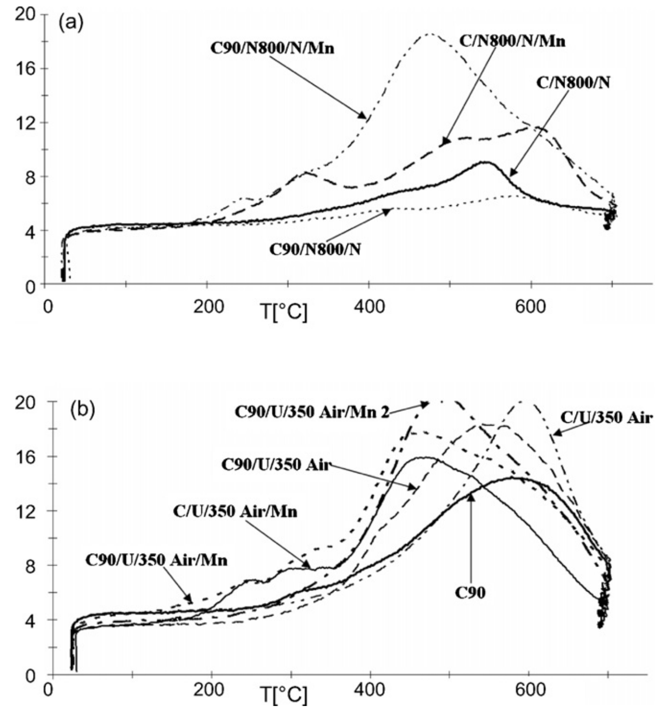

Fig. 2. TPR profiles for the samples under study.

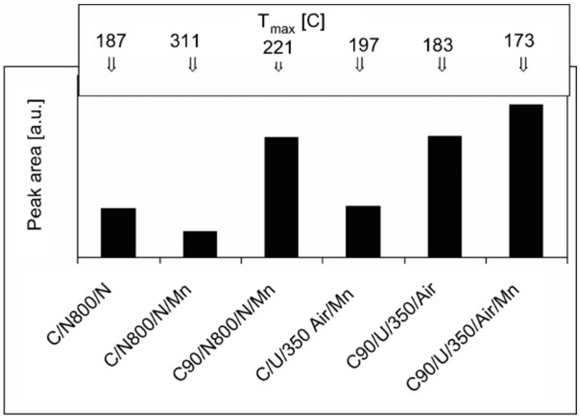

Fig. 3. The area of TPAD peaks and temperature of maximum desorption T_{max}.

3.2. Temperature-programmed desorption of ammonia

The amount of acidic sites for N-modified active carbons and samples additionally promoted with MnO_x is compared in Fig. 3. Both the modification with N-compounds and the promotion with manganese result in the change of the number and the strength of acidic surface sites. The highest number of acidic sites was detected on catalyst C90/U/350 Air/Mn. The following preparation steps seem to influence positively the number of sites:

(i) Pre-oxidation of active carbon (cp. C90/N800/N/Mn versus C/N800/N/Mn and C90/U/350 Air/Mn versus C/U/350 Air/Mn). This may be explained by the following. First of all, oxidation with HNO_3 results in the formation of a large number of acidic sites, as shown previously [22]. Some of these sites are lost by the reaction with N-compounds leading to the formation of basic N-sites, but some obviously survive. Additionally, pre-oxidation of active carbon may influence MnO_x distribution, and thus produce different amounts of NH_3 sorption sites. The formation of different types of acidic sites on pre-oxidized and non-treated samples is additionally indicated in this work by their different strength, as shown by temperature of peak maximum which is higher for C than C90-derived catalysts.

(ii) The treatment of active carbons with urea rather than ammonia (cp. C90/N800/N/Mn versus C90/U/350 Air/Mn and C/N800/N/Mn versus C/U/350 Air/Mn). This is most probably directly correlated with the influence of oxygen-containing surface species which are formed during urea treatment. Such groups may influence MnO_x distribution [2,3,22], as discussed in more detail later.

3.3. X-ray photoelectron spectroscopy

Table 1 summarizes binding energies of Mn $2p_{3/2}$ peaks, as well as the splitting of Mn 3s and the surface composition (as

Table 1
XPS data: binding energy BE of Mn $2p_{3/2}$, the splitting of Mn 3s peak (ΔMn 3s) and surface composition (shown as atomic ratio of Mn/C and O/C) for the studied samples

Catalyst	BE Mn $2p_{3/2}$ (eV)	ΔMn 3s (eV)	Surface atomic ratio (at. %)	
			Mn/C	O/C
C/N800/N/Mn	641.7	5.3	0.200	0.971
C90/N800/N/Mn	641.8	5.2	0.276	1.393
C90/U/350 Air/Mn	642.3	4.6	0.029	1.006
C90/U/350 Air/Mn2	642.2	[a]	0.006	0.913

[a] Under detection level.

Mn/C and O/C surface atomic ratios). Table 2 gives reference data for Mn_2O_3, Mn_3O_4 and MnO_2 [23–26]. The comparison of both tables indicates that oxidation state of MnO_x differs, depending on N-compound pre-treatment. In case of NH_3-treated samples it is lower (Mn_2O_3) than for urea-modified ones (MnO_2). The distribution of MnO_x is, according to the model Kerkhoff and Moulijn [27], related to the intensity ratio of a peak of the active material and that of the support. As this ratio is proportional to the atomic ratios of appropriate elements, Mn/C atomic ratio may give some information on MnO_x distribution on the N-modified carbonaceous materials. From Table 1 it may be derived that distribution on active carbons treated with ammonia at high temperature (both C and C90) and C90 modified with urea is completely different. In the former case Mn/C atomic ratios are high, indicating the deposition of bigger MnO_x aggregates preferentially on the outer surface of active carbon grains, while in the latter the ratio is small which proves much more even distribution over the internal surface. Similar results were obtained in many previous publications concerning the promotion of carbonaceous materials with transition elements compounds. It was established without doubt that pre-oxidation of the active carbons resulted in the formation of oxygen-containing surface species which in turn were anchoring places for Me^{n+} cations [e.g. 2,3,22]. Thus pre-oxidation led to the formation of smaller entities on the surface (small clusters or perhaps in some cases even individual cations) which, because of their size, could be accommodated in relatively narrow pores of carbonaceous materials. On the other hand, the surface of active carbons, which were not initially oxidized, did not offer enough such places to bind the cations and as a result bigger aggregates of MeO_x precipitated preferentially on the outer surface of the grains. This reasoning may well explain the distribution observed for our samples. The treatment of active carbons with ammonia at high temperature leads to the formation of basic sites and the exclusion of some acidic surface sites, as proven before [18,28–30]. The lack (or smaller amount) of acidic centers hinders the formation of smaller MnO_x entities. On the other hand, some new oxygen functionalities are formed during the urea modification procedure as a result of the part of urea decomposing during the curing process to ammonia and carbon dioxide [31]. As a consequence, the sample may be further oxidized by CO_2 and the formed groups may enable more even distribution of MnO_x. It is also possible that curing process which was carried out in air, has an additional positive influence on oxygen-containing surface species, although it was found before that carbonaceous materials oxidized by air have weaker acidity than those treated by concentrated HNO_3 [32] and so it may be expected that their influence on anchoring Mn cations would not be too pronounced.

Table 2
Reference XPS data for manganese peaks: binding energy (BE) and the splitting of Mn 3s (ΔMn3s) [23–26]

Compound	Mn $2p_{3/2}$	ΔMn 3s
MnO	640.5–641.2	5.8
Mn_3O_4	641.2–641.4	5.6
γ-Mn_2O_3, γ-MnOOH	641.5–641.8	5.3
MnO_2	642.0–642.4	4.6

4. Catalytic properties

Fig. 4 compares NO conversion and N_2O formation for the studied catalysts. From Fig. 4 the following conclusions may be made:

- the introduction of MnO_x increased NO conversion in comparison to N-modified active carbons. The extent of the increase depended on the pre-oxidation of active carbon prior to NH_3 or urea treatment, as illustrated by the sequence of NO conversion:
  for NH_3 modification: C90/N800/N/Mn > C/N800/N/Mn
  for urea modification: C90/U/350 Air/Mn > C/U/350 Air/Mn.
- Mn-containing samples activate on-line (cp. C/N800/N/Mn; for the sample C90/N800/N/Mn and C90/U/350 Air/Mn the effect was not registered because activity was almost complete already during the first part of the experiment). This was observed before by Marban and Fuertes [3] and Grzybek et al. [4] for Mn-promoted carbon materials, although it did not find a proper explanation yet. Grzybek et al. [4] suggested that during reaction some manganese nitrate did not decomposed during calcination formed new MnO_x centers. The experimental results of Marban and Fuertes [3], on the other hand, seem to exclude this possibility. In order to solve the problem Marban and Fuertes [3] pre-treated carbon fibers promoted with MnO_x with ammonia or nitrogen oxide before reaction, but the results were not conclusive.
- Selectivity to N_2 decreased after promotion with manganese oxides/hydroxides, leading to a conclusion that MnO_x is the additional source of N_2O in the products in all cases. However, selectivity depended strongly on the temperature of the reaction and the formed amounts of N_2O were small for especially interesting low-temperature SCR (i.e. 140 or 180 °C). Additionally, the amount of formed N_2O depended on several other factors, directly connected to the preparation conditions. The initial pre-oxidation of the support resulted in more selective catalysts. This may be directly correlated to active material distribution, as derived from XPS. Similarly,

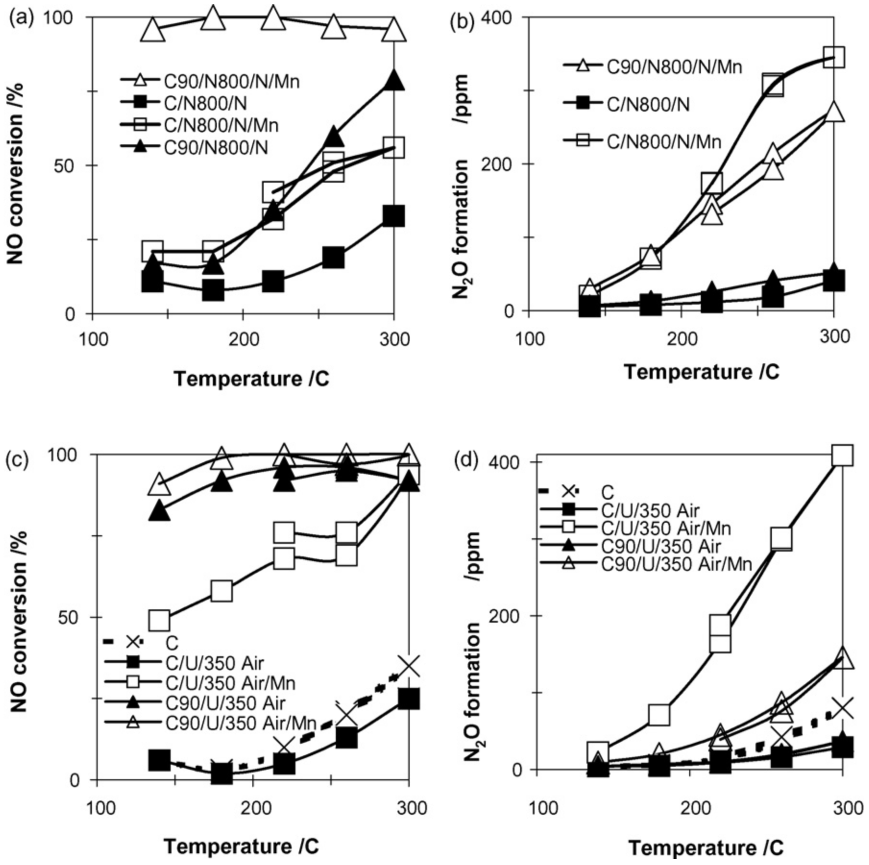

Fig. 4. NO conversion and N_2O formation for the studied samples: (a) NO conversion for active A carbons modified with ammonia and MnO_x; (b) N_2O formation for active carbons modified with ammonia and MnO_x; (c) NO conversion for active carbons modified with urea and MnO_x; (d) N_2O formation for active carbons modified with urea and MnO_x. Reaction conditions: mass of catalysts 400 mg; reaction mixture: 800 ppm NO, NH_3, 3% O_2; flow: 100 ml/min.

as for carbonaceous materials promoted with MnO_x (but not modified with N-compounds [4]), smaller clusters and/or individual cations led to lower formation of dinitrogen oxide while bigger aggregates gave high amounts.

These observations lead to an obvious suggestion for optimisation: smaller amounts of active material (MnO_x) should produce smaller aggregates and thus decrease the tendency to the formation of undesired N_2O. On the other hand, this could result in the loss of activity. Due to the fact that all C90-based catalysts were very active (the registered NO conversion was almost 100%), the experiment was repeated for a smaller amount of catalyst (200 mg, other reaction conditions unchanged) for C90/N800/N/Mn (containing 5 wt.% Mn) and C90/U 350 Air/Mn and C90/U/350 Air/Mn2 containing 5 or 2 wt.% Mn, respectively. Fig. 5 compares NO conversion and N_2O formation for these catalysts; in order to better illustrate the point discussed below, the formation of N_2O on the support C90/U/350 Air was added. As it may be seen from the figure, activity is still very high for C90/U/350 Air/Mn2 (containing 2% Mn), only slightly lower than for C90/U/350 Air/Mn (containing 5 wt.% Mn). On the other hand, the formation of N_2O decreased. This, in comparison with Table 1, confirms the conclusion that the distribution of MnO_x is directly correlated with the formation of the side product. The comparison with the TPR data for the same samples (cp. Fig. 2) indicates that the amount of labile oxygen at temperature range relevant for the reaction (between 140 and 300 °C) is, to a large extent, responsible. No easily reducible oxygen species are available at the lowest temperatures (under 200 °C) either on N-modified active carbons (supports) or the samples containing MnO_x and thus no or little N_2O appears in the products. On the other hand, in the temperature range of ca. 200 to ca. 300 °C, the amount of labile oxygen forms a sequence: C90/N800/N/Mn $\approx$ C90/U/350 Air/Mn $>$ C90/U/350 Air/Mn2 $\approx$ C90/U/350 Air. If in both cases (catalysts with bigger and smaller aggregates of MnO_x) the deposits had the same character, smaller ones should be more easily reduced than bigger ones. As TPR results show that there is less labile oxygen in the case of samples with smaller MnO_x aggregates, it must be therefore assumed that smaller and bigger aggregates are different in character. The possible reason could be a difference in the interaction of MnO_x with active carbon surface. For bigger crystallites the interaction is probably rather weak and the conditions of reduction are more similar to those for pure MnO_x. Smaller aggregates, on the other hand, are probably more strongly bonded through more numerous acidic oxygen functionalities on carbon surface and thus they are less easily reducible. It must be stressed, however, that there is no linear correlation between TPR and XPS.

There is another positive effect of smaller amounts of active material. As it may be observed in Fig. 5a, NO conversion

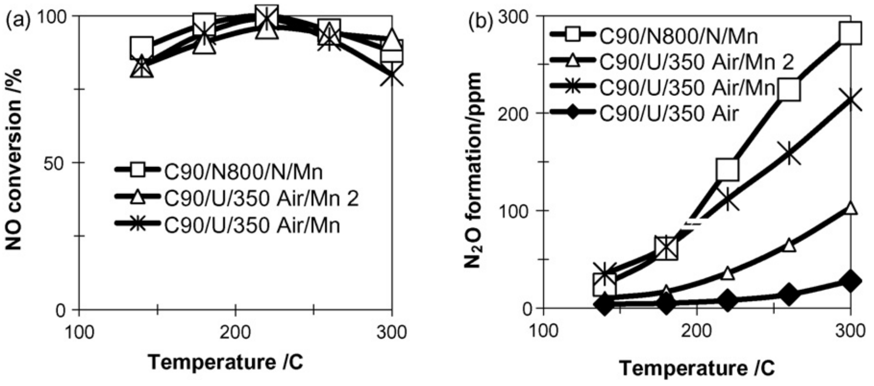

Fig. 5. The comparison of NO conversion and N_2O formation for C90/N800/N/Mn, C90/U/350 Air/Mn and C90/U/350 Air/Mn2. Reaction conditions: mass of catalysts 200 mg; reaction mixture: 800 ppm NO, NH_3, 3% O_2; flow: 100 ml/min.

decreased somewhat for reaction temperatures over 220 °C. The loss was higher for C90/U/350 Air/Mn than for C90/U/350 Air/Mn2. The decrease in NO conversion is most probably connected with the increase in the preferential oxidation of NH_3, leading to the depletion of the amount of reducing agent on-line. This was observed before for active carbons promoted with bigger aggregates of MnO_x.

To conclude, carbonaceous materials modified with nitrogen compounds may be used as supports for transition metal oxides/hydroxides. The efficiency of low-temperature $DeNO_x$ catalysts based on such supports depends, however, strongly on their structure which, in turn, is determined by several preparation conditions. Firstly, the oxidative pre-treatment of active carbon is important. If active carbons are not oxidized prior to the modification with N-compounds, the small starting amount of oxygen functionalities on the original sample (before the N-modification procedure) leads, after promotion with MnO_x, to less efficient catalysts. Secondly, appropriate number of acidic surface groups must be introduced before the promotion of the N-modified support with transition metal oxides/hydroxides. Such groups facilitate the formation of smaller clusters of active material which decreases their reducibility and thus leads to less N_2O in the products. Apart from that, the formation of MnO_x species increases acidity which plays an important role in reaction mechanism, being a site for the sorption of reducing agent. On the other hand, N-surface species which are basic in character play a role of sorption sites for NO and facilitate their oxidation to NO_2, as discussed for carbonaceous materials modified with different N-compounds [17,18,33,34]. The high-temperature treatment with ammonia is less beneficial than the proposed urea treatment followed by curing in air. The former, as shown by Muñiz et al. [29] increases mainly the basicity of the samples and thus was found of advantage for SO_2 removal. The latter influences both basicity (by the introduction of N-surface species) and acidity (through the curing process). Thirdly, the amount of active material has to be carefully optimised. In case of MnO_x, higher amounts lead to an excess in labile surface oxygen which results in the increased tendency to the formation of N_2O, either as a side product of SCR or through oxidation of the reducing agent (ammonia), which may additionally decrease high-temperature $DeNO_x$ activity.

5. Conclusions

It was possible to introduce two functions to carbonaceous materials: basic-N-containing surface species and active material (MnO_x), thus influencing positively low-temperature $DeNO_x$ properties of the system. The overall effect depended to a high extent on the proper choice of the preparation technique for N-promoted active carbon. There was the beneficial effect of:

- active carbon pre-oxidation (C90-based catalysts were more active and more selective than C-based ones),
- urea-introduction procedure, especially the curing process which, through decomposition of adsorbed urea in situ to NH_3 and CO_2, led to the formation of both nitrogen-containing and oxygen-containing surface functionalities.

The N-functionalities introduced onto supports are important for reaction mechanism—they influence basicity and thus facilitate NO adsorption and oxidation. On the other hand, oxygen-containing surface species play a much more complex role. First of all, they determine active material distribution and so the number of acidic sites, necessary for the adsorption of reducing agent (NH_3). Secondly, they indirectly influence reducibility of the samples by determining MnO_x distribution. As a result, the catalysts with more even MnO_x distribution (smaller clusters and/or individual cations) lead to lower amounts of N_2O in the products while bigger aggregates give high amounts of the undesired by-product. The effect may be rationalized assuming that small clusters most probably interact more strongly with the support than bigger aggregates which leads to higher oxygen lability in the latter case than in the former.

The preparation procedure consisting of a series of steps (pre-oxidation of active carbon, impregnation with aqueous urea solution, curing in air at 350 °C and impregnation with aqueous solution of $Mn(NO_3)_2$) results in $DeNO_x$ catalyst active at low-temperature with high selectivity to N_2. Such modification procedure is easier, less costly and less-energy consuming than most often proposed high-temperature modification with ammonia.

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References

[1] M.J. Lazaro, M.E. Galvez, S. Artal, J.M. Palacios, R. Moliner, J. Anal. Appl. Pyrolysis 78 (2007) 301.
[2] G. Marban, A.B. Fuertes, Appl. Catal. B 34 (2001) 55.
[3] G. Marban, A.B. Fuertes, Appl. Catal. B 34 (2001) 43.
[4] T. Grzybek, J. Pasel, H. Papp, Phys. Chem. Chem. Phys 1 (1999) 341.
[5] T. Grzybek, H. Papp, Appl. Catal. B 1 (1992) 271.
[6] Z. Zhu, Z. Liu, S. Liu, H. Niu, T. Hu, T. Liu, Y. Xie, Appl. Catal. B 26 (2000) 25.
[7] Z. Zhu, Z. Liu, S. Liu, H. Niu, Appl. Catal. B 23 (1999) L229.
[8] J. Pasel, P. Käβner, B. Montanari, V. Gazzano, A. Vaccari, W. Makowski, T. Łojewski, R. Dziembaj, H. Papp, Appl. Catal. B 18 (1998) 199.
[9] M. Yoshikawa, A. Yasutake, I. Mochida, Appl. Catal. A 173 (1998) 239.
[10] I. Mochida, M. Ogaki, H. Fujitsu, Y. Komatsubara, S. Ida, Fuel 64 (1985) 1054.
[11] Y. Komatsubara, S. Ida, H. Fujitsu, I. Mochida, Fuel 63 (1984) 1738.
[12] H. Teng, Y.-T. Tu, Y.-C. Lai, C.-C. Lin, Carbon 39 (2001) 575.
[13] L.-Y. Hsu, H. Teng, Appl. Catal. B 35 (2001) 21.
[14] M.E. Galvez, M.J. Lazaro, R. Moliner, Catal. Today 102–103 (2005) 142.
[15] Z.H. Zhu, L.R. Radovic, G.Q. Lu, Carbon 38 (2000) 451.
[16] L. Singoredjo, F. Kapteijn, J.A. Moulijn, J.-M. M-Martinez, H.-P. Boehm, Carbon 31 (1993) 213.
[17] M.-Ch. Huang, H. Teng, Carbon 41 (2003) 951.
[18] G. Marbán, J. Muñiz, A.B. Fuertes, Appl. Catal. B 23 (1999) 25.
[19] G. Szymański, T. Grzybek, H. Papp, Catal. Today 90 (2004) 51.
[20] J. Muñiz, G. Marbán, A.B. Fuertes, Appl. Catal. B 27 (2000) 27.
[21] R.J.J. Jansen, H. van Bekkum, Carbon 32 (1994) 1507.
[22] T. Grzybek, J. Klinik, M. Rogóż, H. Papp, J. Chem. Soc. Faraday Trans. 94 (1998) 2843.
[23] M. Oku, K. Hirokawa, S. Ikeda, J. Electr. Spectr. 7 (1975) 465.
[24] M. Oku, K. Hirokawa, J. Electr. Spectr. 8 (1976) 475.
[25] V. DiCastro, C. Furlani, M. Gargano, M. Rossi, Appl. Surf. Sci. 28 (1987) 270.
[26] J.W. Murray, J.G. Dillard, R. Giovanoli, H.M. Moers, W. Stumm, Geochim. Cosmochim. Acta 49 (1985) 463.
[27] F.P.M.J. Kerkhoff, J.A. Moulijn, J. Phys. Chem. 83 (1979) 1612.
[28] S. Biniak, G. Szymański, J. Sielewski, A. Świątkowski, Carbon 35 (1997) 1799.
[29] J. Muñiz, J.E. Herrero, A.B. Fuertes, Appl. Catal. B 18 (1998) 171.
[30] D. Mang, P. Boehm, K. Stanczyk, H. Marsh, Carbon 30 (1992) 391.
[31] T. Grzybek, J. Klinik, B. Samojeden, V. Suprun, H. Papp, Catal. Today, in print.
[32] T.J. Bandosz, B. Buczek, T. Grzybek, J. Jagiełło, Fuel 14–15 (1997) 1409.
[33] S. Matzner, H.P. Boehm, Carbon 36 (1998) 1697.
[34] Ch.-M. Yang, K. Kaneko, J. Colloid Interface Sci. 255 (2002) 236.