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Nitrogen promoted activated carbons as $DeNO_x$ catalysts. 2. The influence of water on the catalytic performance

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ABSTRACT

The catalytic properties of the activated carbons treated with N-compounds and promoted with manganese oxides were studied in SCR reaction with ammonia in absence and presence of water. The catalysts were characterized by the elemental analysis, low-temperature Ar sorption, thermogravimetric analysis with the analysis of surface species, temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS). The addition of H_2O to SCR decreased activity by 10–20% and increased selectivity to N_2. The catalysts are quite promising for SCR reaction at lower temperatures in the range of 180–260 °C.

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1. Introduction

The removal of NO_x from stack gases is one of the most important environmental issues. Currently, selective catalytic reduction of NO_x with ammonia is widely used in the EU for the off-gas treatment of stationary sources. Most often $V_2O_5/WO_3/TiO_2$ is applied as catalyst. However, the optimum temperature window for this catalyst is between 300 and 400 °C. An attractive alternative for lower temperatures is the application of activated carbons. It was demonstrated that with the use of appropriate additives carbon monoliths could easily be prepared [1]. The activity of carbonaceous materials may be improved by promotion with transition metal oxides/hydroxides of Mn, Fe, Ni, Co, Cu, Cr or V [2–9] or the introduction of surface functionalities, e.g., oxygen or nitrogen containing surface groups [10,11]. Oxygen-containing surface groups play a dual role for activated carbons: on the one hand increasing the activity in SCR (although the effect is much lower than in the case of the promotion with metal oxides) [12–14], and, on the other hand, positively influencing the distribution of the active material. The preparation procedures consisting of a combination of two or three of the mentioned treatments were also reported previously [10,15]. Grzybek et al. [15] showed that pre-oxidized activated carbons further treated either with ammonia or with urea were both more active and selective to N_2 than similarly prepared non-oxidized activated carbons. The promotion of N-treated activated carbons with MnO_x increased additionally the activity, although some deterioration of the selectivity was observed [15]. However, a possible deactivating effect of H_2O on activated carbon based catalysts was rarely studied. As exceptions, the articles of Muñiz et al. [11,16] and Marbán et al. [17] may be mentioned. Muñiz et al. reported that carbon fibers containing N-species, prepared by carbonization of polyacrylamide or treatment of activated carbons by N-compounds, showed a considerable decrease in NO conversion at 150 °C upon the addition of water but the effect became smaller at higher temperatures. Marbán et al. [17] investigated the mechanism of the SCR reaction at 125 °C for MnO_x/activated carbons and also addressed the role of H_2O.

The main aim of this work was to study the influence of the addition of water to a $NO/NH_3/O_2$-mixture on activity and selectivity of activated carbons promoted with N-species or doubly promoted with N- and Mn-compounds.

2. Experimental

2.1. Preparation of samples

Activated carbons modified by nitrogen compounds and promoted with MnO_x were prepared according to the procedure described in more detail elsewhere [10,15]. In short activated carbon, either initially oxidized by HNO_3 (C90;

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Table 1
Characterization data for the supports and catalysts under study: specific surface area S_{BET}, N content from elemental analysis, surface composition and chemical state of Mn as obtained from XPS.

Sample	S_{BET} (m^2/g)	N content (wt.%)	Surface composition			
			N/C (at.%/at.%)	O/C (at.%/at.%)	Mn/C (at.%/at.%)	MnO_x chemical state[a]
C90/U/350 Air	760	4.19	0.036	1.213	–	–
C90/U/350 Air/Mn 2	780	2.15	0.038	0.867	0.007	Mn_2O_3, MnOOH[b]
C/N800/N	978	1.26	0.012	0.188	–	–
C/N800/N/Mn	810	2.01	0.021	0.971	0.200	Mn_2O_3, MnOOH
C90/N800/N	1216	1.43	0.015	0.593	–	–
C90/N800/N/Mn	708	2.26	0.021	1.393	0.276	Mn_2O_3, MnOOH
C90/N800/N–Ar	1212	0.98	0.005	0.502	–	–
C90/N800/N–Ar/Mn	759	1.48	0.026	0.964	0.167	Mn_3O_4, MnO

[a] From Mn 3s splitting.

[b] From binding energy of Mn 2p (Mn 3s under detection level).

$S_{BET} = 1008\ m^2/g$) or untreated (C; producer Gryfskand Hajnówka, Poland; $S_{BET} = 1083\ m^2/g$) was used as starting materials and two preparation procedures were applied. In *procedure* 1: C or C90 was impregnated with an aqueous solution of urea and then cured in air at 350 °C (C/U/350 Air or C90/U/350 Air) and subsequently impregnated with $Mn(NO_3)_2$ (C or C90/U/350 Air/Mn). In *procedure* 2: C or C90 was treated with NH_3 at 800 °C (C/N800 or C90/N800) and cooled under NH_3 flow to room temperature (C/N800/N or C90/N800/N) and subsequently impregnated with $Mn(NO_3)_2$ (C or C90/N800/N/Mn). If not stated otherwise, the content of Mn was 5 wt.%. Of the catalysts described in [10,15] the following were chosen for the SCR tests in the presence of water: C90/U/350 Air/Mn 2% (the most active and selective catalyst), its support C90/U/350 Air, C90/N800/N/Mn (very active catalyst whose selectivity to N_2 was not satisfactory at $T \geq 180\ °C$), C/N800/N/Mn (not very active, and not very selective). Additionally, a new catalyst was prepared by a slightly modified procedure 2 and tested in SCR: C90/N800 was cooled in NH_3 to 300 °C, then in Ar to 100 °C (C90/N800/N–Ar) and subsequently impregnated with Mn (C90/N800/N–Ar/Mn). The resulting catalyst was somewhat less active than C90/N800/N/Mn and much less selective.

2.2. *Characterization of samples*

The details of elemental analysis (the content of N), low-temperature Ar sorption (specific surface area), thermogravimetric analysis (TG/DTG) with the analysis of surface species (type and amount of surface groups), temperature-programmed reduction (TPR) (the amount of labile oxygen) and X-ray photoelectron spectroscopy (XPS) (surface composition) was fully discussed elsewhere [10,15], with the exception of the newly prepared C90/N800/N–Ar/Mn. Characterization data: specific surface area S_{BET}, the N content from elemental analysis, surface composition and the chemical state of Mn as obtained from XPS are summarized for the studied catalysts and supports in Table 1.

2.3. *DeNO$_x$ activity and selectivity*

The catalytic behaviour of the prepared catalysts was studied in a flow-type reactor operated at ambient pressure. In order to choose the appropriate temperature for studying the influence of water, first long-time experiments were carried out at 140 and 180 °C, because the temperature region below 250 °C is the most interesting for industrial applications. Two samples were selected: C90/U/350 Air and C90/U/350 Air/Mn 2%. The tests were carried out as follows: before reaction, the samples were calcined in situ at 250 °C for 2 h in order to decompose manganese nitrate. For the chosen conditions, the presence of rest (undecomposed) manganese nitrate and its further influence on catalytic reaction could be excluded for two reasons: (i) thermogravimetric measurements (TG/DTG) accompanied by the analysis of decomposition products showed $m/e = 30$ peak with a maximum around or below 250 °C, indicating that an appropriate temperature for calcination procedure was chosen and (ii) during calcination NO_2 arising from Mn precursor was decomposed to NO in a catalytic unit installed before NO analyser and then NO was registered in NDIR analyser. After 2 h of calcination no NO was observed any more, testifying to total decomposition of the Mn precursor. After calcination the catalyst was heated to 140 °C and the reaction was carried out for 450 min, followed by another 450 min at 180 °C. The reaction conditions were: mass of catalysts 200 mg; reaction mixture 800 ppm NO, 800 ppm NH_3, 3 vol.% O_2, rest He; flow rate 100 cm^3/min; detection of NO, N_2O, CO_2 was carried out by NDIR (Hartmann and Braun). Since the conversion of NO was not stable at 140 °C even without H_2O, as discussed below, temperatures of 180, 220 and, for comparison 260 °C, were chosen for the experiments to determine the influence of water on SCR. All reaction conditions, i.e. mass of the catalyst, calcination, flow rate and composition in gas stream were the same, as described above. The amount of H_2O, if added, was 0.3 g/h. The experiments were carried out as follows: after calcinations at 220 °C, the catalyst was heated to 180 °C, and SCR was carried out for 50 min in dry flow. Then, water was added and the measurements were continued for 50 min, followed by further 50 min without water on-line; this was repeated at 220 and 260 °C. Additionally, tests with a repeated addition and removal of H_2O were carried out at 220 °C for C90/N800/N–Ar/Mn, in the following way: after calcination, the reaction was carried out without H_2O, then with H_2O, again without and with H_2O for 50, 60, 60 and 50 min, respectively. The sample was cooled and left overnight, and then calcined in He at 220 °C for 50 min and water was repeatedly added and removed from educt flow (exp. II).

3. Results and discussion

3.1. *Influence of the cooling procedure on C90/N800 catalysts*

The cooling step in preparation procedure 2 influenced both the structure and the catalytic performance of C90/N800 catalysts. The support C90/N800/N–Ar contained less nitrogen (1 wt.%) than C90/N800/N (1.4 wt.%), proving the presence of some weakly bound N-species on the surface of the latter which could be introduced when cooling in ammonia and removed when cooling in Ar. This is confirmed by the N/C and O/C ratios measured by XPS (N/C [at.%/at.%] 0.015 and 0.005 and O/C 0.593 and 0.502 for C90/N800/N and C90/N800/N–Ar, respectively). According to the oxidation states of Mn oxides as determined from the splitting of the Mn 3s peak [18] the detected phases are Mn_2O_3 (C90/N800/N/Mn) or MnO/Mn_3O_4 (C90/N800/N–Ar/Mn). Mn/C ratios for both catalysts were relatively high (ca. 0.20), indicating preferential deposition of active material on the outer surface of the activated carbon

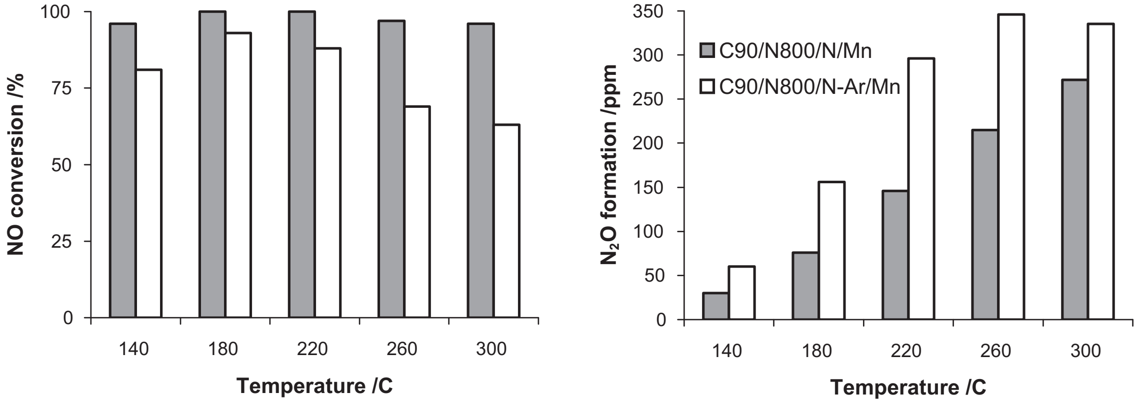


Fig. 1. NO conversion and N_2O formation for C90/N800/N/Mn and C90/N800/N–Ar/Mn.

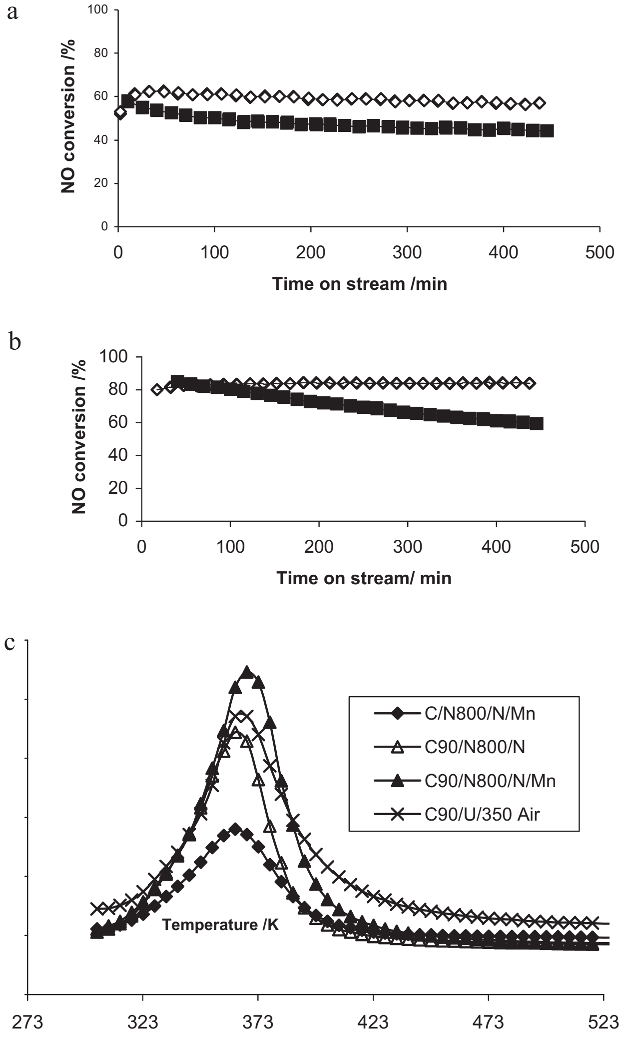
particles. TPR profiles of the catalysts registered in the range of temperatures 30–700 °C, were similar and testified the presence of large amounts of labile oxygen on the surface. NO conversion and the formation of N_2O for these catalysts and their supports are presented in Fig. 1a and b. Although both supports showed very similar SCR behaviour. Mn containing catalysts proved to be different. The observed differences could arise either from (i) the changes in MnO_x distribution which is very sensitive to the type/number of oxygen-containing surface species, as shown before [4] or (ii) the difference in the oxidation state of the active material.

3.2. Long-time performance

Fig. 2a and b compares NO conversions for C90/U/350 Air/Mn 2% and its support at 140 and 180 °C. NO conversion decreased during time on stream at 140 °C and was stable at 180 °C as well as at 220 °C (not shown in the figure). Kijlstra et al. [19] observed a decrease in NO conversion of a MnO_x/Al_2O_3 catalyst in the presence of H_2O and ascribed it to the formation of hydroxyl species both on the active material and the support. These species were claimed to be stable below 150 °C. The TPD signal $m/e = 18$ (cf. Fig. 2c) proves that considerable amounts of H_2O were adsorbed on the surface of the studied catalysts. Water desorption was observed up to 150–180 °C and thus the above mentioned assumption of Kijlstra et al. [19] may also be valid for the catalysts studied here. Another possibility was raised by Marbán et al. [17] who argued that water adsorbed competitively on MnO_x decreasing the number of active Mn species available for the reaction. This implies that the product of SCR, i.e. H_2O has this inhibiting effect since there was no water in the feed. However, neither of the above mentioned arguments explains the conversion deterioration on the carbon support C90/U/350 Air, containing no Mn. Possibly, a slow desorption from microporous supports may also play a role.

3.3. SCR in the presence of H_2O

The influence of the addition of H_2O on SCR performance (NO conversion and the amount of N_2O in the products) is shown in Fig. 3. NO conversion decreased (ca. 10–25%) after introduction of water to the feed; the extent of the decrease depended on the reaction temperature, as already observed before both for N-modified activated carbon [11,16] and MnO_x/Al_2O_3 [19]. However, the decrease in NO conversion was much smaller than in the case of MnO_x/Al_2O_3 [19] and it was totally reversible after removing H_2O. Selectivity to N_2 improved after adding water to the feed, especially at higher temperatures (220, 260 °C). The trend is in agreement with the observations of Kijlstra et al. [19], although their measurements were carried out at lower temperatures. The amount of the formed N_2O decreased stronger as would be expected from the decrease in NO conversion. The reasons for both effects, i.e. decrease in NO conversion and increase in selectivity to N_2, are not totally clear. Water is believed to have an influence on the



Designation in fig. (a) – (b): temperatures: ■ – 413K, ◊ – 453K,

Fig. 2. (a and b) NO conversion versus time on stream for (a) C90/U/350 Air and (b) C90/U/350 Air/Mn 2. (c) TPD desorption profiles ($m/e = 18$).

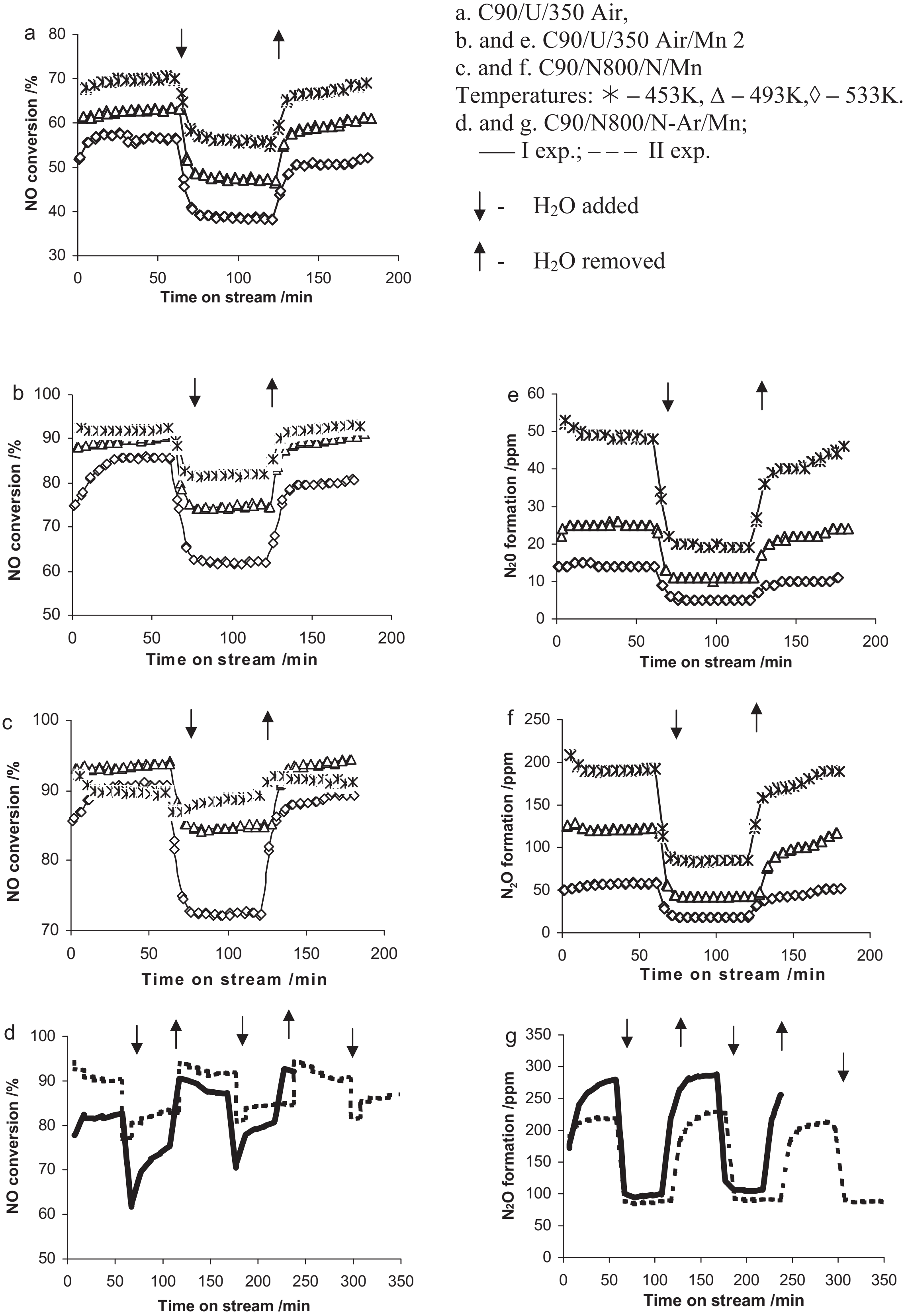


Fig. 3. SCR activity and N_2O formation in the presence and absence of H_2O; within experimental error there was no N_2O in the products for C90/U/350 Air, so appropriate figure was omitted.

adsorption–desorption equilibrium of NO and/or NO_2, although the literature information is not consistent. For experiments carried out at room temperature: (i) Mochida et al. [20] reported a decrease in NO sorption in air of high humidity (80%); (ii) Kong and Cha [21] claimed that the removal of NO at room temperature from a feed consisting of NO, N_2, air and H_2O was almost independent of the concentration of O_2 over 5% and H_2O over 1%, and (iii) Bashkova and Bandosz [22], who studied NO_2 adsorption on urea-treated activated carbons, observed an increase in adsorption from an air–water mixture in comparison to the adsorption from dry air. It must be stressed, however, that the results of these experiments may not be necessarily relevant for mechanistic considerations at higher temperatures. Firstly, oxidation of NO to NO_2 is favoured at lower temperatures and at higher temperatures the equilibrium is shifted towards NO. Secondly, NO_2 is reduced much faster by ammonia than NO, so if the presence of water led to more NO_2 species on the surface, NO conversion should increase and not decrease. On the other hand, there is a general agreement that H_2O competes for surface sites with NO and/or NH_3. According to Kijlstra et al. [19] there is always a surplus of NH_3 on the surface under reaction conditions, so the reduced activity in SCR with H_2O should be explained by the smaller number of NO molecules present on the surface. The smaller effect on the activated carbons studied here in comparison to MnO_x/Al_2O_3 [19] may be explained by the superposition of the negative effect of water and the positive effect of the activated carbon supports which contain N-surface species which are believed to increase NO adsorption [23].

The increase in selectivity was more pronounced for the unselective C90/N800/N/Mn and C/N800/N/Mn (not shown in Fig. 3) than for C90/U/350 Air/Mn 2% which may be explained by the differences in the reducibility of MnO_x species. The former two contain more labile oxygen than the latter, as shown by TPR [15]. Since a part of the N_2O molecules originate from ammonia oxidation, the decrease in N_2O formation may be ascribed to the inhibiting effect of the sorption of H_2O on active species. This is in good agreement with observations of several authors, e.g., Curtin et al. [24] who claimed that water decreased the number of labile oxygen species on the surface and thus restricted the access of NH_3 molecules to oxidation sites. It can be proposed that NO reduction and ammonia oxidation takes place on different sites, because otherwise it is difficult to understand why the decrease in NO conversion is not proportional to the decrease in the amount of formed N_2O molecules. This would agree with the model of Marbán et al. [17] who argued that there are two types of adsorbed ammonia species on the surface: weakly adsorbed via hydrogen bonding (which may lead to amide-type species), and NH_4^+ groups. The former takes part in oxidation of ammonia to N_2 and N_2O and these reactions are inhibited by water. However, it must be kept in mind that the model of Marbán et al. was developed for SCR at low temperature (125 °C) and may not be applicable fully in our case.

From the experimental results and literature findings discussed above a SCR mechanism on the N-modified MnO_x promoted catalysts can be proposed. The route in dry stream on activated carbons without MeO_x is supposed to take place through NO adsorption on oxygen containing surface species, NO oxidation to NO_2, sorption of NH_3 as NH_4^+ or NH_2. Then the reaction may proceed through the subsequent formation of NH_4NO_2 or NH_2NO_2 intermediates decomposing to N_2 and H_2O. The possibility of formation of such intermediates in SCR was postulated by literature for different catalysts [e.g., 25–27]. NO adsorption is rather weak and it is believed that the modification of activated carbons with N-compounds results in an increased adsorption of either NO [23] or NO_2 formed by oxidation of NO [11]. The latter is in good agreement with the basic character of N-species [11]. The matter is, however, not yet solved without doubt and more experimental data are needed. The promotion with active material (transition metal oxides/hydroxides) most probably enhances the NO oxidation and supplies additional acidic sites for ammonia adsorption. Taking into account the dependence of the formation of the by-product N_2O on the degree of reducibility of the studied catalysts, an assumption may be made that only the most reducible sites are the primary centers for ammonia oxidation, either through the reaction of sorbed-NH_2 or more strongly dehydrogenated N-species. In the presence of water in the feed, the promotional effect of the N surface species is partially cancelled and the pool of adsorbed NO species on the surface is decreased. The amount of adsorbed ammonia molecules is also diminished. However, since this reactant is in excess on the surface it is not the limiting factor in the decrease in NO conversion. Simultaneously, the number of the most reducible sites is influenced by water resulting in less of active lattice oxygen available for oxidation of adsorbed ammonia species, thus leading to smaller amounts of the by-product N_2O. Additionally, it must be mentioned that for our catalysts, the amount of active lattice oxygen is directly correlated to the distribution of MnO_x and thus the preparation procedure. As shown before, the formation of oxygen-surface groups on activated carbon supports led to a higher dispersion of MeO_x and simultaneously influenced the interaction with the support [10].

The influence of the repeated introduction and removal of H_2O, studied for C90/N800/N–Ar/Mn at 220 °C is shown in Fig. 3d and g. As may be seen in the figure, NO conversion stabilised at a somewhat higher value and N_2O formation at a slightly lower value after several cycles. This may be caused either by redistribution of manganese oxides/hydroxides and/or the changes in the oxidation state of active material taking place under the prolonged interaction with water. The latter was examined by XPS. Based on the splitting of the Mn 3s peak, it was concluded that Mn_2O_3 was present on the surface after the repeated reaction with H_2O.

4. Conclusions

Activated carbons modified by N-species, promoted with manganese, show an interesting behaviour towards the addition of water in SCR reaction. The NO conversion decreased, the extent of decrease depending on temperature, as observed for many other catalysts. The decrease of activity was, however, totally reversible. On the other hand, selectivity towards the formation of the undesired by-product N_2O was strongly diminished in the presence of water in educt stream, which makes the catalysts quite promising for SCR reaction at lower temperatures in the range of 180–260 °C. The relatively small decrease in NO conversion for n/N-activated carbon catalysts in comparison to Mn/Al_2O_3 systems may be explained by the presence of N surface species which are believed to increase NO adsorption, thus diminishing the negative influence on this process by H_2O. The nature of activated carbon supports is also responsible for the possible improvement in selectivity. As discussed before, the pre-treatment in HNO_3 of the support influenced the distribution of MnO_x species oxides and resulted in less labile oxygen on the surface and in consequence, lower tendency of the catalysts for ammonia oxidation. On the other hand, the same effect can be obtained by adding water to the feed, due to the fact that H_2O blocks labile oxygen from the reaction and less N_2O is formed. The repeated reaction cycles with and without H_2O led to a slight improvement in catalytic performance, possibly due to MnO_x redistribution and/or changes in the oxidation state of active material.

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