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Nitrogen-promoted active carbons as $DeNO_x$ catalysts 1. The influence of modification parameters on the structure and catalytic properties

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Abstract

The influence of modification by post-treatment of active carbon with ammonia or urea on catalytic reduction of NO with ammonia was studied. The amount of nitrogen introduced into the structure depended on the pre-treatment of active carbon. The formed N-species were mainly pyridinic or pyrrole/pyridone in nature. No amine, amide or cyano species were found. Both modification procedures (ammonia or urea) led to the increase in activity in SCR and selectivity to N_2. The extent of the improvement depended on the pre-oxidation of active carbon before N-introduction and was higher for urea than ammonia treatment.

Keywords: $DeNO_x$; Active carbon; N surface groups

1. Introduction

One of the most important tasks in energy production is the decrease of the amount of nitrogen oxides NO_x (NO and NO_2) in outgases which have deleterious influence on environment. Although an industrial solution for medium temperature region (ca. 250–400 °C) already exists (catalysts $V_2O_5/WO_3/TiO_2$) [1], appropriate catalysts for low temperature region (below 250 °C) are still searched. One of the possible solutions are carbonaceous materials [2] which per se are not very active but their $DeNO_x$ catalytic properties may be improved by the modification of surface functionalities [3–9] or promotion with transition metal oxides/hydroxides[2,3,10–13]. Lately the interest in the application of carbonaceous materials with N-containing surface groups for selective catalytic reduction (SCR) of NO with ammonia has been growing [3–8]. The studied catalysts were obtained either by carbonization and activation of N-containing precursors (C-containing materials promoted with different N-compounds or N-containing polymers) [4,7,8] or by post-treatment of active carbons or carbon fibers with NH_3 [3,5] or $(NH_4)_2SO_4$ [6].

The subject of this work was to compare catalytic properties in SCR of NO with ammonia for active carbons containing N groups introduced by post-treatment with ammonia or urea. The influence of the following parameters of preparation on SCR were considered: (a) high temperature NH_3 versus low temperature urea modification, (b) different pre-treatment of the starting active carbon (pre-oxidation or no modification), and (c) in case of urea treatment different atmosphere of curing after N-compound introduction (air or nitrogen).

2. Experimental

Active carbons containing nitrogen surface species were prepared using either urea (route 1) or NH_3 (route 2) as the source of N according to the scheme:

Route 1: active carbon (designation C) → optional oxidation (designation C90) → treatment with NH_3 at 800 °C (designation C/N800/N or C90/N800/N).

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Route 2: active carbon (C) → optional oxidation (C90) → promotion with aqueous solution of urea (C/U or C90/U) → curing either in air or nitrogen at 350 °C (C/U/350 Air; C90/U/350 Air; C/U/350 N_2; C90/U/350 N_2).

The starting material was active carbon N (commercial name) produced by Gryfskand Hajnówka. Oxidation conditions were: conc. HNO_3, $T = 90$ °C, 1 h, followed by washing with distilled water. The starting active carbon contained 0.5 wt.% N, as measured by elemental analysis. After oxidation with HNO_3, the amount of nitrogen increased to 1.0 wt.%. The formed groups may be ascribed to $-NO_2$, as proven before by XPS for similarly treated sample by Grzybek et al. [14]. These groups are, at least partly, removed at relatively low temperature (below 200 °C), as will be discussed later. In route 1, samples C or C90 were dried at 120 °C for 24 h and then impregnated with 5 wt.% of urea using an aqueous solution and incipient wetness technique. The curing procedure in air (flow 5 dcm^3/min) or nitrogen (flow ca. 20 dcm^3/min) for 2 h was followed. Ambient air containing water vapour was chosen instead of synthetic air in order to promote the reaction of in situ decomposition of urea to ammonia. After curing procedure, the samples were cooled to ambient temperature under the flow of nitrogen. The curing in air was prompted by the observations of Pietrzak et al. [15] who found that the reaction of a mixture of solid urea and active carbon in air at ca. 300 °C was most successful. In route 2, active carbon untreated (C) or oxidized (C90) was dried in air at 120 °C for 24 h and then introduced into the oven (PRS 100 W produced by Czylok) preheated to 800 °C, kept under ammonia flow (ca. 1 dcm^3/min) for 2 h and then cooled under NH_3 to room temperature.

The characterization of the prepared samples consisted of: (i) elemental analysis carried out using Elemental Analyser Vario-EL (Elementar-Analyse-Systeme GmbH, Hanau); (ii) specific surface area measurement by low temperature argon sorption at −196 °C using a standard volumetric equipment; (iii) thermal stability and surface oxides studies by thermogravimetric method and temperature programmed desorption of surface oxides TPD. A NETSCH STA409C apparatus equipped with a quadrupole mass spectrometer was used to determine the temperature programmed desorption of NH ($m/e = 15$), H_2O ($m/e = 16,17,18$), CO_2 ($m/e = 44$), CO, N_2 ($m/e = 28$), CN ($m/e = 26$) and NO ($m/e = 30$). The latter was treated as an indication of the existence of both NO and NO_2 species on the surface, as they give the same fragment in mass spectrometer. No separate measurement was carried out for NO_2. The experiments were carried out on a 20 mg sample with 20 mg of Al_2O_3 as a reference. At the beginning of each experiment, the sample was evacuated to 1 mbar in order to remove air and physically adsorbed gases. Then it was linearly heated at the rate of 10 °C/min up to 1000 °C in a stream of helium. The weight losses and the intensities of appropriate mass numbers were recorded as a function of temperature and (iv) surface composition determination by X-ray photoelectron spectroscopy XPS 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 C 1s, O 1s and N 1s and sensitivity factors of Scofield were used to determine 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; GHSV 8000 h^{-1}; before reaction catalysts were heated at 250 °C for 2 h in helium (100 ml/min).

3. Results and discussion

3.1. Characterization of the samples

From *elemental analysis* it may be concluded that: (i) the high temperature ammonia treatment was less efficient in the introduction of stable N-species than using urea, (ii) more groups were introduced onto the pre-oxidized carbonaceous materials in case of urea treatment—3.9 and 2.6 wt.% for C90/U/350 N_2 and C/U/350 N_2; 3.7 and 1.5 wt.% for C90/U/350 Air and C/U/350 Air, respectively. This indicates that surface groups prepared by HNO_3 oxidation are the main anchoring sites in this case.

Specific surface area S_{BET} was measured only for the selected samples in order to determine the general trends. No overall analysis was undertaken because Marbán et al. [8] proved that NO conversion in SCR (with ammonia) on N-containing active carbons was not directly correlated with S_{BET}. The obtained S_{BET} values were: 1008, 1083, 978, 1216, 38, 949 and 758 m^2/g for C, C90, C/N800/N, C90/N800/N, C90/U, C90/U/350 N_2 and C90/U/350 Air, respectively. As the measured values for C and C90 were quite similar (the error of BET method is usually estimated to be ±5%), it indicates that oxidation procedure did not greatly influence the porous structure. The impregnation with urea resulted in a considerable decrease of S_{BET}, testifying to the clogging of pores and/or their inlets by the introduced substance. Curing in air or nitrogen led to the decomposition and/or desorption of the part of the introduced promoter, as is proven by elemental analysis and TG–TPD experiments discussed in detail below, and resulted in specific surface area increasing again. The values are, however, lower than for the starting active carbon—considerably for C90/U/350 Air and slightly for C90/U/350 N_2. It may be speculated that curing in air leads to the reaction of carbon matter to form CO_2.Thus thin walls between smaller pores may be oxidized and subsequently collapse leading to the decrease of S_{BET}. In case of curing in N_2 the effect should be small, as the temperature of 350 °C is too low for efficient carbonization. This is in good agreement with S_{BET} for this sample (949 m^2/g) which is within experimental error the same as for C and only slightly lower than C90. The catalysts obtained by high temperature treatment with ammonia showed the values of S_{BET} either the same as the starting active carbon (C/N800/N) or higher (C90/N800/N). Thus it may be assumed that ammonia can play an additional role of activating agent, as observed before by Mangun et al. [16].

TG–TPD results are summarised in Fig. 1. Fig. 1a–c compares mass losses and TPD $m/e = 44$ (CO_2) and 15 (NH) for

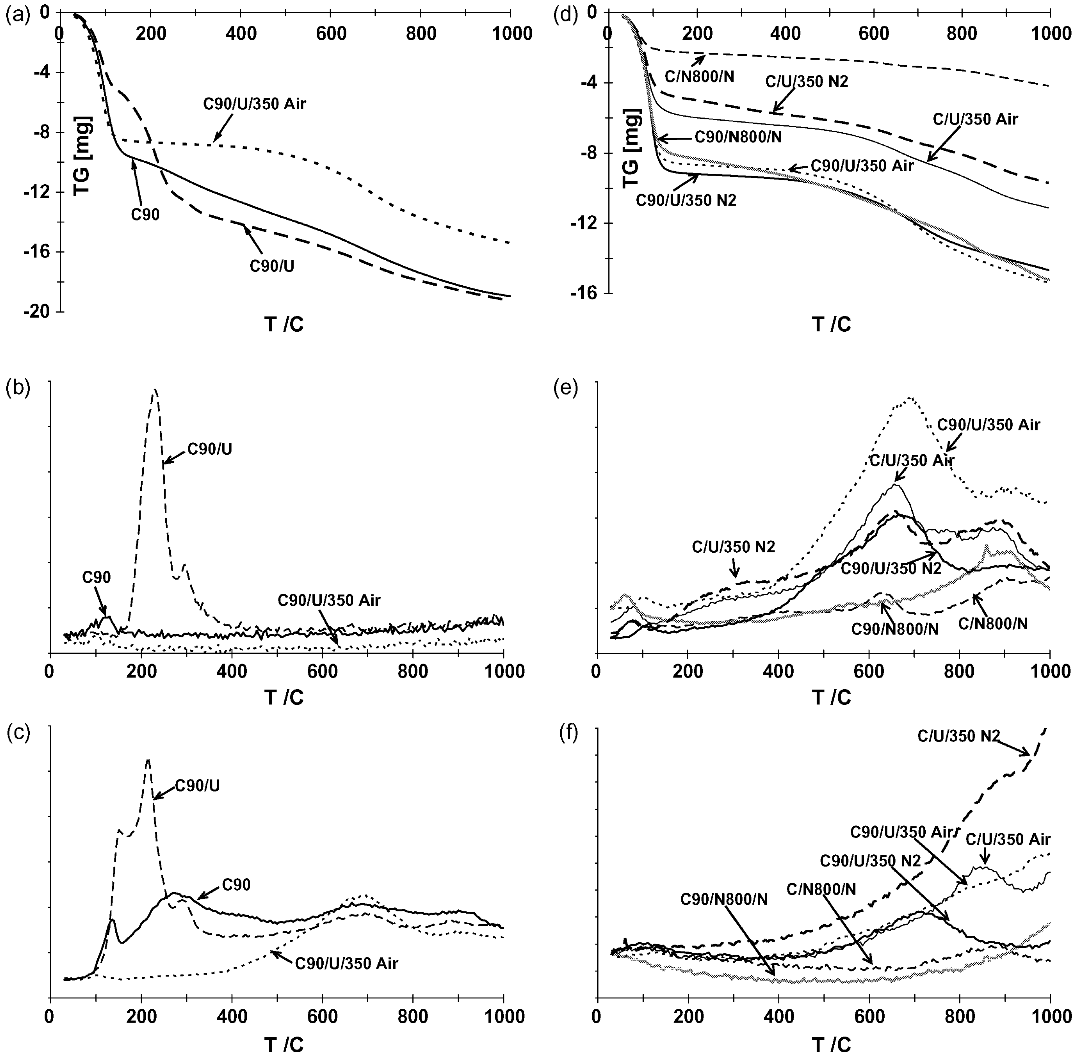

Fig. 1. TG–TPD experiments for the studied catalysts; C90, C90/U and C90/U/350 Air: (a) mass losses, (b) desorption profiles for $m/e = 15$ and (c) desorption profiles for $m/e = 44$; C/N800/N, C90/N800/N, C/U/350 Air, C90/U/350 Air, C/U/300 N_2 and C90/U/350 N_2: (d) mass losses, (e) desorption profiles for $m/e = 44$ and (f) desorption profiles for $m/e = 28$.

C90, C90/U and C90/U/350 Air samples. All three figures exhibit considerable differences. There are two regions in mass loss for C90 (to 120 °C, and 120–1000 °C) and three distinct regions for C90/U and C90/U/350 Air (to ca. 120 °C; 120 °C to ca. 300 °C for C90/U or 120 °C to ca. 550 °C for C90/U/350 Air; to 1000 °C). The first region is connected with desorption of water adsorbed on the surface. The comparison of desorption profiles of $m/e = 15$ (NH, a fragment of NH_3) and 44 (CO_2), indicates that part of urea is relatively weakly chemisorbed on the surface and is decomposed in the temperature region of ca. 200 to ca. 350 °C to ammonia and carbon dioxide. The rest urea forms N-species strongly bonded to the surface, which is proven by the lack of $m/e = 15$ peak for C90/U/350 Air. An additional argument for this reasoning may be derived from the analysis of $m/e = 30$ profile. As mentioned below C90 has a small peak with a maximum at ca. 130 °C which was ascribed before to $-NO_2$ group formed during oxidation with HNO_3 [14]. C90/U/350 Air has a peak in the same position (ca. five times smaller in intensity), indicating that no additional groups containing nitrogen and oxygen introduced onto the surface by curing decompose in the discussed temperature region. The desorption profiles of $m/e = 44$ (CO_2) differ for C90 and C90/U between 30 and 500 °C and are similar above 500 °C.

The differences in mass losses together with the changes in $m/e = 44$ profiles indicate that the number of acidic groups is somewhat smaller for C90/U than C90 and much smaller for C90/U/350 Air than both C90 and C90/U. CO_2 may originate not only from the decomposition of urea but also from the decomposition of surface acidic functionalities (e.g. carboxylic groups). The comparison of CO_2 profile for C90/U (Fig. 1c) with that for $m/e = 15$ (Fig. 1b) indicates that the main maximum at ca. 220 °C and a secondary one at ca. 300 °C have their origin in decomposing urea. On the other hand, another secondary peak for C90/U at ca. 150 °C in $m/e = 44$ profile coincides reasonably well with desorption maximum at ca. 130 °C for C90. This maximum cannot come from urea decomposition because it does not exist in $m/e = 15$ profile for C90/U. This means that $m/e = 44$ profile up to ca. 300 °C for C90/U is a superposition of the two processes—the decomposition of acidic surface species overlapps with urea decomposition. From ca. 250 to 400 °C the C90 profile has, however, a somewhat higher intensity than C90/U, indicating that there are less acidic surface groups for the latter sample. Simultaneously, no CO_2 was registered up to 400 °C for C90/U/350 Air. Thus it may assumed that the mechanism of N-functionalities formation in this case is: urea chemisorbs on some acidic groups on C90, partly desorbing below 400 °C. A part of nitrogen becomes strongly bonded to the surface. A part of urea decomposing during the curing process to CO_2 promotes partial reoxidation of the surface.

Fig. 1d–f compares differently prepared N-containing catalysts. Again mass losses show three temperature regions: to ca. 120 °C, ca. 120 to ca. 400–500 °C and ca. 400–500 to 1000 °C. The low temperature region is connected with H_2O desorption. In the medium temperature region samples show low or very low mass losses, which proves their stability between ca. 120 and 400–500 °C, i.e. also at the temperature range of interest for SCR. High temperature region is connected with desorption of CO_2, as well as species of $m/e = 28$ (either CO or N_2).

The process of curing of urea treated samples in air or nitrogen at moderate temperatures leads to the formation of fairly stable surface groups which start decomposing at ca. 400–500 °C. Some of these are acidic species, as proven by desorption profile of $m/e = 44$. According to Figueiredo et al. [17] CO_2 arises from either carboxyl or lactone groups, or carboxyl anhydrides. Additionally, there is desorption of mass number $m/e = 28$ which may arise from either CO or N_2 (cp. Fig. 1f). The profile is in most cases featuresless and in contrast to non-modified active carbon C or oxidized active carbon C90 [18] there are no well defined CO peaks, except for C90/U/350 N_2 and C/U/350 Air. It is in agreement with Jansen and van Bekkum [19] who observed that oxidation of active carbon with HNO_3 followed by treatment with ammonia below 650 °C resulted in samples with lower oxygen content—especially carbonyl groups were removed.

Preparation route 1 (urea, curing in air or nitrogen) in comparison to route 2 (NH_3, 800 °C) resulted in significantly higher amount of groups decomposing in high temperature region. Moreover, the profiles of $m/e = 44$ and 28 differ for catalysts based on C and C90. It may be therefore concluded that the surface pre-treatment plays an important role in the type and stability of the groups formed during reaction with urea or ammonia.

Neither desorption of $m/e = 15$ (NH) nor 26 (CN) was observed for any sample. Thus the number of decomposing amine, amide or cyano species must be very small, if any. This is in reasonable agreement with literature where cyano groups are concerned, as they were found to decompose at fairly high temperatures. And so Przepiórski et al. [20] who studied active carbon heated in Ar to temperatures between 200 and 1000 °C and then contacted with NH_3 for 2 h, followed by cooling in NH_3 related that TG–TPD experiments showed groups of C=N type still stable 720 °C. Boudou et al. [21] observed HCN in the decomposition products at ca. 927 °C for active carbon treated with mixtures of NH_3 and H_2O, or ammoxidized. On the other hand, the information on amide or imide groups seem rather contradictory. Przepiórski et al. [20] registered groups decomposing to NH_3 at 720 °C while Jansen and van Bekkum [19] observed HCN desorption arising from amide species at ca. 650 °C and lactam and imide species at 950 °C. Taking into account that all these samples had different preparation procedures it must be concluded that NH_3 (NH_2, NH) desorbing groups are strongly influenced by the pre-treatment and post-treatment of the samples.

No $m/e = 30$ desorption was registered for C90/N800/N or C/N800/N. For C90, C90/U and C90/U/350 Air, C90/U/350 N_2 and C/U/350 Air the peak with a maximum around 100–140 °C was registered. The intensity of the peak is ca. 5–8 times higher for C90 than the other mentioned samples. Thus it may be safely assumed that the only groups decomposing to NO (NO_2) are those introduced onto the support during oxidation. Only C/U/350 N_2 has somewhat different $m/e = 30$ desorption profile (maximum between 200 and 380 °C) although the intensity is still small (4.5 smaller than for C90). No reasonable explanation can be offered in this case and more experimental data will be necessary.

X-ray photoelectron spectroscopy studies show two N 1s peaks: around 399.5 eV and 406–407 eV. The latter is connected with NO_2 group. Its presence is easily understood for C90 supports which were oxidized by concentrated nitric acid but in C series it must arise from some contamination of original active carbon which, as shown by elemental analysis, contained ca. 0.5 wt.% N. The peak at lower BE is at 399.5 ± 0.3 eV, i.e. between the position of pyridinic and pyrrolic/pyridone N [7,15,22–24], suggesting a similar amount of both forms. As the intensity of N 1s was low in our case we decided not to fit individual peaks. Pietrzak et al. [15] reported similar amounts (ca. 30% of total N) for both species present on the surface of active carbons treated with urea in the post-treatment stage in a procedure similar to ours. The studies of active carbons treated with ammonia at high temperatures interpreted the results as indicating the presence of pyrrole/pyridone [26] or nitriles which are the product of the decomposition of amides and carboxylates at temperatures over 300 °C (FTIR) [27]. However, the latter group should rather be excluded because no desorption of CN was registered in TPD in our study. On the other hand, although XPS literature data are not very helpful where amine, imine, amide or imides groups are concerned (some authours fix such groups around 398 eV [22] and some at 399.5–400 eV [23,24]), there are some arguments against the presence of higher amounts of such species for urea treated samples. E.g. Burg et al. [25] found by FTIR and XPS that urea modification led to amides, amines and lactams but they disappeared after thermal treatment. Moreover, Meldrum and Rochester [27] confirmed by FTIR the absence of amine structures in NH_3-treated carbonaceous materials. Additionally, quantum chemical calculations of Strelko et al. [29] suggest that modification with NH_3 (or any functional group containing NH_2, and thus urea) should lead to pyrrolic nitrogen during pyrolysis. Thus the peaks observed in our spectra must be interpreted as pyridinic/pyrrolic/pyridone groups.

The consideration of surface composition (atomic ratios of N/C and O/C) indicates that more nitrogen is fixed in both treatments (NH_3—high temperature or urea treatment) if surface is pre-oxidized (cp. N/C 0.012 and 0.015 for C/N800/N and C90/N800/N, respectively; 0.017 and 0.036 for C/U/350 Air and C90/U/350 Air, respectively). There is a large difference in oxygen content between the samples. Those based on C90 have higher O/C ratios than those based on C. From the comparison of C/N800/N and C90/N800/N it may be assumed that some oxygen species formed during oxidative pre-treatment survive the reaction with ammonia at high temperature. This is in good agreement with TPD experiments (*m*/*e* = 28 and 44 profiles) discussed above. In case of urea treated samples, the formed groups must have their origin in the oxidative pre-treatment, as well as in the curing procedure (cp. O/C 0.22 and 1.21 for C/U/350 Air and C90/U/350 Air).

3.2. SCR catalytic properties

Fig. 2a–d compares NO conversion and N_2O formation for the studied samples.

Both treatments (with NH_3 and urea) lead to the increase in NO conversion and selectivity to N_2 but the overall effect is strongly dependent on the pre-oxidation of the support, as well as on the choice of N-precursor.

For ex-ammonia catalysts it was observed that: (i) the gain in NO conversion for pre-oxidized sample (C90/N800/N) was rather small at lower temperatures (up to ca. 180 °C) but increased considerably at higher temperatures (over 180 °C). On the other hand, for the sample based on C (without oxidative pre-treatment), NO conversion increased after the modification with ammonia by ca. 5–10% at lower temperatures but almost no effect was registered at 260 and 300 °C. (ii) N_2O formation was very small at 140 and 180 °C, similarly as for unpromoted active carbon C. For higher experimental temperatures (260 and 300 °C), N_2O production formed a sequence: $C \approx C90/N800/N > C/N800/N$. Taking into account much higher conversion for C90/N800/N than for C, this indicates a considerable increase in selectivity to N_2 for C90/N800/N. (iii) The temperature dependence of NO conversion shows a minimum for samples treated with ammonia at high temperature, as well as for the starting carbon C. It was observed before by several authors [3–5,7] and explained as arising from two different mechanisms of NO removal. At lower temperatures NO is removed by sorption while at the higher temperatures NO reduction prevails.

For ex-urea catalysts it was observed that: (i) NO conversion for active carbons modified with urea was high even at low reaction temperature (140 °C). The requirement was, however, that active carbons be pre-oxidized before N-treatment—if C90 was used, the increase in NO conversion was considerable, for C-based samples the effect was rather small, if any. (ii) The amount of N_2O formed for urea treated carbons was low. In all cases, but especially for ex-C90 samples, selectivity to N_2 was considerably improved. (iii) In contrast to active carbons modified with NH_3, no minimum in NO conversion was registered as a function of temperature for urea treated samples. It must be stated, however, that not all N-modified carbons, described in literature, exhibited such minimum (cp. some of carbons promoted with glucoasamine described by Singoredjo et al. [4]). Possibly the position of the minimum was outside our experimental range.

The improvement of NO reduction activity has obviously its origin in N-species introduced onto the surface. Although no experiment was carried out on C90 and all C90-based samples show higher conversions than C-based ones, the major role of oxygen species in reaction mechanism can be excluded. The

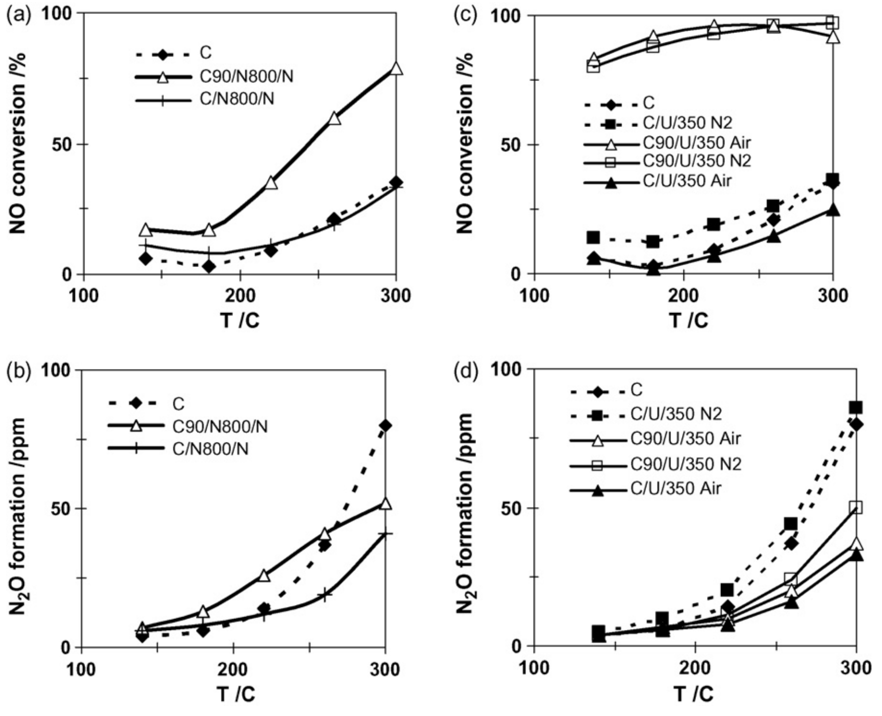

Fig. 2. NO conversion and the formation of N_2O for the catalysts under study.

first argument against the major role of O-functionalities is taken from literature. Szymański et al. [3] observed that the gain in NO conversion was lower for oxidized active carbons than for active carbon first oxidized and then annealed with ammonia at high temperature. Moreover, the dependence of conversion on temperature was different for both samples. Active carbon which was only oxidized showed a maximum in NO conversion at 220 °C. Additionally it was shown that NO conversion decreased after SCR was carried out at higher temperatures. The experiment was carried out with a sequential change of temperature: first NO conversion was measured at 140 °C, then temperature was increased to 180, 220, 260 and 300 °C (exp. a), followed by the measurement at 260 and 220 °C without the removal of the sample (exp. b). In each case, NO conversion was measured for 90 min. It was observed that NO conversions for 220 and 260 in exp. b were smaller than in exp. a. The reason was the decomposition of some of acidic groups (e.g. carboxyl). It must be mentioned that the experiments described in this article were carried out under identical reaction conditions as in this work (mass of catalysts, flow, the composition of reaction mixture) for active carbon of a different producer (CarboTech. Essen, Germany) but oxidized and treated with ammonia under similar conditions: active carbon was oxidized with HNO_3 at 80 °C for 3 h and then treated with ammonia at 900 °C for 2 h. The second argument against the major role of oxygen functionalities is based on an experiment for C90/U/350 Air carried out in a similar way as that described in the above mentioned publication. NO conversions for 220 and 260 °C were the same for exps. a and b and thus the removal of oxygen surface functionalities (at temperatures up to 300 °C) did not influence the catalytic results. Both arguments indicate, that oxygen-containing surface species play a relatively small role in the increase of conversion observed for the studied catalysts.

There are several indications that the increase in NO conversion for N-modified samples is directly correlated to the ability of NO adsorption. This is in good agreement with literature [7,8,30,31]. Matzner and Boehm [30] observed that at low temperature (30 °C) the amount of adsorbed NO increased with the increase in N content in active carbon. Similar conclusions were made by Yang and Kaneko [31]. Huang and Teng [7] found a correlation between temperature programmed desorption of NO and NO conversion. Marbán et al. [8] studied TPD NO in the presence and absence of oxygen and concluded that N-species were adsorption sites for NO_2 which was formed by oxidation of NO. This agrees well with basic character of the discussed N-species [8,16,19,28,32].

The modification of C90 with urea was much more advantageous than with ammonia (at 800 °C). The effect may be, among others, connected with the higher amount of N introduced in the former case, although Huang and Teng [7] observed no direct correlation with the N content from elemental analysis. The possible explanation is offered by Strelko et al. [29] who calculated by quantum mechanic method the influence of N-doping on the decrease of band gap. This change influences catalytic properties of carbon by modifying electron mobility and electron work function. It was found that the combination of pyrrolic and pyridinic surface species leads to the minimum band gap for N content of ca. 2.5 at.%, and such species were observed in our samples.

The second important factor differing both types of modification is the amount of surface oxygen, which originates from pre-oxidation of carbon and, in case of urea treatment, additionally from the process of curing. As these groups to some extent decompose to CO_2 they must be acidic in nature and are obvious sorption sites for NH_3 molecule during the SCR reaction.

4. Conclusions

The influence of modification of active carbon with N-compounds on SCR activity and selectivity was compared. As N-precursors gaseous ammonia at high temperature and an aqueous solution of urea, followed by curing in air or nitrogen at 350 °C were chosen.

The amount of stable nitrogen introduced into active carbons was ca. 1–1.5 wt.% for NH_3 modified samples, and ca. 2–4.5 wt.% for urea treated samples.

Both modification procedures somewhat influenced specific surface area in comparison to the starting active carbon.

The formed N-species are mainly pyridinic and pyrrole/pyridone in nature, as shown by XPS. No amine, amide or cyano species were found, either by XPS or TPD. TPD (surface groups) showed additionally the presence of oxygen-containing acidic surface species whose type/number depended on the oxidative pre-treatment of active carbon, as well as on the curing process.

The N-promoted active carbons showed high stability in the temperature range of importance for SCR, as witnessed by low mass losses in TG.

From the studies of SCR catalytic properties it may be concluded that both used modification procedures led to the increase in activity and selectivity to N_2. The extent of the improvement was dependent on the history of the sample before the introduction of N-compounds. NO conversion increased more for catalysts prepared from pre-oxidized samples.

The procedure of the modification by urea solution, followed by curing in air or nitrogen resulted in much better activity and selectivity to N_2 in comparison to high temperature ammonia treatment. The possible reason may be the higher amounts of N surface functionalities introduced by the former procedure than the latter.

On the whole, it must be remarked that the urea modification procedure is not only much more efficient where SCR catalytic properties of active carbons are concerned, but also much easier and less costly than high temperature NH_3 modification.

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