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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.

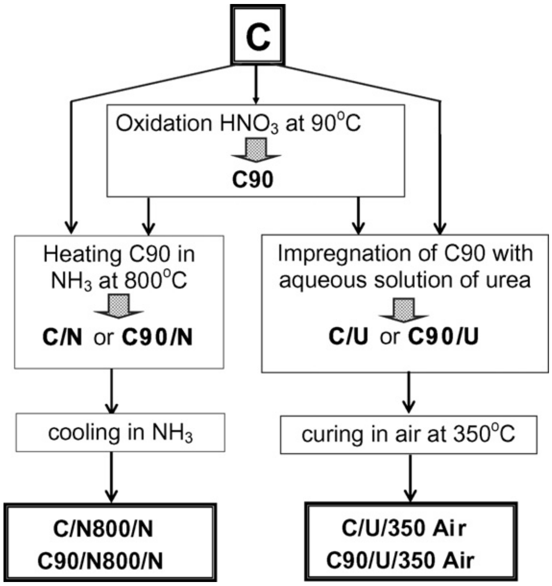

Fig. 1. The scheme of modification of active carbons with N-compounds.

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