

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 N₂. The extent of the improvement depended on the pre-oxidation of active carbon before N-introduction and was higher for urea than ammonia treatment.

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1. Introduction

One of the most important tasks in energy production is the decrease of the amount of nitrogen oxides NO_x (NO and NO₂) in outgases which have deleterious influence on environment. Although an industrial solution for medium temperature region (ca. 250–400 °C) already exists (catalysts V₂O₅/WO₃/TiO₂) [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 NH₃ [3,5] or (NH₄)₂SO₄ [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 NH₃ 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 NH₃ (route 2) as the source of N according to the scheme:

Route 1: active carbon (designation C) → optional oxidation (designation C90) → treatment with NH₃ 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 N₂; C90/U/350 N₂).

The starting material was active carbon N (commercial name) produced by Gryfskand Hajnówka. Oxidation conditions were: conc. HNO₃, $T = 90\text{ }^{\circ}\text{C}$, 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 HNO₃, the amount of nitrogen increased to 1.0 wt.%. The formed groups may be ascribed to –NO₂, 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 dcm³/min) or nitrogen (flow ca. 20 dcm³/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 dcm³/min) for 2 h and then cooled under NH₃ 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 ($m/e = 15$), H₂O ($m/e = 16, 17, 18$), CO₂ ($m/e = 44$), CO, N₂ ($m/e = 28$), CN ($m/e = 26$) and NO ($m/e = 30$). The latter was treated as an indication of the existence of both NO and NO₂ species on the surface, as they give the same fragment in mass spectrometer. No separate measurement was carried out for NO₂. The experiments were carried out on a 20 mg sample with 20 mg of Al₂O₃ 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 NH₃, 3% O₂, 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 N₂ and C/U/350 N₂; 3.7 and 1.5 wt.% for C90/U/350 Air and C/U/350 Air, respectively. This indicates that surface groups prepared by HNO₃ 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 m²/g for C, C90, C/N800/N, C90/N800/N, C90/U, C90/U/350 N₂ 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 N₂. It may be speculated that curing in air leads to the reaction of carbon matter to form CO₂. Thus thin walls between smaller pores may be oxidized and subsequently collapse leading to the decrease of S_{BET} . In case of curing in N₂ 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 m²/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 $m/e = 44$ (CO₂) and 15 (NH) for

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