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Reduction of N_2O over carbon fibers promoted with transition metal oxides/hydroxides

Teresa Grzybek [a,*], Jerzy Klinik [a], Barbara Dutka [a], Helmut Papp [b], Vladimir Suprun [b]

[a] *Faculty of Fuels and Energy, University of Science and Technology, 30-059 Kraków, Poland*
[b] *Faculty of Chemistry and Mineralogy, University of Leipzig, 04103 Leipzig, Germany*

Abstract

Reductions of N_2O on oxides/hydroxides of nickel, cobalt or manganese supported on carbon fibers were studied. Supports and catalysts were characterized by low temperature argon sorption, temperature-programmed desorption (TPD) of surface oxides and temperature-programmed desorption of ammonia (TPAD), X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR). Conversion of N_2O depended on the initial pretreatment of the support, the origin of the effect lying in a different distribution of active material. The differences in distribution influenced also the mobility of surface oxygen. The presence of more labile oxygen resulted in its easier transfer and faster formation of CO_2.

Keywords: N_2O reduction; Carbon fibers; XPS; TPR

1. Introduction

Acid treatment of carbonaceous materials is known to change its surface chemistry. The presence of acidic groups on the surface of carbonaceous materials in turn influences the dispersion of active phase and catalytic activity, as well as selectivity in NO reduction with ammonia or carbons, and NH_3 oxidation to N_2 (and N_2O). NO reduction with carbon on active carbon-supported catalysts [1–8] and NO reduction with NH_3 on both active carbon- and carbon fiber-supported catalysts [9–17] have been studied extensively in recent years. Several interesting facts were observed:

i. There was an influence of the ash content and composition on catalytic reduction of NO with NH_3 [9]. Similar effects were observed for NO reduction with carbon [1].
ii. Acidic pretreatment of carbonaceous materials influenced their activity (cf. SCR activity for carbonaceous materials promoted with oxides/hydroxides of Mn [10–12]). The overall result of acidic pretreatment depended, however, on its conditions. Mainly, the type [11,18,19] and the temperature of acid [10,20] and the time of treatment [11] influenced the catalytic activity through the change in the type and the number of oxygen-containing surface groups. The formation of acidic species such as carboxylic and lactonic groups by the use of HNO_3 [18] or to a smaller extent by H_2SO_4 [11], increased the activity while the formation of more stable surface groups such as carbonyls or phenols by the use of HCl deactivated the catalysts [18].
iii. Selectivity to N_2 in the above-mentioned reactions and thus the presence or absence of N_2O in the products seems to be connected with the crystallite size of MeO_x, smaller crystallites of active material producing less N_2O. This was found for active carbon-supported MnO_x [10] or carbon fibers promoted with NiO [21]. The formation of N_2O is not quite understood. Curtin et al. [22] showed for copper oxide supported on Al_2O_3 that N_2 and N_2O are formed through dissociative chemisorption of NO thus leading to a pool of N species on the surface. They may be converted into N_2 or through the reaction of N with NO into N_2O. A decrease in the availability of surface lattice oxygen species in the

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[*] Corresponding author. Tel.: +48 12 6172119; fax: +48 12 6172066.
E-mail address: grzybek@uci.agh.edu.pl (T. Grzybek).

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reaction system, which may be reduced e.g. by the addition of SO_2 to the feed led to a lower formation of N_2O. Similar effects were found for active carbon-based catalysts or montmorillonites covered with carbon promoted with MnO_x [23].

On the other hand, it is believed that the mechanism of N_2O and NO reduction by carbon are essentially the same and can be summarized as [19]:

- dissociative adsorption of NO connected with N_2 formation either on a active catalyst site S and/or a free carbon site C_f

  $$2S + 2NO \rightarrow 2S{-}O + N_2$$
  $$2C_f + 2NO \rightarrow 2C{-}O + N_2$$

- oxygen transfer between the oxidized catalyst site S–O and carbon site C–O and surface carbon groups

  $$C{-}O \rightarrow C(O)$$
  $$S{-}O \rightarrow C(O)$$

- C_f site regeneration and catalytic site preparation

  $$2C(O) \rightarrow CO_2 + C_f^*$$
  $$2C_f^* + 2NO \rightarrow 2C{-}O + N_2 \rightarrow (CO_2 + C_f^*)$$

This model, however, does not take into account the possibility of higher or lower N_2O formation but only its decomposition. On the whole, it is not yet clear whether N_2O is formed in SCR as a primary product in a reaction parallel to the formation of N_2 and is then decomposed to N_2 on some catalysts in the mechanism suggested by the above-mentioned model or not formed due to lower oxygen availability as suggested by Curtin et al. [22]. Although extensive studies have been carried out on the heterogeneous catalytic decomposition of N_2O using oxide-supported catalysts, much less information is available on N_2O conversion over carbon-supported catalysts. Dandekar and Vannice [24] compared copper supported on active carbon, Al_2O_3, SiO_2 and ZSM-5 for N_2O decomposition. The efficient oxygen scavanging capability of carbon led to higher initial activities on Cu/C catalysts compared to Cu/ZSM-5 but the reaction was accompanied by a high gasification of carbon. The activity of Cu/C depended on the initial pretreatment of active carbon-initial oxidation with HNO_3 leading to an increase in activity in comparison to a heat pretreatment in H_2 at 1223 K, which resulted in no change in comparison to the untreated support. The pretreatment influenced additionally the stability of the catalysts. Labile surface oxygen and its mobility were found to play an important role in controlling the steady state behaviour of Cu. The mechanism was believed to involve dissociative adsorption of N_2O and the transfer of oxygen from active material to the carbon surface to form CO_2 or CO.

N_2O reduction was also studied by Zhu et al. on active carbon promoted with Ni [18] or Cu [19]. The role of oxidative pretreatment of the support was considered as (i) influencing the distribution of active material and, in consequence, providing better contact of catalytic material with carbon, making oxygen transfer easier and (ii) producing acidic groups which are useful for the release of carbon oxygen complexes.

There are, however, still some open questions e.g. how the process of N_2O decomposition on carbonaceous materials is influenced by (a) the amount of acidic groups introduced e.g. by HNO_3 at different temperatures or (b) the choice of metal oxide as active material.

In order to answer these questions, carbon fibers promoted with Ni, Co or Mn oxides/hydroxides were studied as catalysts for N_2O reduction. A detailed characterization of the supports and catalysts was carried out, and the article focuses additionally on how catalyst dispersion is affected by surface chemistry. In order to exclude the uncertain influence connected with the role of ash for the reduction of NO with NH_3 or with carbon, ashless carbonaceous materials, i.e. carbon fibers were used.

2. Experimental

2.1. Catalysts

A commercial carbon fiber Kynol (further designated as K) activated by the producer with water vapour was used as a support in the untreated or pretreated form. The pretreatment of carbon fiber K consisted of the oxidation with 40% aqueous solution of HNO_3 for 1 h either at 343 K or at boiling temperature. In the latter case, two versions of oxidation procedure were used: either in a closed or open system i.e. with or without the recirculation of the formed nitrogen oxides, respectively called methods I and II. The pretreatment parameters and designation of the supports are given in Table 1.

Active material oxides or hydroxides of Ni, Co or Mn (5 wt.% recalculated to the appropriate metal content) were introduced by wet impregnation onto oxidized (K-ox1 or K-ox3) or untreated (K) supports. K-ox2 was omitted, because as will be shown later in the text, the amount of acidic sites is the same for K-ox2 and K-ox3. The active material precursors were nitrates of Ni, Co or Mn.

The following experiments were carried out:

i. Determination of the texture, or in some cases, only the specific surface area by low temperature argon sorption at a relative pressure range p/p_0 of 0–1 or 0.05–0.35,

Table 1
The pretreatment parameters and designation of the studied carbon fibers

Sample	Pretreatment	Temperature	Method[a]
K	None	–	–
K-ox1	40% HNO_3	343 K	I
K-ox2	40% HNO_3	Boiling temperature	I
K-ox3	40% HNO_3	Boiling temperature	II

[a] Method I: in a closed system with a recirculation of the formed nitrogen oxides and method II: in an open system with the removal of the formed nitrogen oxides.