Short communication

TPR study and catalytic performance of noble metals modified Al_2O_3, TiO_2 and ZrO_2 for low-temperature NH_3-SCO

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ABSTRACT

A series of γ-Al_2O_3, TiO_2 (anatase) and mt-ZrO_2 were impregnated with 1.0 wt.% of Cu or Fe and/or with 0.05 wt.% of Pt, Pd or Rh. The obtained samples were tested as catalysts of the selective catalytic oxidation of ammonia. An interesting class of zirconia and titania supported catalysts is based on copper. Modification of these catalysts with noble metals significantly decreased temperature of the ammonia oxidation. Platinum doped catalysts exhibited the highest activity, while rhodium based materials were the most selective catalysts in the studied temperature range. Catalytic performances of tested materials were consistent with their redox properties.

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1. Introduction

Low temperature selective catalytic oxidation of ammonia into nitrogen and water vapour (NH_3-SCO) is potentially considered as an efficient, stable and simple technology for ammonia removal from oxygen-containing waste gases [e.g. [1,2]] (1):

$$NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O. \tag{1}$$

NO and N_2O are the main by-products of this process. Therefore, the effective NH_3-SCO catalysts should operate at a relatively low temperature range and additionally should result in the production of N_2.

Previous studies described physicochemical characterization of copper- or iron-containing commercially available oxides, such as γ-Al_2O_3, TiO_2 (anatase) and mt-ZrO_2 as well as their catalytic performance in both NH_3-SCO and NH_3-SCR processes [3]. In the following studies the deposition of selected noble metals, such as Pt, Pd, or Rh, on the surface of transition metal oxide modified catalysts will be discussed. The idea to prepare and test such catalysts arose from hypothesis about the mechanism of NH_3-SCO process. It was suggested that the selective oxidation of ammonia over copper- or iron-modified oxide supports proceeds according to the internal selective catalytic reduction mechanism (i-SCR). According to i-SCR mechanism noble
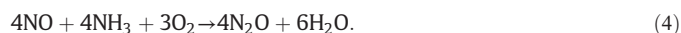
metals (e.g. Pt, Pd and/or Rh) are expected to catalyze ammonia oxidation to NO (Eq. (2)) [4]:

$$\text{step 1}: 4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \tag{2}$$

while transition metals (Cu and/or Fe) are expected to catalyze the NH_3-SCR of NO to nitrogen (Eq. (3)):

$$\text{step 2}: 4NO + 4NH3 + O2 \rightarrow 4N2 + 6H2O. \tag{3}$$
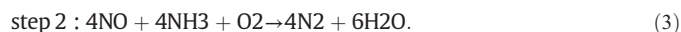
A side reaction can be responsible for N_2O production by reaction of NO with ammonia (Eq. (4)):

$$4NO + 4NH_3 + 3O_2 \rightarrow 4N_2O + 6H_2O. \tag{4}$$

Such catalyst design deliberately based on the principle of bi-functionality will be inevitable to develop high-performance catalysts which can cope with such difficult problems as ammonia oxidation. The types of active components for both functions as well as their ratio are the key parameters determining activity and selectivity of the catalyst. Bi-functional catalyst based on transition and noble metals have been already proposed [e.g. [5–7]]. In particular, the best catalytic properties among Pt, Pd, and Rh modified Mg–(Cu,Fe)–Al hydrotalcite originated mixed metal oxides, were obtained for the platinum doped Cu–Mg–Al–O_x [5].

The above-mentioned report was an inspiration to the presented studies, which are focused on determination of the role of redox properties of modified oxide supports (γ-Al_2O_3, TiO_2 (anatase),

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mt-ZrO$_2$) in the selective oxidation of ammonia. Catalytic performance of the Pt–Cu oxide based catalysts was compared with the reference supported catalysts (Pt deposited on Cu–Mg–Al–O$_x$).

2. Experimental

2.1. Catalyst preparation

A series of Cu- or Fe-doped catalysts with 1.0 wt.% of transition metal of different commercially available oxides such as γ-Al$_2$O$_3$ (Merck), TiO$_2$ (anatase) (Sigma-Aldrich) and mt-ZrO$_2$ (Sigma-Aldrich) were prepared by the incipient wetness impregnation method. Details of both preparation and characterization of copper- or iron-modified samples can be found in previous studies [3]. After calcination at 600 °C for 12 h, materials were further modified with noble metals. The Pt-, Pd-, or Rh-doped catalysts were prepared by incipient wetness impregnation method using Pd(C$_5$H$_7$O$_2$)$_2$, Pt(C$_5$H$_7$O$_2$)$_2$, or Rh(C$_5$H$_7$O$_2$)$_2$ (Sigma-Aldrich) as precursors. Acetylacetonates were dissolved in methanol (Lach-ner, 99.5%) to avoid any modification and/or acidification of the support. The solutions were ultrasonic treated for 30 min. After impregnation, materials with 0.05 wt.% of noble metals were dried in the air, crushed and calcined at 500 °C for 3 h. Catalyst obtained grade grain was in the range of 1.60–3.15 mm.

Platinum modified Cu–Mg–Al–O$_x$ derived from hydrotalcite-like compound was used as reference sample. Details of its preparation, characterization as well as catalytic performance were given in previous studies [5].

2.2. Catalyst characterization

The specific surface areas of calcined catalysts were determined by the BET method. The measurements were performed using a Quantasorb Junior sorptometer (Ankersmit). Prior to the nitrogen adsorption at −196 °C the samples were outgassed in the nitrogen atmosphere at 250 °C for 2 h.

The X-ray diffraction (XRD) patterns of catalytic materials were recorded with a D2 Phaser diffractometer (Brucker) using Cu K$_\alpha$ radiation (λ = 1.54060 Å, 30 kV, 10 mA).

The H$_2$-TPR of the samples was carried out between room temperature and 1100 °C, using a linear heating rate of 5 °C/min. The measurements were performed in a fixed-bed flow microreactor. The TPR runs were carried out in a flown of 5.0 vol.% of H$_2$ diluted in argon. The flow rate was 6 cm^3/min. Evolving water was removed from effluent gas by means of a cold trap. The evolution of hydrogen was detected by microvolume TCD (Valco).

2.3. Catalytic tests

The catalytic experiments were performed in a fixed-bed flow microreactor (i.d., 7 mm; l., 240 mm). The analysis of the reaction products was performed using a QMS detector (PREVAC). Prior to the activity tests the sample of catalyst (100 mg) was outgassed at 500 °C for 1 h in a flow of pure helium (20 cm^3/min). Catalytic tests were performed for the mixture containing: [NH$_3$] = 0.5 vol.%, [O$_2$] = 2.5 vol.%, and [He] = 97.0 vol.%. The total flow rate of the reaction mixture was 40 cm^3/min. The studies were performed in the temperature range of 100–500 °C with the linear heating rate of 10 °C/min. The intensities of the mass lines corresponding to all reactants and possible products were measured at a given temperature for at least 30 min after the reaction had reached a steady-state. The signal of the helium line served as the internal standard to compensate small fluctuations of the operating pressure. The sensitivity factors of the analyzed lines were calibrated using commercial mixtures of gases. The possible changes in the molar flow caused by NH$_3$ conversion were negligible in the diluted reaction mixtures. The differences between the reactor inlet and outlet molar flows of the reactants were used to determine conversion of the reactants.

Additionally, the catalysts were tested in the process of selective catalytic reduction of NO with ammonia (NH$_3$-SCR). The experiments were performed in a fixed-bed flow microreactor (i.d., 7 mm; l., 240 mm). The reactant concentrations were continuously measured using a quadruple mass spectrometer (PREVAC) connected directly to the reactor outlet. Prior to the reaction, each sample (100 mg) of the catalyst was outgassed in a flow of pure helium at 500 °C for 1 h. The following composition of the gas mixture was used: [NO] = [NH$_3$] = 0.25 vol.% and [O$_2$] = 2.5 vol.%. Helium was used as a balancing gas at a total flow rate of 40 cm^3/min.

3. Results and discussion

The specific surface areas of the commercial oxides such as γ-Al$_2$O$_3$, TiO$_2$ (anatase), mt-ZrO$_2$ and their modifications with transition and/or noble metals are presented in Table 1. As it was previously described, copper- or iron-containing supports were characterized by lower specific surface areas comparing to the commercial oxides [3]. Deposition of noble metals, especially rhodium further decreased the specific surface areas of the oxides. This effect was significantly less distinct for a series of the TiO$_2$- and ZrO$_2$-based catalysts.

Powder XRD diffraction patterns obtained for the commercial oxides and their impregnated with transition metals derivatives were presented earlier [3]. In the case of γ-Al$_2$O$_3$, TiO$_2$ (anatase) and mt-ZrO$_2$ modified with transition metals and further with noble metals any phases corresponding to transition and/or noble metals or their oxides were detected in diffractograms of the corresponding samples (results not shown).

The results of H$_2$-TPR studies of the commercial oxides containing both transition metals (Cu, Fe) and/or noble metals (Pd, Rh, Pt) are shown in Fig. 1. TPR studies were performed for all obtained catalytic materials. The H$_2$-TPR profiles recorded for γ-Al$_2$O$_3$ impregnated with noble metals revealed intensive reduction peaks. The Pt-impregnated sample, Al$_2$O$_3$-600–Pt showed a broad reduction profile centered around 190 °C, which can be ascribed to the reduction of amorphous PtO$_x$ species, while the broadening can suggest some interactions with the support [8,9]. In the profile of the Al$_2$O$_3$-600–Rh sample, two peaks centered around 160 and 410 °C appeared, indicating different interactions with the support [10] and/or different dimensions of the RhO$_x$ particles [11]. The negative detector signal observed at temperatures below 100 °C, in the profile of the Al$_2$O$_3$-600–Pd sample, can be attributed to the desorption of hydrogen chemisorbed on the palladium surface or absorbed in the bulk of metallic palladium particle, i.e. β-Pd hydride [12].

For both modified titania or zirconia reduction of PtO$_x$ or PdO$_x$ species were not identified mainly due to partial reduction of oxide supports [3]. Additionally, noble metals supported on TiO$_2$ are known to exhibit strong metal-support-interaction (SMSI) [e.g. [13,14]]. According to previous studies over Rh and Pt catalysts supported on TiO$_2$, the reduction peaks located above 300 °C can be attributed to

Table 1
Specific surface areas and chemical compositions of the catalytic materials.

Sample codes	Al$_2$O$_3$-600– S$_{BET}$ [m^2/g]	TiO$_2$-600–	ZrO$_2$-600–
Pd	106	9	4
Cu–Pd	103	7	4
Fe-Pd	110	7	4
Rh	77	8	4
Cu–Rh	72	9	4
Fe-Rh	77	6	4
Pt	70	9	5
Cu-Pt	66	9	4
Fe–Pt	110	8	3