

Fe₂O₃/Al₂O₃ catalysts for the N₂O decomposition in the nitric acid industry

Grzegorz Giecko^{a,*}, Tadeusz Borowiecki^a, Wojciech Gac^a, Janusz Kruk^b

^a Department of Chemical Technology, Faculty of Chemistry, University of Maria Curie-Skłodowska, M. Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland

^b Institute of Fertilizers, 24-100 Puławy, Poland

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Abstract

Fe₂O₃ catalysts supported on Al₂O₃ were used to remove nitrous oxide from the nitric acid plant simulated process stream (containing O₂, NO and H₂O). Catalysts were prepared by the coprecipitation method and were characterized for their physico-chemical properties by BET, XRD, AFM and TPR analysis. A strong influence of the post-preparation heating conditions on the structural and catalytic properties of the catalysts has been evidenced. Laboratory tests revealed 95% conversion of N₂O at temperature 750 °C and a slight decrease in activity in the presence of H₂O and NO. The catalysts were inert towards decomposition of NO. The pilot-plant reactor and real plant studies (up to 3300 h time-on-stream) confirmed high activity and very good mechanical stability of the catalysts as well as no decomposition of nitric oxide.

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1. Introduction

The main anthropogenic activities producing N₂O are agricultural soil management, fuel combustion in motor vehicles, nitric acid production, stationary fuel combustion, manure management and wastewater treatment. N₂O has been considered as one of the largest contributor to the global anthropogenic greenhouse gas emissions which is over 300 (global warming potential (GWP) is 310 in 100 years time horizon) times more effective than CO₂ in trapping heat in the stratosphere [1]. Nitric acid production is the largest industrial source of nitrous oxide where N₂O is produced as an unwanted by-product of the catalytic oxidation of ammonia. Nitrous oxide abatement from nitric acid plants is one of the most challenging environmental problems in catalysis.

Besides the improvement/optimization of ammonia oxidation catalysts there are three possible options for catalytic decomposition of N₂O in the nitric acid plant. Firstly, the catalysts can be used in the ammonia oxidation chamber just downstream of the NH₃ oxidation catalyst. The second abatement measures remove N₂O from the tail-gas leaving the absorption column before the expander. The third option,

typical end-of-pipe, is to decompose N₂O in a tail-gas downstream of the expander [2–5]. Most of the studies presented in the literature deal with the catalysts for nitrous oxide decomposition for the second and third abatement method because of the mild reaction conditions (temperature between 100 and 500 °C at pressures of 1–12 bar).

This paper concerns the first location of the catalysts which is one of the most promising among the several N₂O abatement methods, but it demands a high stability of the catalyst and a very high selectivity for N₂O decomposition since destruction of NO is unacceptable in the production process. Numerous N₂O decomposition catalysts are known and most of these are based on various metal oxides [5,6] very often supported on zeolite carriers or in the form of metal ion exchanged zeolites [7–12]. However, the practical use of these zeolitic systems in the ammonia oxidation chamber is likely to be problematic due to their deactivation under hydrothermal conditions. Iron zeolites are often used as catalysts for low-temperature tail-gas removal of N₂O with reductants [5]. A reducing agent (methane, propane, LPG and ammonia) is added to the tail-gas leaving the NO₂ absorber. Hydrocarbons are widely used as a reductants and CH₄ is considered as one of the most efficient among them [13,14]. Depending on the type of the reductant, the catalyst used and the reaction conditions the co-addition of hydrocarbon powers the temperature for N₂O reduction over iron zeolites around 100 °C with respect to direct N₂O

* Corresponding author. Tel.: +48 81 5375526; fax: +48 81 5375565.

E-mail address: ggiecko@hermes.umcs.lublin.pl (G. Giecko).

decomposition [5]. One of the commercially implemented processes of N_2O removal using iron-containing zeolites in the presence of NH_3 and CH_4 is Uhde EnviNOx [13].

Most of the efforts to develop catalysts suitable to use in a nitric acid production plant have been made by the companies [15–19]. Among the most promising are the catalysts based on cobalt-oxide spinels (composition $Co_{3-x}M_xO_4$, where $M=Fe, Al$ and $x = 0-2$) supported on cerium oxide developed by Norsk Hydro [20]. Co_2AlO_4/CeO_2 catalyst with the addition of ZrO_2 (0.2 wt.%) showed exceptional activity in decomposing N_2O (over 95%) and stability in the real-plant conditions. The catalyst can be used at a wide temperature range and is stable at varying gas composition, even in the presence of relatively high amounts of water, which often is a problem. Furthermore, NO losses in the real-plant tests occurred to be lower than 0.2%.

The main objective of this paper was to arrive at a versatile, active and thermally stable catalyst for N_2O decomposition at extreme conditions of the ammonia oxidation process with high selectivity for decomposing nitrous oxide without decomposing NO.

2. Experimental

2.1. Catalysts preparation

Fe_2O_3/Al_2O_3 catalysts series were prepared by coprecipitation using the aqueous solutions of iron (III) nitrate and alumina (III) nitrate with sodium (II) hydroxide at different pH of solutions (8.5 and 9.5). The catalysts were dried after precipitation at 105 °C for 24 h and then calcined at 400 °C for 4 h. Afterwards samples were heated at 900 or at 1100 °C for 5 h to simulate the catalyst aging and reactor exotherms. For the pilot-plant studies catalysts were formed in 17 mm × 17 mm × 12 mm Raschig rings and 5 mm × 5 mm pellets.

2.2. Catalysts characterization

The chemical composition of the samples was determined by applying the X-ray fluorescence method (ED-XRF Canberra 1510). The total surface area of the samples was determined by measuring argon adsorption at the temperature of liquid nitrogen in a static-volumetric apparatus, which ensured a vacuum better than 2×10^{-6} kPa. X-ray diffraction studies (XRD) were done in the HZG-4 diffractometer using $Cu K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology of the samples was studied by the atomic force microscopy (AFM) using Nanoscope III (Digital Instruments) microscope.

The temperature-programmed reduction was carried out in the Altamira AMI-1 system. The 0.02–0.05 g catalysts samples (with the grain size equal to 0.2–0.5 mm) were introduced into the quartz reactor (i.d. = 7 mm). A temperature controller maintained the reactor temperature within 1 °C and provided linear temperature programming. The monitoring of the gas composition was followed by means of a mass spectrometry detector HAL 201 RC (Hidden Analytical). During TPR measurements an LN_2 -methanol trap was placed between the

reactor and detector to remove water. In the TPR measurements 6 vol.% H_2 in Ar mixture was applied. The gases were of 99.995% purity and were further purified by OXICLEAR or MnO/SiO_2 traps.

2.3. Activity tests

Catalytic tests were carried out in a tubular quartz reactor using 0.1 g of catalysts shaped in particles with diameters of 0.63–1 mm. The tests were carried out at the atmospheric pressure in the model mixture of gases formed in the ammonia oxidation chamber in the nitric acid plant. The partial pressure of the gases was 5–10 mbar for N_2O , 5–10 mbar for O_2 , 30 mbar NO , 30–60 mbar for H_2O , balance He at different gas mixture compositions. The total flow of the reactant gases amount to 50 or 100 cm^3/min . Individual and combined effects of these gas mixtures on the catalytic performance were investigated. All the samples were heated at 900 °C for 1 h in flowing helium prior to reaction and cooled down in the same gas to the reaction temperature. The reaction temperatures ranged from the ambient up to 800 °C. The products were continuously analyzed by a mass spectrometer (Hidden Analytical HAL201RC) and discontinuously by GC (Fisons GC8000) equipped with the thermal conductivity detector using a Porapak Q 100/120 mesh column. At least three analyses for the GC were averaged for a data point.

Pilot-plant tests were carried out in the three-reactor system. The reactor construction was the same as an industrial one made up from Pt–Rh gauzes and the bed of ceramic Raschig rings in the reference reactor or the catalyst in experimental reactors. Each reactor was fed with the same gas mixture containing 10.7 vol.% of NH_3 in air at the flow rate 45 Nm^3/h (conditions the same as in the real plant). The reaction was carried out at 4.9 bars pressure and at the temperature range 885–890 °C. The measured N_2O concentration (in the reference reactor) was 1200–1300 ppm.

The catalysts were also placed in the real plant ammonia oxidation reactor (ZA “Pulawy”) for 3300 h and then characterized for the mechanical stability and activity towards N_2O decomposition.

3. Results

3.1. The physico-chemical properties of the catalysts

The catalysts were prepared by a coprecipitation method using different amounts of solutions at different pH of the ones. Table 1 shows the composition and total surface area of the samples. The assumption of the preparation step was to prepare series of the catalysts with different Fe/Al ratios. In order to obtain an aging effect, post-preparation thermal treatment of the samples was used. The catalysts are denoted as $FeAl_x-T_y$, where x stands for Fe/Al molar ratio in the samples and y stands for the temperature of post-preparation heating in degrees of Celsius.

The higher thermal treatment of the samples the lower total surface area of the ones.

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