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The influence of modifiers on the activity of Fe_2O_3 catalyst for high temperature N_2O decomposition (HT-deN_2O)

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ABSTRACT

The Fe_2O_3-based catalysts have numerous advantages for HT-deN_2O process applications. The possibility of enhancing their activity by various metal oxide modifiers addition (Al, Zr, Ce, La, Cu, Cr) has been investigated. The catalysts were prepared by the coprecipitation method and their physicochemical properties were characterized by N_2 sorption, XRF and XRD methods. A quartz gradientless reactor was used for activity evaluation at the temperature range of 500–900 °C. The modifiers efficiency was compared and the activity of hematite catalysts at 800 °C was found to increase in the following order: $Cr < Ce < Zr < La < Al < Cu$.

1. Introduction

Nitrous oxide (N_2O) is a harmful gas, contributing to the greenhouse effect (310 times stronger than CO_2) and ozone layer depletion. There are two main sources of N_2O formation: natural processes and industrial activity – mainly nitric acid production by Ostwald method [1]. In the course of catalytic ammonia oxidation process on Pt–Rh gauzes a part of ammonia is converted into nitrous oxide, which, in consequence, causes decrease of nitric acid yield and problems with N_2O emission to the atmosphere [2].

The simplest way of N_2O removal, usually implemented in industrial practice is catalytic high-temperature N_2O decomposition (HT-deN_2O) in a catalytic bed placed behind Pt–Rh alloy gauzes. Moreover, for this process modifications of the ammonia oxidation reactor are not required. Nitrous oxide degrades to gases that are environmentally friendly and abundant in atmosphere, in the course of the following, reaction: $N_2O \rightarrow N_2 + ½O_2$.

HT-deN_2O catalysts are used under stringent process conditions and, additionally, reactor construction limitations imply that the catalysts must fulfil several requirements, they include:

- High activity per bed volume unit so that the lowest possible amount of a catalyst assures high degrees of N_2O conversion;
- Lack of a negative impact on the performance of catalytic gauzes and no decrease of the extent of ammonia oxidation to NO;
- High mechanical strength (resistant to high temperature and high steam concentrations), low and stable pressure drop.

The literature data survey reveals that various catalysts with different formulas, grain shape and physicochemical properties can be utilized in the HT-deN_2O process [3–5]. According to information available from the catalyst manufacturers, the HT-deN_2O catalysts used currently in the industry allow for a radical decrease of N_2O emission, providing a high (>90%) degree of N_2O decomposition [6]. However, continuous restrictions on legal regulations for N_2O emission limits enforce a search for even better catalysts with higher efficiency. This issue is of continuous interest and the preparation of novel more effective catalysts, that could be applied in the industry, constitutes a challenging goal for many research groups.

Different catalysts have been examined as potentially useful for the deN_2O process. They can be divided into: precious metals on oxide or ceramic supports [7], transition metal oxides in a pure form or as spinels [8,9], perovskite oxides [10] and catalysts based on zeolites [11,12], ex-hydrotalcites [13,14].

In a very first attempt to solve the N_2O abatement problem, platinum group metals have become of particular interest for the preparation of active HT-deN_2O catalysts [15]. However, it turned out that the platinum catalysts are sensitive to oxygen and quickly deactivate in the presence of oxygen in nitrous gases. This is in contrast to the palladium and rhodium catalysts, for which the initially low activity increases and stabilizes with time [16]. The efficiency of rhodium has been demonstrated by Gajdej [17], a complete decomposition of N_2O at the temperature >500 °C was achieved already at the 1 wt% rhodium content on Al_2O_3.

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A kind of support influences the activity of platinum group metals in N_2O decomposition. Platinum and palladium supported on $LaCoO_3$ showed definitely higher activity than when supported on Al_2O_3 [18], but the Ir/Al_2O_3 catalyst is more active and less sensitive in the presence of oxygen, especially at higher temperatures [19]. In industrial practice, the platinum group metals catalysts supported on alumina are used [20].

There has been a relatively high interest in cobalt catalysts or other systems promoted or modified with cobalt [21–23]. Co_3O_4 shows high activity in N_2O decomposition process, however, at 820–830 °C [24]. Shen et al. investigated the effects of the support nature on the activity of cobalt catalysts in the deN_2O process [25]. The best results were obtained for the CoO–MgO and Co/ZnO systems. The results of Russo et al. show that the systems based on perovskites of a general formula $LaBO_3$ (where B = Cr, Mn, Fe and Co) are characterized by very good catalytic properties [26]. The highest activity was found for $LaCoO_3$, in the presence of both oxygen-containing and oxygen-free gases. Complete N_2O decomposition for this system was achieved at ca. 550 °C. Similar investigations were carried out for the catalysts based on spinels and the best catalytic properties in the presence of oxygen were obtained for the Mg-Co spinel of the $MgCo_2O_4$-type [8].

Due to the high cost of precious metals and some of the transition metals (e.g. Co) other VIII group metals and rare-earth elements and their mixed oxides have become of great interest as an alternative. A number of catalysts based on mixed oxides have been examined in N_2O decomposition process so far, including La-perovskite [27], Fe-mordenite/cordierite [28], Fe–hexaaluminate or Fe-zeolite [29], Cu- and Zn-spinels [30].

Among the above-mentioned catalysts iron-based ones seem to be promising catalysts for the effective reduction of N_2O emission in nitric acid plants [31,32]. It is known that exchanging iron salts within the ZSM-5 zeolite is an effective method of the preparation of very active catalysts [33]. Despite the low activity of pure hematite for HT-deN_2O [34], another preparation route of the effective HT-deN_2O catalysts is a homogeneous modification of hematite with additives by precipitation of complex hydroxides followed by thermal treatment [35]. Because of a synergy effect mixed oxides are usually more active than pure oxides as can be observed e.g. for the Fe_2O_3/CeO_2 catalyst [36]. In such systems noticeable synergy of oxides has been observed. Hematite as a main component of deN_2O catalysts has many advantages compared to catalysts based on precious metals or other transitions metals oxides, including:

- abundant and low cost, so it can be used in large concentrations;
- manufacture, use and disposal of the catalyst after use are generally harmless from the ecological point of view.

The aim of our research is to investigate the effect of modifiers on the activity and physicochemical properties of iron oxide-based catalysts. It is important to determine whether their activity can be enhanced by the addition of other oxides as promoters.

2. Experimental

2.1. Catalysts preparation

Model samples containing approximately the same amount of Fe_2O_3 (80 wt%) with a different modifiers in the form of oxides of Al, Zr, Ce, La, Cu or Cr were precipitated by adding a ferrous sulfate aqueous solution and a nitrate solution of one of the modifiers to a sodium hydroxide aqueous solution at 80 °C with the final pH value of 10. The catalysts were then dried at 105 °C for 3 h and calcined at 900 °C for 3 h (the industrial operating temperature range for the catalyst in high-temperature deN_2O process is in the range 850–940 °C).

2.2. Catalysts characterization

The chemical composition of the samples was determined by applying the X-ray fluorescence method (XRF PW 2400). The total surface area of the samples was determined by measuring nitrogen adsorption at the temperature of liquid nitrogen and $p/p_o = 0.05–0.3$ using a Micromeritics ASAP® 2050 Xtended Pressure sorption analyzer. X-ray diffraction studies (XRD) were done using a Panalytical Empyrean diffractometer with CuK_α radiation ($\lambda = 1.542$ Å).

2.3. Activity tests

Activity measurements were done in a quartz gradientless reactor [37] at the temperature range of 500–900 °C and pressure 0.1 MPa. A catalyst sample (50–100 mg) grounded to the fraction of 0.16–0.25 mm was placed into the reactor and loaded with a feedstock (GHSV approx. 10000 h^{-1}) containing 1500 ppm N_2O, 1500 ppm NO and N_2 as an inert. The N_2O concentration in the outlet gases was determined by SICK S710 NDIR analyzer. The N_2O decomposition rate constant was calculated from the equation given below, assuming that the reaction kinetics is first order in N_2O concentration [1,34]:

$$k \cdot C_0 \cdot m_{\text{cat.}} = V \cdot (C_i - C_0) \qquad (1)$$

where k is the rate constant [$Ndm^3\ N_2O\ g^{-1}\ h^{-1}$], C_i the inlet concentration of N_2O [ppm], C_0 the outlet concentration of N_2O [ppm], m_{cat} the mass of the catalyst [g], V is the total flow [$Ndm^3\ N_2O\ h^{-1}$].

3. Results and discussion

3.1. The physicochemical properties of the catalysts

The catalysts were prepared by a coprecipitation method. Table 1 shows the composition and specific surface area of the samples.

The data presented in Table 1 clearly show a satisfying accordance of the nominal composition of the samples with the measured composition. The standard deviations from the assumed Fe_2O_3 content (80 wt%) for the individual samples do not exceed 5 wt%. There is a significant influence of a modifier type on the specific surface area of the catalysts, which changes in the range from 2.0 m^2/g to ca. 16 m^2/g. The lowest values of specific surface area were observed for the Fe–Cu and Fe–Ce catalysts (below 5 m^2/g) and the highest for the Fe–Cr (15.8 m^2/g) and Fe–Al (14.6 m^2/g) catalysts.

The XRD patterns of catalysts are shown in Fig. 1. The analysis of the XRD pattern revealed that hematite is a dominant phase in all samples. In the $Fe_2O_3–CeO_2$ catalyst the dominant crystallographic phase (vol.) is hematite (ICDD 01-076-3169). Besides the well-formed iron(III) oxide phase, a weakly crystalline CeO_2

Table 1
Chemical composition and specific surface area of Fe_2O_3-based catalysts.

Catalyst	Composition (wt%)		S_{BET} [m^2/g]
FeAl	78.9% Fe_2O_3	21.1% Al_2O_3	14.6
FeZr	84.4% Fe_2O_3	15.6% ZrO_2	5.3
FeCe	84.8% Fe_2O_3	15.2% CeO_2	3.9
FeLa	82.4% Fe_2O_3	17.6% La_2O_3	7.9
FeCu	78.2% Fe_2O_3	21.4% CuO	2.0
FeCr	82.9% Fe_2O_3	24.3% Cr_2O_3	15.8