



Stainless steel wire mesh-supported potassium-doped cobalt oxide catalysts for the catalytic decomposition of nitrous oxide

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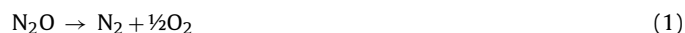
ABSTRACT

Structured catalysts consisting of potassium-doped cobalt oxide supported on stainless steel wire mesh were tested for the decomposition of N₂O under dry and wet conditions. The cobalt oxide catalysts were prepared by the ammonia-evaporation-induced method. Of the several doping procedures tested, dropwise impregnation with potassium carbonate solutions provided the best catalytic results at lower K/Co molar ratios. Kinetic analysis of a potassium-doped catalyst yielded a reaction order on the N₂O partial pressure slightly below unity (0.87). The activation energy values and the natural logarithms of the pre-exponential factors for the different catalysts followed the classical compensation effect. This effect may be the result of a combination of competing reactions on different groups of active centers. Thus, cobalt ions affected by potassium display a low activation energy (~40 kJ/mol), whereas cobalt atoms unaffected by potassium display a higher activation energy equal to that of the undoped catalysts (~106 kJ/mol). The catalytic activity of the catalysts in N₂O decomposition increases with the amount of reducible Co³⁺ ions, although there does not appear to be a direct relation between the amount of Co³⁺ ions and the textural and crystal properties of the catalysts. The addition of water produces some inhibition of the N₂O decomposition reaction on K-doped catalysts, although catalytic activity is completely restored when the water is removed from the reaction stream. The catalysts prepared in this work were found to be among the most active, selective and stable catalysts reported in the literature.

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1. Introduction

Nitrous oxide has been long considered to be as an ozone depletion agent and a greenhouse gas [1]. Well-known anthropogenic sources of N₂O emissions include the adipic acid and nitric acid industries, the fluidised bed combustion of coal and biomass, fertilizer plants and deNO_x treatment techniques, such as SCR and three-way catalysis [2–6]. Awareness of the environmental impact of N₂O has led to an enormous international effort since the Kyoto agreement to reduce anthropogenic N₂O emissions, via a series of clean development mechanism projects [7]. Among the various N₂O reduction techniques considered, thermal decomposition [6,8] and catalytic decomposition [6,9] have been the most widely studied:



It is well known that cobalt-based catalysts present excellent catalytic activities for N₂O decomposition [2,3,10–30]. Typical precursors for cobalt-based catalysts are ion-exchanged

zeolites [3,15,21,22,29] and hydrotalcites [12,28]. The most common cobalt-based catalyst (Co₃O₄ spinel) is fairly stable and suffers no inhibitory effect from the accumulation of oxygen on its surface during reaction at around 300 °C [30]. Doping the cobalt spinel with small amounts of cerium oxide [13] or alkali metals [2,11,14,16] significantly increases the activity of the catalyst. The role of these agents, especially potassium, is to increase the amount of oxygen adsorbed on cobalt ions and to promote the reduction of Co³⁺ to Co²⁺ through an electron donation effect [2,11,16,25,30], thus favouring the desorption of oxygen from the surface of the catalysts, which is the controlling step of N₂O decomposition [13]. Most of these catalysts come in particulate form, and have to be used in packed beds which may lead to uneven gas and temperature distributions and high pressure drops. The use of structured catalysts to overcome these disadvantages, has not been investigated in depth. A study carried out by Pérez-Ramírez et al. [6] on N₂O abatement alternatives in nitric acid plants showed that the structured reactor concept is optimal not only for catalytic N₂O decomposition or reduction in the tail-gas (upstream or downstream of the expander), but also for N₂O decomposition in the process-gas, i.e. below the platinum gauzes. Wang et al. [26] used a ceramic honeycomb support to produce Ni-Co catalysts for N₂O decomposition with good catalytic activity and stability, although

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in their case the support was crushed before being impregnated with the active phase. In this work we have employed a structured reactor based on a novel concept, initially tested for the preferential oxidation of carbon monoxide [31] and the catalytic decomposition of methanol [32]. The reactor consists of a very fine stainless steel wire mesh, coated with mesoporous Co_3O_4 nanowires (catalyst), and rolled up inside a stainless steel pipe (1/4" o.d.). In this kind of reactor, the metal wire mesh provides a large geometric surface area for supporting the catalyst. It also guarantees a negligible pressure drop and good heat transfer through the reactor. In the present study the mesh-supported catalyst was modified with potassium in order to produce the desired increase in catalytic activity. The catalysts obtained were tested for N_2O decomposition in the presence of oxygen and water.

2. Experimental

2.1. Catalyst synthesis

Wire mesh-supported cobalt oxide catalysts were prepared by the ammonia-evaporation-induced method at 90°C for 18 h using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as cobalt precursor. A detailed description of the synthesis procedure can be found elsewhere [31,32].

Two types of stainless steel wire mesh were tested as catalyst supports: M40 (30 μm wire diameter and 40 μm screen opening; smooth fabric) and M25 (25 μm wire diameter and 25 μm screen opening; twill fabric). Before use, both meshes were washed with HNO_3 (4 M) at 60°C for 4 h and then with isopropyl alcohol in an ultrasonic bath for 10 min.

The uncalcined wire mesh-supported cobalt hydroxide catalysts were impregnated with potassium by the dropwise addition of an aqueous solution of K_2CO_3 (0.15–0.21 M) or KOH (0.231 M). After wetting the sample, the excess solution was removed by applying an air stream, followed by vacuum-drying at 60°C for 1 h. The impregnation step was then repeated in order to obtain the desired amount of potassium. The molar ratio of potassium to cobalt (K/Co) ranged between 0 and 0.03. In some specific cases potassium addition was performed by equilibrium impregnation. In this case each sample was immersed in aqueous KOH solutions (0.21 M) and kept under magnetic stirring for several hours. Afterwards, the metal wire mesh was removed from the solution, thoroughly washed with deionised water and vacuum-dried at 60°C .

2.2. Finally all the samples were calcined in air at 400°C for 2 h

The samples were denoted as M-KP-IM-K/Co where M refers to the type of stainless steel wire mesh (M40 or M25), KP is the potassium precursor (KC for potassium carbonate; KO for potassium hydroxide), IM is the impregnation method (DW for dropwise impregnation; EA for equilibrium adsorption impregnation) and K/Co is the molar ratio of the doped metal (from 0.006 to 0.029). Undoped catalysts were simply denoted M25 or M40.

2.3. Catalyst characterisation

The metal contents of the samples were determined by atomic absorption spectroscopy (AAS) and mass spectrometry (ICP-MS). Microscopic images of the samples were obtained using a scanning electron microscope (Zeiss, DSM 942 model). X-ray diffraction (XRD) analyses were carried out with a Bruker instrument (D8 Advance) operating at 40 kV and 40 mA and using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). Crystal size values (d_{XRD}) were estimated from the XRD patterns by means of Scherrer's equation. The instrumental contribution to line broadening was taken into account by using the diffraction pattern of corundum as instrumental standard.

TPR analyses were performed in a chemisorption analyzer (Autochem II) equipped with a TCD detector. For each analysis approximately 80 mg of sample was pre-treated at 400°C for 1 h in an argon flow, cooled down to room temperature and then treated with a 50 mL/min stream of 10 vol% H_2 in argon from 100 to 600°C at $5^\circ\text{C}/\text{min}$.

N_2 adsorption isotherms at -196°C were obtained in a Micromeritics ASAP 2010 volumetric adsorption system. The BET surface area was determined from the isotherm analysis in the relative pressure range of 0.04–0.20.

2.4. Catalytic activity tests

Catalytic activity tests for N_2O decomposition were performed in a six-flow parallel microreactor system that allows up to six samples to be simultaneously tested by means of an automatically operated multiposition valve. Each catalyst consisted of a 5 cm \times 1 cm strip that was rolled up to form a 1 cm-high cylindrical piece. One roll of catalyst was then inserted into each of the six stainless-steel reactors (1/4 in. outer diameter). A stream composed of 1300 ppm N_2O , 0.5 vol% O_2 , 0 or 4 vol% H_2O and 10 vol% Ar in helium was fed into each reactor at a gas hourly space velocity of $\sim 20,000 \text{ h}^{-1}$. Weight hourly space velocities varied in the range 0.08 – 0.10 $\text{g}_{\text{N}_2\text{O}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$, depending on the amount of catalyst loaded onto the metal wire mesh. The samples were first heated in a flow of He at 400°C for 30 min. Then the reactant stream was passed through the catalysts and their catalytic activity and selectivity were evaluated at decreasing temperatures from 400 to 300°C , in 3 h isothermal steps. It was generally found that 30 min after each change in conditions the conversion levels were constant and were thus considered as steady-state values. The transition ramp between each temperature step was performed under a helium atmosphere. The products were analysed on-line by mass spectrometry (OmniStar 3000). N_2O , N_2 , O_2 , and H_2O were quantitatively analysed with the help of previous calibration steps, whereas the evolution of NO and NO_2 was followed from the changes in the mass intensities of the fragments 15 (NO) and 46 (NO_2). By means of this procedure it was possible to know for certain whether any products other than N_2 were formed during the reaction. The conversion parameter, X, represents the fraction of N_2O converted to N_2 and O_2 according to the reaction:



Each experimental conversion point was evaluated after two hours of reaction at the specified temperature. For the kinetic analysis, experiments at different N_2O partial pressures (0.17–0.40 atm) and temperatures (150 – 300°C) were performed. The following potential equation for the reaction rate was used to fit the experimental results:

$$-\frac{dP_{\text{N}_2\text{O}}}{dt} = kP_{\text{N}_2\text{O}}^n \quad (1)$$

where $P_{\text{N}_2\text{O}}$ is the outlet partial pressure of N_2O , n is the reaction order and k is the reaction rate constant, that follows an apparent Arrhenius-type dependence; $k = k_0 \exp[-Ea/(RT)]$. Integral reactor behaviour was employed to solve Eq. (1) and the following expression was used to calculate the values for the reaction rate constant:

$$k = \frac{F_{\text{N}_2\text{O}}^0}{w_{\text{cat}} (P_{\text{N}_2\text{O}}^0)^n} \frac{1 - (1 - X)^{1-n}}{1 - n} \quad (2)$$

Only conversion values below 0.7 were used in this equation.

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