

Development of a new Rh/TiO₂–sepiolite monolithic catalyst for N₂O decomposition

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Abstract

Monolithic catalysts based on Rh/TiO₂–sepiolite were developed and tested in the decomposition of N₂O traces. Several effects such as the presence of NO, O₂ and NO + O₂ in the gas mixture, the catalysts pre-treatment and the metal loading were evaluated. The system was extremely sensitive to the amount of rhodium, passing through a maximum in the catalytic activity at a Rh content of 0.2 wt.%. It has been demonstrated that both NO and O₂ compete for the same adsorption sites as N₂O; however, this effect was not as severe as for other previously reported Rh systems. For NO + O₂ gas mixtures the inhibition effect was stronger than when only NO or O₂ was present. Analysis of the pre-reduced sample by XPS showed Rh mainly in the metal state, even after treatment with N₂O + O₂ mixtures, suggesting that the oxygen consumption observed in the Temperature Programmed Reaction experiments was related to the oxygen uptake by vacancies in the support. The presence of sepiolite in the support preparation and its role as a matrix over which TiO₂ particles were distributed, seems to play an important effect in the migration process of oxygen species through the support vacancies. The Rh/TiO₂ monolithic system is an attractive alternative for the elimination of N₂O traces from stationary sources due to the combination of high catalytic activity with a low pressure drop and optimum textural/mechanical properties.

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1. Introduction

The harmful effect of nitrous oxide (N₂O) in the atmosphere is well known. Although formerly considered innocuous, this gas contributes to the greenhouse effect and the depletion of stratospheric ozone [1]. At the Kyoto protocol conference in 1997 the EU committed itself to reduce the emissions of greenhouse gases by at least 5% below 1990 levels in the period 2008–2012.

Besides agriculture, the main stationary anthropogenic sources are chemical processes such as nitric and adipic acid manufacture, combustion processes, and industrial and municipal nitrogen-containing waste in fluidised-bed reactors [2–5]. Furthermore, N₂O may be produced as an undesirable byproduct in some catalytic processes. Our previous results showed that N₂O was formed in the SCR-NH₃ process, even in the low temperature region (180–230 °C). A temperature increase, and high [NH₃]/[NO_x], [NO₂]/[NO_x] ratios favour

nitrous oxide formation, which was strongly dependent on the catalysts nature [6–8].

These emissions can be reduced by end-of-pipe solutions, employing catalytic technology. The catalytic decomposition of N₂O to nitrogen and oxygen is the most direct method for nitrous oxide elimination, although other processes such as the selective reduction with propane, methane or ammonia are currently being studied. Noble metals such as Rh, Pt, Pd [9,10] and metal oxides, both pure and supported, have been used for the N₂O decomposition reaction [11–13]. In a recent article, Xu et al. highlighted the better performance of Rh catalysts compared to Fe-based materials [14]. The excellent properties of Rh-ZSM-5-based catalysts at relatively low temperatures 250–300 °C have previously been reported by Li and Armor [15] and Obuchi and co-workers [16]. The Rh/TiO₂ system is an interesting material as was demonstrated by Centi et al. showing similar performances to Rh/ZSM-5, operating even at room temperature [17,18]. According to these authors, titania plays an active role in the reaction, due to the presence of oxygen vacancies at the support–Rh particle interface that greatly influence the steady-state activity in the presence of oxygen.

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To date, such materials have been tested only as powder-type model catalysts, whereas for industrial applications, pellets, spheres or monoliths are required. Catalytic results obtained over model catalysts might be far away from the performance of these industrially required systems, where besides the presence of binders, both the preparation methods and the purity of the raw materials differs from those prepared at laboratory scale. The use of monolithic or honeycomb systems is an attractive option for environmental solutions since amongst other advantages they offer the possibility of treating large gas volumes (high space velocities) which may also contain particles, operating with low pressure drop [19].

In a previous article we studied the performance of Rh/Al₂O₃ monolithic catalysts in the decomposition of N₂O and the effect of the gas feed on the reaction rate obtaining a stable catalyst even in the presence of oxygen in the feed [20]. Bearing in mind those observations, the objective of this work was to study the performance of Rh/TiO₂–sepiolite monolithic catalysts in this reaction, focusing on the role that a semiconductor material (titania) plays in the reaction. The morphology of the particles that conforms the support and their distribution within the monolith is examined. The effect of the metal loading, catalyst pre-treatment and the influence of NO, O₂ and NO + O₂ is analysed. The different reactions involved in the overall process, N₂O decomposition, NO to NO₂ transformation are studied. The metal oxidation state after different treatments and the evolution of reactants and products in reaction conditions is further discussed.

2. Experimental

2.1. Monolithic catalyst preparation

Monolithic supports were made by extrusion of a dough prepared by kneading a mixture of TiO₂–anatase (Rhône-Poulenc), sepiolite (Tolsa S.A.) and activated carbon powders with water. The higher performance of a new TiO₂/sepiolite monolithic support prepared with carbon as a pore generating agent (PGA), with respect to the conventional ones has been recently demonstrated [21]. The optimum TiO₂/sepiolite ratio selected to carry out this study was 1:1, since this combines good textural and mechanical properties. The monolithic shaped materials were dried at room temperature for 48 h, then at 110 °C for 24 h and finally treated at 500 °C for 4 h to eliminate the activated carbon. The resulting monoliths presented the following geometric characteristics: square cell size 2.5 mm, wall thickness 0.9 mm, geometric surface 865 m²/m³ and cell density 8.5 cell/cm².

Catalysts were prepared by impregnation of the support with an aqueous solution containing rhodium, using RhCl₃·H₂O (42.44 wt.%, Johnson Matthey). After drying at room temperature the monoliths were further dried at 110 °C and finally treated in an air atmosphere at 500 °C and if required reduced in NH₃/N₂ flow at 400 °C. Catalysts with Rh contents between 0.08 and 0.5 wt.% were prepared. The samples were denominated TiRh_x, where *x* indicates the rhodium loading expressed as mass percentage.

2.2. Catalyst characterisation

Rhodium and chlorine contents were determined by *inductively coupled plasma optical emission spectroscopy ICP-OES* (Perkin-Elmer Optima 3300DV) at $\lambda_{\text{Rh}} = 343.489$ nm and $\lambda_{\text{Cl}} = 725.670$ nm, respectively. The chlorine concentration was below 0.03 wt.%. The surface areas (S_{BET}) were calculated from *nitrogen adsorption* at –196 °C determined with a Carlo Erba Sorptomatic 1800, outgassing the samples overnight at 250 °C to a vacuum of $<1.33 \times 10^{-2}$ Pa to ensure a dry clean surface, free from any loosely bound adsorbed species. The pore volumes were analysed by use of *mercury intrusion porosimetry* (MIP) using CE Instruments Pascal 140/240 porosimeter, after drying the samples at 150 °C overnight. For these measurements the values recommended by the IUPAC [22] for the mercury contact angle (141°) and surface tension (484 mN m⁻¹) were used. The total pore volumes were determined by combination of nitrogen adsorption and mercury intrusion results. The mechanical strength of the monoliths was determined measuring the crushing strength with a Chantillon dynamometer model LTCM with a 1 mm diameter die head.

Scanning Electron Microscopy studies were performed in a ISI DS-130 electron microscope with a Si/Li detector and a Be window of 7 μm thickness. Catalyst samples were coated with gold to minimise charging. Measurements were carried out on both the internal part and surface of the monolith wall.

X-ray photoelectron spectra were acquired with a VG Escalab 200R spectrometer fitted with a monochromated Mg Kα radiation ($h\nu = 1253.6$ eV, $1 \text{ eV} = 1.6302 \times 10^{-19}$ J) 120 W X-ray source and a hemispherical electron analyser. The powdered samples were placed on a sample rod, introduced in a pre-treatment chamber, degassed at 25 °C and 10^{-3} Pa for 5 h prior to being transferred to the analysis chamber. Residual pressure during data acquisition was maintained below 3×10^{-7} Pa. The energy regions of the photoelectrons of interest (Ti 2p, Si 2p, Mg 2p, Rh 3d), were scanned a number of times in order to obtain an acceptable signal-to-noise ratio. Accurate binding energies (± 0.2 eV) were determined by referring to the Ti 2p peak at 485.5 eV.

The temperature programmed reaction experiments of N₂O (TPR-N₂O) were carried out using 2.5 g of shards from monoliths in a stainless steel microreactor of 1 cm diameter, operating with a total flow $F = 275$ ml min⁻¹, $P = 114$ kPa using argon as a gas carrier. To analyse the adsorption desorption processes, a low gas hourly space velocity of 3000 h⁻¹ and a linear velocity of around 0.06 m s⁻¹ at normal conditions were selected. After a pre-treatment at 500 °C with O₂ (5 vol.%) or following reduction with NH₃ at 400 °C (0.5 vol.%) using Ar as a gas balance, the system was cooled to 250 °C in an argon atmosphere. Subsequently, the gas mixture was fed to the reactor, increasing the temperature by steps of 100 °C up to 450 °C ended at 500 °C with a ramp of 10 °C min⁻¹ and maintained at each temperature until the steady state was reached. The detection and quantification of the gases at the microreactor inlet and the desorbed products was performed by mass spectrometry (Balzers Omnistar), using a Channeltron detector, evaluating the following masses: N₂

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