



Mesoporous silica supported Rh catalysts for high concentration N₂O decomposition



Marco Piumetti^a, Murid Hussain^{a,b}, Debora Fino^a, Nunzio Russo^{a,*}

^a Department of Applied Science and Technology, Politecnico di Torino, Corso Duca, degli Abruzzi 24, 10129 Torino, Italy

^b Department of Chemical Engineering, COMSATS Institute of Information Technology, M.A. Jinnah Building, Defence Road, Off Raiwind Road, Lahore 54000, Pakistan

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ABSTRACT

A set of Rh-containing catalysts (Rh-MCM-41, Rh-SBA-15, Rh-KIT-6 and Rh-MCF, nominal Rh content = 1 wt.%) has been prepared by wet impregnation of mesoporous silicas and tested for high concentration N₂O abatement. The physico-chemical properties of the materials have been investigated by means of complementary techniques.

The best performances, in terms of N₂O decomposition, have been achieved for the Rh-MCF catalyst, due to the better textural properties of the MCF silica. In fact, the MCF-type support exhibits three-dimensional mesoporosity with ultra-large cells (up to 40 nm), which allow a uniform distribution of small RhO_x particles (≈1 nm) over the high (internal) surface area of the MCF. Moreover, the Rh active sites are also readily accessible to N₂O molecules.

The most promising catalyst has shown the highest amount of Rh¹⁺ species, the easiest rhodium reducibility and the greatest abundance of Rh surface sites. These important features reflect the different Rh particle sizes and play a role in catalytic activity.

A remarkable relationship between the catalytic activity and the dimension of the RhO_x particles has been observed in the 1–2.5 nm size domain, thus confirming the dispersion-sensitivity of N₂O decomposition over RhO_x nanoparticles.

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1. Introduction

Nitrous oxide (N₂O) is considered a greenhouse gas since it lasts approximately 150 years in the atmosphere, it has 310 and 21 times greater warming potential than CO₂ or CH₄, respectively, and it contributes to the destruction of stratospheric ozone [1–3]. For these reasons, it has recently received a great deal of attention by scientists because of its possible environmental effects [1]. Europe has agreed to reduce greenhouse emissions, including N₂O, to fulfil the Kyoto protocol.

N₂O is produced from both natural and anthropogenic sources. Biological processes, which take place in soils and oceans, are the primary natural sources of N₂O. The main contributors of the anthropogenic sources include fertilizers, nitric acid, adipic acid, caprolactam and glyoxal production, fossil fuels and biomass combustion, as well as sewage treatment [3,4]. Nitric acid and adipic acid production plants are thought to be the largest industrial

sources of N₂O emissions. As a whole, there is a higher N₂O concentration in tail gas emissions from adipic acid plants (usually 20–40% v/v) than from nitric acid production (around 300–3500 ppm). It has in fact been reported that around 10% of N₂O released into the atmosphere each year originates from adipic acid production, and hence great efforts have been made to abate high-concentration N₂O [5,6].

Catalytic N₂O decomposition could be a promising alternative solution, as it makes N₂O abatement possible at the emission source at lower temperatures (300–500 °C) than the conventional thermal abatement technology [3]. Noble metals, metal oxides, mixed oxides, metal or ion exchanged zeolites and supported metal catalysts have been reported in the literature as promising catalysts for N₂O abatement [4–9]. Rhodium or iridium oxides have been found in particular to be more active in the decomposition of N₂O than other oxides. However, their low surface areas contribute to their main disadvantages as catalysts [4,10]. Mesoporous materials with large controlled accessible surface areas could be attractive candidates for N₂O decomposition, since the active phase can be highly dispersed over the support [11]. The discovery of ordered mesoporous molecular sieves, such as SBA-15

* Corresponding author. Tel.: +39 011 0904710; fax: +39 011 0904699.
E-mail address: nunzio.russo@polito.it (N. Russo).

and MCM-41, has sparked interest throughout the scientific community over the last few decades. These mesoporous silicas, first discovered by Mobil researchers, exhibit high surface areas and pore volumes with a highly ordered hexagonal array of large pores; thus, the diffusion of reactants to the catalytic sites is favoured compared to conventional zeolites. Owing to these interesting textural properties, ordered mesoporous materials have opened new and exciting opportunities in the field of heterogeneous catalysis [12–16].

Various types of noble metals supported on mesoporous silicas have recently been developed for low concentration N_2O degradation and for nitric acid plant tail gas treatment application, and these have shown comparatively better activity than conventional catalysts due to the combination of good accessibility, uniform pore size and the high surface area of the mesoporous materials [4,15,17,18].

Rh supported on MCM-41, SBA-15-Conventional (SBA-15-C), Spherical shaped SBA-15 (SBA-15-S) and KIT-6 silica have been explored for the first time for low concentration N_2O degradation in the recent works by the authors [4,18,19]. These Rh-based catalysts had shown good catalytic activity. However, to the best of the authors' knowledge, mesoporous silica supported noble metal (Rh) has not been explored yet for high concentration N_2O abatement in the treatment of adipic acid production plant tail gas.

Therefore, in the current work, an effort has been made to explore mesoporous silica supported Rh catalysts for high concentration N_2O abatement. Moreover, a recent mesoporous silica material, namely mesocellular silica foams (MCF), which features a well-defined three-dimensional (3D) mesoporosity with large pores (up to 40 nm) [20] has been investigated as a potential candidate for this application. Unlike MCM-41 or SBA-15, which have two-dimensional (2D) mesopore structures, MCF is a new three-dimensional (3D) hydrothermally robust material with ultra-large mesopores and uniform spherical cells interconnected by windows with a narrow size distribution [21–23]. This MCF-type material allows a good dispersion of the active phase (RhO_x nanoparticles) and offers advantages, over its more ordered counterparts MCM-41 or SBA-15, in terms of better diffusion of reactants to the catalytic active sites.

MCM-41, SBA-15, KIT-6 and MCF have therefore been studied in the present work as supports for Rh-based catalysts (nominal Rh-content 1 wt.%) in order to obtain active catalysts for the abatement of high concentration N_2O .

The structural and surface properties of the prepared catalysts have been investigated using complementary techniques, including X-ray diffraction (XRD), N_2 physisorption at -196°C , field emission scanning electron microscope (FESEM), transmission electron microscope (TEM), H_2 temperature-programmed reduction (H_2 -TPR), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR) by adsorption of the basic probes (namely CO and NH_3). Hence, the relationship between the physico-chemical properties and the catalytic performance of such materials has been studied.

2. Experimental

2.1. Preparation of the catalysts

Unless otherwise specified, all the ACS grade reagents were obtained from Sigma–Aldrich S.r.l. (Milan, Italy). The MCM-41 support was hydrothermally synthesized with a CTACI (cetyltrimethylammonium chloride surfactant), according to the procedure reported in Ref. [12]. The obtained MCM-41 material was then dried overnight at 100°C , washed with distilled water and calcined at 550°C for 5 h so that it could be used as a support.

The SBA-15 material was prepared by slightly modifying a literature procedure [24]. In a typical synthesis, 4 g of Pluronic P123 triblock copolymer ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_{av} = 5800$) was dissolved in 30 g of bi-distilled water and 160 mL of 2 M HCl solution. Then, 8.5 g of TEOS (tetraethyl orthosilicate) was added and this solution was stirred at room temperature for 24 h. This was followed by ageing at 100°C for another 24 h. Finally, the mixture was filtered, washed with distilled water, dried overnight at 100°C and calcined at 550°C for 5 h.

The KIT-6 support was prepared according to a procedure described elsewhere [25]. Briefly, 6 g of Pluronic P123 was dissolved in 217 g of distilled water and 11.8 g of concentrated HCl. Then, 6 g of 1-butanol (99.5%, Fluka) was added under stirring at 35°C for 1 h. 12.9 g of TEOS was then added dropwise and the final solution was stirred at 35°C for 24 h. The mixture was transferred to a Teflon autoclave and aged at 100°C for 24 h. The solid was then recovered by filtration, washed with distilled water, dried overnight and calcined at 550°C for 6 h.

The MCF support was synthesized by modifying a literature procedure [22], using Pluronic P123 surfactant with 1,3,5-trimethylbenzene (TMB) as the organic swelling agent with TMB/P123 = 0.75 (wt./wt.). In a typical synthesis, 4.0 g of Pluronic P123 and 3.0 g of 1,3,5-trimethylbenzene were dissolved in 150 mL of 1.6 M HCl solution and stirred at room temperature for 5 h. Then, 8.5 g of TEOS was added to the mixture and then stirred at 40°C for 24 h. The milky reaction mixture was transferred to a Teflon autoclave and aged at 100°C for another 24 h in order to increase both the cells and windows size of the foam. The solid product was filtered off, washed with distilled water and dried overnight at 100°C under static conditions. The surfactant was removed by calcination at 600°C for 5 h in air and the final mesoporous MCF material was obtained.

Calcined MCM-41, SBA-15, KIT-6 and MCF supported Rh (nominal Rh content = 1 wt.%) catalysts were synthesized by means of the incipient wetness method, using a rhodium nitrate precursor, followed by drying overnight at 100°C and calcination at 600°C for 6 h in air; the obtained catalysts were denoted as Rh-MCM-41, Rh-SBA-15, Rh-KIT-6 and Rh-MCF, respectively. A detailed description of the synthesis procedures and of the effect of the main operating parameters on the material properties can be found in Refs [12,22,24,25].

2.2. Characterization of the catalysts

Powder X-ray diffraction patterns have been collected on a Philips PW3040 diffractometer using $\text{Cu K}\alpha$ radiation (2θ range = 0.5 – 60° ; step = 0.02° ; 2θ ; time per step = 1 s).

The textural properties of the prepared samples were obtained as follows: the BET (Brunauer–Emmett–Teller) specific surface area (S_{BET}) was measured by means of N_2 sorption isotherms at -196°C on a ca. 30 mg sample previously outgassed at 150°C for 5 h to remove molecular water and other atmospheric contaminants (Micrometrics Tristar II, USA instrument); the total pore volume (V_p) was calculated at $p/p_0 = 0.97$, whereas the micropore volume (V_{micro}) was measured according to the t -plot method; the average pore diameter (D_p) was calculated by either applying the Barrett–Joyner–Halenda (BJH) algorithm to the isotherm desorption branch (MCM-41, SBA-15 and KIT-6 materials) or according to a modified Broekhoff de Boer (BdB) method using Hill's approximation for the adsorbed layer thickness (MCF materials) [26].

Sample morphology was investigated by means of an FESEM (Zeiss MERLIN, Gemini-II column) and TEM (Jeol JEM 3010 operating at 200 kV). The Rh-content was determined through EDS analysis (Oxford X-ACT). Five different spots with a 10–50 nm diameter were selected in representative zones of the sample and the average Rh-content was then calculated.

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