Available online at www.sciencedirect.com

ScienceDirect

Catalysis Communications 8 (2007) 1406–1410

CATALYSIS COMMUNICATIONS

www.elsevier.com/locate/catcom

Direct decomposition of nitrous oxide over Ru/Al_2O_3 catalysts prepared by deposition–precipitation method ☆

P. Siva Sankar Reddy, Nayeem Pasha, M.G.V. Chalapathi Rao, N. Lingaiah, I. Suryanarayana, P.S. Sai Prasad *

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Received 22 May 2006; received in revised form 30 November 2006; accepted 30 November 2006
Available online 5 December 2006

Abstract

Alumina-supported ruthenium catalysts were prepared by the deposition–precipitation (DP) and impregnation (IMP) methods. The catalysts were characterized by BET surface area, X-ray diffraction, temperature-programmed reduction (TPR) and diffused reflectance infra-red spectroscopic (DRIFTS) techniques. The DP catalysts showed higher activity than their IMP analogues. The DRIFTS analysis revealed preferential formation of Ru^{n+} species on the surface of DP catalysts. Both Ru^{n+} and Ru^0 species appeared on IMP catalysts, with the composition of Ru^0 increasing with increase in metal loading. The temperatures at which the peak maxima appeared were higher in the TPR patterns of the DP catalysts, indicating greater interaction between Ru and alumina, which explained the formation of the cationic Ru species. The high activity of the catalysts prepared by DP method was related to the formation of electron deficient Ru sites during the preparation of the catalyst.

Keywords: N_2O Decomposition; Temperature-programmed reduction; X-ray diffraction; Ru Catalyst; DRIFTS

1. Introduction

Nitrous oxide (N_2O) has been recognized as an important greenhouse gas responsible for stratospheric ozone depletion. With a lifetime of 150 years at atmospheric conditions, it also exhibits a global warming potential 310 times that of carbon dioxide. With the increase in concern for environmental protection, efforts have been made to convert N_2O into N_2 and O_2 [1] and in this process catalytic direct decomposition is found to be advantageous.

A large number of catalysts such as bulk and mixed oxides, perovskites, hydrotalcites and transition metal exchanged zeolites are reported to be capable of catalytically decomposing N_2O at elevated temperatures [2–8]. Most of these reports paid attention to the mechanistic understanding and kinetics of decomposition. Supported oxides are more effective in practical applications due to the higher dispersion of active species as the support affords higher specific surface area. In most of the works alumina was used as a support with one among Pd, Cu, Co, Mn, Rh, Ru, Fe and Cr as active component. Catalysts based on Co, Cu, Ru and Rh exhibit higher catalytic activity than the others [9–15].

Considerable information exists on the activity of Ru/Al_2O_3 in the complete decomposition of N_2O to N_2 at high temperatures. Zeng and Pang [16] reported that the decomposition with negligible inhibition by oxygen follows a first-order reaction with N_2O adsorption as the rate-limiting step. Wang and Zeng [17] observed excellent catalytic activity and stability of Ru/Al_2O_3 catalysts under dry and wet N_2O feeds. Pinna et al. [18] examined N_2O decomposition over Ru supported on ZrO_2. N_2O acted as an oxidant for the reduced ruthenium sites and as a reductant for the over-oxidized sites. Recently, Marnellos et al.

☆ IICT Communication No. 060511.

* Corresponding author. Tel.: +91 40 2719 3163; fax: +91 40 2716 0921.
E-mail address: saiprasad@iict.res.in (P.S. Sai Prasad).

1566-7367/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.catcom.2006.11.039

[19] have studied the effect of metal loading and pretreatment procedure over Ru/Al_2O_3 catalysts and proposed a reaction mechanism in the presence of poisonous gas like SO_2. In the present investigation, an attempt has been made to study the influence of method of preparation of Ru/Al_2O_3 catalysts by adopting the impregnation and deposition precipitation methods. By means of DRIFTS spectra of CO adsorbed on the catalysts, the nature of active species has been identified. The enhancement in the decomposition activity is explained in terms of the difference in the nature of active species formed on the surface of the catalysts.

2. Experimental

2.1. Catalyst preparation

Two different sets of catalysts were synthesized. The first set, comprising three catalysts with 1, 3 and 5 wt% Ru loading, was prepared by conventional impregnation of Al_2O_3 (Harshaw Al-39996 R, crushed and sieved to 18/25 BSS mesh) with the aqueous solutions of $RuCl_3$ (Aldrich, Analar grade) of required concentrations adopting the wet impregnation method. The second set (with 1 and 3 wt% Ru) was prepared by the deposition–precipitation method. Typically the support γ-Al_2O_3 was first dispersed in an aqueous solution of $RuCl_3$. A quantity of 1 M Na_2CO_3 was slowly added to the $RuCl_3$ solution until the pH value of the mixture reached 10.5. The suspension was then maintained at the same pH for 1 h during the precipitation process. The resulting solid was washed with deionized water several times until no chloride ion was detected by silver nitrate solution. All the catalysts were evaporated to dryness on a water bath and dried at 120°C (12 h) in air. Finally they were calcined at 500 °C for 5 h in air. The catalysts were designated as DP and IMP, where the former refers to deposition–precipitation and the latter to impregnation method, respectively. The extent of metal loading is represented by the number that follows the above abbreviation, as for example, IMP 1 represents the catalyst prepared by the impregnation method and contains 1 wt% Ru on the surface of alumina.

2.2. Characterizations

The specific surface areas of the catalyst samples were estimated using the N_2 adsorption at −196 °C by the single-point BET method, using a Micromeritics Plus Chemisorb 2700 instrument. Before measurements, the samples were oven-dried at 393 K for 12 h and flushed in situ with He gas for 2 h. X-ray powder diffraction patterns were obtained with a Siemens D5000 diffractometer, using Cu Kα radiation (1.5406 Å). The measurements were recorded in steps of 0.045° with a count time of 0.5 s in the 2Θ range of 2–80°. Identification of the phases was made with the help of the JCPDS files. Temperature-programmed reduction of the catalysts was carried out in a flow of 10% H_2/Ar gas mixture at a rate of 30 ml/min with a temperature ramp of 10 °C/min. Before the TPR run, the catalysts were pretreated with argon at 300 °C for 2 h. The hydrogen consumption was monitored using a thermal conductivity detector. DRIFTS experiments were performed with an Excalibur Series, Digilab, USA, IR spectrometer equipped with an MCT detector and a high-pressure, high-temperature DRIFTS cell (Harrick) fitted with KBr windows allowing to record spectra at different temperatures under controlled atmosphere. The cell was connected to a flow reaction system at atmospheric pressure. The temperature was monitored through a thermocouple in direct contact with the sample. Spectra were acquired at a resolution of $2\ cm^{-1}$, typically averaging 100 scans. The samples were initially flushed with helium and then were activated at 400 °C at a ramping rate of 10 °C/min in flowing 10% H_2 balanced by argon gas mixture. After 1 h, the sample was flushed and cooled to room temperature in the flow of helium. The sample was then allowed to adsorb CO by flowing a gas mixture containing 1% CO balanced by helium at a total flow rate of 30 ml/min for 1 h. The spectrum of adsorbed CO was obtained by the difference between the absorbance of the sample before and after adsorption of CO.

2.3. Activity measurements

The catalytic decomposition of N_2O was carried out in a fixed-bed reactor. A fresh catalyst ($\approx$0.5 g), diluted with the same size and amount of quartz powder, was loaded in the reactor for each run. Prior to catalyst testing, the catalysts were pretreated at 400 °C for 1 h in a flow of hydrogen (10% H_2 in helium mixture) to activate and stabilize the catalysts. The flow rate of high purity N_2O (5000 ppm in He) gas was measured by a mass flow controller (Aalborg, USA). The total flow rate used for each run was 60 ml min^{-1} (yielding a space velocity of 7200 h^{-1}). After the catalyst had attained steady-state over a period of 2 h at each temperature, the effluent gas was analyzed by a micro gas chromatograph (Varian CP-4900 TCD) using a Molecular Sieve 5A column (for the analysis of O_2, N_2) and a Poraplot column (for that of N_2O).

3. Results and discussion

The XRD patterns of the air calcined catalysts are shown in Fig. 1. The major diffraction peaks indicate the presence of γ-Al_2O_3 (JCPDS file no. 10-0425) predominant in these catalysts with peaks at 2θ: 36.5°, 46°, 62°, and 67°. Spectral characteristics of RuO_2 phase are also observed (JCPDS file no. 40-1290) [17]. The intensity of RuO_2 peak is very low in the case of 1 wt% Ru catalysts. By increasing the metal content to 3 and 5 wt%, an increase in intensity of the peaks is observed.

BET surface areas of IMP 1, IMP 3 and IMP 5 catalysts are recorded as 174, 165 and 159 m^2/g, respectively; whereas DP 1 and DP 3 catalysts have displayed 143 and