ELSEVIER
Catalysis Today 68 (2001) 237–244
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Catalytic decomposition and reduction of N_2O on Ru/MCM-41 catalyst

S. Kawi*, S.Y. Liu, S.-C. Shen

Department of Chemical and Environmental Engineering, National University of Singapore,
10 Kent Ridge Crescent, Singapore 119260, Singapore

Abstract

Three different types of Ru/MCM-41 catalysts were prepared by impregnating MCM-41, which had a high surface area of $1200\,m^2\,g^{-1}$ and a very uniform mesoporous size of 27 Å, with $RuCl_3$ or $Ru(OH)_3$ or $Ru_3(CO)_{12}$. The catalysts were characterized by surface area and pore size distribution. The state of Ru and its dispersion on MCM-41 surface was studied by XPS and chemisorption, respectively. The conversion of nitrous oxide to nitrogen and oxygen, by catalytic decomposition and reduction reactions, was studied using the synthesized Ru/MCM-41 catalysts. The effects of the amount of Ru loading, the type of Ru precursor, catalyst pore size, as well as the presence of oxygen, carbon monoxide, and moisture in the feed stream on the catalyst activities for the catalytic decomposition and reduction of N_2O were investigated. The results show that the Ru/MCM-41 catalyst prepared from $Ru(OH)_3$ as the catalyst precursor and having a 5 wt.% Ru loading is promising for the catalytic decomposition and reduction of N_2O. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: N_2O decomposition; Catalyst; MCM-41; Ruthenum

---

1. Introduction

Nitrous oxide has been considered as an environmental pollutant because it is a relatively strong greenhouse effect gas and it can cause the destruction of ozone in the stratosphere. It is mainly produced in some chemical processes, such as nylon manufacturing process. It is also produced in the catalytic deNO$_x$ process as N_2O was found to be the main by-product when Pt-based catalysts were used [1–3]. Catalytic approaches to decompose nitrous oxide could be an effective way to protect our environment. A large number of catalysts such as metal oxides, mixed oxides, perovskite-type oxides, hydrotalcites, and transition metal exchanged zeolites are known to be capable of catalytically decomposing N_2O to its elements at elevated temperatures [4–10]. However, most of these previous reports paid attention to the mechanistic understanding and kinetics of the decomposition rather than the N_2O conversion levels.

The disadvantages of metal oxides and mixed metal oxides as catalysts are mainly due to their very low surface areas. For example, on ZSM-5, which is the most widely used zeolite, Rh and Ru were reported to be the most active metals; the order of the catalyst activity was as follows: Rh, Ru > Pd > Cu > Fe > Pt > Ni > Mn [4]. For each supported metallic species on ZSM-5, the catalyst activity depended on the metal loading dramatically [11]. However, the exchange capacity of metal in the pores of ZSM-5 is

---

* Corresponding author. Tel.: +65-8746312; fax: +65-7791936.
E-mail address: chekawis@nus.edu.sg (S. Kawi).

PII: S0920-5861(01)00283-8

not high, hence limiting the application of ZSM-5 as the support for the metallic component.

For a practical application, catalyst supports having high surface area are more attractive because the active catalyst component could be highly dispersed on their surface. MCM-41, which is a family of mesoporous material, possesses some unique properties, such as: very high surface area (above $1000\,\mathrm{m^2\,g^{-1}}$), uniform pore size (tunable from 20 to 100 Å) [12,13] and relatively hydrophobic nature. The novel properties of MCM-41 are believed to be useful to increase not only the loading of transition metal in the pores as high as possible, but also with good dispersion so that the reactor volume required to achieve complete N_2O conversion can be as small as possible. The advantages of a small reactor are its low capital cost and its low operating cost as it could minimize the energy consumption during operation. This paper reports the results of the effects of Ru precursors, the amount of Ru loading on MCM-41, impregnation method, the presence of oxygen and carbon monoxide and moisture in the feed stream on the catalytic performance of the catalyst for N_2O conversion by catalytic decomposition and reduction.

2. Experimental

2.1. Preparation of MCM-41

MCM-41 was prepared according to the synthesis method reported by Beck et al. [13]. The synthesis of MCM-41 was carried out as follows: 4.9 g of $NaAlO_2$ was dissolved in 38 ml of water with stirring. To this solution, 94 g of tetraethylammonium hydroxide solution (20%), which was prepared by the ion-exchange of cetyltrimethylammonium bromide with the OH form of Amberlite® IRA-400 ion-exchange resin, was added and stirred for 5 min, followed by the addition of 96 g of colloidal silica (40%). A 210 g of cetyltrimethylammonium hydroxide solution was added to the resulting mixture. The resulting gel was stirred for 45 min before it was transferred to teflon-lined autoclaves. The crystallization was carried out by heating the autoclaves at 100°C for 2 days. The solid sample was recovered by filtration, thorough washing with deionized water and drying at 80°C overnight. The sample was then calcined in air at 580°C for 12 h at a rate of $1^\circ\mathrm{C\,min^{-1}}$. The ratio of Si/Al was calculated to be 10:1.

2.2. Impregnation of MCM-4 with Ru

Ru was supported onto MCM-41 materials by three different routes, as follows. In the first route, 1 g of calcined MCM-41 was added to a 2.5 ml solution of $RuCl_3$. The mixture was then stirred overnight to allow $RuCl_3$ transport into the pores of MCM-41. Water was then removed under vacuum at room temperature. The sample was dried at 80°C and subsequently calcined in air at 600°C for 8 h using a ramping rate of $1^\circ\mathrm{C\,min^{-1}}$.

In the second route, 1 g of calcined MCM-41 was added to a 2.5 ml solution of $RuCl_3$, and the mixture was stirred overnight to allow $RuCl_3$ transport into the pores of MCM-41. 1 ml of NaOH solution was then added to the mixture under stirring, causing $RuCl_3$ to react with NaOH to form $Ru(OH)_3$, which was precipitated out onto the pore surface of MCM-41. The amount of NaOH was adjusted to a molar ratio of $OH^-/Cl^- = 1{:}1$. The solid sample was recovered by filtration, washed with deionized water to remove all the chloride, dried at 80°C, and then calcined in air at 600°C for 8 h using a ramping rate of $1^\circ\mathrm{C\,min^{-1}}$.

In the third route, 1 g of MCM-41 was mixed with a dichloromethane solution of $Ru_3(CO)_{12}$. The mixture was stirred overnight to allow $Ru_3(CO)_{12}$ diffuse into the pores of MCM-41. The solvent was then removed by vacuum. The solid sample was dried and calcined in air at 500°C for 8 h using a ramping rate of $1^\circ\mathrm{C\,min^{-1}}$.

2.3. Impregnation of ZSM-5 with Ru

A 1 g of commercially available ZSM-5 was added to a 2.5 ml solution of $RuCl_3$ under stirring, and the mixture was stirred overnight to allow $RuCl_3$ transport into the pores of ZSM-5. NaOH solution (1 ml) (molar ratio of $OH^-/Cl^- = 1{:}1$) was then added to the mixture under stirring to allow the reaction between Ru^{3+} and OH^- take place, forming the $Ru(OH)_3$ precipitate onto the pore surface of ZSM-5. The solid sample was recovered by filtration, washed with deionized water to remove all the chloride, dried at 80°C, and then calcined in air at 600°C for 8 h using a ramping rate of $1^\circ\mathrm{C\,min^{-1}}$.

2.4. Catalyst characterization

2.4.1. BET measurement

The support MCM-41 material and the Ru-impregnated MCM-41 were characterized by surface area measurement and pore size distribution determination. The N_2 adsorption/desorption data were collected on a NOVA-1000 gas sorption analyzer (Quantachrome Corp.) using a continuous procedure at 77 K.

2.4.2. H_2 chemisorption

AutoSorb-1-C (Quantachrome) was used to measure the Ru dispersion of 5 wt.% Ru/MCM-41 by H_2 chemisorption at 30°C. Prior to analysis, the sample was reduced in H_2 at 500°C for 45 min. Based on the H_2 adsorption isotherm and extrapolation to $P = 0$, the mono-layer chemisorbed volume V_m was obtained. The Pt dispersions were calculated from V_m by assuming Pt_s:H_2 = 2:1.

2.4.3. XPS determination

The status of surface ruthenum species on MCM-41 was characterized by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS analytical instrument. An Mg Kα X-ray source ($h\nu = 1253.6$ eV) with an analyzer pass energy of 80 eV was operated at 10 mA and 15 kV. The pressure in the XPS analysis chamber was less than 10^{-9} Torr.

2.5. Catalyst testing

To minimize pressure drop, the catalyst was pelletized, crushed and sieved and the particles having mesh No. 40–60 were used for the reaction test. Catalyst (0.2 g) was loaded in the reactor for each run. Prior to the catalyst testing, the catalysts were pretreated at 400°C for 90 min in a flow of oxygen (25% in He) to activate and stabilize the catalysts.

The catalytic conversion of N_2O (by catalytic decomposition or reduction reaction) was carried out in a fixed-bed microreactor. The flow rates of high purity gases, such as N_2O (10 vol.% in He), He (99.999%), O_2 (99.995%), and CO (99.95%) were measured by four mass flow controllers (Gossen 5875). The total flow rate used for each run was 27 ml min^{-1} (yielding a space velocity of 4,000 h^{-1}). The typical N_2O feed composition used for each reaction was 10 vol.% N_2O balanced by He. The catalytic decomposition and catalytic reduction of N_2O was carried out in the absence and presence of CO, respectively.

The gas mixture before and after reaction was analyzed online by an HP6890 gas chromatograph using a thermal conductivity detector. The column used for separation was Porapak Q (4 m long and a diameter of 1/8 in.). The GC oven temperature was set at 80°C. Helium was used as the carrier gas with a flow rate of 25 ml min^{-1}.

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows that MCM-41 has a surface area of 1,200 m^2 g^{-1} and a pore size of about 27 Å, which are similar to those reported in the literature [12,13]. After impregnation with Ru, the surface areas of the resulting materials drop to about 560–900 m^2 g^{-1}, depending on the type of Ru precursor and Ru loading. Generally, the catalyst having higher Ru loading has lower surface areas and those prepared from $Ru(OH)_3$ has higher surface area than those prepared from $RuCl_3$. It should be noted that the calcination treatment of MCM-41 in air at 600°C did not cause any significant reduction of surface area and pore size under the conditions studied.

The pore size of Ru/MCM-41 prepared from $RuCl_3$ was smaller than 16 Å. It was found that Ru/MCM-41 prepared from $RuCl_3$ always had smaller pore size and these smaller pore size seemed not to depend on Ru loading, as even 0.5 wt.% Ru loading had already

Table 1
Physical properties of Ru-MCM-41 prepared from $Ru(OH)_3$ and from $RuCl_3$[a]

Sample	Ru loading (wt.%)	Surface area (m^2 g^{-1})	Pore diameter (Å)
Ru-MCM-41			
	0	1240	27
	0.5	900 (760)	25 (<16)
	1.5	825 (740)	23 (<16)
	5.0	815 (705)	19 (<16)
	10.0	781 (560)	<16 (<16)

[a] Values in parenthesis are for Ru/MCM-41 samples prepared from $RuCl_3$.

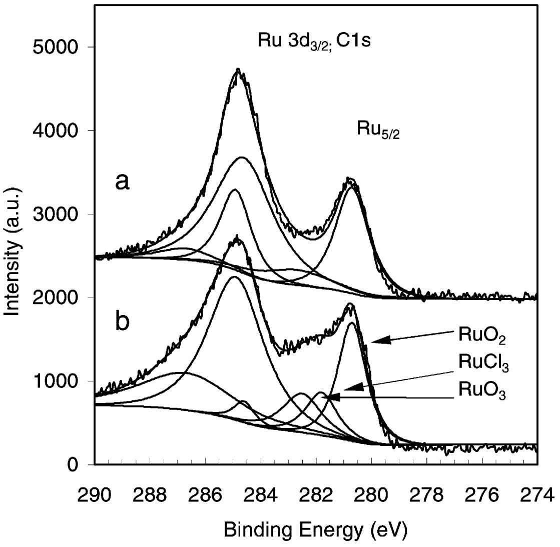

Fig. 1. XPS spectra of Ru/MCM-41 catalysts with 5 wt.% Ru loading: (a) prepared from $Ru(OH)_3$; (b) prepared from $RuCl_3$.

caused the pore size to be smaller than 16 Å. On the other hand, using $Ru(OH)_3$ as the precursor, the resulting Ru-MCM-41 had relatively larger pore size. For example, with a 0.5 wt.% Ru loading, the pore size of Ru/MCM-41 prepared from $Ru(OH)_3$ was 23 Å, which was larger than those sample prepared from $RuCl_3$ (<16 Å). In terms of the resulting surface area and pore size, it can be concluded that $Ru(OH)_3$ is a better precursor for impregnation than $RuCl_3$.

The status of surface ruthenium species on MCM-41 was characterized by XPS. The binding energies of Ru_{3d} for Ru species are 280.1 eV for Ru metal, 281.8 eV for $RuCl_3$, 280.7 eV for RuO_2, and 282.5 eV for RuO_3. Fig. 1 shows that RuO_2 and RuO_3 species exist on the surface of MCM-41 for the catalysts prepared from both $RuCl_3$ and $Ru(OH)_3$ precursors. Curve-fittings using a combination of RuO_2 and RuO_3 also give satisfactory results for the catalyst prepared from $Ru(OH)_3$. However, for the catalyst prepared from $RuCl_3$, the curve-fitting with only RuO_2 and RuO_3 has a large deviation between 280.7 and 282.5 eV. Therefore, one more Ru species, i.e. $RuCl_3$ (which has a binding energy at 281.8 eV) is suggested to be present on the catalyst surface. An optimally fitted curve could be obtained by fitting against the Ru_{3d} spectrum using a combination of RuO_2 and RuO_3 oxides and $RuCl_3$. The result indicates that $RuCl_3$ could not be fully decomposed and oxidized by calcination under air after calcination at 580°C. Similarly, it has been reported that chloride-bonded Ru species existed on the catalyst surface after calcination below 600°C due to the incomplete decomposition of $RuCl_3$ [14].

3.2. Effect of Ru loading on catalyst activity

Using the unsupported MCM-41 as the catalyst, N_2O decomposition reaction was carried out at temperatures between 200 and 500°C. Fig. 2 shows the N_2O conversion results. It is clear that its catalytic activity is very low even at high temperature (e.g. 500°C), showing that MCM-41 is not active in the decomposition of N_2O. As it has been reported in the literature that the catalytic activity of Ru/ZSM-5 increased with the increase in the Ru loading [11], Ru loading was varied in this study from 0.5 to 10 wt.%.

Fig. 2 also shows that N_2O could be substantially decomposed in the presence of Ru on MCM-41 and the conversion level for the decomposition of N_2O increased with the increase of the reaction temperature. As shown in Figs. 2 and 3, for the Ru/MCM-41 catalysts prepared either from $Ru(OH)_3$ or $RuCl_3$, the catalyst activity increased as the Ru loading increased from 0.5 to 5.0 wt.% and then decreased as the Ru loading increased from 5.0 to 10.0 wt.%. The result shows that there is a maximum Ru loading (around 5.0 wt.%) on Ru/MCM-41 catalysts for the maximum

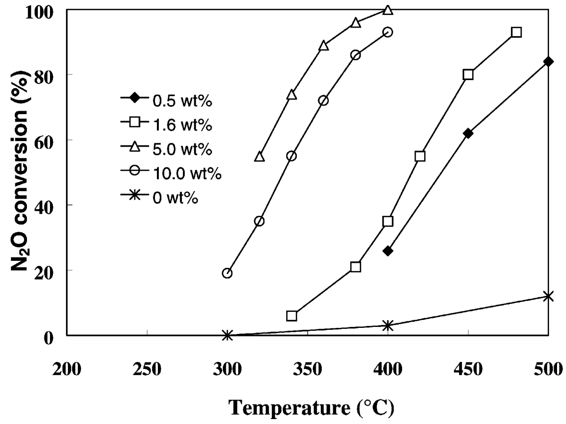

Fig. 2. Effect of Ru loading on the conversion of N_2O decomposition on Ru/MCM-41 catalysts prepared from $Ru(OH)_3$.

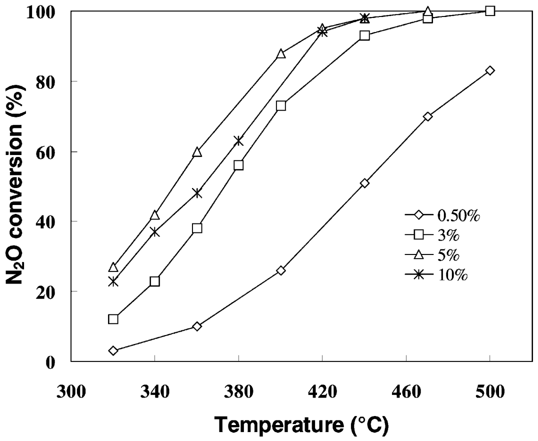

Fig. 3. Effect of Ru loading on the conversion of N_2O decomposition on Ru/MCM-41 catalysts prepared from $RuCl_3$.

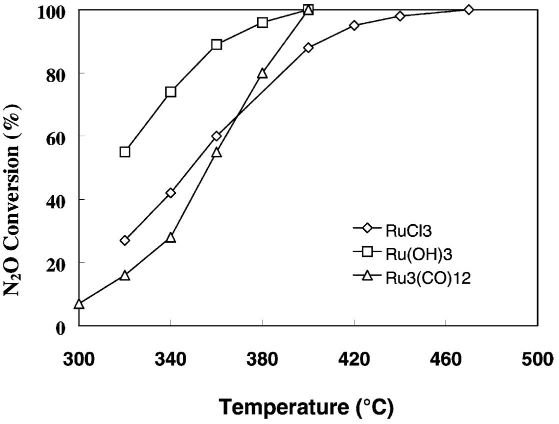

Fig. 4. Effect of Ru precursor on the catalytic activity of N_2O decomposition on Ru/MCM-41 (Ru loading: 5 wt.%).

conversion of N_2O. This result is not surprising as overloading of metallic species on the catalyst support generally causes the aggregation of the metal into bigger particles, which may then block the openings of the pores and affect the mass transport of reactants to the catalytic sites inside the pores. The possible blockage of Ru particles in the pores of MCM-41 at high Ru loading is evidenced by the significant reduction of the pore size and surface area of the resulting Ru-impregnated MCM-41. Similar observation has also been reported by Cui et al. [15] for Ni, Mo-supported MCM-41. It is worthwhile to note that the most effective Rh loading in Rh/ZnO catalyst for N_2O decomposition [5] has been reported to be around 0.5 wt.%, which is much lower compared to Ru-MCM-41 due to the very low surface area of ZnO.

3.3. Effect of Ru precursors on catalyst activity

To see more clearly about the effect of Ru precursors on the decomposition of N_2O, the activities of 5.0 wt.% Ru/MCM-41 catalysts prepared from different Ru precursors are plotted and compared in Fig. 4. It can be seen that the catalytic activity of the catalyst prepared from $Ru(OH)_3$ is much higher than that prepared from $RuCl_3$. This may be explained by the effect of the different surface area and pore volume of the catalysts prepared from different precursors. As shown in Table 1, Ru/MCM-41 prepared from $Ru(OH)_3$ always has higher surface area and pore volume than that prepared from $RuCl_3$, indicating that the dispersion of Ru prepared from $Ru(OH)_3$ was better than that prepared from $RuCl_3$. This is confirmed by H_2 chemisorption results. Under the same Ru loading (5.0 wt.% loading), the Ru/MCM-41 catalyst prepared from $Ru(OH)_3$ has a Ru dispersion of 8.4%, which is higher than that prepared from $RuCl_3$ which has a Ru dispersion of 6.7%. Similar observation has been reported that Fe_2O_3 could be better dispersed on γ-Al_2O_3 than $FeCl_3$ [16,17]. Another reason why $Ru(OH)_3$ is a better precursor than $RuCl_3$ for the preparation of Ru/MCM-41 catalyst for N_2O decomposition is probably due to the presence of traces of chlorine, which might be catalyst poison, on the catalyst prepared from $RuCl_3$. The poisoning effect of the residual Cl in Rh/NaY catalyst has been reported by Yuzaki et al. for N_2O decomposition reaction [18].

At temperatures lower than 400°C, the activity of the catalyst prepared from $Ru_3(CO)_{12}$ was lower than that prepared from $Ru(OH)_3$; however, both catalysts achieved a 100% conversion of N_2O at 400°C. Comparing with Ru/MCM-41 catalysts prepared from $RuCl_3$ and $Ru(OH)_3$, the Ru/MCM-41 catalyst prepared from $Ru_3(CO)_{12}$ had a steeper conversion versus temperature curve, indicating that the activation energy of the catalyst prepared from $Ru_3(CO)_{12}$ was higher than the other two catalysts. All these results show that impregnation of $Ru(OH)_3$ as the Ru precursor on MCM-41 provides a Ru/MCM-41 catalyst having the highest activity for N_2O decomposition.

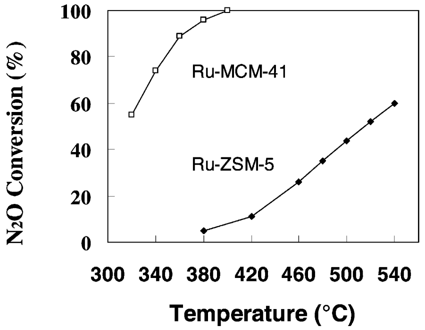

Fig. 5. Comparison of the activities between Ru/MCM-41 and Ru/ZSM-5 catalyst for N_2O decomposition (Ru loading for both catalysts: 5 wt.%).

3.4. *Effect of pore size on catalyst activity*

Fig. 5 shows a comparison of the catalyst activity for N_2O decomposition between Ru/MCM-41 and Ru/ZSM-5, with both catalysts prepared from $Ru(OH)_3$ as the Ru precursor and having 5.0 wt.% of Ru loading. It can be clearly seen that Ru/MCM-41 has much higher activity for N_2O decomposition than Ru/ZSM-5 throughout the whole range of reaction temperatures. This result may be explained by the fact that ZSM-5 has much smaller pores. Upon high loading of Ru onto ZSM-5, most of the pores have probably been filled with Ru oxide particles. Hence, under the same Ru loading, the number of catalytic sites available on Ru/ZSM-5 for N_2O decomposition is much less than that on Ru/MCM-41. Similarly, Satsuma et al. [19] found that N_2O decomposition was a structure-sensitive reaction as there was a strong dependence of the initial and steady state activities on the catalyst surface area; the steady state reaction rate per surface area increased linearly with the surface area. In this study, the specific surface area of Ru/MCM-41 is much higher than that of Ru/ZSM-5, thus contributing to the better activity of Ru/MCM-41 for N_2O decomposition.

3.5. *Effect of moisture on catalyst activity*

Qi et al. [6] reported that the presence of water in the feed stream significantly decreased the activity of ZSM-5 supported catalysts for N_2O decomposition. This inhibiting effect of water was attributed to the blockage of zeolite cages by water molecules, thus reducing the number of active sites to only those on the surface of the zeolites. As moisture always exists in the gas stream containing N_2O, it is important to study the effect of moisture on the catalyst activity of Ru/MCM-41 system for N_2O decomposition. In this study, water was introduced into the feed stream by passing the feed stream of N_2O (10% in He) through a water bubbler. The concentration of water in the feed stream was adjusted to be around 3 vol.%. The feed composition used in our study for the effect of moisture on the catalyst activity was as follows: H_2O = 3 vol.%, N_2O = 10 vol.% and He = 86 vol.%. Fig. 6 shows that there was some small effect of water vapor on the decomposition of N_2O on Ru/MCM-41 catalysts. Generally, the effect of moisture was generally less on Ru/MCM-41 catalyst prepared from $Ru(OH)_3$ than that prepared from $Ru_3(CO)_{12}$; the difference between the activities of these two catalysts in the presence of moisture became clearer at higher reaction temperatures. The present data are not enough to elucidate the effect of moisture on the decomposition of N_2O on Ru/MCM-41. However, it is believed that water molecules are unlikely to block the channels of MCM-41 as MCM-41 has much larger pore size and is relatively more hydrophobic than ZSM-5 [20,21]. The slight inhibition effect of water on the decomposition of N_2O on Ru/MCM-41 indicates that there might be some competitive adsorption between water and N_2O molecules on the same catalytic sites. This

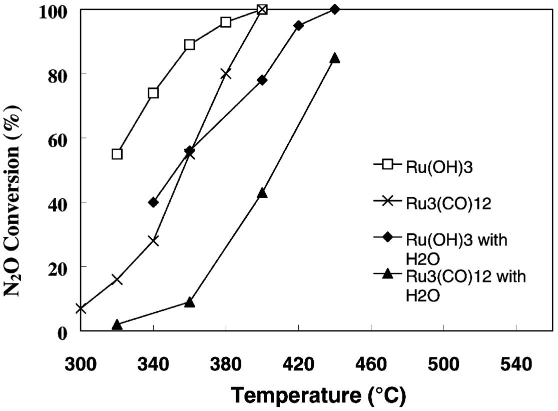

Fig. 6. Effect of water in the feed stream on the activity of Ru/MCM-41 for N_2O decomposition (H_2O concentration in the feed stream: 3 vol.%).

competitive adsorption between water vapor and reactants has been extensively studied by Kim et al. [22].

3.6. Effect of oxygen in the feed stream on catalyst activity

Oxygen has been reported to be inhibiting the decomposition of N_2O [23]. Although Ru, especially Ru-exchanged ZSM-5, was found to be very active in the decomposition of N_2O, however it has been found that there was a strong inhibition in the decomposition of N_2O using Ru-supported catalyst system operating in a feed stream containing a high concentration of oxygen (around 5 vol.%), especially at low temperature region [24]. In order to find the effect of oxygen on the decomposition of N_2O on Ru/MCM-41, the catalyst was tested in a feed stream containing 4 vol.% of oxygen. The ratio of N_2O/O_2 was adjusted to be 2.5/1. The feed composition used in our study on the effect of oxygen on the catalyst activity was as follows: $N_2O = 10$ vol.%, $O_2 = 4$ vol.% and He = 86 vol.%.

Fig. 7 shows the results of the catalytic activity of Ru/MCM-41 for the decomposition of N_2O in the presence of O_2. It is clear that, using Ru/MCM-41 catalyst system, the inhibition of oxygen was much lower than those reported in the literature (about 30% lower). Hence, in term of practical application in the presence of oxygen, Ru/MCM-41 catalyst has an advantage over the other Ru-supported catalysts.

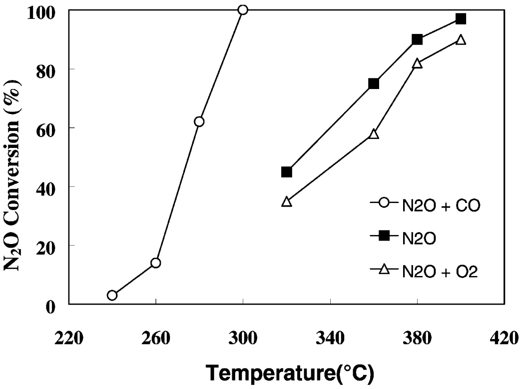

Fig. 7. Effect of O_2 and CO in the feed stream on the decomposition of N_2O on Ru/MCM-41 catalyst (both O_2 and CO concentrations in the feed stream: 4 vol.%).

3.7. Effect of reductant in the feed stream on catalyst activity

According to the generalized reaction mechanism [25], some reductants such as CO, NO, and SO_2 help to remove the surface oxygen species generated during the decomposition of adsorbed N_2O on the surface active site* as follows.

$$N_2O + {}^* \leftrightarrow N_2O^* \tag{1}$$

$$N_2O^* \rightarrow N_2 + O^* \tag{2}$$

$$2O^* \leftrightarrow O_2 + 2^* \tag{3}$$

$$N_2O + O^* \rightarrow N_2 + O_2 + {}^* \tag{4}$$

In this study, CO was added to the feed stream and used as a reductant to investigate the effect of CO on the decomposition of N_2O on Ru/MCM-41 catalysts. The feed composition used in the investigation of the effect of CO on the catalyst activity was: $N_2O =$ 10 vol.%, CO = 4 vol.% and He = 86 vol.%. Fig. 7 shows that CO could considerably enhance the conversion of N_2O on Ru/MCM-41. In fact, a complete conversion of N_2O could be achieved in the presence of CO at 300°C, which is a much lower reaction temperature than those achieved without CO. No excess CO was observed in the exhaust stream of the reaction. The products were CO_2 and N_2, as confirmed by GC-MS analysis, indicating that all of the CO introduced in the feed stream had been oxidized to CO_2. The absence of CO in the exhaust stream is of importance as the slippage of unused CO in the exhaust stream could cause other environmental problems. This result shows that CO, which is present in the system and is itself a pollutant, could be used as a reactant or reductant to decompose N_2O completely at much lower temperatures, hence minimizing the energy consumption and minimizing the release of CO into atmosphere.

4. Conclusions

A series of Ru-MCM41 catalysts were prepared by impregnating different Ru precursors on MCM-41 having a Si/Al ratio of 10:1. It was found that, among these catalysts, Ru/MCM-41 catalyst prepared from $Ru(OH)_3$ was the most active for the catalytic decomposition of N_2O, achieving a complete decomposition of N_2O at 400°C using a loading of 5.0 wt.% Ru. The catalyst activity was enhanced significantly when some CO was introduced into the feed stream, where the complete conversion of N_2O was achieved at 300°C. The presence of moisture and oxygen in the feed stream was found to slightly decrease the catalyst activity, probably due to the competitive adsorption between these species with N_2O on the catalytic sites.

Acknowledgements

This research has been supported by a research grant from the National University of Singapore (RP 3982687).

References

[1] E. Joubert, T. Bertin, J.C. Menezo, J. Barbier, Appl. Catal. B: Environ. 23 (1999) L83.

[2] R. Long, R.T. Yang, Catal. Lett. 52 (1998) 91.

[3] D.K. Captain, K.L. Robert, M.D. Amirdis, Catal. Today 42 (1998) 93.

[4] Y.J. Li, J.N. Armor, Appl. Catal. B 1 (1992) L21.

[5] P. Ciambelli, E. Garufi, R. Pirone, G. Russo, F. Santagata, Appl. Catal. B 8 (1996) 333.

[6] J. Qi, A. Obuchi, G.R. Bamwenda, A. Ogata, H. Yagita, S. Kushiyama, K. Mizuno, Appl. Catal. B 12 (1997) 277.

[7] V. Zholobenkot, Mendeleev Commun. (1993) 67.

[8] H.C. Zeng, J. Lin, W.K. Teo, J.C. Wu, K.L. Tan, J. Mater. Res. 10 (1995) 545.

[9] G.I. Panov, V.I. Sobolev, A.S. Kharitonov, Catal. Sci. Technol. 3 (1991) 171.

[10] S. Sato, R. Takahashi, T. Sodesawa, K. Yuma, Y. Obata, J. Catal. 196 (2000) 195.

[11] Y.-F. Chang, J.G. McCarty, E.D. Wachsman, Appl. Catal. B 6 (1995) 21.

[12] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Besk, Nature 359 (1992) 710.

[13] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.

[14] K.W. Kim, E.H. Leea, J.S. Kimb, K.H. Shinc, K.H. Kimd, Electrochim. Acta 46 (2001) 915.

[15] J. Cui, Y.-H. Yue, Y. Sun, W.-Y. Dong, Z. Gao, Stud. Surf. Sci. Catal. 105 (1997) 687.

[16] Y.C. Xie, X.P. Xu, G.B. Wu, Y.Q. Tang, in: Proceedings of the 4th Chinese Congress on Catalysis, Tianjin 1-E-29, 1988.

[17] T. Yashioka, J. Koezuka, H. Ikoma, J. Catal. 16 (1970) 264.

[18] K. Yuzaki, T. Yarmizu, S.-I. Ito, K. Kunimori, Catal. Lett. 47 (1997) 173.

[19] A. Satsuma, R. Akahori, M. Kato, S. Komai, H. Yoshida, T. Hattori, J. Mol. Catal. A 155 (2000) 81.

[20] C.Y. Chan, H.X. Li, M. Davis, Microporous Mater. 2 (1993) 17.

[21] P.T. Branton, P.G. Hall, M. Treguer, K.S.W. Sing, J. Chem. Soc., Faraday Trans. 91 (1995) 2041.

[22] M.H. Kim, I.-S. Nam, Y.G. Kim, Appl. Catal. B 12 (1997) 125.

[23] A.G. Anshits, E.V. Kondratenko, E.N. Voskresenskaya, L.I. Kurteeva, N.I. Pavlenko, Catal. Today 46 (1998) 211.

[24] K. Li, X.F. Wang, H.C. Zeng, Chem. Eng. Res. Dev. 75 (1997) 807.

[25] J.N. Armor, T.A. Braymer, T.S. Farris, Y. Li, F.P. Petrocelli, E.L. Weist, S. Kannan, C.S. Swamy, Appl. Catal. B 7 (1996) 397.