ELSEVIER

Catalysis Today 29 (1996) 103-107

CATALYSIS TODAY

Selective reduction of nitrogen oxides with various organic substances on precious metal catalysts under a high GHSV condition

A. Obuchi, A. Ogata, H. Takahashi, J. Oi, G.R. Bamwenda, K. Mizuno

Atmospheric Environmental Protection Department, National Institute for Resources and Environment, 16-3 Onogawa, Tsukuba, Ibaraki 305 Japan

---

Abstract

Performances of Pt and Rh catalysts for the selective reduction of NO were investigated using various reducing agents under high gas hourly space velocity (GHSV). Higher activities were attained when olefins were used for both Pt and Rh catalysts, and when oxygen containing substances such as methyl *tert.*-butyl ether (MTBE) were used in the case of Rh catalysts. Selectivity toward N_2 for the NO converted was from 7% to 38% for Pt catalysts and from 45% to 67% for Rh catalysts. A comparison of N_2O decomposition rates on these catalysts has shown that gaseous N_2O is not a principal intermediate in the pathway for N_2 formation. The high selectivity toward N_2 for Rh/Al_2O_3 at low GHSV conditions is attributed to an additional catalytic effect of Al_2O_3, which can reduce NO_2 with propylene at temperatures as low as 350°C.

Keywords: NO_x reduction; Pt catalyst; Rh catalyst; GHSV

---

1. Introduction

Platinum-group metal catalysts have excellent activity and durability for the selective catalytic reduction (SCR) of nitrogen oxides (NO_x) using organic substances at temperatures as low as 200–300°C [1–8]. However, although Pt catalysts have the highest activity at low temperatures, they have a low selectivity toward N_2 while emitting N_2O, which is suspected to be one of the green-house effect and ozone layer destruction gases. Rh catalysts exhibit good selectivity, but more efficiency is needed from an economical point of view. In this study, the effect of the reducing agents on the performance under high GHSV and factors affecting the selectivity toward N_2 were investigated for Pt and Rh catalysts.

2. Experimental

Catalysts made of 0.2 to 6 wt.-% Pt and Rh supported on γ-Al_2O_3 (Sumitomo Chemicals, KHS-24, 60–150 mesh) or silica gel (Davison 950, 80–200 mesh) were prepared by an impregnation method using $H_2PtCl_6 \cdot 6H_2O$ and $RhCl_3 \cdot 3H_2O$ as precursors. The catalysts (10 mg to 2 g) were packed in a quartz glass tube. The internal diameter of the tube was either 4, 8 or 16 mm, depending on the amount of the catalyst used. The catalytic activity was mea-

SSDI 0920-5861(95)00287-1

sured between 200 and 600°C, with a reactant gas composed of NO = 1000 ppm, hydrocarbons = 3000 ppm C, O_2 = 5% in He at a flow rate of 160 ml/min. The effect of the reducing agent was examined using 0.03 g of the catalysts, which corresponds to 190000 h^{-1} in GHSV. Gaseous hydrocarbons were supplied in the form of a standard gas diluted in He (Takachiho Trading). Methanol, ethanol, acetone and MTBE were added in the reactant gas by vaporizing the liquids at 0°C at a determined flow rate of He.

3. Results and discussion

Fig. 1a and Fig. 1b show NO conversion on a 6 wt.-% Pt/Al_2O_3 and a 6 wt.-% Rh/Al_2O_3, respectively, using various reducing agents. In the case of the Pt catalyst, olefins showed higher activities, the NO conversion reaching 57% at 200°C when *iso*-butene was used as the reductant. On the contrary, the efficiencies of paraffins and oxygen-containing substances were poor. Although not shown here, CO also acted as a poor selective reductant. In the latter case, a maximum NO conversion of 7% was attained. In the case of Rh/Al_2O_3, the active temperature range was generally about 50°C higher than that of the Pt catalyst. Not only olefins but also oxygen-containing substances, other than methanol, such as MTBE and acetone, showed higher efficiencies, the NO conversion reaching 46% at 275°C when MTBE was used as the reducing agent. On Rh/Al_2O_3 at temperatures above 300°C, MTBE seems to react with NO after decomposing into *iso*-butene and methanol, since, the temperature dependencies for MTBE and *iso*-butene almost coincide with each other in this temperature region. Also, the efficiency of paraffins was higher compared to that in the case of the Pt catalyst.

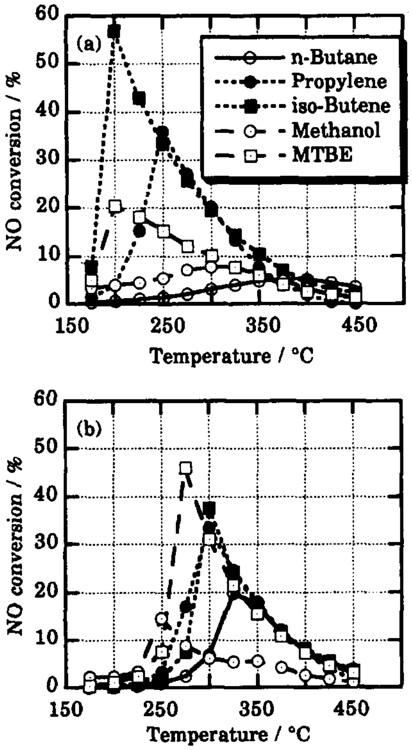

Fig. 1. Effect of the reducing agent on NO conversion over (a) 6 wt.-% Pt/Al_2O_3 and (b) 6 wt.-% Rh/Al_2O_3 catalysts. Catalyst weight = 0.03 g, total flow rate = 160 ml/min, reactant composition: NO = 1000 ppm, O_2 = 5% and hydrocarbons = 3000 ppm C in He.

Table 1
Selectivity to N_2 at maximum NO conversion

Reductant	Catalyst	
	6 wt.-% Pt/Al_2O_3	6 wt.-% Rh/Al_2O_3
Propane	38 [a] (375)	45 (325)
n-Butane	37 (400)	46 (325)
iso-Butane	– (350)	46 (325)
Ethylene	25 (250)	50 (325)
Propylene	28 (250)	59 (300)
1-Butene	32 (250)	65 (300)
iso-Butene	24 (200)	67 (300)
Methanol	7 (325)	56 (250)
Ethanol	19 (200)	60 (300)
Acetone	18 (350)	58 (300)
MTBE	24 (200)	64 (275)

[a] Percentage of N_2 produced relative to NO converted.
Numbers in the parenthesis indicate the temperature (°C) at maximum NO conversion.

Table 1 shows the selectivity toward N_2 at maximum NO conversion temperatures. The rest of NO was mostly converted to N_2O. The selectivity on Pt/Al_2O_3 was generally very low, ranging from 7 to 38%. In the case of Rh/Al_2O_3, the selectivity ranged from 45 to

67% and was relatively poor compared with that under low GHSV (ca. 90% at 5700 h^{-1}) [1].

From the chemistry point of view, it may be assumed that in the SCR process N_2O is an intermediate toward N_2. Fig. 2 shows the temperature dependence of N_2O conversion on the same catalysts as in Fig. 1. In the case of Pt/Al_2O_3 (Fig. 2a), N_2O conversion was negligible in the presence or absence of propylene, in the examined temperature range. Rh/Al_2O_3 had much higher activity for N_2O conversion to N_2, nonetheless this conversion was lower than 25% below 325°C, and much lower than any value of the selectivity for the Rh catalyst listed in Table 1. It can thus be concluded that gaseous N_2O is not a major intermediate leading to the formation of N_2 in the SCR process with hydrocarbons, either on Pt/Al_2O_3 or Rh/Al_2O_3. Note that curves (c) and (d) represent N_2O conversion without and with 1.1% water vapor, respectively, in the absence of propylene. Curve (b) presenting N_2O conversion in the presence of propylene lies between curves (c) and (d), suggesting that the N_2O conversion observed in the presence of propylene is actually not through a reduction process but through a direct decomposition process whose rate is somewhat lowered by water vapor produced by the oxidation of propylene.

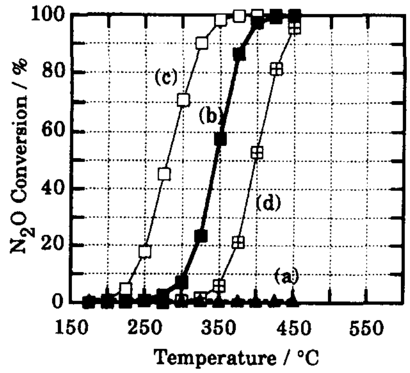

Fig. 2. N_2O conversion over (a) 6 wt.-% Pt/Al_2O_3 and (b), (c), (d) 6 wt.-% Rh/Al_2O_3 catalysts under a high GHSV condition. Catalyst weight = 0.03 g, total flow rate = 160 ml/min, reactant concentration: N_2O = 950 ppm, O_2 = 5%, C_3H_6 = 3000 ppm C, H_2O = 1.1%, in He. Reactant composition: (a), (b) $N_2O+O_2+C_3H_6$; (c) N_2O+O_2; (d) $N_2O+O_2+H_2O$.

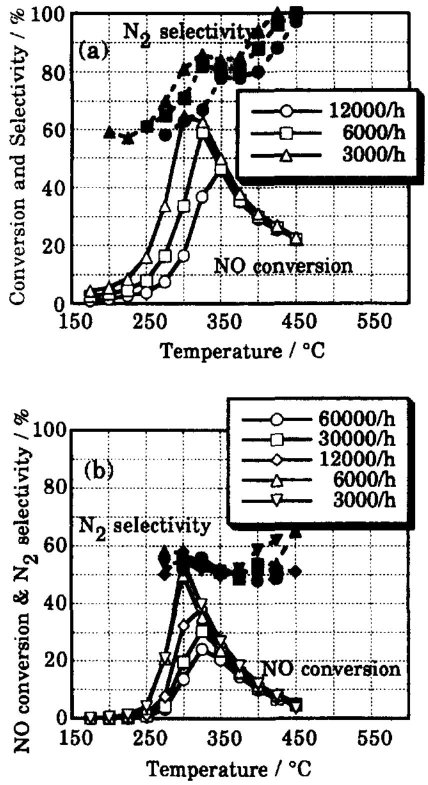

Fig. 3. Effect of the space velocity on NO conversion and selectivity to N_2 in the reaction $NO+C_3H_6+O_2$ over (a) 1 wt.-% Rh/Al_2O_3 and (b) 1 wt.-% Rh/SiO_2, NO = 1000 ppm, C_3H_6 = 3000 ppm C, O_2 = 5%.

Variation of the selectivity toward N_2 was investigated in more detail for Rh catalysts. Fig. 3a and Fig. 3b show the effect of the space velocity (GHSV) on NO conversion and selectivity to N_2 on a 1 wt.-% Rh/Al_2O_3 and Rh/SiO_2, respectively. In the case of Rh/Al_2O_3, the lower the GHSV, the higher the NO conversion and the selectivity to N_2, whereas in the case of Rh/SiO_2, the selectivity was practically constant (50%–60%) as the GHSV was lowered, while NO conversion increased. It should be noted that the selectivity observed here for Rh/SiO_2 almost coincides with that for Rh/Al_2O_3 under much higher GHSV conditions (see Table 1), for Rh catalysts supported on other inert oxides such as ZrO_2, TiO_2 and ZnO, and for pure Rh [9]. These results indicate that Rh has an intrinsic selectivity toward N_2 of around 50%–60% at its maximum activity temperature. In a similar way, Pt seems to have an intrinsic selectivity to N_2 of 20%–40% at its maximum activity temperature. These findings lead us to conclude that the selectivity of Pt and Rh can not be improved so drastically.

The data in Fig. 3a shows that Al_2O_3 seems to play a certain role in improving the selectivity. Fig. 4 shows the catalytic activities of pure Al_2O_3 and SiO_2 for the SCR of NO_2 with propylene. Compared with NO, the NO_2 conversion on Al_2O_3 was remarkably increased, especially at temperatures above 350°C. Also, an excellent selectivity toward N_2 was noted above 375°C. In contrast, SiO_2 had little catalytic activity for this reaction.

Fig. 5 shows the catalytic activities of Pt/Al_2O_3, Rh/Al_2O_3 and Al_2O_3 for the oxidation of NO into NO_2 under the same GHSV conditions as those in Fig. 1. It is clearly shown that part of the NO is oxidized into NO_2 on both Pt/Al_2O_3 and Rh/Al_2O_3 at temperatures above 200 and 300°C, respectively, while Al_2O_3 has negligible activity for this reaction. Consequently, we conclude that the improvement of the selectivity for Rh/Al_2O_3 at lower GHSV conditions results from a successive process of NO oxidation to NO_2 on Rh sites, followed by the SCR of NO_2 with propylene on Al_2O_3.

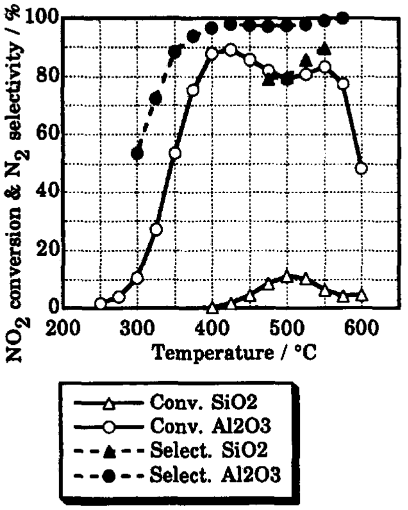

Fig. 4. Selective reduction of NO_2 by C_3H_6 over Al_2O_3 and SiO_2. Catalyst weight: Al_2O_3 = 0.1 g, SiO_2 = 1.0 g, total flow rate = 160 ml/min, reactant: NO_2 = 1000 ppm, C_3H_6 = 3000 ppm C, O_2 = 5% in He.

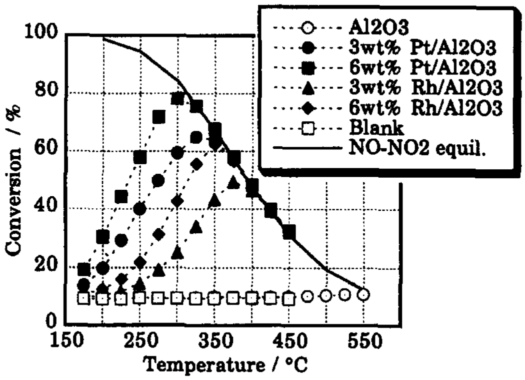

Fig. 5. NO conversion into NO_2 over Pt and Rh catalysts. Reactant: NO = 1000 ppm, O_2 = 5%, catalyst weight = 0.03 g. The GHSV condition is the same as in Fig. 1 (= 190000 h^{-1}).

4. Summary

This study has shown that: (1) under high GHSV (190000 h^{-1}), higher activities were generally attained when olefins were used for both Pt/Al_2O_3 and Rh/Al_2O_3, in addition to oxygen containing substances such as MTBE and acetone for Rh/Al_2O_3, (2) the type of the reducing agent does not affect the selectivity under high GHSV conditions, (3) gaseous N_2O is not a major intermediate for the formation of N_2 and (4) for the improvement of the selectivity, combined use of Rh and a large proportion of Al_2O_3, which catalyzes the SCR of NO_2 formed by the oxidation of NO on Rh, seems to be a promising alternative.

References

[1] A. Obuchi et al., Appl. Catal. B, 2 (1992) 71.
[2] G. Zhang, T. Yamaguchi, H. Kawakami and T. Suzuki, Appl. Catal. B, 1 (1992) L15.

[3] M. Sasaki, H. Hamada, Y. Kintaichi and T. Ito, Catal. Lett., 15 (1992) L15.

[4] H. Hirabayashi, H. Yahiro, N. Mizuno and M. Iwamoto, Chem. Lett., (1992) 2235.

[5] Y. Nishizaka and M. Misono, Chem. Lett., (1993) 1295.

[6] W. Held, A. König, T. Richter and L. Puppe, SAE Paper 900496 (1990).

[7] B.H. Engler, J. Leyrer, E.S. Lox and K. Ostgathe, SAE Paper 930735 (1993).

[8] R. Burch and S. Scire, Appl. Catal. B, 3 (1994) 295.

[9] A. Ogata, A. Obuchi, G.R. Bamwenda, J. Oi and K. Mizuno, Proc. 1st World Congress on Environmental Catalysis, Pisa, 1995, p. 347.