CHEMISTRY LETTERS, pp. 1295-1298, 1993.

Catalytic Reduction of Nitrogen Monoxide by Methane over Palladium-Loaded Zeolites in the Presence of Oxygen

Yukiko NISHIZAKA and Makoto MISONO*
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Palladium ion-exchanged H-ZSM-5 showed a high catalytic activity for the removal of dilute nitrogen monoxide in the presence of methane and oxygen at 350-550 °C. The presence of palladium and (protonic) acidity is essential for the high activity.

Catalytic reduction of nitrogen monoxide by hydrocarbons is a promising measure for the removal of dilute nitrogen monoxide from engine exhausts which contain significant amount of oxygen, and the reaction has recently been studied by many research groups by using various types of hydrocarbons and catalysts.1-4) However, there have been very few studies which utilize methane as the reductant,5-7) although it is desirable in the case of gas engine that the reductant hydrocarbon is methane which is contained in the exhaust gas. The difficulty encountered with methane is that it is the least reactive hydrocarbon. So highly active catalysts are needed for the activation of methane, but those catalysts tend to rapidly combust methane by utilizing oxygen without consuming nitrogen monoxide. So methane is regarded to be a non-selective reductant.8) As for the catalysts, noble metals are rarely useful when methane is used as the reductant. Platinum-doped zeolites were reported to be efficient for the reduction of nitrogen monoxide by propene or ethene at a low temperature region, but a large amount of dinitrogen oxide is produced9-11) and methane has not been reported to be an efficient reductant.

We wish to report here that the combination of palladium and strongly acidic ZSM-type zeolites is efficient for the catalytic reduction of nitrogen monoxide by methane in the presence of oxygen.

H-ZSM-5 was prepared by ion exchange of Na-ZSM-5 in an aqueous solution of ammonium nitrate, followed by calcination at 500 °C for 4 h. Ce-H-ZSM-5 was prepared by ion exchange of H-ZSM-5 in an aqueous solution of cerium acetate. Palladium, platinum and ruthenium ion-exchanged ZSM-5 catalysts were prepared at room temperature by using aqueous solutions of $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ or $Pd(NO_3)_2 \cdot 1.8H_2O$, $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ and $[Ru(NH_3)_6]Cl_3$, respectively. The obtained catalysts were calcined in air at 500 °C for 2 h. Hereafter palladium ion-exchanged H-ZSM-5 and Ce-H-ZSM-5 will be abbreviated as Pd-H-ZSM-5 and Pd-Ce-H-ZSM-5, respectively. The reactions were usually carried out with a flow reactor by passing a gas mixture of 1000 ppm NO, 2% O_2 and 2000 ppm methane in helium at a rate of 150 cm^3 min^{-1} over 0.5 g of catalysts

(GHSV: 9000 h^{-1}). The effluent gases were analyzed by gas chromatography and a NOx meter. The catalytic activity was evaluated by the extent of conversion of NO into N_2.

Typical results are shown in Fig. 1; the conversions of nitrogen monoxide into dinitrogen in Fig. 1a and the conversions of methane to COx in the corresponding experiments in Fig. 1b. The reduction of nitrogen monoxide started to proceed when the oxidation of methane was initiated with increase in the reaction temperature. This is similar to the cases with other hydrocarbons,[1-4] and indicates that the oxidation of hydrocarbons is closely coupled with the reduction of nitrogen monoxide. As shown in Fig. 1a, Pd-H-ZSM-5 and Pd-Ce-H-ZSM-5 were the most efficient, while Pd-Na-ZSM-5 and Na-ZSM-5 were inactive, and H-ZSM-5 was moderately active. The activity of the former two catalysts is of comparable order with Co- and Ga-ZSM-5 reported in the literature,[5,6] if the slight differences in the reaction conditions are considered. Neither Pd nor PdO was detected by XRD for Pd-H-ZSM-5 after use, indicating high dispersion of Pd in ZSM. It was remarkable that the product from nitrogen monoxide was essentially dinitrogen. The highest conversion to dinitrogen oxide was only 7.1% which was observed at 400 °C over Pd-H-ZSM-5 catalyst.

Close comparison of these results demonstrates that the combination of palladium and acidity is essential in the present systems, as explained below. If one looks at Fig. 1b, there were little differences between Pd-H-ZSM-5 and Pd-Na-ZSM-5 and between H-ZSM-5 and Na-ZSM-5 in the catalytic activity for methane oxidation, although the presence of palladium obviously accelerated the methane conversion in accordance with the low-temperature activity of Pd-H-ZSM-5 and Pd-Ce-H-ZSM-5 for the removal of nitrogen monoxide as shown in Fig. 1a. In other words, the activity for methane oxidation does not depend on the acidity of zeolite (H- or Na-type), while the acidity is indispensable for the reduction of nitrogen monoxide by methane, as the activity for its removal was in the order; H-ZSM-5 based catalysts ≫ Na-ZSM-5 based catalysts = 0. Since the oxidation

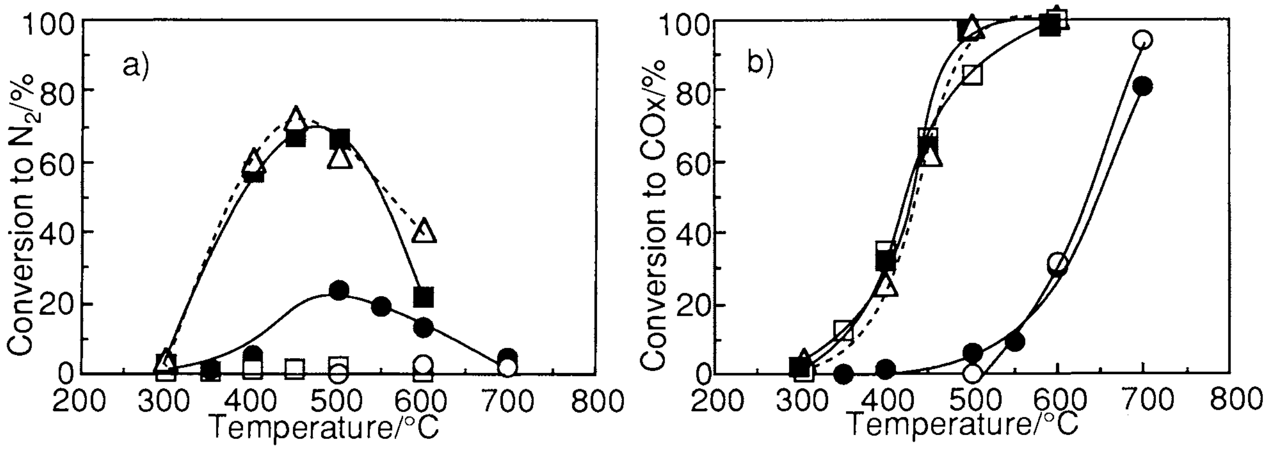

Fig. 1. Reduction of NO by methane over several catalysts as a function of reaction temperature. a) Reduction of NO to N_2. b) Conversion of methane to COx.

○:Na-ZSM-5, □:Pd-Na-ZSM-5, ●:H-ZSM-5, ■:Pd-H-ZSM-5, △(······):Pd-Ce-H-ZSM-5.

NO: 1000 ppm, CH_4: 2000 ppm, catalyst weight: 0.5 g, flow rate: 150 cm^3 min^{-1} (GHSV: 9000 h^{-1}), Pd loaded: 1 wt%.

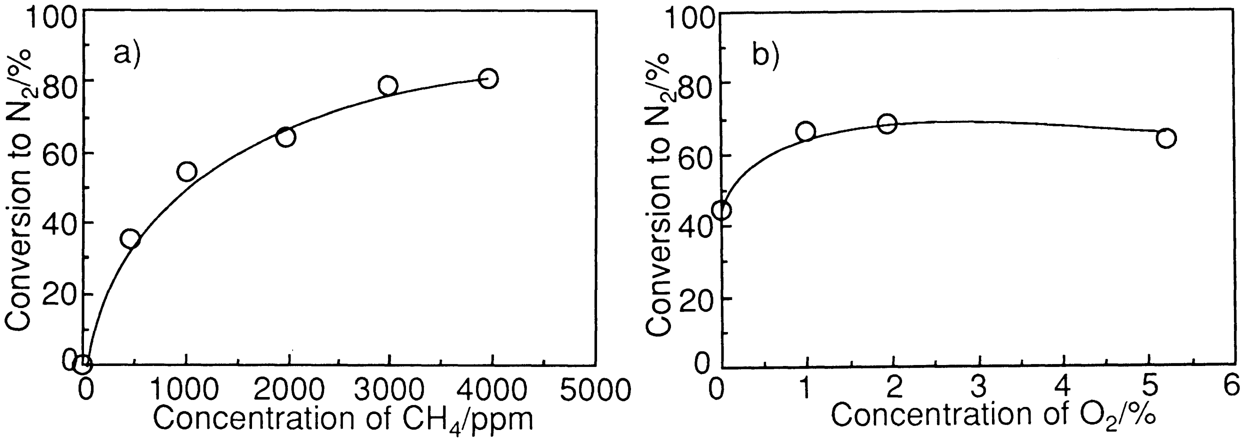

Fig. 2. Pressure dependencies of reduction of NO over Pd-H-ZSM-5 (Pd: 1 wt%) at 450 °C.
a) Dependency on methane. b) Dependency on oxygen. Reaction conditions other than the partial pressures are the same as in Fig. 1.

of methane little differed between the H- and Na-form catalysts (Fig. 1b), the acidity probably plays more important roles in the activation of nitrogen monoxide, although the possible influence on the state of palladium can not be eliminated.

As for the selectivity of hydrocarbon utilization which is defined as in the previous work[4)] by the ratio of the number of NO molecules converted to N_2 to the number of methane molecules converted to COx, Pd-H-ZSM-5 and Pd-Ce-H-ZSM-5 showed high selectivity below 400 °C, but it decreased gradually as the reaction temperature increased. The selectivities at 400 °C were still as high as those observed for $NO-C_3H_6-O_2$ system with Ce-zeolite.[4b)]

The effects of the concentration of methane and oxygen are shown in Fig. 2. The concentration of methane showed apparent reaction order of 0.4. On the other hand, nitrogen monoxide was reduced to a certain extent even in the absence of oxygen in contrast with the other cases[4,6)] and the increase in its concentration had only a small effect at this temperature.

Results with several other catalysts are collected in Table 1. The increase of the Pd loading level enhanced modestly the activity. Pd-H-ZSM-5 was not effective for the reduction by propene under the present reaction conditions, probably due to rapid oxidation of propene. Cu-ZSM-5 which is a good catalyst for the reduction by ethene or propene was a poor catalyst in the case of methane. As for the starting materials of palladium, $Pd(NO_3)_2$ was also effective, but $PdCl_2$ gave poor results probably due to incomplete exchange which may have resulted in poor Pd dispersion. Pd supported on alumina was also a poor catalyst. Pt was not effective as a noble metal component, while Ru showed medium activity. Ce-ZSM-5 prepared from H-ZSM-5 was modestly active.

This work was presented at the 65th National Meeting of the Chemical Society of Japan, March 1993. The authors acknowledge Tosoh Corp. for the kind donation of ZSM-5 sample.

Table 1. Reduction of NO by Methane over Various Catalysts

Catalyst	Loading/wt%	Conversions into N_2 and COx[a] /%				
		300°C	400°C	450°C	500°C	600°C
Pd-H-ZSM-5[b]	0.1	0 (0.2)	7.6 (3.8)	20.1 (9.1)	27.0 (15.0)	20.6 (34.4)
Pd-H-ZSM-5[b]	0.5	1.0 (1.2)	34.0 (13.3)	51.4 (19.6)	57.4 (26.1)	56.7 (78.3)
Pd-H-ZSM-5[b]	1	2.9 (2.3)	57.4 (32.5)	67.1 (64.0)	66.5 (97.5)	21.8 (100)
Pd-H-ZSM-5[c]	1	2.7 (2.1)	57.1 (31.3)	66.0 (83.4)	51.1 (96.9)	25.0 (97.0)
Pd-H-ZSM-5[d]	0.7	0.3 (1.1)	5.0 (22.1)	18.2 (42.2)	34.8 (59.0)	5.6 (98.1)
Pt-H-ZSM-5	1.9	0.9 (0.7)	4.0 (7.1)	10.0 (17.9)	15.1 (41.0)	3.1 (98.0)
Ru-H-ZSM-5	-	0.1 (0.1)	6.9 (4.9)	19.9 (15.4)	30.0 (34.1)	13.9 (87.8)
Cu-ZSM-5	3.9	0.9 (1.0)	4.5 (33.9)	4.3 (71.4)	3.7 (95.8)	3.4 (100)
Pd-Y[e]	1	0 (0)	0 (4.5)	-	0.5 (34.3)	3.2 (73.0)
Pd/Al_2O_3	2.7	2.5(47.9)	1.9 (99.3)	1.5 (100)	1.1 (100)	-
Ce-H-ZSM-5	-	0 (0)	4.5 (3.7)	12.7 (9.8)	23.8 (23.3)	14.4 (72.4)
$NO+C_3H_6+O_2$ reaction						
Pd-H-ZSM-5[b]	1	18.7(21.2)	14.0 (100)	-	1.1 (100)	-

Reaction conditions: NO 1000 ppm, CH_4 or C_3H_6 2000 ppm, O_2 2%, He balance.

Catalyst weight: 0.5 g (GHSV: 9000 h^{-1}).

a) Conversions into COx are given in parentheses. b) Pd from $[Pd(NH_3)_4]Cl_2 \cdot H_2O$. c) Pd from $Pd(NO_3)_2 \cdot 1.8H_2O$. d) Pd from $PdCl_2$. e) Pretreated in an H_2 flow for 2 h, then in an He flow for 2 h at 500 °C.

References

1) M. Iwamoto, H. Yahiro, Y. Yu-u, S. Shundo, and N. Mizuno, *Shokubai*, **32**, 430 (1990); S. Sato, Y. Yu-u, H. Yahiro, N. Mizuno, and M. Iwamoto, *Appl. Catal.*, **70**, L1 (1991).
2) W. Held, A. König, T. Richter, and L. Puppe, SAE Paper 900496 (1990).
3) Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki, and T. Ito, *Catal. Lett.*, **6**, 239 (1990).
4) a) M. Misono and K. Kondo, *Chem. Lett.*, **1991**, 1001; b) C. Yokoyama and M. Misono, *ibid.*, **1992**, 1669.
5) Y. Li and J. N. Armor, *Appl. Catal. B*, **1**, L31 (1992).
6) K. Yogo, M. Ihara, I. Terasaki, and E. Kikuchi, *Chem. Lett.*, **1993**, 229.
7) Y. Kawai, W. Kobayashi, K. Sekizawa, K. Kobayashi, and K. Nomura, 64th National Meeting of the Chemical Society of Japan, Niigata, 1992, 3E303.
8) M. Iwamoto and H. Hamada, *Catal. Today*, **10**, 57 (1991).
9) Japan Patent 1989-135541, 1991-232533 (Toyota Motors).
10) G. Zhang, T. Yamaguchi, H. Kawakami, and T. Suzuki, *Appl. Catal. B*, **1**, L15 (1992).
11) H. Hirabayashi, H. Yahiro, N. Mizuno, and M. Iwamoto, *Chem. Lett.*, **1992**, 2235; 10th Forum on Environmental Catalysis, Tokyo, No. 26, October 1992.

(Received April 23, 1993)