Enhancement of Tolerance to the Humidity by Chemical Vapor Deposition of Silicon Alkoxide on Pd-Mordenite Catalyst in the Reaction of NO, Methane and Oxygen

Masaki Suzuki and Miki Niwa*
Department of Materials Science, Faculty of Engineering, Tottori University, Koyama-cho, Tottori 680

(Received December 11, 1995)

In order to enhance the tolerance of Pd loaded on zeolite catalyst to the humidity, chemical vapor deposition of silicon alkoxide has been studied in the reduction of NO by methane in the presence of oxygen. The suppression of activity by the added water vapor was able to be reduced or almost disregarded by the deposition of silica.

Recently, much attention has been paid to the development of catalyst for NOx reduction using hydrocarbons as reductant. Among them, Cu-ZSM5 has been most extensively studied by many researchers since the independently development by Iwamoto[1] and Held et al.[2] Utilization of methane as a reductant molecule which was available most usually was reported by Kikuchi et al[3] and by Li and Armor[4] using Ga- and Co-ZSM5, respectively. However, these are deactivated during the reaction under the conditions of high temperature and humidity due to the collapse of zeolite structure. Furthermore, the activity is often suppressed by the presence of water vapor. The most important current requirement to the development of NOx removal catalyst is therefore the enhancement of the tolerance against heat and humidity. We will now report the chemical vapor deposition (CVD) of silicon alkoxide to enhance the tolerance of the Pd-mordenite catalyst to the humidity in the reaction of NO, methane and oxygen. The Pd-zeolite catalyst for the reduction of NO using methane was first reported by Misono et al.[5]

The Pd-mordenite catalyst was prepared by an ion exchange method using $Pd[(NH_3)_4]Cl_2$ solution. Decationized mordenite, JRC-Z-HM10 or -HM20, (reference catalyst of Catalysis Society of Japan, silica to alumina molar ratio was *ca.* 10 or 20, respectively) was kept in the solution at 353 K for 24 hrs, followed by thoroughly washing with deionized water. The content of Pd was measured by ICP (inductively coupled plasma) emission spectroscopy, after it was digested by HF solution; the loading of Pd was 0.39 and 0.46 wt% on HM10 and HM20, respectively. Thus prepared catalyst was treated in flowing N_2 at 773 K for 4 h, and used for subsequent experiments. The method of CVD of silicon alkoxide has been described elsewhere.[6] The sample of metal loaded zeolite was used for the CVD without further treatment.

Before the reaction, thus prepared catalyst was treated in flowing He at 773 K for 1 h. 150 ml min^{-1} of mixture of NO, O_2 and methane (NO, 1000 ppm; CH_4, 1000 ppm; O_2, 1%; He, balance) was fed into 0.5 g of the catalyst, and the outlet gas was analyzed by gas chromatography (Hitachi) and NOx meter (Horiba).

Figure 1 shows the change of catalytic activity at the temperature ranges 473 - 823 K not only by the deposition of 2.0 wt % silica but also by the addition of 1.0 mol% water vapor to the reaction system on the unmodified and modified Pd loaded on HM10. As usual, the conversion of NO into N_2 went through a maximum value against the reaction temperature, because the combustion of methane into carbon dioxide occurred preferentially at higher temperatures. On the other hand, the conversion of CH_4 increased gradually with increasing temperature.

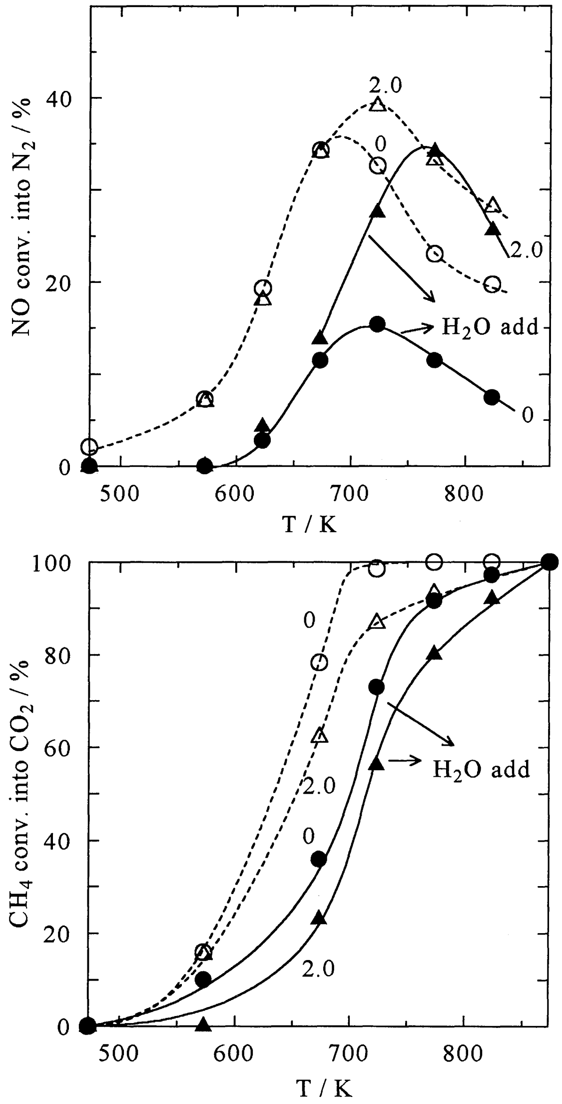

Figure 1. Change of activity by the addition of water vapor on the Pd/mordenite(HM10) unmodified (○●) and 2.0 wt % silica deposited (△ ▲). Open symbol, without the addition of water: closed symbol, with the addition of 1 mol% water.

The deposition of silica on the external surface of the zeolite by CVD changed the activity of Pd/HM10; the conversion of CH_4 was suppressed, while the conversion of NO was enhanced above 700 K. It seemed that the temperature at which the

Table 1. Conversion of NO into N_2/% at 723 K without and with added water [a)]

SiO_2 deposited /wt%	Pd/HM10 H_2O un-added	Pd/HM10 H_2O added	Pd/HM20 H_2O un-added	Pd/HM20 H_2O added
0	32.6	15.4 (13.7)	26.1	21.7
2	37.3	27.2 (27.5)	25.7	27.2
4	35.3	29.0	24.2	24.6

[a)] Water was added usually by 1 mol%, except 10 mol% only at the cases shown by the parenthesis.

maximum activity was obtained shifted to a higher one by the deposition of silica.

Addition of water vapor to the reaction system suppressed the conversions of NO and CH_4 on unmodified Pd/HM10. On the 2.0 wt% silica deposited Pd/HM10, however, the suppression of NO conversion due to water vapor was small above 700 K, while significant below 650 K. Thus, the conversion of NO measured with added water was much higher on the silica deposited Pd/HM10 than on unmodified one above 700 K. However, the conversion of CH_4 was suppressed by the added water both on unmodified and modified catalysts.

Table 1 shows the change of NO conversion by the addition of 1.0 or 10 mol% water on unmodified and 2 - 4 wt% silica deposited Pd loaded on HM10 and HM20. The deposition of silica on Pd/HM20 changed little the conversion of NO, unlike as on Pd/HM10. The addition of water on the Pd/HM20 suppressed the conversion, while little on the silica deposited Pd/HM20. In other words, the deposition of silica improved the activity of Pd/HM20 so that the activity was maintained even by the addition of water. Only in the cases of HM10, 10 mol% water was added to the reaction system; we confirmed almost the same enhancement effect by the deposited silica on the 2 wt% silica deposited Pd/HM10.

It was observed that the change of catalyst activity by added water vapor occurred reversibly as for the reaction conditions of 10 mol% water vapor at 723 K on the 2 wt% silica deposited HM10.

Thus, we have a simple conclusion about the effect of deposited silica on the reduction of NO; the suppression of activity by water vapor on the Pd/HM catalyst is able to be reduced or disregarded by the deposition of silica. The extent of the modification depends on the zeolite as well as on the reaction temperature; it may be related to the reaction mechanism, but it has not been clarified yet.

Two kinds of effect are considered about the deposited silica on the zeolite based on our previous investigations. These are a fine control of the pore-opening size and an inactivation of the external surface of zeolites. Dependence upon the silica to alumina molar ratio of zeolite was indicated for the pore-opening size control,[7] but not for the inactivation of the external surface.[8] The effect by the deposited silica on the activity thereby may be related to the pore-opening size control, because it was significant only on the HM10 where the pore-opening size was easily controlled. On the other hand, the tolerance of the catalyst to the humidity was embedded irrespective of the composition of zeolite, though the extent of enhancement of stability seemed to be outstanding on HM10. It may thereby be caused by both the inactivation of the external surface and/or the pore-opening size control. More precise characterization of the zeolite catalysts and knowledge of the reaction mechanism will be required to sufficiently explain the effect of deposited silica.

This study was supported by a Grant in Aid for Scientific Research on Priority Areas No.07242251 from the Ministry of Education, Science, Sports and Culture of Japan.

References

1 M. Iwamoto, Preprint of Catalytic Technology for Removal of Nitrogen Monoxide, Tokyo, January, (1990), p.17.

2 W. Held, A. Konig, T. Richter and L. Puppe, SAE paper 900496, 1990.

3 K. Yogo, M. Ihara, I. Terasaki and E. Kikuchi, *Chem. Lett.*, **1993**, 229.

4 Y. Li and J. N. Armor, *Appl. Catal.*, B, **1**, L31 (1992).

5 Y. Nishizaka and M. Misono, *Chem. Lett.*, **1993**, 1295.

6 M. Niwa, S. Kato, T. Hattori, and Y. Murakami, *J. Chem. Soc., Faraday I*, **80**, 3135 (1984).

7 T. Hibino, M. Niwa, Y. Kawashima, and Y. Murakami, in *Chemistry of Micro Porous Crystals*, Eds by T. Inui, S. Namba, and T. Tatsumi, Kodansha, Tokyo (1991), p.151.

8 T. Hibino, M. Niwa, and Y. Murakami, *Zeolites*, **13**, 518 (1993).