Catalytic reduction of NO by hydrocarbons over a mechanical mixture of spinel Ni–Ga oxide and manganese oxide

Laiyuan Chen, Tatsuro Horiuchi * and Toshiaki Mori

Ecoceramic Lab, Ceramics Technology Department, National Industrial Research Institute of Nagoya, 1-1 Hirate-cho, Kita-ku,
Nagoya 462-8510, Japan
E-mail: horiuchi@nirin.go.jp

Received 25 February 1999; accepted 25 May 1999

NO reduction with propylene over Mn_2O_3, spinel Ni–Ga oxide and their mechanical mixtures has been investigated. Mn_2O_3 has no activity to NO reduction, but has a high activity for NO oxidation to NO_2. Spinel Ni–Ga oxide showed an apparent activity to NO reduction only at temperatures above 400 °C. Mixing of Mn_2O_3 to the Ni–Ga oxide resulted in a significant enhancement of NO reduction in the temperature range of 250–450 °C. The optimal Mn_2O_3 content in the mixture catalyst was about 10–20 wt%. It is suggested that the synergetic effect of Mn_2O_3 and Ni–Ga oxide plays an important role in the catalysis of NO reduction. The Ni–Ga oxide and Mn_2O_3 mixture catalyst is superior to Pt/Al_2O_3 and Cu-ZSM-5 by showing a higher NO reduction conversion, resistance to water and negligible harmful by-product formation. Other lower hydrocarbons C_2H_4, C_2H_6 and C_3H_8 also give a maximum NO reduction conversion as high as 50%. The difference from using C_3H_6 is that the temperature at the maximum NO reduction is higher than it is with C_3H_6.

Keywords: catalytic NO reduction, spinel nickel–gallium oxide, manganese oxide

1. Introduction

The selective reduction of NO during lean exhaust mixture conditions remains a challenging problem both in academia and industries, especially for mobile NO_x resources. In recent years, extensive attention has been paid to the selective reduction of NO by hydrocarbons for automobile exhaust control. As far as this research is concerned, the two principal types of active catalysts for this reaction are zeolite (ZSM-5) and precious metal (Pt) based catalysts [1]. It is now recognised that zeolite based catalysts are not suitable to automobile application because of the poor hydrothermal stability of zeolite. The precious metal based catalysts are of high stability even in the presence of water and SO_2. However, the formation of nitrous oxide, a greenhouse effect gas, is a serious problem and the operating temperature window is narrow. Apparently, the development of new type of catalyst is necessary.

Physical mixture catalysts, based on a bifunctional mechanism of NO oxidation and subsequent reduction, have been shown to be active for NO reduction with hydrocarbons. Misono et al. [2,3] found that mechanically mixing of Mn_2O_3 or CeO_2 to Ce-ZSM-5 considerably enhanced the rate of NO reduction by propylene, especially in the low-to-medium temperature range. Mechanically mixing of Mn_2O_3 with Au/Al_2O_3 [4] and 2%Co/CeO_2 with spinel Ni–Ga oxide [5] have also been found to enhance the NO conversion to N_2 with propylene and widen the temperature window by exhibiting a high activity at a lower temperature. A similar enhancement was also observed for the NO_x reduction with CH_4 over a physical mixture of Co/Al_2O_3 and H-zeolite [6].

In this study, mechanical mixtures of Ni–Ga oxide and Mn_2O_3 have been investigated for NO reduction by lower hydrocarbons. It is found that the mixture with a 10–20 wt% amount of Mn_2O_3 exhibits a high activity toward NO reduction in the presence of excess oxygen and water in the low-to-medium temperature range. The possible mechanism of NO reduction with C_3H_6 over the mixture is also discussed.

2. Experimental

Spinel Ni–Ga oxide (Ni/Ga = 1 : 3, BET surface area 38.6 m^2/g) was prepared by co-precipitation by adding 25% ammonia solution to the mixed aqueous solution of gallium nitrate and nickel nitrate. The final pH was adjusted to about 8.5. Then the precipitate was filtered and washed with Milli-Q water, dried at 100 °C overnight and calcined in static air at 700 °C for 24 h. Mn_2O_3 powder (BET surface area 4.2 m^2/g) was prepared by decomposing manganese acetate in air at 550 °C for 10 h. A 0.5%Pt/Al_2O_3 catalyst was prepared by impregnating γ-Al_2O_3 powder with an appropriate amount of aqueous solution of H_2PtCl_6. Another reference catalyst, Cu-ZSM-5 with an exchange level of 78%, was prepared by an ion exchange method. An NH_4 form of ZSM-5 zeolite (JRC-Z5-25H, a reference catalyst from the Catalysis Society of Japan) was used as the starting material for the preparation of Cu-ZSM-5. Both

---

[*] To whom correspondence should be addressed.

Pt/Al_2O_3 and Cu-ZSM-5 catalysts were dried at 120 °C overnight and calcined in air at 550 °C for 8 h. The structures of the spinel Ni–Ga oxide and Mn_2O_3 were confirmed by XRD analysis (figure 1). XRD spectra were recorded using an MXP powder diffractometer with a Cu K_α radiation and operated at 40 kV and 20 mA.

Mixture catalysts were prepared by mechanically mixing different amounts of Ni–Ga oxide and Mn_2O_3 (by varying the Mn_2O_3 content in the range of 3.3–50 wt%), and milling in a mortar for about 10 min until the light green color of Ni–Ga oxide became gray or black upon the amount of Mn_2O_3. Prior to reaction test, the catalyst powder (0.3 g) was pretreated with flowing pure O_2 at 500 °C for 1 h, or treated in an oxygen flow with 20% water at 600 °C for 1 h, when the catalyst activity was evaluated in the presence of water. It was noticed that the mechanical mixing and the subsequent heating processes did not result in any change of the structures of spinel Ni–Ga oxide and Mn_2O_3. Separate Ni–Ga oxide and Mn_2O_3 phases were still present in the mixture.

NO reduction reaction was performed by using a fixed-bed flow reactor. The feed mixture consisted of 773 ppm NO, 579 ppm C_3H_6, 2.5% O_2, and N_2 as the balance gas. The total gas flow rate was 145 ml/min (corresponding to a space velocity of about 40000 h^{-1} for the mixture of Ni–Ga oxide with 10 wt% Mn_2O_3) when the reactant stream contained no water. When other hydrocarbons were used, the flow rate and the feed composition were the same as above except that there was a minor difference in hydrocarbon concentrations. In the presence of water, the feed composition was 618 ppm NO, 463 ppm C_3H_6, 2% O_2 and 20% water with N_2 as a balance gas, and the total flow rate was 175 ml/min (corresponding to a space velocity of about 48000 h^{-1} for the mixture of Ni–Ga oxide with 10 wt% Mn_2O_3). NO and NO_2 concentrations were analyzed with a HORIBA CLA-510SS NO_x analyzer. Other products were analyzed using a Shimadzu 8A GC equipped with a TCD. The concentrations of C_3H_6, CO_2 and N_2O were analyzed by a Porapak Q column. A molecular sieve 5A column was used to monitor the formation of CO. With all the catalysts tested, hydrocarbons were oxidized to CO_2 and H_2O, no CO was produced. Over the Ni–Ga oxide and Mn_2O_3 mixture catalyst, NO was converted mainly to N_2 with a small amount of NO_2. The formation of other N-containing compounds like N_2O and NH_3 was not detected. However, over the Pt/Al_2O_3 catalyst, a significant amount of N_2O as well as NO_2 was produced. Formation of a trace amount of NH_3 and N_2O was observed with the Cu-ZSM-5 catalyst.

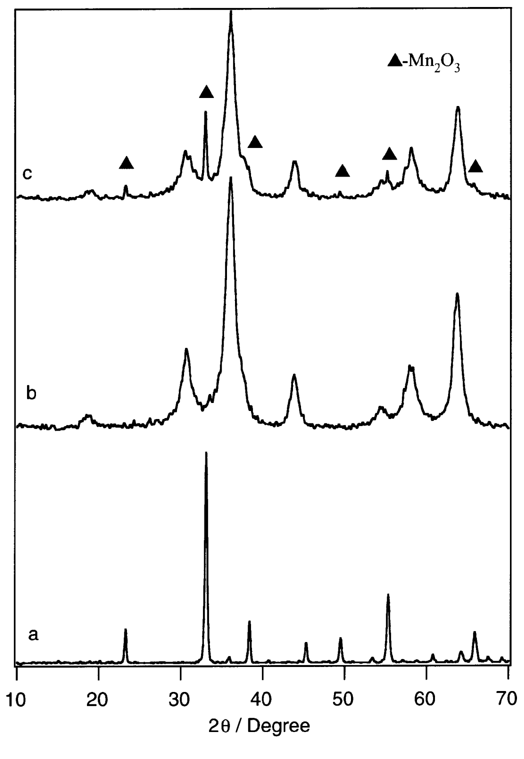

Figure 1. XRD patterns of (a) Mn_2O_3, (b) spinel Ni–Ga oxide, and (c) a mechanical mixture of spinel Ni–Ga oxide with 10 wt% Mn_2O_3.

3. Results and discussion

The NO reduction activities of the spinel Ni–Ga oxide, Mn_2O_3 and mixtures of Ni–Ga oxide and Mn_2O_3 with different Mn_2O_3 contents are shown in figure 2, as a function of reaction temperature. Mn_2O_3 showed virtually no activity toward NO reduction to N_2. Spinel Ni–Ga oxide itself exhibited a NO reduction conversion of 12% at 400 °C,

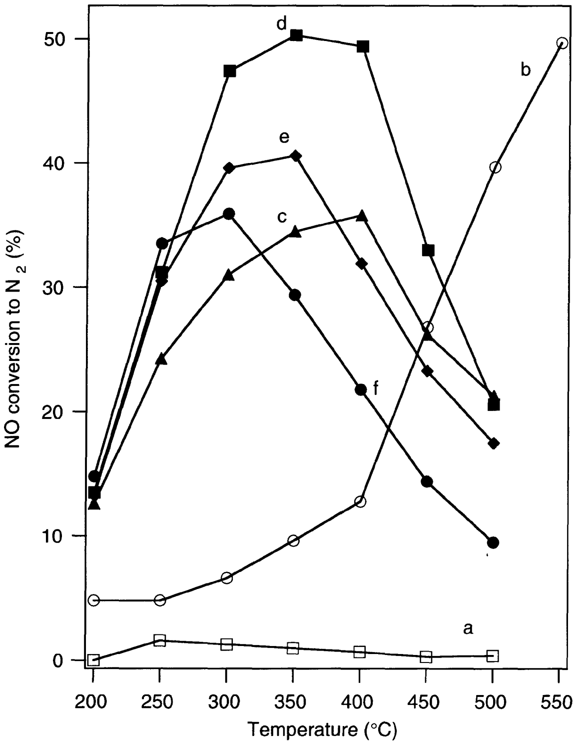

Figure 2. NO reduction conversion as a function of temperature over (a) Mn_2O_3, (b) spinel Ni–Ga oxide, and mixtures of Ni–Ga oxide with different amounts of Mn_2O_3: (c) 3.3 wt%, (d) 10 wt%, (e) 30 wt%, (f) 50 wt%. Reaction conditions: 773 ppm NO, 579 ppm C_3H_6, 2.5% O_2, N_2 balance gas, flow rate 145 ml/min, catalyst weight 0.3 g.

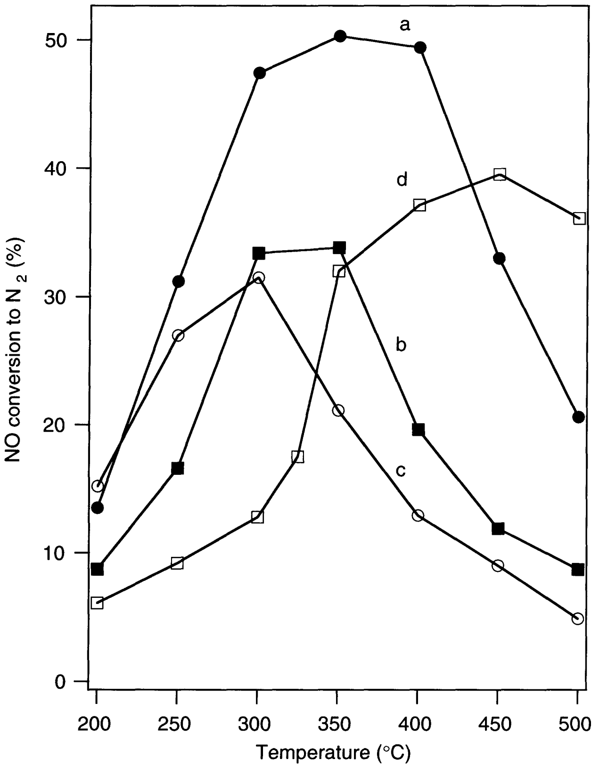

Figure 3. A comparison of NO reduction with propylene over (a) a mixture of Ni–Ga oxide with 10 wt% amount of Mn_2O_3, (b) a mixture of Ni–Ga oxide with 10 wt% amount of 2%Co/CeO_2, (c) 0.5%Pt/Al_2O_3, and (d) Cu-ZSM-5. Reaction conditions were the same as those in figure 2.

a noticeable NO reduction conversion was observed only at temperatures higher than 400 °C. However, with the addition of Mn_2O_3 to Ni–Ga oxide, the onset temperature for NO reduction with propylene greatly decreased, and a significant enhancement of NO reduction conversion was observed in the low and medium temperature range. It is important to note that the amount of Mn_2O_3 is a crucial factor in determining the catalytic performance of the mixture catalyst. The mixture with 10 wt% Mn_2O_3 showed a NO reduction conversion of about 50% in the temperature range of 300–400 °C, and a NO reduction conversion of over 30% in the range of 250–450 °C. The Ni–Ga oxide mixture with a 20 wt% amount of Mn_2O_3 showed much the same NO reduction conversion. With the increase of Mn_2O_3 content in the catalyst, the starting temperature for NO reduction decreased. However, if the Mn_2O_3 content was over 30 wt%, a low NO reduction conversion was observed. The most possible reason is that excess Mn_2O_3 catalyses the propylene complete oxidation with O_2 before it can react with NO. On the other hand, if the Mn_2O_3 content was too low (3.3 wt%), NO reduction took place at a relatively high temperature and the total NO reduction conversion was also low. Apparently, the optimal Mn_2O_3 content in the mixture catalyst for NO reduction is between 10 and 20 wt%.

The Ni–Ga oxide and Mn_2O_3 mixture exhibited a much higher NO reduction conversion compared to Pt/Al_2O_3 and Cu-ZSM-5 (figure 3). Under the same reaction conditions, the maximum NO reduction conversion to N_2 was 50% over the mixture of Ni–Ga oxide with 10 wt% Mn_2O_3, whereas it was 31 and 36% over the 0.5%Pt/Al_2O_3 and Cu-ZSM-5 catalysts, respectively. The results in figure 3 demonstrate that the NO reduction conversion is much higher and the operating temperature window is wider for the mixture of Ni–Ga oxide with 10 wt% amount of Mn_2O_3 than those of the Pt/Al_2O_3 catalyst. From the comparison with Cu-ZSM-5, it is seen that the NO reduction conversion is higher and the NO reduction temperature is lower for the mixture of Ni–Ga oxide with 10 wt% Mn_2O_3. Another advantage of the Ni–Ga oxide and Mn_2O_3 mixture catalyst is the negligible formation of harmful by-product. A significant amount of N_2O (its selectivity was about 50%), a greenhouse effect gas, was produced on the Pt/Al_2O_3 and a noticeable amount of NH_3 and N_2O was formed with the Cu-ZSM-5 catalyst, whereas the formation of N_2O and NH_3 was negligible over the mixture of Ni–Ga oxide and Mn_2O_3.

From figure 2, we can see that the NO conversion over the mixture of Ni–Ga oxide with 10 wt% Mn_2O_3 is not just a simple addition of those of Mn_2O_3 and Ni–Ga oxide. Misono et al. [3] proposed a two-step bifunctional mechanism for this type of catalysts. According to this mechanism, NO is first oxidized to NO_2 over Mn_2O_3, then NO_2 reacts with propylene over Ni–Ga oxide. The enhancement of NO conversion is attributed to the fact that the reaction of NO_2 with C_3H_6 is easier and occurs at a lower temperature over the spinel Ni–Ga oxide than the reaction of NO and C_3H. While this mechanism is true for the reaction over the mixture of Ni–Ga oxide and Mn_2O_3, we want to emphasise the synergetic effect of Mn_2O_3 and Ni–Ga oxide. From figure 4(a), we can see that the maximum NO oxidation conversion to NO_2 over pure Mn_2O_3 is lower than 30%. If the NO reduction takes place by following a simple two-step mechanism, the maximum NO reduction conversion would be less than 30%. This apparently cannot account for the maximum NO reduction conversion of 50% over the mixture of Ni–Ga oxide with 10 wt% Mn_2O_3. It is suggested that the intimate contact of Mn_2O_3 and Ni–Ga oxide promotes both the NO oxidation and the subsequent reduction with C_3H_6 simultaneously. In fact, if Mn_2O_3 and Ni–Ga oxide were not mixed, that is, they were separated by a thin layer of quartz wool, and Mn_2O_3 was placed above the bed of Ni–Ga oxide, the final NO conversion was quite low (figure 4(b)). This result once again demonstrates that the synergetic effect of Ni–Ga oxide and Mn_2O_3 plays a crucial role. Possibly the spillover of the adsorbed NO_2 and C_xH_y species from Mn_2O_3 to a neighbouring Ni–Ga oxide is an important step. The role of isolated Mn_2O_3 possibly is to oxidize NO to NO_2 and activate C_3H_6 as well. If the catalyst was prepared by impregnating Ni–Ga oxide with manganese acetate, the manganese oxide was finely dispersed over the Ni–Ga oxide (no Mn_2O_3 phase was detected in the XRD measurement); the resulting catalyst showed almost no activity toward NO reduction (figure 4(c)). Highly dispersed manganese species show an

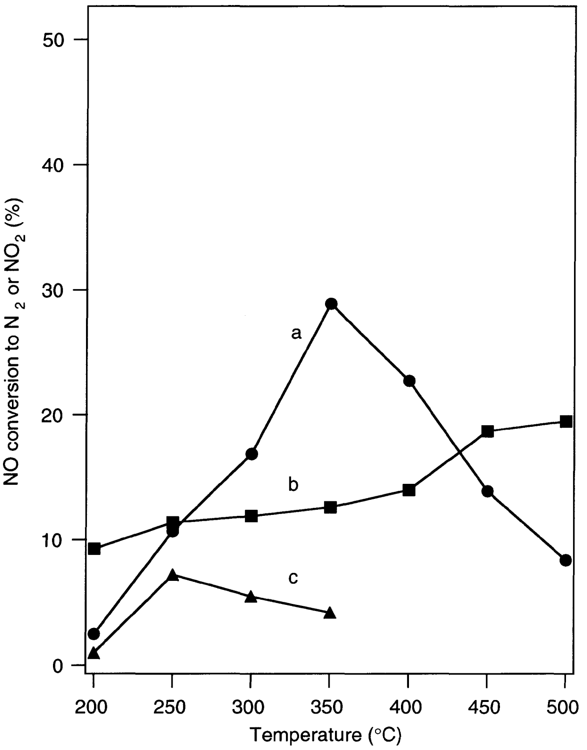

Figure 4. NO oxidation conversion to NO_2 over Mn_2O_3 (a), and NO reduction with propylene over (b) the separate bed of Mn_2O_3 (up) and Ni–Ga oxide (down) and (c) Mn-impregnated Ni–Ga oxide (corresponding to a Mn_2O_3 content of 10 wt%). NO reduction conditions were the same as those in figure 2.

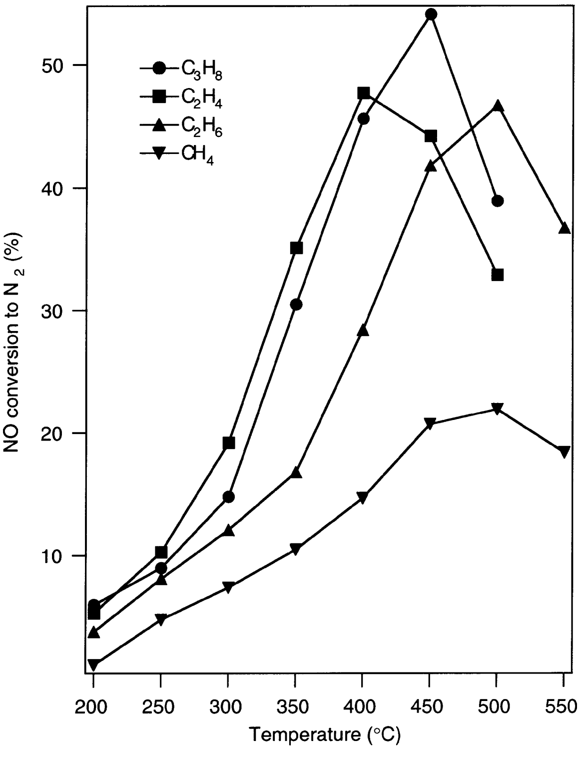

Figure 5. NO reduction with different hydrocarbons over a mixture of Ni–Ga oxide and 10 wt% Mn_2O_3. Reaction conditions were the same as those in figure 2, except the concentrations of hydrocarbons: 579 ppm C_3H_8, 596 ppm C_2H_4, 568 ppm C_2H_6 and 585 ppm CH_4.

extremely high activity to C_3H_6 oxidation by O_2, therefore, C_3H_6 is consumed by O_2 before it can react with NO.

NO reduction by other lower hydrocarbons (CH_4, C_2H_4, C_2H_6 and C_3H_8) over the mixture of Ni–Ga oxide with a 10 wt% amount of Mn_2O_3 has also been investigated, and the results are shown in figure 5. It can be seen that all these lower hydrocarbons but CH_4 gave a maximum NO reduction conversion of about 50%, which is near to that of C_3H_6. It is interesting to note that even the saturated alkanes C_2H_6 and C_3H_8 gave a high NO reduction conversion. The most inert hydrocarbon CH_4 also showed a NO reduction conversion of 20% at 450–500 °C. These results once again indicate that the mixture of Ni–Ga oxide and Mn_2O_3 is a promising catalyst for NO reduction as a wide range of hydrocarbons can be used as reductants. It is noticed that the onset temperature of NO reduction as well as the temperature at the maximum NO reduction was much lower for the NO reduction with C_3H_6 than with other hydrocarbons. This possibly is due to the reason that the conversions of C_2H_4, C_2H_6 and C_3H_8 take place at a relatively higher temperature compared to that of C_3H_6. This assumption also explains the low NO reduction conversion with CH_4. A noticeable CH_4 conversion was observed only at temperatures of about 500 °C. However, at such a high temperature, the conversion of NO to NO_2 is thermodynamically unfavourable. The maximum NO oxidation and CH_4 conversion cannot take place at the same temperature

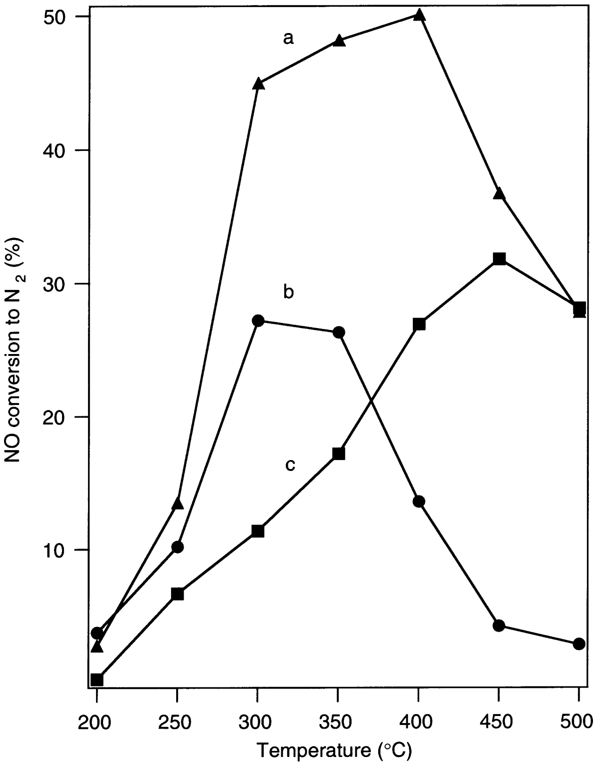

Figure 6. Influence of water on NO reduction with propylene over (a) a mixture of Ni–Ga oxide with 10 wt% Mn_2O_3, (b) 0.5%Pt/Al_2O_3, and (c) Cu-ZSM-5 catalysts. Reaction conditions: 618 ppm NO, 463 ppm C_3H_6, 2% O_2, 20% water, N_2 as the balance gas, flow rate 175 ml/min, catalyst weight 0.3 g.

range. As a result, the NO reduction conversion is low with CH_4 as a reductant.

In the absence of oxygen, the mixture catalyst of Ni–Ga oxide with a 10 wt% Mn_2O_3 showed a NO reduction of 5.6% at 350 °C. With the introduction of 2.5% oxygen, the NO reduction conversion increased sharply to 50%. Further increase in oxygen concentration from 2.5 to 15% resulted in a slight decrease of NO reduction from 50 to 46%. It is important to note that the Mn_2O_3 and Ni–Ga oxide mixture catalyst showed an excellent stability even with the presence of 20% water in the reaction stream. By comparing figure 6 with figure 3, it can be seen that the presence of water showed only a minor influence on the NO reduction in the low temperature range. At a high temperature, the activity to NO reduction was even enhanced slightly by the presence of water. In contrast, the activities of both Pt/Al_2O_3 and Cu-ZSM-5 catalysts were suppressed significantly by the presence of water, especially for the Cu-ZSM-5 catalyst.

4. Conclusions

Mechanically mixing of Mn_2O_3 to the spinel Ni–Ga oxide resulted in a significant enhancement of NO reduction in the low and medium temperature range. The optimal Mn_2O_3 content in the mixture was about 10–20 wt%. An excess amount of Mn_2O_3 led to an extremely high propylene consumption rate by complete oxidation with oxygen, which rendered a low NO reduction conversion, whereas too less amount of Mn_2O_3 in the mixture showed little improvement in NO reduction. The synergetic effect of Mn_2O_3 and Ni–Ga oxide plays an important role in the catalysis of NO reduction. The Ni–Ga oxide and Mn_2O_3 mixture catalyst is superior to Pt/Al_2O_3 and Cu-ZSM-5 by showing a higher NO reduction conversion, resistance to water and negligible harmful by-product formation. Other lower hydrocarbons C_2H_4, C_2H_6 and C_3H_8 also give a maximum NO reduction conversion as high as that of C_3H_6, the only difference is that their temperatures at the maximum NO reduction are much higher than it is with C_3H_6. The presence of water led to a minor decrease in NO reduction at the low temperature, but showed a slight increment at a high temperature.

Acknowledgement

LC is grateful to Japan International Science and Technology Exchange Center (JISTEC) for an STA fellowship.

References

[1] Fritz and V. Pitchon, Appl. Catal. B 13 (1997) 1.
[2] C. Yokoyama and M. Misono, Catal. Lett. 29 (1994) 1.
[3] M. Misono, Y. Hirao and C. Yokoyama, Catal. Today 38 (1997) 157.
[4] Ueda and M. Haruta, Appl. Catal. B 18 (1998) 115.
[5] Y. Yuu and H. Matunosako, Nippon Kagaku Kaishi 2 (1998) 141.
[6] J.Y. Yan, H.H. Kung, W.M.H. Sachtler and M.C. Kung, J. Catal. 175 (1998) 294.