

Enhancement by water vapour of catalytic reduction of NO by propene over mechanically mixed Mn_2O_3 and Sn-ZSM-5

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The first example where the presence of water vapour considerably enhances the rate of the reaction NO , C_3H_6 , $\text{O}_2 \rightarrow \text{N}_2$, CO_x , H_2O in the entire range of reaction temperature (250–500 °C) is found when a mechanical mixture of Mn_2O_3 and Sn-ZSM-5 is used as a catalyst.

Catalytic reduction of NO by using hydrocarbons in the presence of an excess of oxygen has attracted much attention. In addition to early reports on Cu-zeolites,^{1–3} many other catalysts have been reported.^{4–6} However, the most serious problem encountered is the retarding effects caused by the presence of water vapour which is inevitably contained in combustion effluents. Two such effects are observed; rapid reversible inhibition and slow but irreversible degradation of catalytic activity. Here, we report a catalytic system which solves the former problem caused by water vapour.

We have recently reported that the activity of Ce ion-exchanged zeolites^{7–9} for the reduction of NO by propene was enhanced by the mechanical mixing of them with Mn_2O_3 or CeO_2 .¹⁰ This promotional effect was explained based on several experimental results by a bifunctional mechanism, in which Mn_2O_3 or CeO_2 accelerates the oxidation of NO to NO_2 and the subsequent steps between NO_2 and propene are catalysed by Ce-ZSM-5. If one admits this mechanism, there arise much wider opportunities for the selection of catalysts; that is, the combination of two catalyst components by mechanical or chemical mixing. For example, a certain metal ion-exchanged zeolite that has previously been regarded inactive could be an efficient catalyst when mixed with Mn_2O_3 or CeO_2 .

In this work, we examined the combination of various metal ion-exchanged ZSM-5 systems with Mn_2O_3 by mechanical mixing and its resistance to water vapour. Mn_2O_3 was chosen since there was an indication in our previous study that the activity of Mn_2O_3 for the oxidation of NO was relatively resistant to water vapour.

Mn_2O_3 ($6.7 \text{ m}^2 \text{ g}^{-1}$) was mixed in a mortar for ca. 20 min with Sn-ZSM-5 which was prepared by ion-exchange of Na-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 23.8$) with an aqueous solution of SnCl_2 . Ce-ZSM-5 prepared as in the previous study was similarly mixed.¹⁰ The ion-exchange levels of Sn and Ce were 100 and 15%, respectively. The $\text{Mn}_2\text{O}_3/\text{M-ZSM-5}$ ratios in the mechanical mixtures were 1 : 1 in mass. The details of the preparation have been described in a previous paper.¹⁰ Hereafter the mechanically mixed catalysts will be denoted by Mn + M-Z.

The reactions were performed with a fixed-bed flow reactor as described previously.^{7–10} A gas mixture of 1000 ppm NO, 500 ppm propene, 2% O_2 and 5.7% H_2O (in He) was ordinarily fed to 0.5 g of a catalyst at a rate of $150 \text{ cm}^3 \text{ min}^{-1}$ (space velocity = 10^4 h^{-1}). The catalysts were treated at 500 °C for 2 h in He. The reaction temperature was lowered stepwise from 500 °C.

Fig. 1 shows the influence of the presence of water vapour on NO + C_3H_6 + O_2 reaction catalysed by three catalysts; Mn_2O_3 , Sn-Z and Mn+Sn-Z.

As for the reaction in the absence of water vapour, N_2 was not formed at all with Mn_2O_3 , although the oxidation of propene readily took place, as reported previously.¹⁰ Sn-Z alone showed only low conversions of NO to N_2 . The rate was considerably

enhanced when mechanical mixtures of Sn-Z with Mn_2O_3 were used as catalysts. The phenomena are consistent with the case of the Mn + Ce-Z mixture,¹⁰ and indicate the bifunctional mechanism in which Mn_2O_3 accelerates the oxidation of NO to NO_2 and the subsequent reactions between NO_2 and propene proceed over Sn-Z.

In the presence of water vapour, the catalysts studied previously¹⁰ showed lower activities as reported for other catalysts in the literature.¹¹ In contrast, in the case of Mn + Sn-Z, the presence of water vapour greatly enhanced the conversion of NO to N_2 in the entire temperature range (250–500 °C). It was noted that the conversion of C_3H_6 to CO_x also increased.

Fig. 2 shows the dependence of the partial pressure of water vapour on NO + C_3H_6 + O_2 reaction catalysed by Mn + Sn-Z. The conversion of NO to N_2 substantially increased in the presence of a small amount of water vapour (1%) and slightly increased further upon increasing the partial pressure of water vapour. The oxidation of C_3H_6 to CO_x and the selectivity also increased, but the increase in the selectivity was more significant. Here, the selectivity is defined by the ratio of the oxidation of C_3H_6 used for the reduction of NO to the entire oxidation of C_3H_6 ; % selectivity = $100 \times (\text{number of oxygen atoms from NO consumed for oxidation of propene})/(\text{number of total oxygen atoms consumed for oxidation of propene})$.⁸ Thus, in the case of Mn + Sn-Z the presence of water vapour enhanced the conversion of NO to N_2 , the conversion of C_3H_6 to CO_x and the selectivity.

The promotional effect of water vapour was confirmed by examination of the response of the reaction to the supply of water vapour. When the % conversion of NO to N_2 reached an almost constant value at 350 °C, the supply of water vapour was

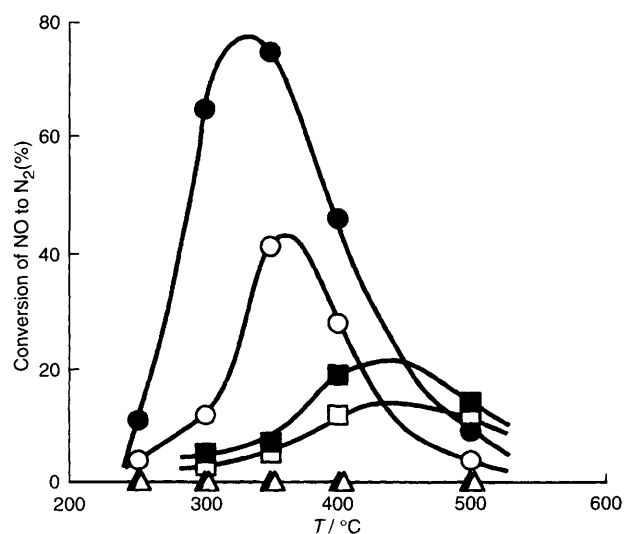


Fig. 1 The influence of the presence of water vapour on the reaction NO , C_3H_6 , $\text{O}_2 \rightarrow \text{N}_2$, CO_x , H_2O . Mn + Sn-Z (●, ○), Sn-Z (■, □), Mn (▲, △). Solid symbols (●, ■, ▲) indicate the results obtained in the presence of water vapour, and open symbols (○, □, △) in its absence. NO: 1000 ppm; C_3H_6 : 500 ppm; O_2 : 2%; H_2O : 5.7%; total flow rate: $150 \text{ cm}^3 \text{ min}^{-1}$. Catalyst mass: Mn (0.25 g) + Sn-Z (0.25 g).

stopped and the conversion dropped immediately and slowly decreased further. When the supply of water vapour was resumed, the conversion rapidly returned to approximately the same initial level. This reversible response suggests that the enhancement by water vapour is not attributable to a change in the catalyst, but rather to the direct involvement of water in the reaction path.

In contrast to Mn + Sn-Z, retarding effects by water were observed for all other catalysts as described previously. For example, in the absence of water vapour, both Mn + Ce-Z and Mn + Na-Z showed high activities, the maximum conversions of NO to N₂ being 84 and 65% at 250 °C, respectively.¹⁰ However, the presence of 5% water vapour drastically lowered

the conversion to 7 and 0%, respectively. Therefore, the enhancement by water vapour for Mn + Sn-Z is probably unique to Sn-Z. Slight enhancement by water vapour may be noted for Sn-Z (Fig. 1). It has been reported that Sn was a good additive to Al₂O₃ for the reduction of NO by methanol.¹²

Among the catalysts reported so forth, Pt-zeolites show the highest resistance to water vapour and the activity changes little in the presence of water vapour.¹³ However, with Pt-zeolites NO is removed only in a narrow range of reaction temperature and a significant amount of N₂O is formed together with N₂. To our knowledge, the Mn + Sn-Z catalyst is the first example in which the activity is enhanced by the presence of water over the entire temperature range.

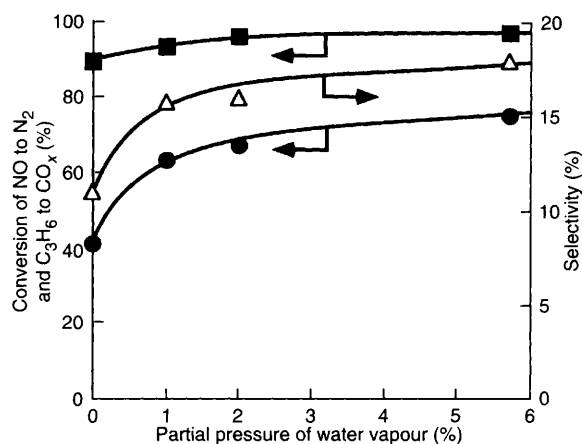


Fig. 2 The dependence of the partial pressure of water vapour on the reaction $\text{NO}, \text{C}_3\text{H}_6, \text{O}_2 \rightarrow \text{N}_2, \text{CO}_x, \text{H}_2\text{O}$ catalysed by Mn + Sn-Z. Conversion of NO to N₂ (●), conversion of C₃H₆ to CO_x (■), and selectivity (△). NO: 1000 ppm; C₃H₆: 500 ppm; O₂: 2%; H₂O: 5.7%; total flow rate: 150 cm³ min⁻¹. Catalyst mass: Mn (0.25 g) + Sn-Z (0.25 g). Selectivity: see text.

References

- 1 Volkswagen, *Ger. Offen DE*, 3 642 018, 1987; Toyota, *Japan Kokai*, 100919, 1988.
- 2 M. Iwamoto, *Proc. of Meeting of Catalytic Technology for Removal of Nitrogen Oxides*, Catalysis Society of Japan, 1990, p. 17.
- 3 W. Held, A. König, T. Richter and L. Puppe, *SAE Paper*, 1990, 900469.
- 4 H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, *Appl. Catal.*, 1991, **70**, L15.
- 5 K. Yogo, S. Tanaka, M. Ihara, T. Hishiki and K. Kikuchi, *Chem. Lett.*, 1992, 1025.
- 6 Y. Li and J. N. Armor, *Appl. Catal.*, 1992, **B1**, L31.
- 7 M. Misono and K. Kondo, *Chem. Lett.*, 1991, 1001.
- 8 C. Yokoyama and M. Misono, *Chem. Lett.*, 1992, 1669.
- 9 C. Yokoyama and M. Misono, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 557.
- 10 C. Yokoyama and M. Misono, *Catal. Lett.*, 1994, **29**, 1.
- 11 M. Shelef, C. N. Montreuil and H. W. Jen, *Catal. Lett.*, 1994, **26**, 277.
- 12 M. Tabata, H. Hamada, F. Suganuma, T. Yoshinari, H. Tsuchida, Y. Kintaichi, M. Sasaki and T. Ito, *Catal. Lett.*, 1994, **25**, 55.
- 13 H. Hirabayashi, H. Yahiro, N. Mizuno and M. Iwamoto, *Chem. Lett.*, 1992, 2235.

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