

Oxidation of NO to NO₂ on a Pt-MFI zeolite and subsequent reduction of NO_x by C₂H₄ on an In-MFI zeolite: a novel de-NO_x strategy in excess oxygen

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Intermediate addition of reductant (C₂H₄) into an NO+O₂ stream between an oxidation catalyst for NO to NO₂ (Pt-MFI) and a reduction catalyst for NO_x to N₂ (In-MFI), a so-called IAR method, is shown to be very effective in selectively reducing NO to N₂ in the presence of excess oxygen.

The selective catalytic reduction of NO by hydrocarbons (SCR-HC) in the presence of excess oxygen is a potential method to remove NO_x from various exhausts.¹ Although there have been many discussions on the reaction mechanism of the SCR-HC, the concept that NO is oxidized to NO₂ by oxygen and then the resulting NO₂ reacts with hydrocarbons to form an active intermediate is widely suggested on various catalysts.^{2,3} Several efforts have been devoted to separate the functions of catalysts; for example, platinum and Mn₂O₃ are reported to be active for the oxidation of NO to NO₂ in the reaction system NO + O₂ + CH₄ on Pt/In/MFI⁴ and NO + O₂ + C₃H₆ on Mn₂O₃ + Ce-MFI,⁵ respectively. One of the most significant problems in these systems is that the oxidation catalyst for NO might be active for oxidation of the hydrocarbons, which would result in a decrease in the efficiency of the reductant. In the case of CH₄ as reductant, Pt can be used for NO oxidation because of the low oxidation activity of Pt towards CH₄.⁴ With C₃H₆, Mn₂O₃ or CeO₂ should be employed because Pt or the other oxide catalysts are too active for C₃H₆ oxidation.⁵

It is well known that diesel exhausts contain very small amounts of unburned hydrocarbons. Thus addition of fuels or hydrocarbons into the diesel exhausts is required to reduce NO by the SCR-HC method. On the basis of the above reaction mechanism and the necessity of hydrocarbon addition, we propose here a novel strategy to reduce NO selectively, *viz.* the intermediate addition of a reductant into the NO-containing exhaust between an oxidation catalyst of NO and a reduction catalyst to N₂ (IAR method). In the present experiments Pt-MFI and In-MFI catalysts⁶ have been employed as the model oxidation and reduction catalysts, respectively, in the reaction system NO + O₂ + C₂H₄.

Platinum and indium ion-exchanged MFI zeolites were prepared by a conventional method from aqueous tetraamineplatinum(II) nitrate and indium(III) nitrate solutions, respectively. The Si/Al molar ratio of the parent MFI zeolite was 11.7. The ion-exchange levels of Pt-MFI and In-MFI prepared were 101 and 83%, respectively. The zeolites were pressed, crushed and sieved to obtain particles of 250–425 μm. Catalytic reduction was carried out in a conventional flow system with twin quartz reactors and the flow diagram is shown in Fig. 1. The twin reactors were placed in a single furnace. The Pt-MFI catalyst was mounted in the first reactor and the In-MFI in the second. A mixture of NO, O₂ and He (balance) (total flow rate, 124 cm³ min⁻¹) was introduced into the first reactor. The reductant, C₂H₄, diluted in He (26 cm³ min⁻¹) was then added into the NO + O₂ mixture between the first and the second reactors. One can change the flow route of the NO + O₂ mixture to the bypass from the first reactor to evaluate the effect of the first catalyst bed. Before the catalytic reaction, the catalysts were pretreated *in situ* at 773 K for 3 h in a He flow. The reactants were 1000 ppm of NO, 857 ppm of C₂H₄, 2% of O₂

(helium balance) and the total flow rate of gases was 150 cm³ min⁻¹. A gas chromatograph was employed to measure the respective concentrations of ethene, nitrogen, nitrous oxide, carbon dioxide and carbon monoxide. An NO_x analyser was used to determine the degree of oxidation of NO to NO₂.

First, the effectiveness of Pt-MFI as the oxidation catalyst of NO was investigated and the results are plotted in Fig. 2. The conversion of NO to NO₂ on Pt-MFI was maximal at 523 K. Decrease in conversion at higher temperatures is due to the limitation of the equilibrium as clearly shown in Fig. 2. In the absence of the Pt-MFI catalyst, only a very small amount of NO₂ was produced under the present experimental conditions. One can therefore conclude that the Pt-MFI zeolite is a very active catalyst for the oxidation of NO to NO₂ and the catalytic activity is much higher than reported previously.^{5,7} After the pretreatment, X-ray diffraction analysis of the Pt-MFI catalyst showed the formation of Pt particles on the MFI zeolite, which is in good agreement with a previous report.⁸ The reproducibility of the results of Fig. 2 was very good within the temperature range 473–873 K and no deactivation of the Pt-MFI catalyst upon NO₂ formation was observed.

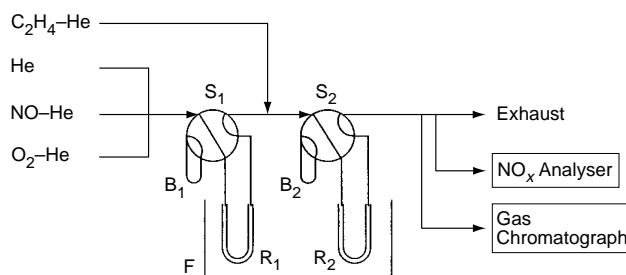


Fig. 1 Flow system for SCR-HC by IAR method. B1 and B2, bypaths of the reactors; F, furnace; R1 and R2, reactors; S1 and S2, six-way valves.

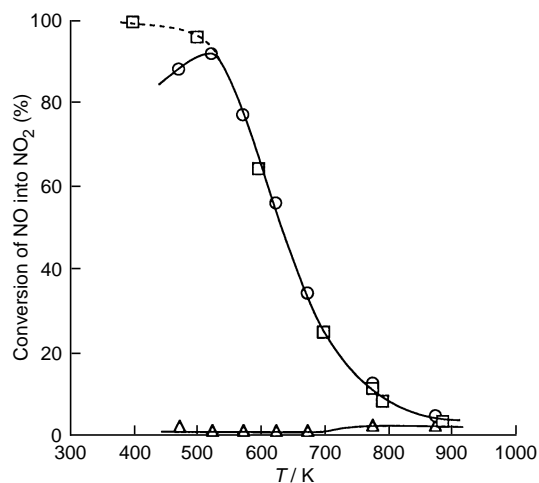


Fig. 2 NO₂ formation in the NO + O₂ reaction on Pt-MFI (○). NO to NO₂ conversions without Pt-MFI (△) and under equilibrium (□) are also shown.

In Fig. 3, the activities of four kinds of catalytic systems are shown: (i) a series combination of the Pt-MFI catalyst (0.4 g) and the In-MFI catalyst (0.4 g) (Pt/In), (ii) the In-MFI catalyst alone (0.4 g) (In), (iii) physically mixed Pt-MFI (0.4 g) and In-MFI (0.4 g) catalysts (Pt + In) and (iv) a series combination of the Pt-MFI catalyst (0.4 g) and the parent Na-MFI catalyst (0.4 g) (Pt/Na). Fig. 3 clearly shows the great difference between the results of the Pt/In and the In systems. With Pt-MFI as the oxidation catalyst, the catalytic activity of In-MFI for NO reduction was greatly enhanced at 473–623 K. At the same time conversion levels of C₂H₄ also increased. It is evident that the increments of NO and C₂H₄ conversions are due to the formation of NO₂ on Pt-MFI. Fig. 3 also indicates formation of

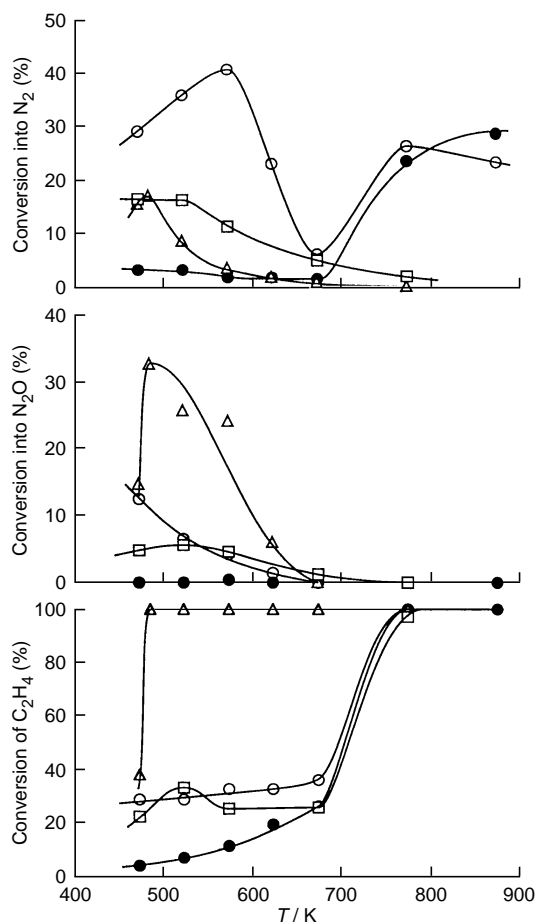


Fig. 3 Reduction of NO by the IAR method on Pt/In (○), In (●), Pt + In (△) and Pt/Na (□) systems. The experimental conditions are described in the text.

N₂O at 473–623 K. This might suggest the easy formation of N₂O in the presence of NO₂, although the reaction mechanism is, as yet, not clear.

The results on the Pt/In and In systems at 773–873 K were approximately the same. Taking the small amount of NO₂ formed at 773–873 K (Fig. 2) into consideration, the activity in this temperature region would result from the catalysis of In-MFI itself to the NO + O₂ + C₂H₄ mixture.

The results of the Pt/In system can be compared with those of the Pt + In system. The degree of conversion of NO to N₂ for the latter was much lower than that of the former as shown in Fig. 3, and almost the same as that of the Pt-MFI alone, as reported in a previous paper.⁸ Therefore it follows that only Pt-MFI in the mixture of Pt-MFI and In-MFI is the active phase while In-MFI is essentially inactive. In addition, the results on the Pt/Na system reveal that indium ions are more effective than sodium ions in promotion of the catalytic reaction of NO₂ with hydrocarbons.

In conclusion, the results show the great effectiveness of the IAR method to reduce NO by hydrocarbons in the presence of an excess of oxygen. Although the effect of water addition to the system is yet to be investigated, it is clear that there is no longer a need to develop or search for catalysts which can oxidize NO to NO₂ but not oxidize the reductant, if we employ this method. There are many possible combinations of oxidation and reduction catalysts, depending on the condition of the exhausts and the nature of the reductants.

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References

- 1 M. Iwamoto and H. Yahiro, *Catal. Today*, 1994, **22**, 5.
- 2 H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, *Appl. Catal.*, 1991, **70**, L15.
- 3 Y. Li and J. N. Armor, *J. Catal.*, 1994, **150**, 376; C. Yokoyama and M. Misono, *J. Catal.*, 1994, **150**, 9; M. Shelef, C. M. Montreuil and H. W. Jen, *Catal. Lett.*, 1994, **26**, 277; D. B. Lukyanov, G. Still, J. L. d'Itri and W. K. Hall, *J. Catal.*, 1995, **153**, 265; T. Beutel, B. J. Adelman, G.-D. Lei and W. M. H. Sachtler, *Catal. Lett.*, 1995, **32**, 83; K. A. Bethke, C. Li, M. C. Kung and H. H. Kung, *Catal. Lett.*, 1995, **31**, 287.
- 4 M. Ogura, S. Hiromoto and E. Kikuchi, *Chem. Lett.*, 1995, 1135; E. Kikuchi, M. Ogura, N. Aratani, Y. Sugiura, S. Hiromoto and K. Yogo, *Catal. Lett.*, 1996, **27**, 35.
- 5 C. Yokoyama and M. Misono, *Catal. Lett.*, 1994, **29**, 1.
- 6 E. Kikuchi, M. Ogura, I. Terasaki and Y. Goto, *J. Catal.*, in the press.
- 7 A. Yu. Stakheev, C. W. Lee, S. J. Park and P. J. Chong, *Catal. Lett.*, 1996, **38**, 271.
- 8 H. K. Shin, H. Hirabayashi, H. Yahiro, M. Watanabe and M. Iwamoto, *Catal. Today*, 1995, **26**, 13.

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