CHEMISTRY LETTERS, pp. 407-410, 1991.

Cocation Effect in Catalytic Property of Copper Ion-Exchanged ZSM-5 Zeolites for the Direct Decomposition of Nitrogen Monoxide

Shuichi KAGAWA,* Hiroshi OGAWA, Hiroshi FURUKAWA, and Yasutake TERAOKA
Department of Industrial Chemistry, Faculty of Engineering,
Nagasaki University, Nagasaki 852

The coexistence of metal cations such as alkaline earth and transition metal cations with Cu ions in ZSM-5 zeolites promoted the catalytic activity of Cu ion for the direct decomposition of nitrogen monoxide at temperatures above 450 °C. The promotion effect was found to depend on the ion exchange mode.

The high and stable steady-state activity of Cu ion-exchanged ZSM-5 zeolite (Cu-Z) for the direct decomposition of nitrogen monoxide (NO) was reported in 1986 by Iwamoto et al.[1)] This finding has triggered recent studies by which several catalyst systems have been revealed to show the substantial NO decomposition activity.[2)] However, Cu-Z is still the most active and promising: catalysis for NO decomposition reaction of Cu-Z was recently summarized by Iwamoto.[3)] It was reported that the NO decomposition activity of Cu-Z was dependent on the amount of Cu ions incorporated as well as the aluminum content of host zeolites.[1b,3,4)] Another way to modify the catalytic property of Cu-Z may be the incorporation of additional metal cations (cocations) to give two-ingredient zeolite catalysts, as reported on Cu ion-exchanged Y-type zeolites.[5)] This letter describes the effects of cocations on the NO decomposition activity of Cu-Z and has revealed the strong cocation effect enhancing the catalytic performance at temperatures above 450 °C.

The starting materials were Na-ZSM-5 zeolites with SiO_2/Al_2O_3 molar ratio of 23.3 (Z2) or 40.4 (Z4) supplied by Tosoh Corporation. Catalysts obtained by ion-exchanging Na-ZSM-5 with an aqueous cupric acetate solution[4)] are termed Na(**a**)-Cu(**b**)-Z. Two-ingredient zeolite catalysts were prepared by the successive ion exchange with an aqueous solution of acetate or nitrate of cocation M and then with an aqueous cupric acetate solution (referred to as normal ion exchange mode), and the resulting catalysts are termed M(**a**)-Cu(**b**)-Z. Ni-coexistent catalysts were also prepared by the successive ion exchange in the reverse sequence (Cu(**a**)-Ni(**b**)-Z) or by the simultaneous ion exchange with a mixed aqueous solution of Cu and Ni acetates (Cu(**a**)Ni(**b**)-Z). Contents of metal cations were measured by means of atomic absorption and flame emission techniques after the samples were dissolved in an HF solution: **a** and **b** in parentheses of the catalyst notation are the cation contents in terms of ion exchange level[6)] and bar sign "-" in parentheses means that the content of the corresponding cation is undetermined. In two-ingredient catalysts examined in this study, traces of Na ions were not detected, indicating that all Na ions were outgoing during the ion exchanges. The NO decomposition reaction was carried out in a fixed-bed flow reactor. The reaction gas (0.48 vol% NO in He) was fed at a rate of 15.0 cm^{3}·min^{-1} over 1.0 g (W/F=4.0 g·s·cm^{-3}) or 0.48 g (1.9 g·s·cm^{-3}) catalyst pre-heated at 500 °C for 1 h in a He stream. The activity was evaluated in terms of the conversion of NO into N_2 ($(2[N_2]_{out}/[NO]_{in})\times100$) after 2 - 3 h on stream, where the reaction practically reached a steady state.

Figure 1 shows temperature dependencies of NO decomposition activities of Na(21)-Cu(83)-Z2 and Ni(60)-Cu(75)-Z2 between 100 and 700 °C. For both catalysts, N_2O formation was dominant below 300 °C, and above that temperature N_2 formation (direct decomposition of NO) was observed. In good agreement with previous reports,[1b,4] the decomposition activity of Na-Cu-Z2 reached a maximum at 450-500 °C and decreased with an increase in temperature at higher temperatures. The activity of the Ni-coexistent catalyst also showed a volcano-shape dependence on temperature. However, the temperature for the maximum activity shifted to around 550 °C and the Ni-coexistent catalyst was more active than the Na-Cu-Z2 catalyst above 500 °C. This shows that the cocation effect in the catalytic property for NO decomposition of Cu ion-exchanged ZSM-5 is the promotion of activity at elevated temperatures. Thus, hereafter, the cocation effect will be evaluated at temperatures above 400 °C.

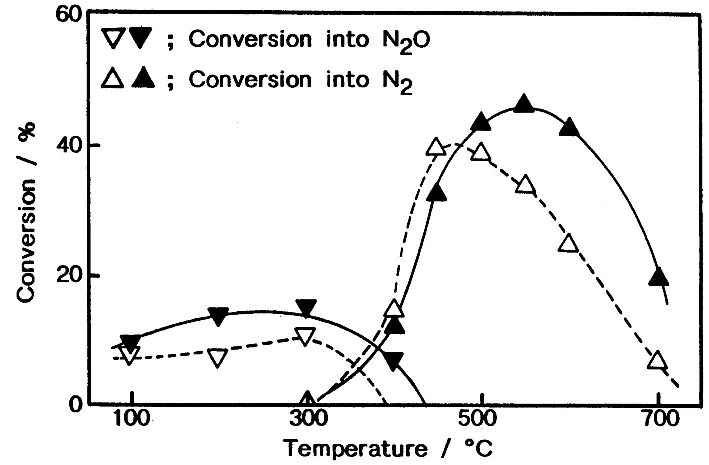

Fig. 1. NO decomposition over Na(21)-Cu(83)-Z2 (△, ▽) and Ni(60)-Cu(75)-Z2 (▲,▼). W/F=1.9 g·s·cm^{-3}, P_{NO}=0.48 vol%.

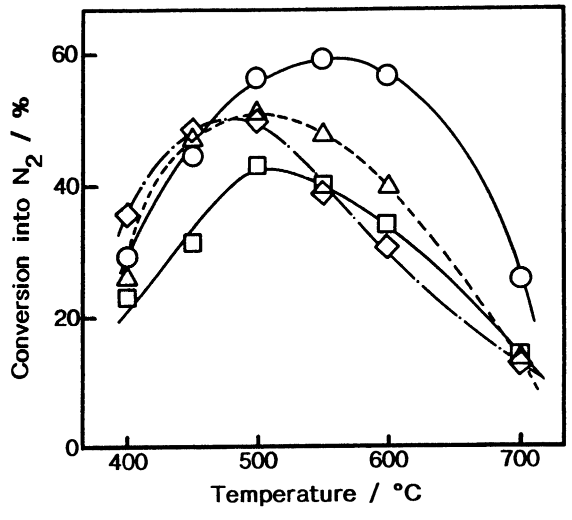

Fig. 2. Effect of the ion exchange mode on NO decomposition activities of Ni-coexistent Cu ion-exchanged Z2 catalysts. W/F=4.0 g·s·cm^{-3}, P_{NO}=0.48 vol%. (○) Ni(60)-Cu(75)-Z2, (△) Cu(79)Ni(51)-Z2 (□) Cu(68)-Ni(51)-Z2, (◇) Na(21)-Cu(83)-Z2

The cocation effect was found to depend significantly on the ion exchange mode, as shown in Fig. 2 for Ni-coexistent catalysts. The promotion of activity at higher temperatures was observed prominently in Ni(60)-Cu(75)-Z2 prepared by the normal ion exchange mode, slightly in Cu(79)Ni(51)-Z2 prepared by the simultaneous mode, and hardly in

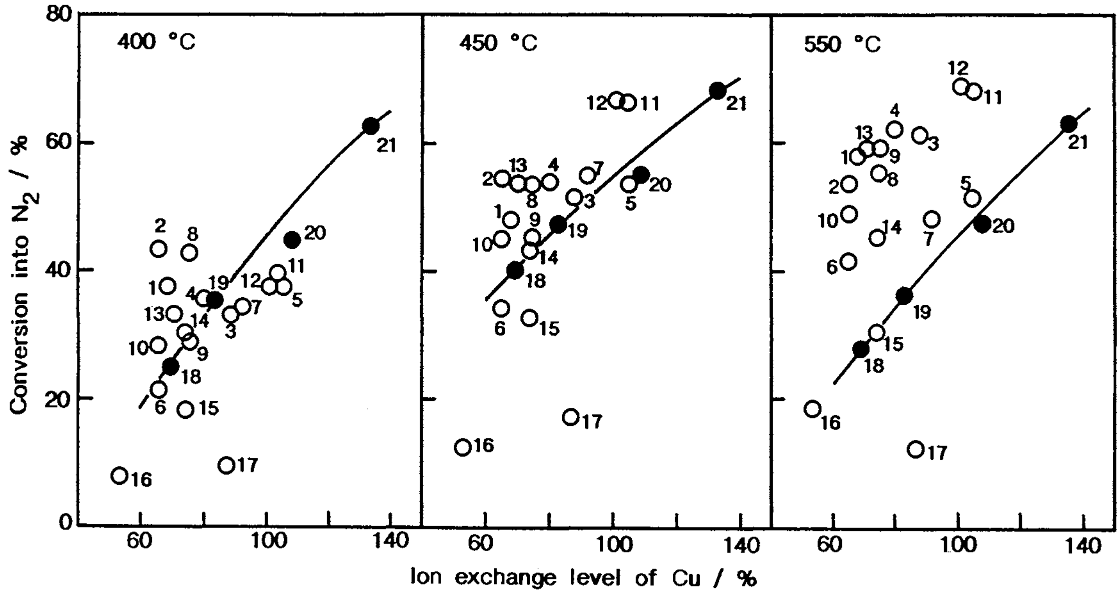

Fig. 3. NO decomposition activities of two-ingredient Z2-based catalysts.
—— ; Correlation line of Na-Cu-Z2, W/F=4.0 g·s·cm^{-3}, P_{NO}=0.48 vol%.
1. Mg(48)-Cu(68)-Z2, **2.** Ca(45)-Cu(65)-Z2, **3.** Sr(23)-Cu(88)-Z2, **4.** Ba(-)-Cu(80)-Z2,
5. Cr(22)-Cu(105)-Z2, **6.** Mn(-)-Cu(65)-Z2, **7.** Fe(41)-Cu(92)-Z2, **8.** Co(65)-Cu(75)-Z2,
9. Ni(60)-Cu(75)-Z2, **10.** Zn(48)-Cu(65)-Z2, **11.** Y(-)-Cu(105)-Z2, **12.** Ag(-)-Cu(101)-Z2,
13. Pt(-)-Cu(70)-Z2, **14.** Pb(-)-Cu(74)-Z2, **15.** Li(31)-Cu(74)-Z2, **16.** K(56)-Cu(53)-Z2,
17. Cs(-)-Cu(87)-Z2, **18.** Na(64)-Cu(69)-Z2, **19.** Na(21)-Cu(83)-Z2, **20.** Na(-)-Cu(108)-Z2,
21. Na(0)-Cu(133)-Z2.

Cu(68)-Ni(51)-Z2 prepared by the reverse mode. This is in marked contrast with the results of Cu ion-exchanged Y-type zeolites[5)] that NO decomposition activities of two-ingredient zeolite catalysts at 500 °C were little dependent on the sequence of ion exchange of Cu and a cocation. It follows that the strong cocation effect in Cu ion-exchanged ZSM-5 zeolites appears only when the normal ion exchange mode is employed.

NO decomposition activities of Z2-based catalysts prepared by the normal ion exchange mode are summarized in Fig. 3, where the conversion into N_2 at 400, 450,and 550 °C is plotted against the ion exchange level of Cu. Points above and below the correlation line of Na-Cu-Z2 indicate the positive and negative cocation effects, respectively. At 400 °C, some cations like Ca and Co show the positive effect while others like Cs show the negative effect. Roughly speaking, however, points of two-ingredient catalysts are distributed around the correlation line, indicating that at this temperature the NO decomposition activity is determined almost exclusively by the loading of Cu ions irrespective of cocations. At 450 °C, points of cocations with some exceptions tend to be on or above the correlation line. At 550 °C, points of cocations except Fe, Cr,and alkali metals are located far above the correlation line, indicating the appearance of the strong cocation effect enhancing the specific activity of Cu ion: at a constant ion exchange level of Cu, the activity of a two-ingredient catalyst is higher than that of the corresponding Na-Cu-Z2 by 20-30% of conversion into N_2. These results confirm again the foregoing observation that the strong cocation effect comes out above 450 °C. It was reported that the NO decomposition activity of Cu ion-exchanged Y-

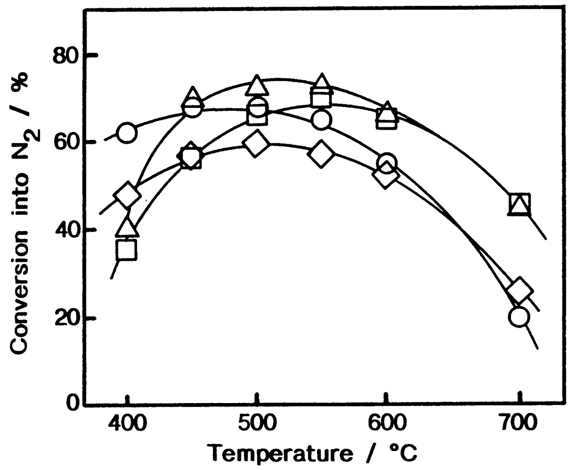

Fig. 4. Cocation effect in Z4-based catalysts. W/F=4.0 g·s·cm^{-3}, P_{NO}=0.48 vol%.
(◇) Na(0)-Cu(174)-Z4, (△) Mg(43)-Cu(128)-Z4
(□) Ni(58)-Cu(123)-Z4, (○) Na(0)-Cu(133)-Z2

type zeolite was increased by the coexistence of Co and Ni while was decreased by that of Ca, Mn, Fe and Zn.$^{5)}$ In ZSM-5 zeolites, on the other hand, the positive cocation effect was observed with many cations irrespective of valency, ionic size and chemical nature. It was confirmed that the activity of Ag(-)-Cu(101)-Z2 which is the most active two-ingredient Z2-based catalyst was not deteriorated even after 50 h on stream at 500 °C.

The cocation effect in Z4-based catalysts is demonstrated in Fig. 4. The comparison between activities of Na-Cu-Z2 and Na-Cu-Z4 suggests that, in addition to the increasing specific activity per Cu ion,$^{1b,3)}$ the more siliceous Z4 matrix is inherently more effective in suffering less decrease of activity at higher temperatures than the Z2 matrix. It is noted that the strong cocation effect, coupled with the inherent nature of Z4 matrix mentioned above, made Mg(43)-Cu(128)-Z4 and Ni(58)-Cu(123)-Z4 catalysts more active than Na(0)-Cu(133)-Z2 above 500 °C; contents of Cu ions in Mg- and Ni-coexistent catalysts are about a half of that in Na(0)-Cu(133)-Z2.

The origin of the cocation effect is not yet clarified. However, it is clear that the cocation effect results not from the direct participation of cocations in NO decomposition catalysis but from the modification of the state, location and/or property of Cu ions because catalysts without Cu did not show any NO decomposition activity.

References

1) a) M. Iwamoto, H. Furukawa, Y. Mine, F. Uemura, S. Mikuriya, and S. Kagawa, J. Chem. Soc., Chem. Commun., **1986**, 1272; b) M. Iwamoto, H. Furukawa, and S. Kagawa, "New Developments in Zeolite Science Technology," ed by Y. Murakami et al., Elsevier, Amsterdam (1986), p.943.

2) H. Shimada, S. Miyama, and H. Kuroda, Chem. Lett., **1988**, 1797; Y. Teraoka, H. Fukuda, and S. Kagawa, ibid., **1990**, 1; H. Hamada, Y. Kintaichi, M. Sasaki, and T. Ito, ibid., **1990**, 1069; H. Yasuda, N. Mizuno, and M. Misono, J. Chem. Soc., Chem. Commun., **1990**, 1094.

3) M. Iwamoto, "Future Opportunities in Catalytic and Separation Technology," ed by M. Misono et al., Elsevier, Amsterdam (1990), p.121.

4) M. Iwamoto, H. Yahiro, Y. Mine, and S. Kagawa, Chem. Lett., **1989**, 213.

5) M. Iwamoto, H. Yahiro, T. Kutsuno, S. Bunyu, and S. Kagawa, Bull. Chem. Soc. Jpn., **62**, 583 (1989).

6) Ion exchange level is defined on the basis of the following nominal ion exchange reaction:
$n\ Na^+(Z) + M^{n+}(S) = M^{n+}(Z) + n\ Na^+(S)$ (Z : in zeolite, S : in solution),
where, n is 1 for Li, K, Cs, and Ag, 2 for Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, and Pb, 3 for Cr and Y, and 4 for Pt.

(Received November 28, 1990)