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Influence of cocations on catalytic activity of copper ion-exchanged ZSM-5 zeolite for reduction of nitric oxide with ethene in the presence of oxygen

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The coexistence of alkaline earth (Ca and Sr) and transition metal (Fe, Co and Ni) cations with Cu ions in ZSM-5 zeolite is effective in the promotion of the maximum activity and the expansion of the active temperature range for the reduction of nitric oxide with ethene in the presence of excess oxygen.

Keywords: Nitric oxide; selective reduction; ethene; oxidizing atmosphere; copper ion-exchanged ZSM-5; cocation effect

1. Introduction

The catalytic reduction of nitric oxide (NO) by hydrocarbons in the presence of excess oxygen is now considered to be the most practicable for the removal of NO_x emitted from diesel engines and lean combustion engines. It has been reported that the reaction is catalyzed by the following catalysts; copper ion-exchanged zeolites [1–4], proton-form zeolites [5], rare earth ion-exchanged zeolites [6], alumina with and without transition metal additives [4,7,8], silica-alumina [8,9] and Fe-silicate [10]. We reported previously [11] that the incorporation of additional metal cations (cocations) into Cu ion-exchanged ZSM-5 was effective in promoting catalytic performance for the direct decomposition of NO, $2NO \rightarrow N_2 + O_2$. In addition, the cocation effect depended strongly on the ion exchange mode; the successive ion exchange with cocations and then copper ions gave the most efficient catalysts. The cocation effect has been also ascertained in the catalysis of NO reduction by ethene in an oxidizing atmosphere, as reported in this paper.

2. Experimental

Copper ions and cocations were introduced into Na-ZSM-5 (SiO_2/Al_2O_3 = 23.3, Tosoh Corporation), which was washed overnight with 0.1 M $NaNO_3$ aqueous solution, by a conventional ion exchange procedure at 333 K [11,12]. After the ion exchanges, samples were filtered and washed thoroughly with deionized water, followed by drying overnight at 383 K. Catalysts obtained by ion-exchanging Na-ZSM-5 with aqueous solutions of cupric acetate and ferric nitrate are termed Na(a)-Cu(b)-ZSM-5 and Na(a)-Fe(b)-ZSM-5, respectively. Two-ingredient ZSM-5 catalysts were prepared by successive ion exchange with an aqueous solution of acetate or nitrate of cocation M and then with an aqueous cupric acetate solution (M(a)-Cu(b)-ZSM-5). Contents of metal cations, which were measured by means of atomic absorption and flame emission techniques after the samples were dissolved in a hydrofluoric acid solution, were presented in parentheses of the catalyst notation in terms of ion exchange level, (nM/Al) × 100; the oxidation number of cations (n) is 1 for Na, 3 for Fe and 2 for others. Details concerning the catalyst preparation are given in table 1. It is noted that the total exchange level ($a + b$) for most catalysts exceeds 100. This may be due to the participation of hydroxylated species of metal cations such as $Cu(OH)^+$ in the ion exchange reaction [13].

The catalytic reduction of NO was carried out with a fixed-bed flow reactor. The reaction gas, NO (3000 ppm)-C_2H_4 (3000 ppm)-O_2 (2%)-He (balance), was fed at a rate of 15 cm^3 min^{-1} over 0.1 g of catalyst which was treated beforehand in a He stream at 773 K for 1 h. The effluent gas was analyzed by gas chromatography, and the NO reduction activity was evaluated in terms of the conversion of NO into N_2, $(2[N_2]_{out}/[NO]_{in} \times 100$.

3. Results and discussion

Temperature dependence of NO reduction by ethene over Co(65)-Cu(75)-ZSM-5 is depicted in fig. 1. The conversion of NO into N_2 increased sharply

Table 1
Preparation of metal ion-exchanged ZSM-5 zeolite catalysts

Catalyst	First ion exchange [a]	Second ion exchange [a]
Na(0)-Cu(112)-ZSM-5	*aq.* $Cu(CH_3COO)_2$ (6.1 mM)	*aq.* $Cu(CH_3COO)_2$ (6.1 mM)
Na(34)-Fe(68)-ZSM-5	*aq.* $Fe(NO_3)_3$ (4.1 mM)	——
Ca(45)-Cu(65)-ZSM-5	*aq.* $Ca(NO_3)_2$ (6.1 mM)	*aq.* $Cu(CH_3COO)_2$ (12.2 mM)
Sr(23)-Cu(88)-ZSM-5	*aq.* $Sr(NO_3)_2$ (6.1 mM)	*aq.* $Cu(CH_3COO)_2$ (12.2 mM)
Fe(61)-Cu(92)-ZSM-5	*aq.* $Fe(NO_3)_3$ (4.1 mM)	*aq.* $Cu(CH_3COO)_2$ (12.2 mM)
Co(65)-Cu(75)-ZSM-5	*aq.* $Co(NO_3)_2$ (6.1 mM)	*aq.* $Cu(CH_3COO)_2$ (12.2 mM)
Ni(60)-Cu(75)-ZSM-5	*aq.* $Ni(CH_3COO)_2$ (6.1 mM)	*aq.* $Cu(CH_3COO)_2$ (12.2 mM)

[a] 333 K; 12 h; zeolite/aqueous solution = 10 g/1 dm^3.

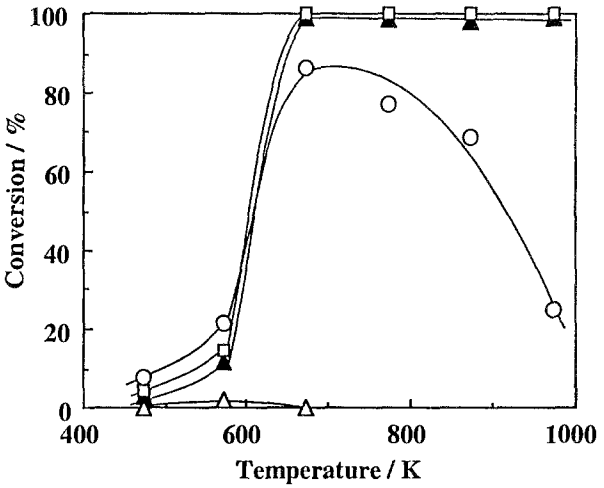

Fig. 1. Reduction of NO by ethene in the presence of oxygen over Co(65)-Cu(75)-ZSM-5. ○: Conversion of NO into N_2, □: Conversion of C_2H_4, ▲: Conversion of C_2H_4 into CO_2, △: Conversion of C_2H_4 into CO.

with increasing temperature and reached a maximum at 673 K. The conversion of ethene increased steeply between 573 and 673 K and was 100% above 673 K. Ethene was converted into CO_2, although a slight amount of CO was detected at 573 K. The material balance with respect to carbon was between 98–100%, indicating that carbonaceous deposits were not formed on the catalyst under the present reaction condition. Common to all the catalysts investigated were two characteristic features observed in fig. 1 that ethene is completely converted into CO_2 above 673 K and the maximum NO reduction activity is attained at 673 K.

The overall reaction of the reduction of NO by ethene in the presence of oxygen can be written as follows:

$$2x\mathrm{NO} + y\mathrm{C_2H_4} + (3y - x)\mathrm{O_2} \rightarrow x\mathrm{N_2} + 2y\mathrm{CO_2} + 2y\mathrm{H_2O}. \quad (1)$$

It was reported that the reaction over Cu ion-exchanged zeolites proceeded by the reduction of NO with partially oxidized intermediates of hydrocarbons and that this main reaction competed with the oxidation of the intermediates (or hydrocarbons) by O_2 [7]. Accordingly, the sharp increase in NO reduction activity below 673 K which is accompanied with the sharp increase in ethene conversion is due to the increasing activity toward the main reaction. Above 673 K where the conversion of ethene is 100%, on the other hand, the decreasing conversion into N_2 with increasing temperature is due to the decreasing selectivity to the main reaction, in other words, the decreasing x/y ratio in eq. (1).

NO reduction activities of two-ingredient catalysts are shown in fig. 2 as a function of reaction temperature, together with that of Na(0)-Cu(112)-ZSM-5. Above 673 K, the two-ingredient catalysts showed higher activity than Na(0)-

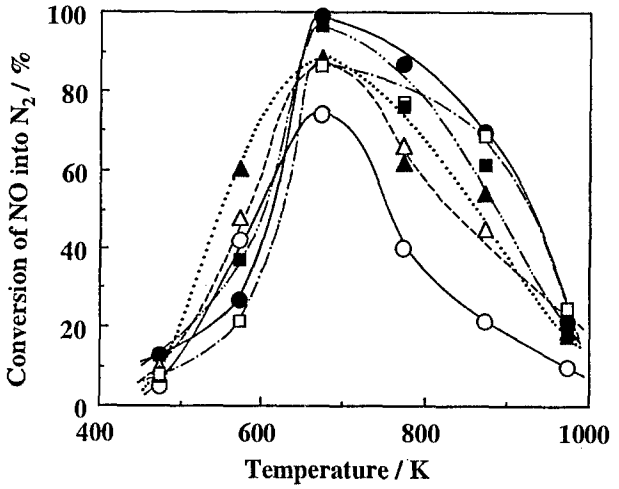

Fig. 2. Cocation effect in catalytic activity of Cu ion-exchanged ZSM-5 catalysts for the reduction of NO by ethene in the presence of oxygen. ○: Na(0)-Cu(112)-ZSM-5, ●: Ca(45)-Cu(65)-ZSM-5, △: Sr(23)-Cu(88)-ZSM-5, ▲: Fe(61)-Cu(92)-ZSM-5, □: CO(65)-Cu(75)-ZSM-5, ■: Ni(60)-Cu(75)-ZSM-5.

Cu(112)-ZSM-5 though the conversion into N_2 at each temperature and the temperature dependence of the activity differed among the catalysts. At 573 K, on the other hand, the change in activity by introducing cocations (cocation effect) was different depending on the kind of cocations; the Fe-coexistent catalyst was superior to, the Sr- and Ni-coexistent catalysts were comparable to Ca- and Co-existent catalysts were inferior to Na(0)-Cu(112)-ZSM-5 in activity. Although ion exchange levels of Cu ions and cocations are different from each other, the results shown in fig. 2 are sufficient to verify how effective the coexistence of alkaline earth and transition metal cations with Cu ions is in promoting the catalytic performance for the reduction of NO by ethene in the presence of oxygen. The cocation effects revealed in this study are the promotion of the maximum activity at 673 K and the expansion of the active temperature range.

As we reported previously, the catalytic activity of Cu ion-exchanged ZSM-5 for the direct decomposition of NO was enhanced above 723 K by the incorporation of cocations [11]. The cocation effect in the NO decomposition catalysis is expected to result from the modification of the property of Cu ions because Cu is a sole ingredient active for the direct decomposition of NO [14]. For the selective reduction of NO, however, situations may be somewhat different. Because the reaction is catalyzed by zeolite catalysts ion-exchanged with various cations [4,7], the direct participation of cocations in catalysis is strongly expected. As shown in fig. 3, Fe ion-exchanged ZSM-5 was more active for the selective reduction of NO than Cu ion-exchanged ZSM-5 at 573 K. Thus the higher activity of the Fe-coexistent catalyst at 573 K (fig. 2) is convincingly

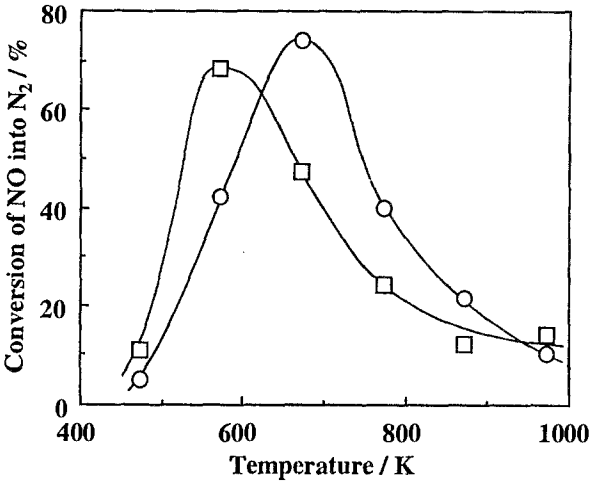

Fig. 3. NO removal activity in Na(0)-Cu(112)-ZSM-5 (○), and Na(34)-Fe(68)-ZSM-5 (□) in the presence of ethene and oxygen.

attributed to the contribution of Fe ions which are superior to Cu ions in activity at lower temperatures. As mentioned above, an increase in NO reduction activity of the two-ingredient catalysts above 673 K originates from the increasing selectivity toward the main reaction, that is, the suppression of the combustion of ethene or its oxidized intermediates. This might be due to the chemical and/or physical change of Cu ions; locations, aggregation state, electronic state, decrease in net concentration, etc. For full understanding and evaluation of the cocation effect in the selective reduction of NO, further studies should be necessary concerning the dependence of the activity on ion exchange level of Cu ions and cocations, reaction mechanism and characterization of catalysts.

In conclusion, the incorporation of additional metal cations to Cu ion-exchanged ZSM-5 was proved to result in the enhancement of the maximum activity as well as the expansion of the active temperature range for the reduction of NO by ethene in the presence of oxygen. The present results suggest one possible way to modify the catalytic performance of Cu ion-exchanged zeolite catalysts which are presently most active catalysts for the selective reduction of NO.

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