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CATALYTIC REDUCTION OF NITRIC OXIDE WITH AMMONIA OVER TRANSITION METAL ION-EXCHANGED Y ZEOLITES

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Catalytic reduction of nitric oxide with ammonia was studied over transition metal ion-exchanged Y zeolite (Me-Y) catalysts. Among various catalysts used, Cu(II)-Y was found to be of particular interest, exhibiting low temperature activity and an unusual catalytic activity-temperature profile with a maximum at 120°C. It was also observed that the catalytic activity was enhanced considerably when a second cation, especially Co(II) or Fe(III), was co-exchanged together with Cu(II) in Y zeolite. Such phenomena were discussed briefly.

The removal of nitrogen oxides from exhaust gases is a subject of current importance for the environmental preservation. One way to remove nitric oxide is the catalytic reduction of NO with adequate reducing agents, and various combinations of catalysts and reducing agents have been tested so far, using mainly metal$^{(1),(2)}$ or metal oxide$^{(3),(4),(5)}$ catalysts. The authors report here some of interesting catalytic behaviors of transition metal ion-exchanged Y zeolites in the catalytic reduction of nitric oxide with ammonia.

Transition metal ion-exchanged Y zeolites (Me-Y) were prepared from Linde NaY zeolite by conventional ion-exchange procedures. In the case of binary cation-exchanged zeolites (Me_1, Me_2)-Y in which Me_1 and Me_2 denote different cationic species, the component cations were exchanged consecutively and the degree of ion-exchange was determined

Table 1. The selectivity to N_2 or N_2O in the NO - NH_3 reaction

Catalyst	Reaction Temp. (°C)	Selectivity N_2(%)	N_2O(%)	NO Conv. (%)
Pt(II)-Y	135	57	43	21.1
Pd(II)-Y	143	70	30	15.5
Co(II)-Y	82	64	36	19.0
Co(III)-Y	430	77	23	24.4
Cu(II)-Y	100	70	30	19.0
Fe(III)-Y	248	69	31	16.8
Cu-Pd-Y	160	72	28	34.3
Cu-Ni-Y	130	61	39	24.5
Cu-Fe-Y	150	68	32	31.2
Cu-Co-Y	190	78	22	21.4
Co_3O_4	159	56	44	29.5
CuO	237	93	7	35.9
Pd(3%)-SiO_2	200	46	54	21.9

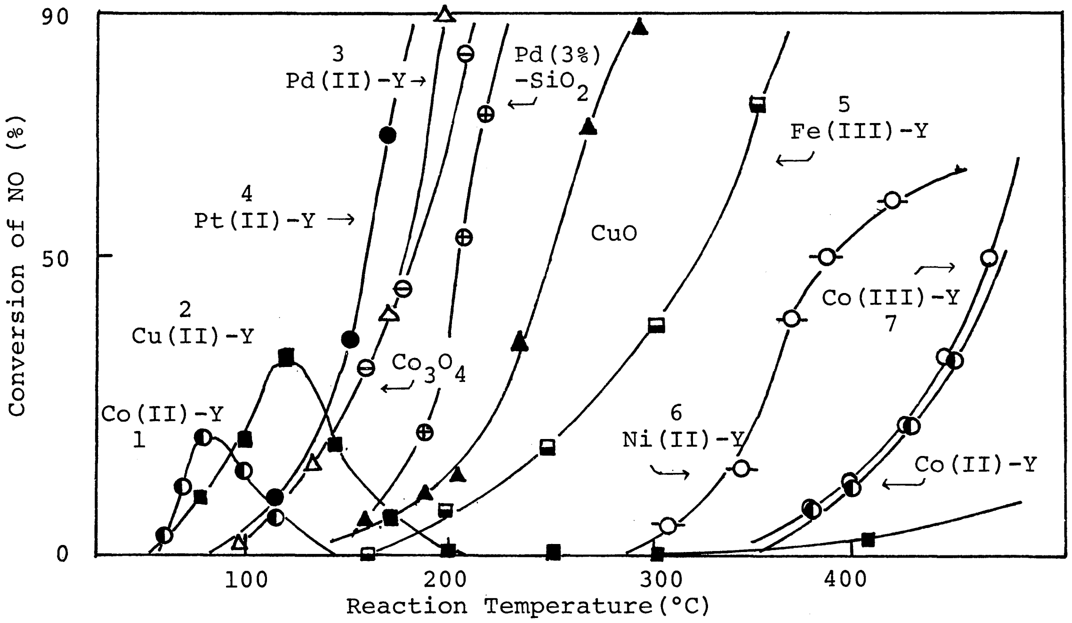

Fig. 1. Catalytic activity of various transition metal ion exchanged Y-type zeolites for the NO-NH_3 reaction. NO: 1.8ml/min,NH_3: 1.2ml/min, He: 57ml/min,contact time: 1g·sec/ml.
The degree of ion exchange was as follows.
1. Co(II)-Y : 70%, 2. Cu(II)-Y : 68%, 3. Pd(II)-Y : 48%,
4. Pt(II)-Y : 52%, 5. Fe(III)-Y : 75%, 6. Ni(II)-Y : 80%,
7. Co(III)-Y : 95%.

by fluorometry.

The catalytic reaction was carried out in a fixed bed flow reactor under an atmospheric pressure. Gaseous mixture of NO and NH_3, diluted with helium, was passed through catalysts at a fixed contact time of 1 g·sec/ml. The gaseous composition was analyzed by gas chromatography before and after the reaction, using following column packings; Molecular Sieve 13X for N_2 and NO, Porapak Q for N_2O, and Chromosorb 104 for NH_3.

Figure 1 shows experimental results on the catalytic activity of Me-Y toward NO-NH_3 reaction tested over wide ranges of temperature. The conversion of NO at a fixed contact time was taken as a measure of catalytic activity and was plotted against reaction temperature for individual catalyst used. Plots for a few representive metal oxide catalysts are also included for comparison. The reaction products were N_2, N_2O and H_2O in all cases with selectivities for N_2 and N_2O shown in Table 1. It is noted that selectivities to N_2 were ca. 60-80% on all the cation-exchanged zeolite catalysts exhibiting a relatively minor variation with the cationic species exchanged.

As is clearly seen from Fig. 1, the catalytic activity of Me-Y as well as its temperature dependence differed largely with the cationic species. Pe(II)-Y and Pd(II)-Y, known to be active in many other reactions, were highly active in this case, too, whereas Fe(III)-Y, Ni(II)-Y and Co(III)-Y were much less active. All these catalysts showed monotonous activity increases with the increase in temperature.

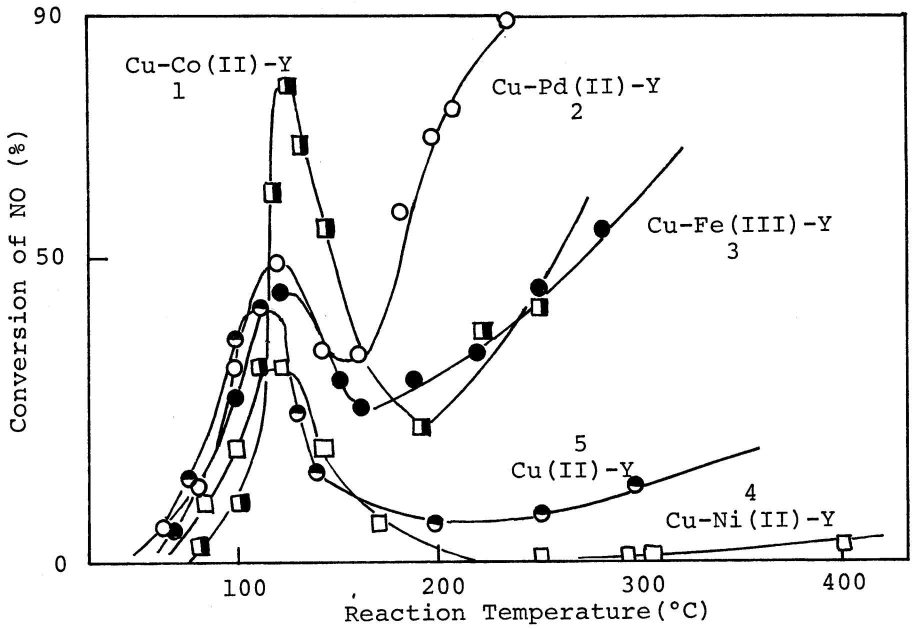

Fig. 2. Catalytic activity of binary transition metal ion-exchanged Y-type zeolites for the NO-NH_3 reaction. NO: 1.8ml/min, NH_3: 1.2ml/min, He: 57ml/min.
The degree of ion exchange was as follows.

1. Cu(II) : 31%, Co(II) : 62%
2. Cu(II) : 32% , Pd(II) : 21%
3. Cu(II) : 36%, Fe(III) : 62%
4. Cu(II) : 58% , Ni(II) : 38%
5. Cu(II) : 68%.

The catalytic activity were in the order of

$$\mathrm{Pt(II)\text{-}Y} \gtrsim \mathrm{Pd(II)\text{-}Y} >> \mathrm{Fe(III)\text{-}Y} > \mathrm{Ni(II)\text{-}Y} > \mathrm{Co(III)\text{-}Y}.$$

The most interesting were, however, the cases of Cu(II)-Y and Co(II)-Y, both of which showed low temperature activities but with complex temperature dependences.

In the case of Cu(II)-Y, the catalytic activity, detectable at a temperature as low as 50°C, increased with the increase in reaction temperature until about 120°C where a maximum activity was attained. At higher temperatures the activity first decreased with temperature to a negligibly small value, thus resulting in a bell-shaped correlation between catalytic activity and temperature, and then increased only gradually above 200°C. The activity decrease on the right side of the bell was not due to degenerative change of the catalyst but an essential phenomenon, because the activity curve could be retraced quite reversibly by changing temperature.

A seemingly similar maximum in the activity-temperature curve was observed over freshly prepared Co(II)-Y, though only in the first experiment where reaction temperature was raised stepwise. In this case, however, the activity decrease after the maximum was irreversible, and catalyst remained inactive even when temperature was lowered. The change in color of the catalyst suggested that Co(II) in zeolite was oxidized during the experiment to Co(III) which was inactive at this temperature range. Moreover, at higher temperature, the catalytic activity was confirmed to coincide with that of Co(III)-Y.

The same kind of experiment was performed on binary metal ion-exchanged Y zeolite catalysts (Me_1, Me_2)-Y in which Me_1 was fixed to Cu(II)(Fig. 2). The catalytic activity-temperature profile showed an activity maximum responsible to Cu(II) near 120°C and an activity increase due to the second component cation at the higher temperature region. Quantitatively, however, the catalytic activities of binary systems were not mere summations of those of single component systems but showed additional promoting effects. For example, (Cu(II), Fe(III))-Y exhibited a specific activity 2.4 times as high as that expected from Cu(II)-Y and Fe(III)-Y, at 120°C. The promoting effect was in particular pronounced with (Cu(II), Co(II))-Y, over which conversion of NO more than 80% was attained at 125°C.

As mentioned above, Cu(II)-Y showed an unusual catalytic behavior, i.e., the bell-shaped dependence of activity on temperature, toward the NO-NH_3 reaction system. Since such a phenomenon was not ovserved in the NO-NH_4 or NO-H_2 system, it is suggested that the coordination of NH_3 molecules to Cu(II) in zeolite is related to this phenomenon. In fact, Vansant et al.(6),(7) reported that NH_3 adsorbed on Cu(II) to form a square planar ammine complex $Cu(NH_3)_4^{2+}$ in the zeolite cavity at low temperature, and that partial desorption of NH_3 at ca. 100°C gave a distorted tetrahedral complex with one NH_3 per Cu(II) ion. It was also reported that the complete removal of NH_3 from the complex resulted in the migration of Cu(II) ion from the super cage of zeolite to the sodalite cage. Considering these facts, we tentatively propose the mechanism of NO reduction with ammonia that NO and NH_3 molecules coordinate to a common metal ion in zeolite and the interaction between them leads to the reduction of NO. The promoting effect of binary systems may be resulted from possible facilitation of any charge transfer process included in the catalysis. Further studies to investigate these interesting problems are in progress.

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