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Enhancement of Catalytic Activity of Copper Ion-Exchanged Y Type Zeolites for the Decomposition of Nitrogen Monoxide

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Synopsis. Catalytic activity of Y zeolites containing copper ions (CuY) for decomposition of nitrogen monoxide was enhanced through additional exchange of other metal ions or evacuation treatment around 923—973 K. In the first case, Co^{3+} or Ni^{2+} ions increase the catalytic activity while Ca^{2+}, Mn^{2+}, Fe^{2+}, and Zn^{2+} diminish the catalytic activity of CuY. In the second case, the catalytic activity of CuY evacuated at 973 K was twice that of CuY without the evacuation treatment, which is discussed in connection with the increment of Cu ions active for the decomposition.

Decomposition of nitrogen monoxide (NO) has been reported to be catalyzed over partially copper(II) ion-exchanged Y zeolites (CuY).[1] This process is the simplest method for the removal of harmful NO because any reducing agents or absorbents are not necessary.[2] Very recently we have also reported that copper ion-exchanged ZSM-5 zeolites are more active than the CuY.[3] However, much more metal ions can be exchanged into Y-type zeolite lattice than into ZSM-5, and Y zeolite can be synthesized more easily and more cheaply. From the viewpoint of practical use of the zeolite catalyst, therefore, it would be very desirable to enhance the catalytic activity of the CuY. In the present work, we have found two possible ways; an additional exchange of other metal ions or evacuation treatments at higher temperatures caused an increase in the catalytic activity of the decomposition.

Experimental

Experimental apparatus and procedures were similar to those reported previously.[1,3] The reactant gas containing 5 vol% of NO and 95% helium was passed through the catalyst bed at 773 or 823 K and the extents of conversion of NO and to N_2 and O_2 were measured by gas chromatography. The total flow rate of feed gases was 30 $cm^3\ min^{-1}$, catalyst weight being 2.0 g. Zeolite samples prepared by the conventional ion exchange of a NaY zeolite (Linde SK-40). In the two-component zeolites (containing copper ion and additional metal ion), zeolites were ion-exchanged first with copper ion and then with the other metal ion, or in the reverse order. Exchange levels of copper and other metal ions in the two component systems were each ca. 30%.

Results and Discussion

The decomposition activities of the two-component zeolites at 773 K are summarized in Table 1. The reaction products at this temperature were N_2, O_2, and NO_2. The formation of N_2O was not observed. In the table it should be noted that the extent of converted NO was approximately twice as much as that of produced N_2. This is due to the oxidative reaction of NO with generated O_2 to yield NO_2, $2NO+O_2 \rightarrow 2NO_2$ as discussed in the previous paper.[1]

Two interesting observations should be pointed out concerning Table 1. First the activity was increased by the coexistence of Co^{3+} or Ni^{2+}, while Ca^{2+}, Mn^{2+}, Fe^{2+}, and Zn^{2+} ions diminished the decomposition ability of CuY. Secondly, the catalytic activities of the two-component zeolites were little dependent on the order of ion exchange, as shown in the table. This fact suggests that the locations of metal ions over various exchangeable sites are decided by the difference between preferences of two kinds of metal ions toward the sites and not by the order of ion exchange.

It was confirmed in separate experiments that Co^{3+} or Ni^{2+} exchanged zeolites (without Cu^{2+} ions) showed no catalytic activity for the NO decomposition, while these ions had an effect for enhancement of the catalytic activity of the CuY. This suggests that the Co^{3+} or Ni^{2+} ions presumably occupy preferentially inner sites S_I and/or $S_{I'}$ which are generally inert for the catalytic reactions, and more Cu^{2+} ions would locate on the super cage-sites. However, one can not deny the possibility that some interaction of Cu^{2+} with Co^{3+} (or Ni^{2+}) resulted in the enhancement of the activity.

Next, pretreatments for the activation of a CuY zeolite (exchange level=70%) were examined. In a pretreatment, the zeolite sample was heated to 773 K in a dynamic vacuum, exposed to oxygen for 30 min, and then reevacuated for 30 min at the same temperature to remove such impurities on the zeolite surface as water, carbon dioxide, and possibly hydrocarbons. Subsequently, the sample was again heated to a desired temperature in a dynamic vacuum and evacuated at this temperature for 1 h. The catalytic run was carried out at 823 K and the results are shown in Fig. 1. It is

Table 1. Catalytic Activities of Various Two Components Zeolites Containing Copper(II) Ions for the Decomposition of Nitrogen Monoxide at 773 K

Exchanged metal ion	CuMY[a] Conversion(%)[b] of NO	CuMY[a] Conversion(%)[b] to N_2	MCuY[a] Conversion(%)[b] of NO	MCuY[a] Conversion(%)[b] to N_2
Cu	10.5	6.4	—	—
Ca-Cu	4.4	2.9	7.4	3.6
Mn-Cu	6.1	3.7	10.6	4.1
Fe-Cu	6.7	3.0	5.9	5.3
Co-Cu	13.5	7.1	12.2	6.1
Ni-Cu	15.5	8.4	16.6	11.4
Zn-Cu	9.2	5.0	6.7	3.0
Ag-Cu	7.5	7.1	8.9	6.4

a) CuMY indicates the order of ion-exchange first with copper ion and then with another metal ion, while MCuY was ion-exchanged in the reverse order. b) These values were calculated on the basis of the amount of NO fed.

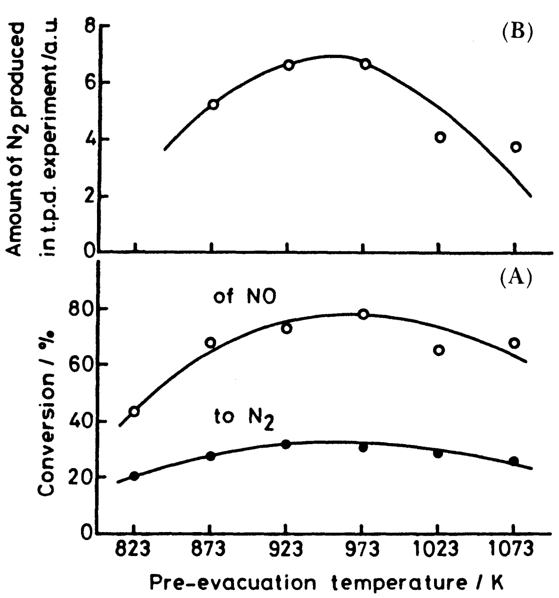

Fig. 1. Effect of the pre-evacuation temperature of the CuY zeolite (70%) on the catalytic activity for the NO decomposition at 823 K (A) and on the amounts of N_2 generated in TPD experiments (B).

evident that the evacuation at higher temperatures caused an increase in decomposition activity of the CuY, though too high evacuation temperatures resulted in a decrease in catalytic activity. The activity of the CuY evacuated at 973 K attained a level of two times as great as that of CuY without the evacuation treatment. The best temperature for evacuation were in the range 923—973 K. No deterioration of the effectiveness of the catalyst was found even after 10 h of continuous service.

To gather more evidence for the activity change of CuY catalysts, temperature programmed desorption (TPD) profiles of NO absorbed on the respective catalysts were investigated by means of the experimental method similar to that of Ref. 4. The amounts and temperatures of NO and N_2O desorbed remained roughly unchanged irrespective of the evacuation treatment. By contrast, the amounts of N_2 desorbed during the TPD procedures were dependent on the evacuation temperatures, though the desorption temperature did not change with the treatment. The amounts of N_2 are plotted in Fig. 1(B) as a function of the evacuation temperatures, indicating a bell-shaped dependence. It is noteworthy that the dependences of catalytic activities in flow system on the evacuation temperature is almost the same as that of N_2 formation in the TPD experiments. It was further confirmed in a separate TPD experiment that N_2 molecules did not chemically adsorb on the CuY surface at room temperature, indicating that the desorption of N_2 in the TPD experiments of adsorbed NO is due to the decomposition or reaction of some surface intermediates. Therefore, it follows that the increase in catalytic activity due to the evacuation around 923—973 K results from the increment of the number of active sites for the decomposition and not from the increment of turnover frequency per active site.

We have recently suggested that the active sites for the decomposition reaction would be copper(I) ions on zeolites.[3] In addition, it has also been reported that an evacuation treatment at higher temperatures above 873 K resulted in the desorption of oxygen molecules.[5,6] The desorption of oxygen would cause formation of copper(I) ions from copper(II) ions owing to charge transfer from anionic oxygen species to metal ions, which would result in the increase in the activity. The decrease in activity of CuY evacuated above 1023 K might be due to partial destruction of the zeolite lattice,[7] though we could not observe it by X-ray analysis.

In conclusion, the additional ion exchange of Co^{3+} or Ni^{2+} or the evacuation treatment around 923—973 K have been shown to enhance the catalytic activity of the CuY for the NO-decomposition.

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