CHEMISTRY LETTERS, pp. 213-216, 1989.

Excessively Copper Ion-exchanged ZSM-5 Zeolites as Highly Active Catalysts for Direct Decomposition of Nitrogen Monoxide

Masakazu IWAMOTO,* Hidenori YAHIRO, Yoshihiro MINE,+
and Shuichi KAGAWA+
Department of Industrial Chemistry, Faculty of Engineering,
Miyazaki University, Miyazaki 889-21
+Department of Industrial Chemistry, Faculty of Engineering,
Nagasaki University, Nagasaki 852

Repeated ion exchange of the ZSM-5 zeolite using aqueous copper(II) acetate solution was found to bring about excess loading of copper ions above 100% of exchange level. The catalytic activities of the resulting Cu-ZSM-5 zeolites for direct decomposition of nitrogen monoxide were very high and increased with increasing exchange level. The activity did not decrease even after 30 h of continuous service.

The catalytic removal of nitrogen monoxide (NO) from exhaust streams can be carried out by either reduction with gaseous reductant or decomposition without any reducing agents. At the present, the former process was preferentially employed in industries and automobiles,1) though the latter is simpler and cheaper than the former. This is due to the fact that to date no suitable catalyst of consistently high activity for the latter process has been found. Very recently, however, we have reported that the catalytic decomposition successfully proceeds on various copper ion-exchanged zeolites2-5) and the ZSM-5 zeolite is the most suitable for the reaction.3,4) It is very desirable to enhance the catalytic activity of the Cu-ZSM-5, since highly active catalysts could be used in practical processes and might change the current catalytic reduction process to new decomposition one. We wish here to report that several ion exchange between Na^+ and Cu^{2+} brought about excess loading of copper ions on the ZSM-5 zeolite and the resultant zeolites are very active for the decomposition of NO.

The parent ZSM-5 (represented by Z) zeolite with SiO_2/Al_2O_3 molar ratio of 23.3 was supplied by Tosoh Corporation. The zeolite was ion-exchanged with usual procedure; that is, the zeolite was washed with dilute $NaNO_3$ solution, ion-exchanged in aqueous copper(II) acetate solution, washed with water, and dried at 383 K overnight. The degree of ion exchange was measured by using atomic adsorption spectrometry after the Cu-Z samples were dissolved in HF solution.

To get zeolites with high extents of ion exchange, the parent zeolite underwent several ion exchange treatments. For example, ca. 15 g of the ZSM-5 zeolite was ion-exchanged in 1 dm^3 of copper(II) acetate solution with concentration of 10 - 11 mmol dm^{-3} overnight, and separated from the solution by filtration. The obtained wet cake was again ion-exchanged in new copper solution. After the desired repetition of the ion exchange treatment, the sample was washed with water and dried. Three or more ion-exchange procedure resulted in the excess loading of copper ions above 100% of exchange level, where the extent of ion exchange was calculated under the assumption that one copper(II) ion can be exchanged for two sodium(I) ions. The similar phenomenon has also been reported by Namba and Yashima.6) This is very interesting in the field of ion exchange; the reason for this phenomenon and the state of copper ions on the zeolite are the problems to be solved in the future. The degree of ion exchange of the copper zeolites prepared were 30-143%. These samples have been called Cu-Z-143 (cation - zeolite structure - degree of exchange), hereafter.

The measurement of catalytic activity was performed by using a fixed-bed flow reactor. Experimental apparatus and procedures were essentially similar to those reported previously.2) The reactant gas contained 1.0 vol% of NO and 99.0% of helium, its flow rate was 15 cm^3 min^{-1}, and the catalyst weight was 1.0 g.

The catalytic activity of each Cu-Z sample for the NO decomposition was measured as a function of reaction temperature. The results of Cu-Z-143 are shown in Fig. 1 as an example. It is obvious that the catalytic activity appeared around 573 - 623 K, the maximum activity was observed at 723 - 823 K, and at higher temperatures the degrees of conversions decreased with increasing temperature. The temperature dependence shown in the figure is in good agreement with that reported previously for the Cu-ZSM-5 zeolites with low ion exchange level.3,4) It should be noteworthy that, when the reaction temperature was again set at 773 K after the experiment at 923 K, the degree of conversions of NO and into N_2 and O_2 were the same as those of the original samples within experimental errors. Thus, the decrement of the catalytic activity at higher temperatures is not attributable to the deactivation of the catalyst. It is presumably due to change of the reaction mechanism, the rate-limiting step, and/or the state of active sites in the catalyst.

At low temperatures, a small amount of N_2O was produced and above 673 K it could not be detected. This indicates that N_2O would be one of the intermediate products during the NO

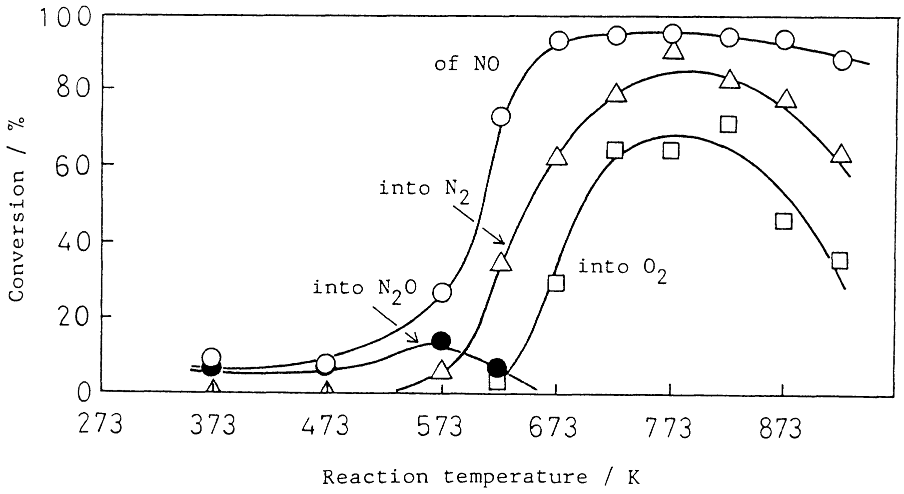

Fig. 1. Temperature dependence of decomposition of NO over Cu-Z-143 at 4.0 $g\cdot s\cdot cm^{-3}$ and P_{NO} = 1.0%.

decomposition and the decomposition of N_2O is faster than that of NO at higher temperatures, which are in accord with the results on Cu-Y zeolites.[2)] As shown in Fig. 1, the degree of conversion of NO was not equal to that of N_2 and O_2 formation. The discrepancy between the amounts of NO consumed and of N_2 produced was approximately equal to that between N_2 and O_2 generated. Furthermore, the formation of NO_2 was confirmed by mass and IR spectrometers, though quantitative analysis of NO_2 was not carried out. Based on these results, the disagreement among the amounts of NO reacted, N_2 and O_2 produced can be attributed to the formation of NO_2 which can not be detected by usual gas chromatography. Namely, a part of O_2 generated through the decomposition would further react with unreacted NO to yield NO_2.

The correlation between the catalytic activity and the exchange level of copper ion is depicted in Fig. 2, where the results at 723 K are summarized. Clearly, two interesting observations can be pointed out. First, the conversions of NO and into N_2 and O_2 show S-shaped dependence on the exchange level; the decomposition rate was very small on low-exchanged Cu-Z zeolites but increased rapidly above ca. 50% of exchange level. Two interpretations can be proposed to explain the phenomenon. The first explanation is the concept that there are two or more kinds of cation sites in the ZSM-5 framework, one of which is most easily exchanged with a copper ion but it is an inert site for the decomposition like S_I in the Y-type zeolite. This might be supported by the fact that at least two kinds of sites exist in the ZSM-5.[7)] The second one is the idea that the NO decomposition proceeds only under cooperation of two adjacent active sites. At the present, it remains unsolved which is correct.

The second interesting point is the catalytic activities of the Cu-Z samples with 100% or more exchange level; the decomposition rate to N_2 and O_2 monotonously increased with increasing exchange levels in this region. This indicates that the copper ions excessively loaded into the ZSM-5 zeolite is effective for the decomposition reaction, though their states are unknown. At the best result in the present experiment, the conversion into N_2 was 80 - 85%, revealing that NO was nearly perfectly decomposed to N_2 and O_2 under these reaction conditions. This result suggests that excess

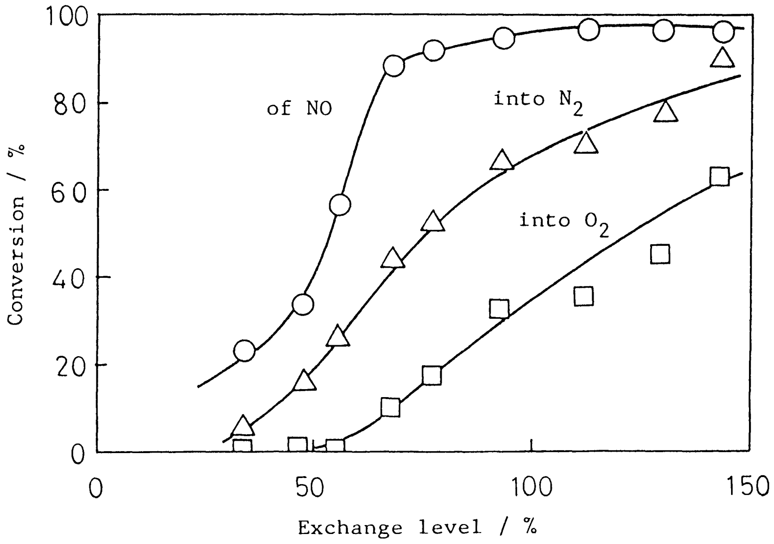

Fig. 2. Correlation between exchange level of copper ions and the conversions of NO and into N_2 and O_2. T = 723 K, W/F = 4.0 g·s·cm^{-3}, P_{NO} = 1.0%.

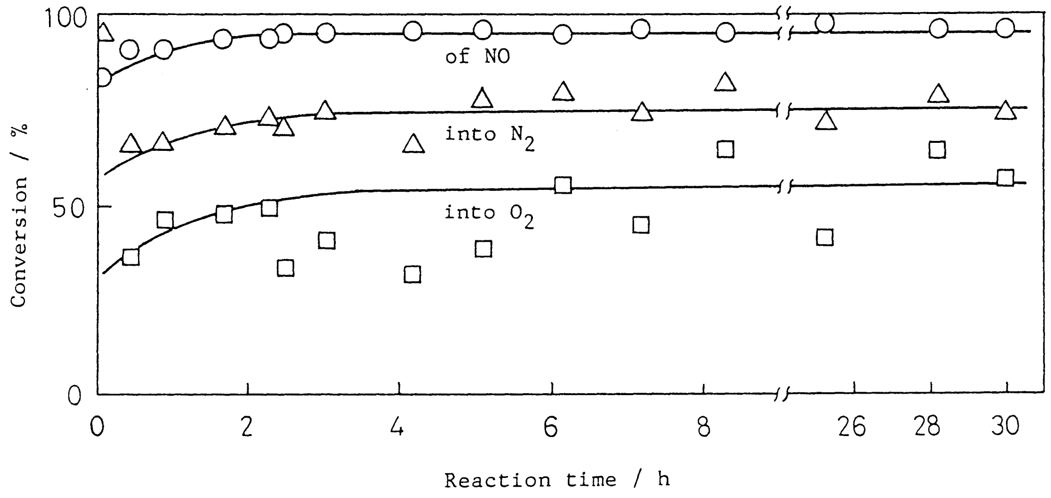

Fig. 3. Time course of NO decomposition over Cu-Z-112 at $4.0\ g\cdot s\cdot cm^{-3}$, P_{NO} = 1.0%, and T = 723 K.

loading of copper ions as well as dual metal ion exchange[5)] is one possible way to develop more active catalyst for the NO decomposition.

The variation of decomposition over Cu-Z-112 with reaction time is shown in Fig. 3. The extents of conversion of NO and into N_2 and O_2 were gradually increased with reaction time up to ca. 3 h and turned into a steady state process. No deterioration of the effectiveness of the catalyst was found at this temperature even after 30 h of continuous service; in the present work an experiment of greater than 30 h was not carried out. The conversions of NO and into N_2 and O_2 under the steady state process were approximately 95%, 75%, and 55%, respectively.

The above results indicate that excessively copper ion-exchanged ZSM-5 zeolites are highly active and stable catalysts for the decomposition of NO.

References

1) A. Crucq and A. Frennet, "Catalysis and Automotive Pollution Control," Elsevier, Amsterdam (1987), pp. 1-96.
2) M. Iwamoto, S. Yokoo, K. Sakai, and S. Kagawa, J. Chem. Soc., Faraday Trans. 1, 77, 1629-1638 (1981).
3) M. Iwamoto, H. Furukawa, and S. Kagawa, "New Development in Zeolite Science Thechnology," ed by Y. Murakami et al., Elsevier, Amsterdam (1986), p. 943.
4) M. Iwamoto, H. Yahiro, and K. Tanda, Stud. Surf. Sci. Catal., in press.
5) M. Iwamoto, H. Yahiro, T. Kutsuno, S. Bunyu, and S. Kagawa, Bull. Chem. Soc. Jpn., in press.
6) S. Namba and T. Yashima, private communication.
7) W. J. Mortier, "Compilation of Extra Framework Sites in Zeolite," Butterworth Sci., London (1982), p. 53.

(Received October 11, 1988)