Copper(II) Ion-exchanged ZSM-5 Zeolites as Highly Active Catalysts for Direct and Continuous Decomposition of Nitrogen Monoxide

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ZSM-5 zeolites containing Cu^{2+} ions showed unusually high and steady state activity for the catalytic decomposition of nitrogen monoxide; for example, the degrees of conversions of NO, and of conversion into N_2 and O_2 were 97, 85, and 70%, respectively, at 823 K with a contact time of 10.0 g s cm^{-3} over 73% exchanged Cu-ZSM-5.

The removal of nitrogen monoxide (NO) from exhaust streams remains an important problem which has been studied extensively; catalytic reduction using a reductant such as ammonia has been employed in industry *etc.*[1] However, the catalytic decomposition of NO, which would provide the simplest method from most points of view, has not yet been carried out successfully because the oxygen contained in the feed gas or generated through the decomposition of NO poisons the activity.[1,2] The only exception is the Cu^{2+} ion-exchanged Y-type zeolite which we have already reported, the catalytic activity of which was not high, however.[3] We report here that Cu^{2+}-exchanged ZSM-5 zeolites show very high and stable catalytic activity for the NO decomposition.

The ZSM-5 zeolite with a silica/alumina molar ratio of 50 was supplied by Toyo Soda Mfg. Co. Ltd. The zeolite was ion-exchanged in aqueous copper(II) acetate of appropriate concentration, and experiments were performed using a fixed-bed flow reactor described elsewhere.[3] The reactant gas was a mixture of 4 vol% of NO and 96 vol% of helium, the flow rate was 15 cm^3 min^{-1}, and the catalyst weight was 1.0 g, unless otherwise stated.

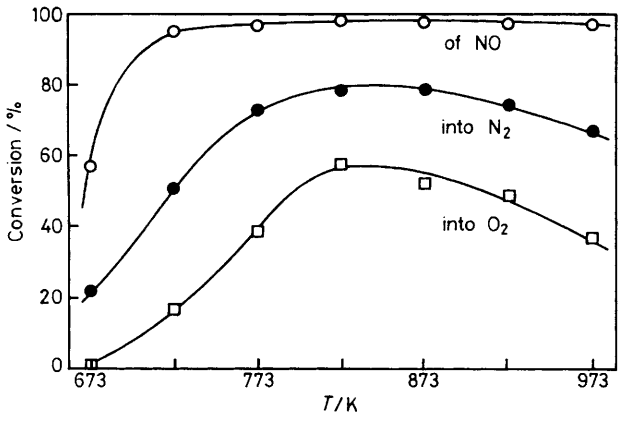

Figure 1. Temperature dependence of catalytic activity of Cu-ZSM-5-73 for NO decomposition with a contact time of 4.0 g s cm^{-3}.

The variation with reaction time of the catalytic activity of Cu-ZSM-5 zeolites for NO decomposition was first examined. The extents of conversion of NO, and of conversion into N_2 and O_2 gradually *increased* with reaction time, reaching a steady state for reaction times greater than about 6 h. For example, at 773 K with Cu-ZSM-5-54 (54 is the degree of ion-exchange) the respective values were 92, 50, and 12% initially , and 95, 64, and 33% after 8 h. No deterioration of the effectiveness of the catalyst was found at this temperature even after 30 h of continuous use; we did not continue experiments beyond 30 h. This contrasts with the finding that some supported metal oxide catalysts are active only in the reduced states.[2,4] The discrepancy between the amounts of NO consumed and of N_2 and O_2 produced can be attributed to the formation of NO_2 as described previously.[3,5]

The temperature dependence of the decomposition reaction is shown in Figure 1. The conversion of NO reached 95% or more above 723 K, and maximum activity was observed around 823 K. This result can be compared with that for the Cu-Y zeolite previously studied; for example, over a Cu-Y-62 catalyst (silica/alumina = 4.8) at 823 K the conversions of NO, and the conversions into N_2 and O_2 were 36, 19, and 0%, respectively.[3] It is clear that the catalytic activity of Cu-ZSM-5 is much higher than that of Cu-Y; such high activity is unprecedented. In addition, since the capacity for ion exchange of the zeolite is determined by the Al content, these results suggest that the catalytic activity per Cu^{2+} ion exchanged is much greater for ZSM-5 than for the Y zeolite.

The effect of contact time on the distribution of the products was investigated at 823 K for Cu-ZSM-5-73. The respective conversions of NO, and the conversions into N_2 and O_2 were 73, 33, and 0% at 0.5 g s cm^{-3} contact time; 94, 49, 12 at 1.0; and 97, 85, 70 at 10.0. These data demonstrate that 90% or more NO could be removed for contact times of 1.0 g s cm^{-3}, and the conversions in N_2 and O_2 increased with increasing contact time. It is noteworthy that at 10.0 g s cm^{-3} NO was almost completely decomposed to give N_2 and O_2.

These results indicated that ZSM-5 is an excellent carrier for Cu^{2+} ions in the catalytic decomposition reaction, so we examined the catalytic activities of other metal ion-exchanged ZSM-5 zeolites, despite the fact that the Y zeolites exchanged by other metal ions showed no activity.[3] Among Co^{3+}-, Fe^{3+}-, Zn^{2+}-, and Mg^{2+}-exchanged ZSM-5, Co-ZSM-5 exhibited stable catalytic activity, but this was so small that, for example, Co-ZSM-5-80 gave a degree of NO removal of only 7.9% at 923 K and 4.0 g s cm^{-3}. Thus, only Cu^{2+}-exchanged zeolites appear to be active for NO decomposition.

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