Activity of Copper(II)-Exchanged Y-Type Zeolites in the Catalytic Decomposition of Nitrogen Monoxide

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Summary Among several metal ion-exchanged Y-type zeolites tested, only the copper(II)-exchanged zeolite exhibited appreciable activity for the catalytic decomposition of NO above 450 °C, and was not poisoned by either oxygen or water vapour.

The catalytic decomposition of NO to N_2 and O_2 is one of the simplest methods for NO removal from exhaust streams. However, no practical catalyst of consistent high activity has been developed as yet that will effect this decomposition directly.[1] Previous investigations on suitable catalysts have dealt almost exclusively with noble metals or metal oxides, and little is known about the catalytic activities of metal ion-exchanged zeolites. However, cobalt(II) ion-exchanged Y-type zeolite [$Co^{II}Y$] has been reported to exhibit a little activity, and to be poisoned by trace amounts of water vapour.[2] Hence we have investigated the catalytic activities of several metal ion-exchanged Y-type zeolites, such as $Mn^{II}Y$, $Cu^{II}Y$, $Zn^{II}Y$, and $Co^{III}Y$. Among them, only $Cu^{II}Y$ exhibited any activity; the others were inactive under conditions similar to those described below. This observation is of interest because $Cu^{II}Y$ is the most effective catalyst for the reduction of NO with NH_3 among various transition metal ion-exchanged Y-type zeolites,[3] as is CuO for the decomposition of NO among various metal oxides.[4] We report here the results of an investigation on $Cu^{II}Y$.

$Cu^{II}Y$-36 and -69 (the numbers represent exchange levels) were prepared by ion-exchange of $Na^{I}Y$ (Linde, SK-40) with aqueous solutions of cupric sulphate and acetate, respectively. Reactions were carried out in a fixed bed flow reactor under atmospheric pressure. The reactant gas containing 4% of NO in He was passed through the catalyst bed at a fixed contact time, usually 1·4 g of catalyst × s per cm³ gas. The gas composition was analysed before and after the reaction by g.l.c. using Porapak Q for N_2O, and molecular sieve 13X for O_2, N_2, and NO. Reaction temperatures were restricted to <550 °C to avoid destruction of the zeolite structure. Prior to each reaction run, the catalysts were heated at 500 °C for 2 h under He.

Table. Catalytic decomposition of NO at 500 °C in gaseous mixture containing 4% of NO in helium

Catalyst	Contact time/ g-cat. × s/ cm³-gas	Conversion of NO/% (A)	Conversion into N_2/%[a] (B)	Conversion into O_2/%[a] (C)
$Cu^{II}Y$-36	1·4	10·0	4·8	trace
$Cu^{II}Y$-69	1·3	28	16	trace
,,	4·0	58	29	0·5
,,	7·8	88	43	5·0

[a] Percentage of NO converted into N_2 or O_2.

The experimental data on the decomposition of NO at 500 °C are given in the Table. The catalytic activity increased with the exchange level of copper(II) ion. The main products were N_2, O_2, and NO_2. The extent of formation of O_2 was negligibly small until $>50\%$ conversion of NO. Although the amounts of NO_2 formed could not be determined directly by g.l.c., the fact that $(A - B)/(A - C) = ca.\ 1/2$ (see Table) shows that the remainders in the total nitrogen and oxygen balances can be attributed to the formation of NO_2, which was actually confirmed by mass spectrometry. No deterioration of the effectiveness of the catalyst was found at this temperatue even after 20 h of continuous service.

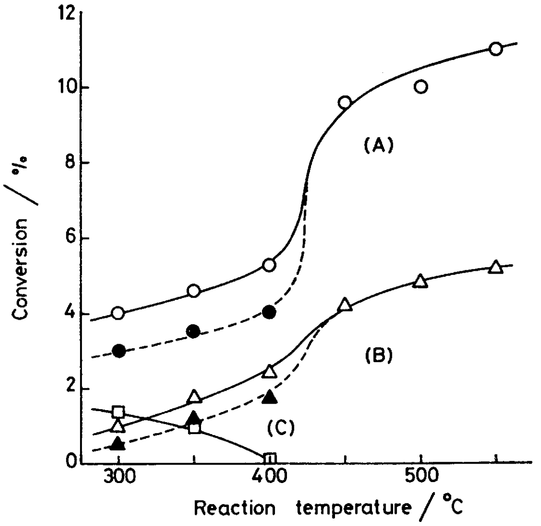

FIGURE. Catalytic decomposition of NO over $Cu^{II}Y$-36 with a gas containing 4% of NO at a contact time 1·4 g of catalyst × s per cm^3 of gas. The solid line and broken line refer to the data at 20 min and 100 min, respectively, after the start of reaction. (A), conversion of NO; (B), conversion into N_2; (C), conversion into N_2O.

The temperature dependence of the catalytic activity is depicted in the Figure. In the range 300—400 °C, the activity decreased with reaction time. The Figure depicts the data 20 min and 100 min after the start of reaction. In this temperature range, N_2O was formed as well as N_2. The activity increased markedly in the range 400—450 °C. After reaction at 400 °C for 5 h, and then heating at 500 °C under He, the catalyst released a considerable amount of O_2. This coincides with the results of a study of the temperature-programmed desorption of O_2 from $Cu^{II}Y$ in that a large desorption peak occurred at *ca.* 400 °C reaching a maximum at 460 °C.[5] The activity of the $Cu^{II}Y$ catalyst was decreased by treating the catalyst with a stream of O_2 at 400 °C, and was restored to its initial state by heating at 550 °C for 30 min. These results show that O_2, either formed by the reaction or present in the reactant gas, is adsorbed on the $Cu^{II}Y$ catalyst below 400 °C and acts as a poison; however it is not adsorbed above 450 °C. Further, pretreatment with a gas containing 1% of water vapour in He at 500 °C for 1 h does not affect the efficiency of the catalyst. Any NO_2 detected above 450 °C may arise from the homogeneous gas phase reaction of unchanged NO with O_2 formed by the decomposition of NO.†

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† A further mechanistic investigation of the decomposition of NO has shown that, over $Cu^{II}Y$, NO_2 decomposes to give NO and O_2.

[1] See for example, J. W. Hightower and D. A. Leirsburg, 'The Catalytic Chemistry of Nitrogen Oxides,' eds. R. L. Klimsch and J. G. Larson, Plenum, London, 1975, p. 63.
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