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Catalytic Reduction of NO with Ammonia over Cu(II) NaY

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The mechanism of the catalytic reduction of NO with NH_3 over Cu(II) ion-exchanged Y-type zeolites [Cu(II) NaY] was examined by kinetic and isotopic tracer studies as well as relevant studies on the transient reaction of reduced catalysts. The rate of the NO–NH_3 reaction showed dependence on the partial pressures of both No and NH_3, in accordance with the Langmuir–Hinshelwood type of rate equation. The isotopic tracer studies using ^{15}N-labeled ammonia and NO indicated that N_2 was mainly formed by bi-molecular reaction between NO and ammonia, while the nitrogen atom of nitrous oxide came soley from NO. These results support the reaction mechanism previously proposed. It has been shown that the "bell-shaped" catalytic activity–temperature relation of Cu(II) NaY is associated with the redox change of copper ions. The reoxidation step of Cu(I) ions to Cu(II) was studied in detail by allowing the reduced catalyst to react with gaseous mixtures of NO and NH_3 under various conditions. The results showed that Cu(I) ions were oxidized to Cu(II) by coupling with the stoichiometric disproportionation reaction of NO. The reaction was strongly promoted by the coexistence of NH_3. Based on these results, the mechanism and the rate-determining step of the catalytic NO–NH_3 reaction were discussed.

INTRODUCTION

The catalytic reduction of NO with NH_3 has been studied extensively over various metal or metal oxide catalysts (*1–6*). The most favorable feature of the use of NH_3 as the reducing agent is the selective reduction of NO in the presence of oxygen (*5*), and in some cases even the promoting effect of coexisting oxygen has been reported (*6*). This feature of the NO–NH_3 reaction is a great advantage in practical applications to processes for NO removal from industrial effluents. For this reaction we have found that, apart from the metal or metal oxide catalysts examined so far, partly cupric-ion-exchanged Y-type zeolite [Cu(II) NaY] exhibits excellent as well as unique catalytic activity (*7–10*). The catalytic activity of Cu(II) NaY becomes detectable at temperatures as low as 50°C and shows a bell-shaped temperature dependence with the maximum activity appearing at ca. 120°C [curve (a) of Fig. 1]. Subsequent studies in a flow system showed that the catalytic activity related well with the oxidation state of copper ions in zeolite [curve (b) of Fig. 1]. A reaction mechanism has been proposed which is rather complex but includes two key steps. One is a surface reaction step between NO and NH_3 both adsorbed on a Cu(II) ion which causes the reduction of the Cu(II) ion to Cu(I), and the other is a disproportionation reaction of NO (*11, 12*) in which produced NO_2 reoxidizes the Cu(I) ion to the original Cu(II) state. Recently, Williamson and Lunsford studied the same catalytic reaction in a closed circulating system (*13*).

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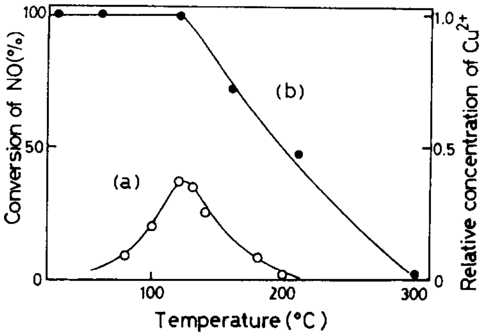

FIG. 1. Temperature dependence of catalytic activity (a) and Cu(II) concentration (b) of Cu(II) NaY catalyst (flow reaction). Feed, NO (3%) + NH_3 (2%) + He; contact time, 1.0 g·sec/ml.

Although their results are essentially in agreement with ours in many respects, there are significant differences as to the reaction kinetics and the reaction mechanism proposed. In this report, we have further examined the catalytic NO–NH_3 reaction using a closed circulating system and tried to verify our reaction mechanism based on the reaction kinetics, ^{15}N-isotope tracer experiments, and some experiments on the regeneration of Cu(II) ions from Cu(I).

EXPERIMENTAL

The partly Cu(II)-ion-exchanged zeolite catalysts, Cu(II) NaY, were prepared as described elsewhere (*10*). Samples with three exchange levels of 7, 47, and 64% were prepared. It will be shown later that the copper ions in the fresh catalysts prepared in this way consist of Cu(I) and Cu(II).

The closed circulating system was equipped with a U-shaped Pyrex glass tube reactor and a circulating pump. The total volume of the system was 200 cm^3, and the circulating rate was 50 cm^3/min under atmospheric pressure. NO and NH_3 were introduced as gaseous mixtures of adequate compositions. A TCD gas chromatograph was attached to the system for the analysis of the gas phase. A 13X molecular sieve column was used for N_2 and NO, and a Porapak Q column was used for N_2O.

For the tracer experiments, ^{15}N-labeled ammonia ($\bar{N}H_3$) with ^{15}N tracer enriched to 99.2% was purchased from British Oxygen Co., Ltd. After $\bar{N}H_3$ was allowed to react with NO over Cu(II) NaY, the reaction products were analyzed with a mass spectrometer (Hitachi RMU-6E). The fractions of the amounts of labeled nitrogen in the total nitrogen, $\bar{N}N/(N_2 + \bar{N}N)$, were obtained from the peak heights at $m/e = 28$ and $m/e = 29$, and those of labeled nitrous oxide, $\bar{N}NO/(N_2O + \bar{N}NO)$, were similarly obtained from those at $m/e = 44$ and $m/e = 45$.

RESULTS

Pretreatment of Catalysts

In a fixed-catalyst-bed flow reactor, a catalyst reaches a stationary working state during prolonged use under given conditions. In a closed circulating system, however, the state of the catalyst may be changed during the course of the reaction, and the result may be different depending on the initial catalyst state.

Figure 2 illustrates the time courses of the NO–NH_3 reaction over fresh Cu(II) NaY catalysts at 90, 73, and 20°C (room temperature). In each case a large amount of N_2O evolved at the first stage of reaction, far exceeding the amount of N_2 formation. This contrasts with the steady catalytic reaction in a flow system for which the reaction selectivity (N_2/N_2O) has been shown to be exactly equal to 2 at zero contact time (*9*). Moreover, the rates of N_2O formation in the present case (the slopes of the curves) decreased with time more rapidly than that of N_2 formation. At 90°C the former diminished to almost a half of the latter after 30 min, thus increasing the selectivity toward 2. The change in reaction selectivity was slower at 73°C. In this case the reaction was discontinued at 120 min by evacuation, and a second run was carried out under the same reaction conditions. In the second run, the N_2 formation slightly exceeded the N_2O formation. Such repeated use of the same catalyst increased the reaction selectivity further up to the final steady value of 2.

Such an evolution of excess amount of N_2O over fresh catalysts can be interpreted as a transient phenomenon due to reduced copper ions, Cu(I), coexisting with Cu(II) in the fresh catalysts. As described in detail later, Cu(I) ions in the zeolite cavities react with the reactant gases, resulting in oxidation to Cu(II) and evolution of N_2O. It is estimated from the amount of excess N_2O formed that Cu(I) ions amount to roughly 40% of the total copper ions in the fresh catalysts. Based on these results, every fresh catalyst was subjected to repeated runs until a steady selectivity was reached, prior to the use for kinetic and tracer experiments. The samples treated in this way are hereafter called pretreated catalysts.

Reaction Kinetics

Previously we reported that the rate of the $NO-NH_3$ reaction over Cu(II) NaY catalysts in a fixed-bed flow reactor was first order in NO and nearly 0.5 order in NH_3 at 110 and 140°C (*8–10*). The kinetic data could be analyzed in terms of a Langmuir–Hinshelwood-type rate equation which was derived by assuming a surface reaction between strongly adsorbed NH_3 and weakly adsorbed NO:

$$r_{N_2} = \frac{dp_{N_2}}{dt} = \frac{kK_{NO}K_{NH_3}p_{NO}p_{NH_3}}{(1 + K_{NH_3}p_{NH_3})^2}, \quad (1)$$

where r_{N_2} is the rate of N_2 formation, t is reaction time, k is a rate constant, K_{NO} and K_{NH_3} are equilibrium adsorption constants of NO and NH_3, respectively, and p_{N_2}, p_{NO}, and p_{NH_3} show the partial pressures of N_2, NO, and NH_3, respectively.

Recently, however, Williamson and Lunsford reported that, in a closed circulating system, the rate was first order in NO but zero order in NH_3 (*13*). Moreover, the selectivity, N_2/N_2O, of their results was strongly dependent upon reaction temperature, increasing with temperature, for example, from 0.5 at 79°C to 3.7 at 149°C. Considering the transient phenomenon previously described over fresh catalysts, the extremely low selectivity at lower temperatures appears to be due to coexisting Cu(I)

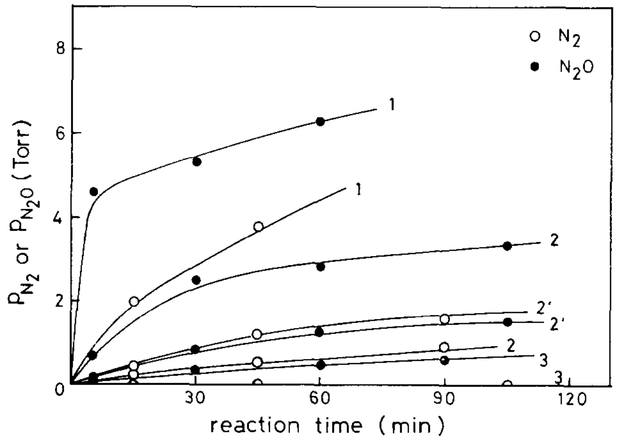

FIG. 2. Time courses of N_2 and N_2O formed over fresh Cu(II) NaY (64%, 0.1 g). Reaction temperature and initial partial pressures in Torr: (1) 90°C; NO, 30, NH_3, 62; (2) 73°C; NO, 83; NH_3, 72; (2′) 73°C, second run (see text); NO, 80; NH_3 69; (3) 20°C (room temperature); NO, 35; NH_3, 92.

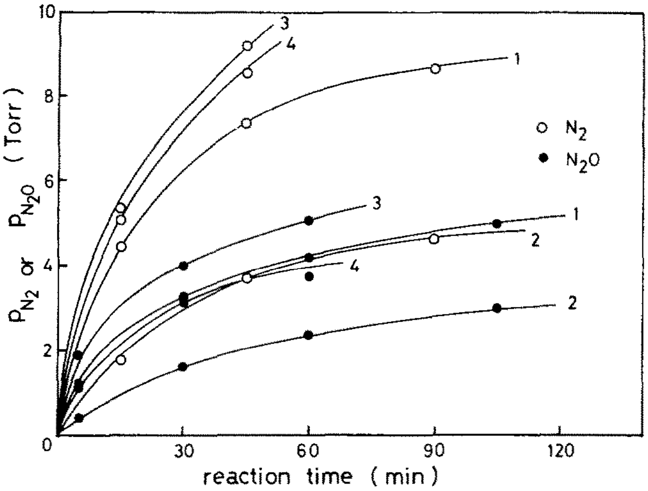

FIG. 3. Time courses of N_2 and N_2O formed at 110°C over pretreated Cu(II) NaY (64%, 0.1 g). Initial partial pressures in Torr: (1) NO, 37; NH_3, 39; (2) NO, 40; NH_3, 16; (3) NO, 38; NH_3, 44; (4) NO, 40; NH_3, 22. In (3) and (4), NH_3 (70 Torr) was preadsorbed followed by a brief evacuation (see text).

ions, while the values much larger than 2 at higher temperatures are likely to have resulted from the consecutive decomposition of the formed N_2O. We observed that, over pretreated Cu(II) NaY, the selectivity N_2/N_2O increased gradually with reaction time; e.g., it was 2.0, 2.6, and 3.0 after the reaction for 5, 30, and 45 min at 110°C, respectively, in a circulating system.

From these considerations, we reexamined the dependence of the rate of the NO–NH_3 reaction on the partial pressure of NH_3 using a closed circulating system. Figure 3 shows reaction curves for various initial NH_3 pressures ($p^0_{NH_3}$) at $p^0_{NO} \simeq 40$ Torr and 110°C [the superior (^{0}) denotes initial states]. Gaseous mixtures of NO and NH_3 were introduced after evacuating the pretreated catalyst for 30 min at the reaction temperature in the experiments of curves 1 and 2. In the runs of curves 3 and 4, however, preadsorption of NH_3 (70 Torr) followed by brief evacuation (1 min) was additionally manipulated between the catalyst evacuation and the introduction of reactants. Comparison of the curves indicates that the reaction rates were enhanced by the NH_3 preadsorption. This is because NH_3 adsorbs on the catalyst considerably (*9*). The preadsorption of NH_3 also affected the apparent reaction order. As shown in Fig. 4 the apparent reaction order of the initial rate was 0.24 or 0.92 in $p^0_{NH_3}$ with or without the preadsorption of NH_3, respectively. It is considered that in the former case the presence of preadsorbed NH_3 somewhat masked the effect of the change in $p^0_{NH_3}$, while the high reaction order in the latter case resulted either from considerable decreases in NH_3 pressure due to adsorption or from an incomplete equilibration of NH_3 adsorption at the first stage of reaction. It appears that the true reaction order is therefore between these two extremes, in agreement with the result (reaction order, $\simeq$0.5) of the flow experiments.

The applicability of the rate Eq. (1) was examined in the integral form. With an approximation that the partial pressures of NO and NH_3 change only as a result of the overall reaction,

$$4NO + 2NH_3 \rightarrow 2N_2 + N_2O + 3H_2O, \quad (2)$$

Eq. (1) is integrated into the following form:

$$\frac{1}{p_{NO}^0 p_{NH_3}^0 - 2A^2}\tan^{-1}\frac{p_{N_2} - A^2}{(p_{NO}^0 p_{NH_3}^0/2) - A^2} + \frac{K_{NH_3}^2}{2} p_{N_2} - [K_{NH_3} - K_{NH_3}^2 A] \times \ln|p_{N_2} - (p_{NO}^0/2)| = kK_{NO}K_{NH_3}t + C, \quad (3)$$

where A and C are the constants defined by the following equations:

$$A = (p_{NH_3}^0/2) - (p_{NO}^0/4) \quad (4)$$

$$C = \frac{1}{p_{NO}^0 p_{NH_3}^0 - 2A^2} \times \tan^{-1}\frac{-A^2}{(p_{NO}^0 p_{NH_3}^0/2) - A^2} - [K_{NH_3} - K_{NH_3}^2 A]\ln(p_{NO}^0/2). \quad (5)$$

Since K_{NH_3} has been shown to be 1.1×10^{-2} $Torr^{-1}$ from the kinetic experiments in the flow system, the left side of Eq. (3), L, can be calculated by using observed values of p_{N_2} and plotted vs reaction time for different $p^0_{NH_3}$ and p^0_{NO}. The analysis was applied only to the reaction curves obtained with NH_3 adsorption to avoid too many complications due to adsorption. It was approximated that changes in partial pressures of NH_3 and NO due to adsorption or desorption were negligible. The results are shown in Fig. 5. The slopes of the lines of the figure should be equal to $kK_{NO}K_{NH_3}$, which was 4.2×10^{-7} sec^{-1} $Torr^{-2}$ on average at 110°C. The corresponding value in the flow system was 1.9×10^{-6} sec^{-1} $Torr^{-2}$. The agreement appears to be reasonable considering the approximations made for the present analysis.

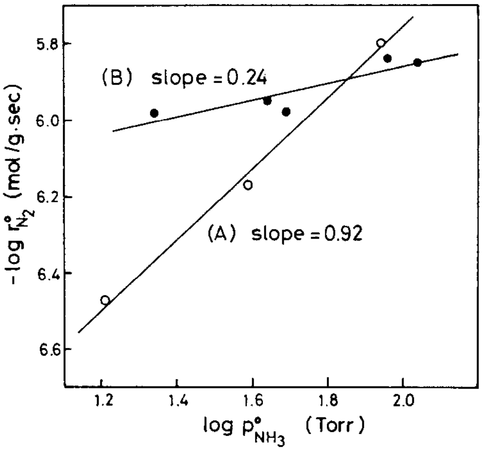

FIG. 4. Dependence of initial rate of N_2 formation on partial pressure of NH_3 over Cu(II) NaY (64%) at 110°C. (A) Without NH_3 preadsorption; NO, 30 Torr; (B) after NH_3 preadsorption (70 Torr), followed by brief evacuation; NO, 30 Torr.

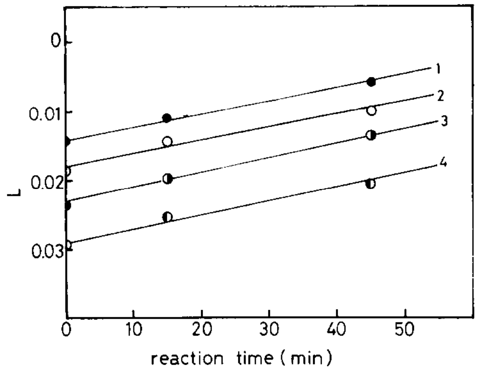

FIG. 5. Verification of Eq. (3). Cu(II) NaY (64%), 110°C. Initial partial pressure in Torr: (1) NO, 28; NH_3, 110; (2) NO, 27; NH_3, 92; (3) NO, 26; NH_3, 49; (4) NO, 32; NH_3, 22.

Isotopic Experiments

The reaction between NO and ^{15}N-labeled ammonia over the pretreated Cu(II) NaY catalysts was carried out in the closed system at 92 to ~140°C with various initial pressures of NO and $\bar{N}H_3$. The reaction produced nitrogen and nitrous oxide which were partly labeled. The scrambling of ^{15}N isotope in the reaction products was shown in Table I. The fractions of the labeled nitrogen in the total nitrogen, $\bar{N}N/(N_2 + \bar{N}N)$, were ca. 0.90, while those of the labeled nitrous oxide, $\bar{N}NO/(\bar{N}NO + N_2O)$, were almost negligible. Thus the isotope scramblings of the

TABLE 1

^{15}N Isotope Scrambling in Reaction Products

Catalyst	Temperature (°C)	p_{NO}^0 (Torr)	$p_{\tilde{N}H_3}^0$ (Torr)	$\frac{\tilde{N}N}{\tilde{N}N + N_2}$	$\frac{\tilde{N}NO}{\tilde{N}NO + N_2O}$	N_2/N_2O	Conversion (%)
Cu(II)NaY (7%)	140	109	21	0.88	0.01	3.1	24.4
Cu(II)NaY (64%)	140	43	34	0.87	0.01	2.0	36.1
Cu(II)NaY (64%)	114	44	35	0.90	0.01	2.6	72.9
Cu(II)NaY (64%)	110	18	50	0.90	0.02	2.3	97.5
Cu(II)NaY (64%)	92	45	35	0.89	0.02	2.9	79.6

two products are quite different from each other, in agreement with the results of Williamson and Lunsford (*13*). Such results indicate that the pathways for the formation of nitrogen and nitrous oxide are different.

The high percentages of $\tilde{N}N$ show that the nitrogen forms mainly by a reaction between NO and ammonia, while the low values of $\tilde{N}NO$ show its formation from NO molecules only.

$$\left.\begin{array}{l}\mathrm{NO}\\ \tilde{\mathrm{N}}\mathrm{H}_3\end{array}\right]\rightarrow \tilde{\mathrm{N}}\mathrm{N}$$

$$\mathrm{NO} \longrightarrow \mathrm{N_2O}(\rightarrow \mathrm{N_2})$$

The consecutive decomposition of nitrous oxide, though very slow, forms only unlabeled N_2 molecules. This probably explains the production of small amounts ($\simeq$10%) of unlabeled nitrogen.

Reoxidation Process of Cu(I) Ion

As reported previously (*10*), Cu(II) NaY catalysts turn white when heated up to 300°C in the NO–NH_3 atmosphere. ESR spectra show that Cu(II) ions are reduced to Cu(I) in this process. Upon contacting with the NO–NH_3 atmosphere at lower temperatures, the reduced Cu(I) ions are reoxidized to Cu(II) accompanied by simultaneous evolution of N_2O. In this study, we examined this reoxidation step quantitatively in a closed circulating system. Cu(II) catalysts were first reduced by the NO–NH_3 mixture at 300°C for 1 hr. The white color of the catalyst confirmed the reduction to Cu(I). The catalysts were then evacuated for 1 hr and cooled to reaction temperatures *in vacuo*, at which gaseous mixtures of NO and NH_3 were introduced. Figure 6 shows the time courses of reaction. It is seen that the initial rate of N_2O formation far exceeds N_2 formation, in contrast to the steady catalytic reaction where reaction selectivity, N_2/N_2O, is nearly equal to 2. Apparently one must consider two kinds of reaction here. One is the oxidation of Cu(I) ions, and the other is the catalytic NO–NH_3 reaction over Cu(II) ions. The former is associated with the excess amounts of N_2O formation compared with the case of steady catalytic reaction. When the N_2 formation due to the consecutive decomposition of N_2O is negligible, the excess amount of N_2O, $V_{N_2O,ex}$, should then be given by

$$V_{N_2O,ex} = V_{N_2O} - \tfrac{1}{2}V_{N_2}, \tag{6}$$

where V_{N_2O} and V_{N_2} are the observed amounts of N_2O and N_2, respectively.

The partial pressure of the excess N_2O, $p_{N_2O,ex}$, thus estimated, is also shown in Fig. 6. The excess N_2O formation decreased rapidly with time due to both the consumption of NO reactant and the consecutive decomposition of N_2O. Upon evacuation of the system followed by introduction of a fresh NO–NH_3 mixture, excess N_2O formation appeared again. When such an experiment was repeated, excess N_2O evolution was much diminished

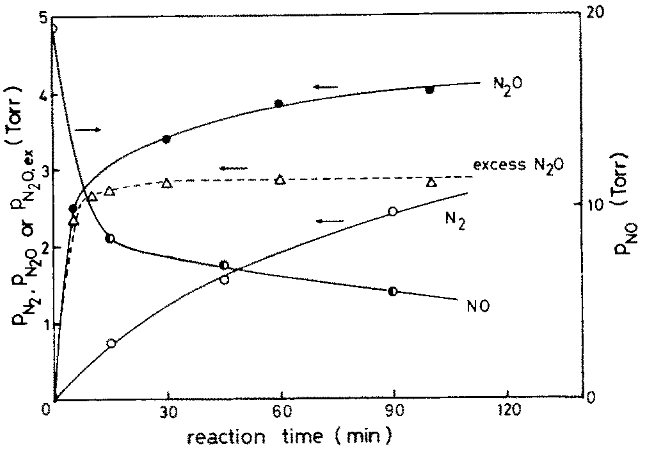

FIG. 6. Time courses of the reaction between reduced catalyst and gaseous mixtures of NO (20 Torr) and NH_3 (45 Torr) at 73°C.

after three to five repetitions. In Table 2, the total amounts of excess N_2O produced over such repeated runs are compared with the amounts of copper ions to be oxidized. It is seen that roughly 1 mol of excess N_2O is produced during the oxidation of 1 mol of Cu(I) ions. The slight disagreement seems to be due, at least partly, to neglecting the consecutive decomposition of N_2O.

In separate experiments, determination of the stoichiometry between the consumed NO and the produced excess N_2O was attempted. Since NO is also consumed by the steady catalytic reaction [Eq. (2)], the amount of NO used to produce the excess N_2O is given by

$$V_{NO,ex} = \Delta V_{NO} - 2V_{N_2}, \tag{7}$$

where ΔV_{NO} is the total amount of the consumed NO. Here the adsorption of NO on the catalyst is assumed to be negligible. The experiments were performed only at lower temperatures where the catalytic reaction proceeded slowly. The ratios of $V_{NO,ex}/V_{N_2O,ex}$ in various runs are listed in Table 3. Although they are a little larger than 3, we consider the true stoichiometry to be 3. The observed deviation from 3 resulted from two reasons. First, we have neglected the adsorption of NO on the catalyst. If it is assumed that one NO molecule adsorbs on the Cu(II) ion formed by the oxidation, the deviation can be as large as unity at maximum. Second, $V_{N_2O,ex}$ is a little underestimated as mentioned before.

It should be added that the excess N_2O formed come solely from NO, though its formation is enhanced by the presence of NH_3 as shown below. This was confirmed by using $\bar{N}H_3$. After the reduction by a NO–$\bar{N}H_3$ mixture at 300°C, the catalyst was exposed to the NO–$\bar{N}H_3$ mixture at lower temperatures similarly as above. The mass-spectrometric analysis of the gaseous products indicated that the nitrous oxide contained only unlabeled nitrogen. It is concluded that 1 mol of Cu(I) ion is

TABLE 2

Amounts of Excess N_2O Evolved by Reaction of Reduced Catalysts with NO and NH_3

Catalysts	Temperature (°C)	No. of Cu ions exchanged ($\times 10^{-4}$ mol)	$V_{N_2O,ex}$ ($\times 10^{-4}$ mol)
CuNaY (47%)	20	1.5	1.1
CuNaY (64%)	112	1.0	0.72
CuNaY (64%)	20	1.0	0.82
CuNaY (64%)	20	1.0	1.1

TABLE 3

NO Consumption for Excess N_2O Formation

Catalyst	Temperature (°C)	$V_{NO,ex}/V_{N_2O,ex}$ (mol/mol)
CuNaY (64%)	20	4.4
CuNaY (64%)	20	3.4
CuNaY (64%)	20	3.8
CuNaY (64%)	73	3.2

oxidized to Cu(II) associated with the consumption of 3 mol of NO and the evolution of 1 mol of N_2O.

Kinetic experiments on the re-oxidation of Cu(I) ions showed that the rate of the excess N_2O formation was strongly dependent on the partial pressures of both NO and NH_3. Figure 7 shows the effects of the initial pressures of NO and NH_3 on the initial rate of excess N_2O formation, $r^0_{N_2O,ex}$, which can be expressed as follows:

$$r^0_{N_2O,ex} = k(p^0_{NH_3})^{1.6}(p^0_{NO})^{1.0} \quad (8)$$

Equation (8) indicates that NH_3 contributes significantly to the reaction rate although NH_3 itself cannot be a reactant. Such a contribution of NH_3 is likely to appear in the following two ways: It has been well established that the Cu(II) ions in the exchanged Y-type zeolite occupy the locked-in sites (I, I′, and II′) in the dehydrated state, but are pulled out toward the supercage upon the admission of complex-forming molecules such as H_2O, NH_3, and pyridine (*14*). A similar effect can naturally be expected between Cu(I) ions and NH_3 in the present case; that is, NH_3 pulls out the Cu(I) ions of the locked-in sites into the supercage where NO can attack the ions. Moreover, the coordination of NH_3 to Cu(I) lowers the redox potential between Cu(I) and Cu(II), which is probably the second contribution of NH_3 to the reaction.

DISCUSSION

In the NO–NH_3 reaction over Cu(II) NaY catalysts, the rate of NO reduction increases in proportion to the exchange level of Cu(II) ions. This proportionality indicates that the reaction occurs on a single copper ion, being assisted by complex formation. In addition, the "bell-shaped" temperature dependence of catalytic activity suggests the incorporation of the redox change between Cu(II) and Cu(I). Based on these considerations, we have proposed the following mechanism (*10*):

$$\mathrm{Cu(II)(NH_3)}_n + \mathrm{NO} \rightarrow [\mathrm{Cu(II)(NH_3)}_n\mathrm{NO}] \rightarrow \mathrm{Cu(I)(NH_3)}_m + \mathrm{N_2} + \mathrm{H_2O} + (n-m-1)\mathrm{NH_3} + \mathrm{H^+(ads)} \quad (9)$$

$$\mathrm{H^+(ads)} + \mathrm{NH_3} \rightarrow \mathrm{NH_4^+(ads)} \quad (10)$$

$$\mathrm{Cu(I)(NH_3)}_m + 3\mathrm{NO} \rightarrow \mathrm{Cu(II)(NH_3)}_m\mathrm{NO_2^-} + \mathrm{N_2O} \quad (11)$$

$$\mathrm{Cu(II)(NH_3)}_m\mathrm{NO_2^-} + \mathrm{NH_4^+(ads)} \rightarrow \mathrm{Cu(II)(NH_3)}_m + \mathrm{N_2} + 2\mathrm{H_2O} \quad (12)$$

$$\mathrm{Cu(II)(NH_3)}_m + (n-m)\mathrm{NH_3} \rightarrow \mathrm{Cu(II)(NH_3)}_n \quad (13)$$

$$4\mathrm{NO} + 2\mathrm{NH_3} \rightarrow 2\mathrm{N_2} + \mathrm{N_2O} + 3\mathrm{H_2O} \quad (14)$$

In this multistep NO–NH_3 reaction, the key steps are (9) and (11); in (9) NO and NH_3 react with each other in the coordination sphere of Cu(II) ions accompanying the reduction to Cu(I) ions, which are reoxidized in (11) by the action of NO. The above mechanism is supported by the present study as discussed below.

(i) In the above mechanism, N_2 is formed from NO and NH_3 molecules in (9)

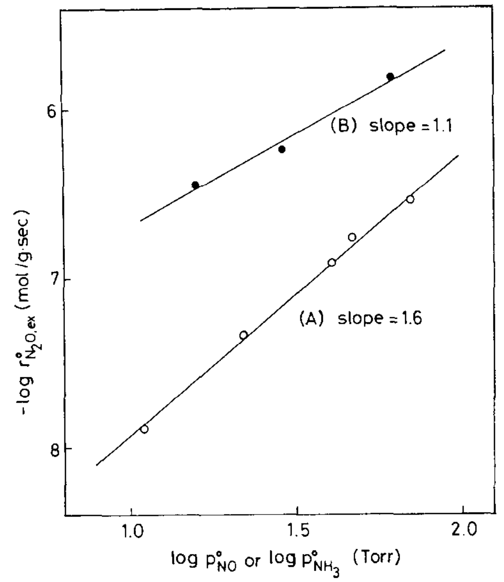

FIG. 7. Effect of the partial pressures of NH_3 at $p_{NO}{}^0 = 20$ Torr (A) and NO at $p_{NH_3}{}^0 = 70$ Torr (B) on the initial rate of excess N_2O formation over reduced catalyst at 90°C.

and (12), while N_2O is formed from NO molecules only in (11). These schemes agree well with the results of the present isotopic studies.

(ii) The rate equation and the rate-determining step (*10*) previously obtained or proposed were confirmed by the present study. The shift of the rate-determining step with temperature is discussed later.

(iii) The experiments on the oxidation of Cu(I) ions with $NO\text{–}NH_3$ mixtures showed that the molar ratio of Cu(I):NO consumed:N_2O evolved was roughly 1:3:1. This is consistent with Eq. (12). Moreover, this reaction necessitates the presence of NH_3, which suggests that this step is essentially a disproportionation reaction of NO (*11, 12*),

$$3NO \rightarrow N_2O + NO_2, \qquad (15)$$

facilitated by a Cu(I)–ammine complex, the product NO_2 being used to oxidize Cu(I) ions. Further details of the reaction as well as of the succeeding steps, however, should be clarified by ir spectra or other methods.

In relation to the rate-determining step of the overall reaction, it is interesting to compare the specific rates of steps (9) and (11). The rate of step (11) can be represented by the initial rate of excess N_2O formation ($r^0{}_{N_2O,ex}$) observed on the admission of gaseous mixtures of NO and NH_3 over reduced catalysts [Cu(I) state]. The observed values of $r^0{}_{N_2O,ex}$ under $p^0{}_{NH_3} = 26$ Torr and $p^0{}_{NO} = 47$ Torr are plotted against temperature in Fig. 8. The figure

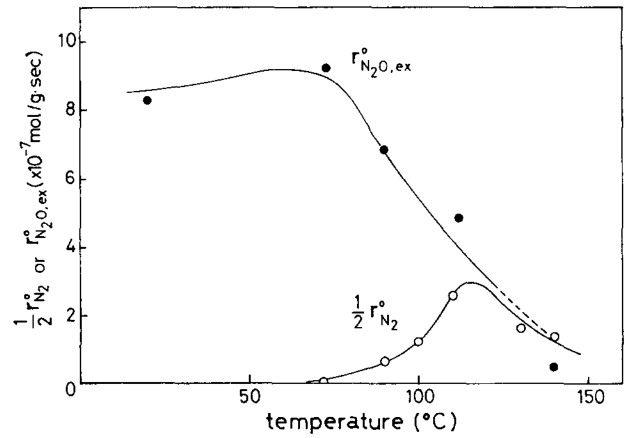

FIG. 8. Comparison of the initial formation rates for N_2 and excess N_2O on introduction of NO (26 Torr) and NH_3 (47 Torr) over pretreated and reduced CuNaY (64%), respectively.

also shows $r^0_{N_2/2}$, one-half the initial rate of N_2 formation observed on introduction of the same gaseous mixture over the pretreated catalyst, in which the copper ions existed as Cu(II) below ca. 120°C (see Fig. 1). If the catalytic cycle of steps (9) to (13) is correct, $r^0_{N_2/2}$ should be equal to the rate of NO consumption in step (9) below ca. 120°C. Apparently, $r^0_{N_2O,ex}$ is much larger than $r^0_{N_2/2}$ in that temperature region, which justifies the previous assumption that step (9) is rate-determining in the catalytic reaction. Above ca. 120°C, however, $r^0_{N_2/2}$ decreases with a rise in temperature, and the comparison with $r^0_{N_2O,ex}$ shows that the overall reaction rate becomes controlled by the rate of the Cu(I) oxidation [step (11)]. The decrease of $r^0_{N_2O,ex}$ with increasing temperature is likely to be associated with an increasing difficulty in forming the Cu(I)-ammine complex at higher temperatures.

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