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# Effects of Coexisting Gases on the Catalytic Reduction of NO with $NH_3$ over Cu(II) NaY

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The effects of coexisting $H_2O$, $O_2$, and $SO_2$ on the NO–$NH_3$ reaction over Cu(II)NaY were examined from a standpoint of practical application to NO removal processes. It is found that water vapor lowered the rate of NO reduction, and the effect was analyzed in terms of the adsorption of $H_2O$ on Cu(II) ions in competition with $NH_3$ and NO. On the contrary, the coexistence of oxygen caused an excellent promoting effect especially at temperatures higher than 120°C, where the catalytic rate had a negative temperature coefficient in the absence of oxygen. Moreover, in the reaction products, no $N_2O$ was detected in contrast to the case in the absence of oxygen. It is proposed that the coexisting oxygen participates in the reoxidation of Cu(I) ions in the catalytic cycle, which is otherwise to be completed in association with a disproportionation reaction of NO. Sulfur dioxide showed an inhibition effect. In the presence of $SO_2$ (100 ppm), the catalytic activity declined rapidly during reaction to a stationary value. The stationary rate of NO reduction increased with a rise in temperature from 100 to 260°C. X-Ray analysis revealed that a part of zeolite framework of the deactivated catalysts was destroyed due to the formation of sulfates.

## INTRODUCTION

Catalytic reduction of NO with $NH_3$ is one of the most important methods for removing $NO_x$ from industrial effluents. It has a great advantage in that NO is selectively reduced in the presence of oxygen (*1*, *2*). Plant tail gases contain oxygen, water vapor, sulfur oxides, and other components together with NO. Such coexisting constituents often bring about unfavorable influences on the $NO_x$ removal process. For example, noble metal catalysts for NO reduction are easily inhibited in the presence of sulfur oxides. Therefore, from a practical standpoint, it is very important to examine the effects of coexisting components on the NO–$NH_3$ reaction.

We have already reported the interesting low-temperature activity of Cu(II) ion-exchanged Y-type zeolites (Cu(II) NaY) for the NO–$NH_3$ reaction (*3*–*6*). The phenomenon has also been confirmed by Williamson and Lunsford (*7*). The reaction mechanism has been studied especially in relation to the unique activity–temperature profile. However, there has been no study on the effects of coexisting gases on the catalytic reaction yet, although the low-temperature performance arouses particular interests in applying the reaction for industrial effluents. In this report, we pursued the effects of coexisting water vapor, oxygen, and sulfur dioxide on the catalytic NO–$NH_3$ reaction over Cu(II) NaY.

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## EXPERIMENTAL METHODS

The partly Cu(II)-exchanged Y-zeolite catalysts, Cu(II) NaY, were prepared by the conventional ion-exchange method (*6*). The catalysts with two Cu(II)-exchange levels of 64 and 60% were used in this study.

The catalytic reactions were performed in a fixed-bed flow reactor made with Pyrex glass tubes. The gases, NO, $NH_3$, $O_2$, $SO_2$, He, and $N_2$ were fed from commercially available cylinders without further purification. Water vapor was fed by supplying degassed water to an evaporator (100°C) equipped in the flow line by means of a microfeeder.

The composition of feed was selected variously as described below. The highest concentrations of NO and $NH_3$ were fed to examine the effect of $H_2O$; NO(3%)-$NH_3$ (2%)-$H_2O$ (0-47%)-He (balance). The effect of $O_2$ was, however, investigated in more diluted system to minimize the gas-phase reaction between NO and $O_2$; NO (0.4%)-$NH_3$ (0.4%)-$O_2$ (0-4%)-He (balance), or NO (160 ppm)-$NH_3$ (200 ppm)-$O_2$ (4%)-$N_2$ (balance). The effect of $SO_2$ was examined only in the presence of oxygen; NO (160 ppm)-$NH_3$ (160-370 ppm)-$O_2$ (4%)-$N_2$ (balance).

The feed and effluent were analyzed as follows. Nitrogen oxides, NO and $NO_2$, were analyzed by means of a chemiluminescent detection method (Yanagimoto ECL-77A). The other gases except for $NH_3$ were analyzed by TCD gas chromatography by using the following columns, molecular sieve 13X at room temperature for $N_2$ and $O_2$, Porapak Q at room temperature for $N_2O$, and Chromosorb 104 at 94°C for $SO_2$. Ammonia was analyzed by absorption spectrophotometry (*8*). After being absorbed in 0.5% boric acid solution, $NH_3$ was converted into "indophenol-blue" ($\lambda_{max} = 638$ nm) with phenol and sodium hypochlorite. The absorbance was measured with a Hitachi 200-10 spectrophotometer.

The rate of NO reduction and the selectivities to $N_2$ and $N_2O$ were measured at various temperatures in each system. The structure of catalysts was examined by X-ray diffraction.

## RESULTS

### *Effect of Water Vapor*

The effect of coexisting water vapor on the catalytic NO-$NH_3$ reaction over Cu(II) NaY was examined in the temperature region of 80 to 200°C. Figure 1 shows the activity-temperature relationships obtained when water vapor was fed to 0, 8, and 47%. Obviously water vapor lowers the conversion of NO without changing the characteristic bell-shaped profile. It is confirmed that the selectivities to $N_2$ and $N_2O$ were not affected by water vapor. The rate of NO reduction at 120°C is plotted against the partial pressure of water vapor in Fig. 2, which shows the inhibition effect of water vapor almost inversely proportional to its partial pressure. This effect was interpreted in terms of the competitive adsorption or coordination of $H_2O$ to Cu(II) ions as described below.

In the absence of added water vapor, we have proposed that the rate-determining step of the NO-$NH_3$ reaction is a Langmuir-Hinshelwood type of reaction between $NH_3$ and NO both of which are strongly and weakly adsorbed on copper

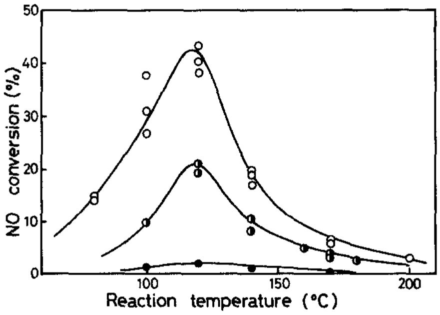

FIG. 1. Influence of water vapor on the NO-$NH_3$ reaction over Cu(II)NaY (64%). Feed: $p_{NO} = 3\%$, $p_{NH_3} = 2\%$, $p_{H_2O} = 0\%$ (○), 8% (◑), 47% (●), He balance. SV = 1800 $hr^{-1}$

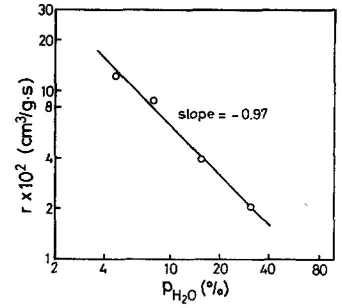

FIG. 2. Influence of the partial pressure of $H_2O$ on the rate of NO–$NH_3$ reaction over Cu(II)NaY (64%). Reaction temperature = 120°C, $p_{NO}$ = 3%, $p_{NH_3}$ = 2%.

ions, respectively (*4–6*). The following rate equation has been derived.

$$r = \frac{kK_{NO}K_{NH_3}p_{NO}p_{NH_3}}{(1 + K_{NH_3}p_{NH_3})^2}, \tag{1}$$

where $k$ is a rate constant, $p_{NO}$ and $p_{NH_3}$ are the partial pressures of NO and $NH_3$, and $K_{NO}$ and $K_{NH_3}$ are the adsorption equilibrium constants. In the present system, if $H_2O$ is competitively adsorbed on Cu(II) ions, the rate equation should be modified as follows.

$$r = \frac{kK_{NO}K_{NH_3}p_{NO}p_{NH_3}}{(1 + K_{NH_3}p_{NH_3} + K_{H_2O}p_{H_2O})^2}, \tag{2}$$

where $p_{H_2O}$ and $K_{H_2O}$ are the partial pressure and adsorption equilibrium constant of $H_2O$, respectively. Under the condition that $p_{NO}$ and $p_{NH_3}$ are constant, Eq. (2) is transformed into the following form,

$$1/r^{\frac{1}{2}} = k_1(k_2 + K_{H_2O}p_{H_2O}), \tag{3}$$

where $k_1 = (kK_{NO}K_{NH_3}p_{NO}p_{NH_3})^{-\frac{1}{2}}$, and $k_2 = 1 + K_{NH_3}p_{NH_3}$. Equation (3) requires $1/r^{\frac{1}{2}}$ to increase linearly with $p_{H_2O}$. The fitting of the experimental data to Eq. (3) is satisfactory as shown in Fig. 3. The straight line gives $K_{H_2O} = 73 \sim 97\ \text{atm}^{-1}$, when $K_{NH_3}$ is assumed to be $260 \sim 360\ \text{atm}^{-1}$ as reported previously (*5*).

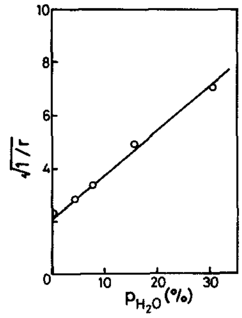

FIG. 3. Examination of Eq. (3).

*Effect of Oxygen*

It has been reported that the NO–$NH_3$ reaction over catalysts such as $V_2O_5$ is largely promoted by the presence of oxygen (*2*). The effect of oxygen in the present case was investigated at feed compositions with moderately concentrated as well as very diluted NO and $NH_3$. Figure 4 shows the results on the moderately concentrated system at four oxygen concentrations. As the most marked effect, oxygen promoted the rate of NO reduction, especially at temperatures above 120°C, where in the absence of oxygen the rate falls as temperature rises. Owing to this promoting effect, the bell-shaped temperature–activity profile no longer appeared. The results on the diluted system with $p_{NO}$ = 160 ppm and and $p_{NH_3}$ = 200 ppm in the presence of 4% oxygen are shown in Fig. 5. Figure 5 shows that NO is completely consumed above ca.

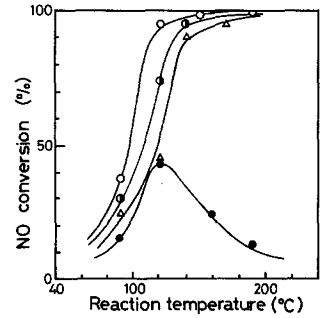

FIG. 4. Influence of oxygen on the NO–$NH_3$ reaction over Cu(II)NaY (64%). SV = 1800 hr⁻¹, $p_{NO}$, $p_{NH_3}$ = 0.4%, $p_{O_2}$ = 0% (●), 0.3% (△), 2% (◑), 4% (○).

100°C. Moreover, it reacts with nearly equimolecular amounts of $NH_3$. This stoichiometry is different from that (2:1) observed in the absence of oxygen, and suggests that the course of NO–$NH_3$ reaction is modified by coexisting oxygen.

We have confirmed that the rate of NO oxidation with $O_2$ is very slow under the similar conditions both in the presence and in the absence of Cu(II) NaY catalysts.

Table 1 shows two examples of the feed and effluent compositions at 90 and 120°C. Unlike the case without oxygen addition where the selectivity ratio to $N_2O$ and $N_2$ was nearly equal to 1:2, the NO–$NH_3$–$O_2$ system gave $N_2$ exclusively without detectable formation of $N_2O$. The stoichiometry of consumed NO: consumed $O_2$: produced $N_2$ was nearly equal to 4:1:4, indicating the following overall reaction.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O. \quad (4)$$

Such effects of oxygen will be discussed later.

TABLE 1

Stoichiometry of NO–$NH_3$ Reaction over Cu(II)NaY (64%) in the Presence of Oxygen

| Reaction temperature (°C) | Composition | | Increment or decrement (%) | Conversion of NO (%) |
|---|---|---|---|---|
| | Feed (%) | Effluent (%) | | |
| 90 | NO 0.40 | 0.30 | 0.10 | 25 |
| | $N_2$ 0.89 | 1.01 | 0.12 | |
| | $O_2$ 0.31 | 0.29 | 0.02 | |
| | $N_2O$ 0 | 0 | 0 | |
| 120 | NO 0.40 | 0.23 | 0.17 | 43 |
| | $N_2$ 0.93 | 1.13 | 0.20 | |
| | $O_2$ 0.29 | 0.25 | 0.04 | |
| | $N_2O$ 0 | 0 | 0 | |

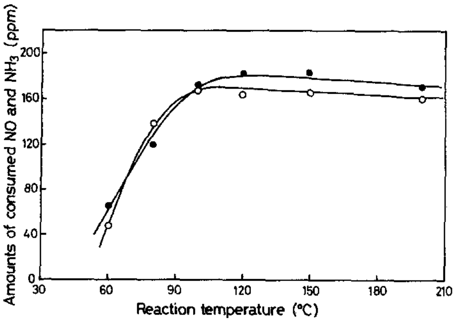

FIG. 5. Temperature profile of the amounts of consumed NO (○) and $NH_3$ (●) over Cu(II)NaY (64%). Feed rate = 200 cm³/min, SV = 6000 hr⁻¹, $p_{NO}$ = 160 ppm, $p_{NH_3}$ = 200 ppm, $p_{O_2}$ = 4%, $N_2$ balance.

*Effect of Sulfur Dioxide*

It is sulfur oxides ($SO_2$ and $SO_3$) that have been reported to cause unfavorable effects on the catalytic NO reduction except for a few cases (*9*). In this study, the effects of $SO_2$ were examined by introducing $SO_2$ in the NO–$NH_3$–$O_2$ system. Figure 6 shows the time courses of the NO conversion at 100, 200, and 260°C with a feed composition of NO (160 ppm), $NH_3$ (160 ppm), $O_2$ (4%), and $SO_2$ (100 ppm). The conversion of NO fell in the initial periods to attain stationary values at 100 and 200°C. The catalytic activity could not be recovered in 3 hr after removing $SO_2$ from the feed. Such initial decay is not apparent at 260°C in the figure, because the space velocity (SV) applied (6000 hr⁻¹) was so small that all of NO fed was consumed even on the deactivated catalyst at 260°C. It was confirmed, however, that at SV = 100,000 hr⁻¹ the NO conversion fell from a initial value of 93% to a stationary value of 88% in 7 hr at 260°C with the same feed composition as above. It is noted that the stationary conversion level is higher at a higher temperature. In the

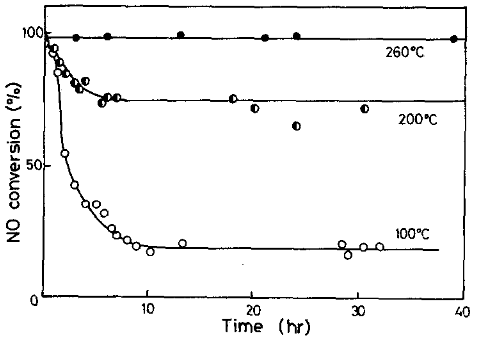

FIG. 6. Time courses of the NO–$NH_3$ reaction over Cu(II)NaY (60%) in the presence of $SO_2$. Feed rate = 200 cm³/min, SV = 6000 hr⁻¹, $p_{NO}$, $p_{NH_3}$ = 160 ppm, $p_{SO_2}$ = 100 ppm, $p_{O_2}$ = 4%, $N_2$ balance.

separate experiments, the concentration of $NH_3$ was increased from 160 ppm ($NH_3$/NO = 1.0) to 370 ppm ($NH_3$/NO = 2.2), but there were no significant differences in the results.

## DISCUSSION

Previously we proposed the following reaction mechanism of NO–$NH_3$ reaction over Cu(II) NaY in the absence of oxygen (*6*).

$$
\begin{aligned}
&\mathrm{Cu(II)\,(NH_3)_{\mathit{n}} + NO \rightarrow} \\
&\quad \mathrm{[Cu(II)\,(NH_3)_{\mathit{n}}NO] \rightarrow} \\
&\quad \mathrm{Cu(I)\,(NH_3)_{\mathit{m}} + N_2 + H_2O} \\
&\qquad \mathrm{+\ (\mathit{n}\text{-}\mathit{m}\text{-}1)NH_3 + H^+\,(ads)} && (5) \\
&\mathrm{H^+\,(ads) + NH_3 \rightarrow NH_4^+\,(ads)} && (6) \\
&\mathrm{Cu(I)\,(NH_3)_{\mathit{m}} + 3NO \rightarrow} \\
&\qquad \mathrm{Cu(II)\,(NH_3)_{\mathit{m}}NO_2^- + N_2O} && (7) \\
&\mathrm{Cu(II)\,(NH_3)_{\mathit{m}}NO_2^- + NH_4^+\,(ads) \rightarrow} \\
&\qquad \mathrm{Cu(II)\,(NH_3)_{\mathit{m}} + N_2 + 2H_2O} && (8) \\
&\mathrm{Cu(II)\,(NH_3)_{\mathit{m}} + (\mathit{n}\text{-}\mathit{m})NH_3 \rightarrow} \\
&\qquad \mathrm{Cu(II)\,(NH_3)_{\mathit{n}}} && (9) \\
\hline
&\mathrm{4NO + 2NH_3 \rightarrow 2N_2 + N_2O + 3H_2O} && (10)
\end{aligned}
$$

The scheme contains two key steps, (5) and (7), in which Cu(II) ions are reduced and regenerated, respectively. In Eq. (5), which is rate determining at the lower temperature region, NO and $NH_3$ react with one another after being adsorbed on Cu(II) ions in the supercage of zeolite. If $H_2O$ is present in the system, it is also adsorbed on the Cu(II) ions in competition with $NH_3$ and NO, thus obstructing the rate of NO–$NH_3$ reaction. This effect of water vapor requires the addition of an inhibition term in the rate equation as written in Eq. (2). The adsorption equilibrium constant of $H_2O$ thus evaluated (73 ~ 97 $\mathrm{atm}^{-1}$) is reasonably large but still smaller than that of $NH_3$ (260 ~ 360 $\mathrm{atm}^{-1}$). In the solution system, the first stability constant of Cu(II) complex (log $K_1$),

$$\mathrm{Cu^{2+} + L \overset{K_1}{\rightleftharpoons} Cu^{2+}L}, \qquad (11)$$

has been tabulated to be 2.85 and 4.34 for L = $H_2O$ in $CH_3NO_2$ and $NH_3$ in $NH_4NO_3$ solution, respectively (*10*). This indicates that $NH_3$ coordinates to Cu(II) ions more strongly than $H_2O$ does in the solution system. A similar tendency is seen in the present case of adsorption in $NH_3$ and $H_2O$ on Cu(II) ions exchanged in a zeolite framework.

On the other hand, the promoting effect of oxygen is associated with the regeneration steps of Cu(II) ions. In the absence of $O_2$, the regeneration of Cu(II) ions from Cu(I) is achieved through a disproportionation reaction of NO (*11, 12*) (Eq. (7)). Although the rate of this reaction is larger than that of Eq. (5) at the lower temperature region, it decreases rapidly around 120°C and above, giving rise to the reverse temperature dependence of the overall catalytic rate.

In the presence of oxygen, however, it is supposed that reoxidation of Cu(I) ions is achieved with oxygen, with the disproportionation reaction of NO and the subsequent steps (Eqs. (7) and (8)) being bypassed. The oxidation of Cu(I) ions exchanged in zeolite with $O_2$ was reported in many studies (*13–15*). The mechanism of NO–$NH_3$ reaction including the reoxidation of Cu(I) ions with oxygen is shown below.

$$
\begin{aligned}
&\mathrm{Cu(II)(NH_3)_{\mathit{n}} + NO \rightarrow} \\
&\quad \mathrm{[Cu(II)(NH_3)_{\mathit{n}}NO] \rightarrow} \\
&\quad \mathrm{Cu(I)(NH_3)_{\mathit{m}} + N_2 + H_2O} \\
&\qquad \mathrm{+\,(\mathit{n}\text{-}\mathit{m}\text{-}1)NH_3 + H^+(ads)} && (5) \\
&\mathrm{Cu(I)(NH_3)_{\mathit{m}} + \tfrac{1}{4}O_2 + H^+(ads) \rightarrow} \\
&\qquad \mathrm{Cu(II)(NH_3)_{\mathit{m}} + \tfrac{1}{2}H_2O} && (12) \\
&\mathrm{Cu(II)(NH_3)_{\mathit{m}} + (\mathit{n}\text{-}\mathit{m})NH_3 \rightarrow} \\
&\qquad \mathrm{Cu(II)(NH_3)_{\mathit{n}}} && (9) \\
\hline
&\mathrm{NO + NH_3 + \tfrac{1}{4}O_2 \rightarrow N_2 + \tfrac{3}{2}H_2O} && (13)
\end{aligned}
$$

Equation (13) accounts for the observed stoichiometry of reaction. This mechanism also explains why $N_2O$ is not formed in the presence of oxygen. Clearly Eq. (12) is not a simple reaction but consists of a few elementary reactions. However, further details of the reaction have not been investigated.

The effect of $SO_2$ was found to be an undesirable one, as has been reported in other catalytic systems. The inhibition effect of $SO_2$ was marked at temperatures not exceeding 260°C. It was noticed, however, that the inhibition took place in a rather characteristic way. That is, the deactivation of catalytic activity appeared at the initial periods of reaction until a stationary activity was attained. It should be noted that the stationary activity exhibited a normal temperature dependence as shown in Fig. 7. These facts suggest that the working state of catalysts is altered in the presence of $SO_2$. It has been reported in many other catalytic systems that the deactivation caused by $SO_2$ is associated with the sulfate formation of catalysts. Therefore, the catalysts used in the present study were subjected to X-ray diffraction analysis. As a result, it was revealed that the zeolite structure after use at 100, 200, and 260°C was partly destroyed with a new diffraction line appearing at $d$ = 7.42 Å. The new line can be ascribed to $(NH_4)_3Al(SO_4)_3$ which shows the strongest diffraction line at $d$ = 7.50 Å. The formation of such sulfate compounds agrees well with the facts that $SO_2$ was not detected in the effluent and that when the catalysts were immersed in water after use, $SO_4^{2-}$ ions were detected in the filtrates. It is considered that, in the $NO–NH_3–O_2–SO_2$ system, the introduced $SO_2$ is catalytically oxidized to $SO_3$ which then reacts with $NH_3$, $H_2O$, and zeolite framework to form $(NH_4)_3Al(SO_4)_3$. Thus the deactivation of catalysts is reasonably attributed to the destruction of the zeolite framework sustaining copper ions inside. The stationary activity after deactivation is probably exerted by the copper ions or cupric sulfate which are now supported on the produced sulfate compounds. It is added that the rate of NO reduction at the stationary state is estimated to be nearly the same order of magnitude as that observed over a cupric sulfate catalyst supported on alumina (*16*).

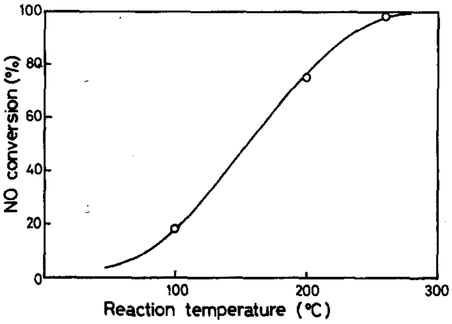

FIG. 7. Temperature profile of NO conversion from the results in Fig. 6.

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