Mechanism of the Reduction of Nitric Oxide with Ammonia over Cu(II) Ion-Exchanged Zeolites

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The catalytic NO reduction with NH_3 over Cu(II) ion-exchanged zeolite was studied with special attention to the temperature dependence of catalytic activity which reaches maximum at *ca.* 120 °C. ESR study showed that in the catalytic system all the exchanged copper ions exist as Cu(II) up to *ca.* 120 °C, above which Cu(II) ions decrease with a rise in temperature. The reaction rates measured at 110 and 140 °C were found to show similar dependence on both NO and NH_3 partial pressures, indicating that the reaction mechanism does not differ much. By lowering temperature the Cu(I) ions formed at higher temperatures were reoxidized to Cu(II), accompanied by N_2O formation due to the disproportionation of NO. From the results and the IR spectroscopic data a reaction mechanism was proposed. It includes a step in which NO reacts with NH_3 adsorbed to Cu(II) ions to give rise to the evolution of N_2 and the reduction of Cu(II) ions, and steps in which Cu(II) ions are regenerated accompanying the evolution of N_2+N_2O.

The catalytic reduction of nitrogen oxide with ammonia is important from the standpoint of removal of air pollutants. For the reduction we found that Cu(II) ion-exchanged zeolite exhibits pronounced unique catalytic activity.[1,2] In addition to the significant catalytic activity shown at temperatures below 100 °C, a characteristic bell-shaped temperature dependence with a maximum appearing at *ca.* 120 °C was observed. This catalytic reaction is not only of practical importance with its low temperature performance, but it also gives a case in which complex formation and redox change of the exchanged metal ions within the zeolite framework take place reversibly. These are in marked contrast to the case of Co(II) ion-exchanged zeolites, first reported by Windhorst and Lunsford,[3] in which Co(II) ions are reactive to the mixture of NO and NH_3 in a similar temperature region but are irreversibly oxidized to unreactive Co(III).

The catalytic NO reduction with NH_3 over Cu(II) ion-exchanged zeolite, however, remains unclarified as regards the path and mechanism of the reaction and the role of copper ions. We have investigated the problems by means of ESR spectroscopy, IR spectroscopy, and reaction kinetics. Efforts were made to elucidate the bell-shaped correlation between the catalytic activity and temperature. A kind of temperature jump method was applied to pursue the transient phenomena observed when the catalytic system was forced to shift from one stationary state to another, especially in relation to the regeneration step of Cu(II) ions from Cu(I).

Experimental

Partly Cu(II) ion-exchanged zeolites, Cu(II)NaY and Cu(II)NaX, were prepared by treating Linde Y and X zeolites with aqueous $CuSO_4$ solutions. The ion-exchanged samples were thoroughly washed with deionized water and dried at 100 °C. The ion-exchange levels of Cu(II) were determined by X-ray fluorometry.

The ESR spectra of Cu(II) ions were recorded in the X-band region at room temperature with a Hitachi 771 spectrometer, by using 2,2-diphenyl-1-picrylhydrazyl (DPPH) standard ($g=2.0036$).

IR spectra were recorded with a JASCO-IR-G spectrophotometer in the double beam absorbance mode. The infrared cell consists of a Pyrex glass fitted with potassium bromide windows. The cell allowed heating of the sample wafer at elevated temperatures measured with a thermocouple in contact with the wafer. The sample wafer, 20 mm diameter, was prepared by pressing the exchanged zeolite powder (*ca.* 10 mg) at 100 kg/cm^2.

Stationary as well as non-stationary reactions between NO and NH_3 were carried out in a fixed bed flow reactor under an atmospheric pressure. The gas composition was analyzed by gas chromatography.

Results

Oxidation State of Copper Ions. For the catalytic NO reduction with NH_3, Cu(II) ion-exchanged zeolite exhibits catalytic activity with unique temperature dependence.[1,2] A typical activity *vs.* temperature profile of a convex bell-shape is exemplified by curve (a) in Fig. 1 where activity is given in terms of the conversion of NO. The reaction products are N_2, N_2O, and H_2O.

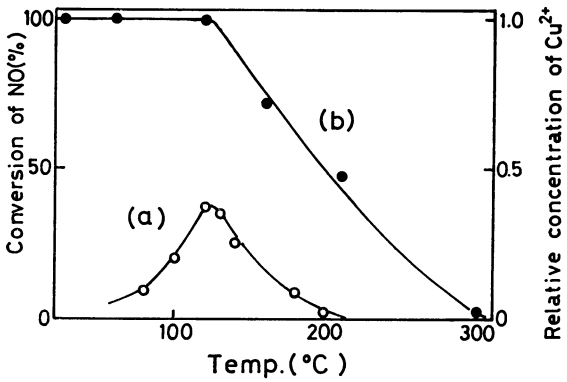

Fig. 1. Changes in catalytic activity (a) and in Cu(II) concentration (b) with temperature in the catalytic NO–NH_3 reaction over copper ion-exchanged Y zeolites.
Feed; NO (3%)+NH_3 (2%)+He,
Contact time; 1.0 g·s/mol.

The selectivity for N_2O ($N_2O/(N_2+N_2O)$) is little influenced by the reaction temperature. It seems that such an activity profile is correlated with the change in oxidation state of the copper ions present in the zeolite framework, as observed by the change in the coloration of catalysts. The correlation was first examined by ESR study as follows.

Cu(II)NaY zeolite with 60% cation exchange (150 mg) was loaded as a catalyst bed in a Pyrex glass tube of o.d. 3.5 mm, which was thereafter connected to a gas flow system. After heating the catalyst bed to the desired temperature, a stream (10 cm^3/min) of gas mixture of NO (3%), NH_3 (2%), and He (95%) was introduced. The same composition and contact time as those used to obtain curve (a) in Fig. 1 were selected. After treatment for 4 h, which was found to be sufficient for the catalytic system to reach a stationary state, the catalyst was purged of the gaseous compounds at the same temperature for 15 min by He stream. The Pyrex glass tube containing the catalyst was then removed from the flow system, and the catalyst was subjected to ESR measurement at room temperature. Figure 2

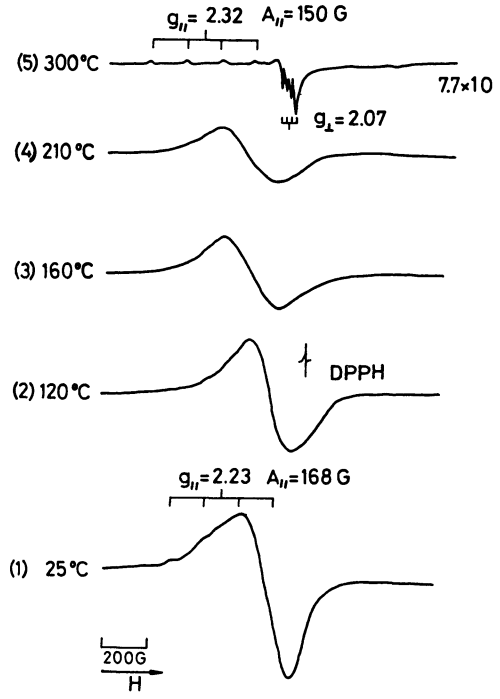

Fig. 2. ESR spectra of Cu(II) ions for a 60% copper ion-exchanged Y zeolites treated by NO (3%)+NH_3 (2%) at various temperatures.

shows ESR spectra of Cu(II) ions recorded after the treatment at various temperatures. All the spectra were taken for one and the same sample by subjecting it to repeated treatment. The signals except (5) turned or nearly turned in to symmetric ones due to high Cu(II) concentrations. Spectra (1) and (2) can be ascribed to square planer $Cu(II)(NH_3)_4$ ($g_{//}$=2.23, $A_{//}$=1.68 G),[4] while (3) and (4) agree with the spectra recorded for partially dehydrated Cu(II)NaY. The decrease in Cu(II) concentration at elevated temperatures made the hyperfine structure of the signal to appear in spectrum (5); g values ($g_\perp$=2.07, $g_{//}$=2.32, $A_{//}$=150 G) show that the Cu(II) center is dehydrated and probably located at site I or I'.[5] It is evident that the Cu(II) ions exchanged in the zeolite exist mostly as tetraammine complexes below 120 °C, above which the complexes are replaced by partially or entirely dehydrated Cu(II) ions. No particular evidence was obtained for the formation of distorted tetrahedral Cu(II)–NH_3 complexes reported by Vansant and Lunsford.[5]

By double integration of the ESR signals the concentrations of Cu(II) ions were determined relative to that obtained after the treatment at 25 °C. They are plotted against temperatures (curve (b), Fig. 1). The Cu(II) concentration remains up to 120 °C, but decreases monotonously at higher temperatures. The decrease in Cu(II) concentration is related to that in catalytic activity shown by curve (a). However, agreement of the two curves is not satisfactory in detail. With rise in temperature, the activity falls more rapidly than Cu(II) concentration. At 200 °C, the activity is almost completely lost but the Cu(II) concentration remains near 50% level. The discrepancy seems to be correlated to the distribution of Cu(II) ions over several sites in the zeolite framework; the Cu(II) ions present above 200 °C are mostly located at inactive "locked-in" sites within the sodalite cage or hexagonal prism.

In dehydrated Cu(II)NaY zeolite, Cu(II) ions show rather strong preference to the "locked-in" sites.[6,7] In the presence of water or ammonia, however, the the Cu(II) ions are pulled toward the supercage by complex formation as reported by Huang and Vansant.[8] Under the present reaction conditions, the catalytic activity of Cu(II)NaY catalyst at 120 °C has been found to be proportional to the Cu(II) ion-exchanged level.[2] This indicates that at temperatures below 120 °C the Cu(II) ions are dominantly present in the supercage and act as active catalytic sites. Above 120 °C, however, the present ESR study shows that complex formation of Cu(II) with NH_3 or water molecules becomes increasingly difficult. This might be the reason for the Cu(II) ions returning to the "locked-in" sites at higher temperatures. The decrease in catalytic activity above 120 °C (curve (a)) results from a decrease in Cu(II) concentration within the supercage, which is caused partly by the reduction of Cu(II) ions to Cu(I) and partly by the migration of Cu(II) ions towards the "locked-in" site.

Reaction Kinetics. The reaction kinetics of the NO reduction with NH_3 over Cu(II)NaY catalysts was studied at 110 and 140 °C in a flow system. The temperatures were so chosen as to include the temperature for maximum activity (120 °C). As a result, the reaction rates at both temperatures were found to be expressed by empirical equations of the following form;

$$r = -\frac{dP_{NO}}{dt} = k_1 P_{NO}^n P_{NH_3}^m, \quad (1)$$

where P_{NO} and P_{NH_3} denote the partial pressures of nitrogen oxide and ammonia, respectively, and k_1 is a rate constant. P_{NO} and P_{NH_3} were varied in the range 0.01—0.08 atm. The reaction orders, n and m, obtained at 110 and 140 °C are given in Table 1. The difference in reaction temperature affects both n and m only slightly.

Table 1. Reaction orders on NO and NH_3 (Eq. 1) in the NO and NH_3 reaction over a Cu(II)NaY catalyst (Contact time; 1.0 g · s/cm³)

Temp (°C)	n	m	k[a]
110	1.0	0.63	2.45×10^{-4}
140	0.92	0.53	0.79×10^{-4}

a) Mols NO/s · (atm) $^{n+m}$ · g.

The rate data were found to satisfy the following expression within experimental errors at both temperatures.

$$r = \frac{k_2 P_{NO} P_{NH_3}}{(1+K_{NH_3}P_{NH_3})^2}. \quad (2)$$

This was derived by assuming a Langmuir-Hinshelwood type of reaction between weakly adsorbed NO and strongly adsorbed NH_3. Here, K_{NH_3} is the adsorption equilibrium constant and k_2 is a constant. It turned out subsequently, however, that the rate data also satisfy the equation

$$r = \frac{k_3 P_{NO} P_{NH_3}}{(1+K_{NH_3}P_{NH_3})}, \quad (3)$$

which implies that NO weakly adsorbs on sites different from those for NH_3 or that a Redeal type of reaction takes place between NO and adsorbed NH_3. Differentiation between (2) and (3) was difficult on the basis of kinetic data only. However, the results of IR study suggest that (3) appears to be more appropriate. The kinetic scheme does not change much for the two temperatures. Kinetic study also revealed that selectivity of the N_2O formation is slightly dependent upon the contact time as shown in Fig. 3. The selectivity ratio N_2/N_2O was extrapolated to exactly 2: 1 at contact time 0. The increase of the ratio at longer contact times indicates a consecutive reduction of N_2O to N_2.

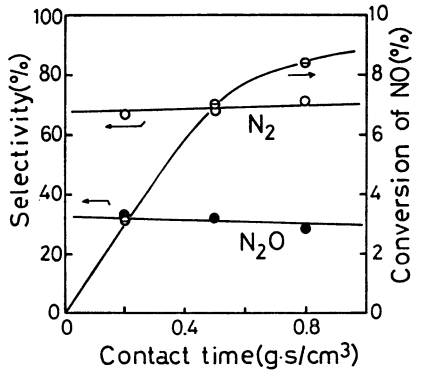

Fig. 3. Effect of the contact time on the conversion and selectivity of the NO–NH_3 reaction.

IR Study on NO–NH_3 Reaction. IR study was carried out to pursue *in situ* the reaction between NO and NH_3 over Cu(II)NaY catalysts. NH_3 undergoes adsorption on both the zeolite skeleton and the Cu(II) ions exchanged. The latter amounts to 3—4 NH_3 molecules per Cu(II) ion at room temperature in agreement with the result of Lunsford *et al.* who reported the formation of tetraammine complexes of Cu(II) ions in the zeolite cavity.[4] As for the NO adsorption, *ca.* one NO molecule is adsorbed per Cu(II) ion at room temperature with no detectable adsorption on the zeolite skeleton.

The results of IR spectroscopic study of the reaction at room temperature are shown in Figs. 4 and 5. A 32% Cu(II) ion-exchanged zeolite was used. The zeolite wafers were evacuated for 4 h at 400 °C in the IR cell before experiments. Introduction of NO over Cu(II)NaY gave curve 2 in Fig. 4. A strong absorption band at 1910 cm^{-1} is attributable to the stretching of the

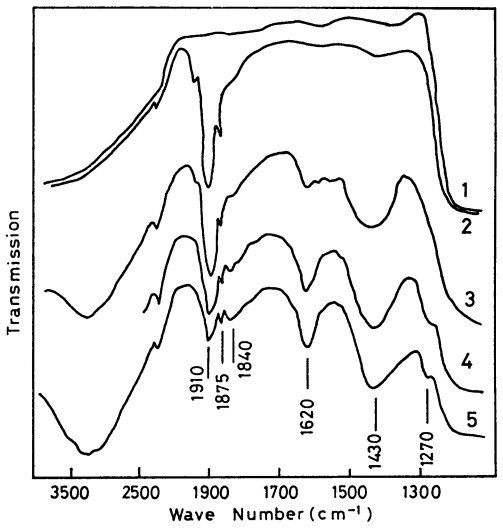

Fig. 4. Infrared spectra produced on introduction of NH_3 over a Cu(II)NaY preadsorbing NO (recorded at 25 °C). (1) Cu(II)NaY after evacuation at 400 °C for 4 h. (2) 30 min after the exposure to NO (49.5 Torr) at 25 °C. (3), (4), and (5) 30, 60, 180 min after the introduction of NH_3 (8 Torr) to (2), respectively.

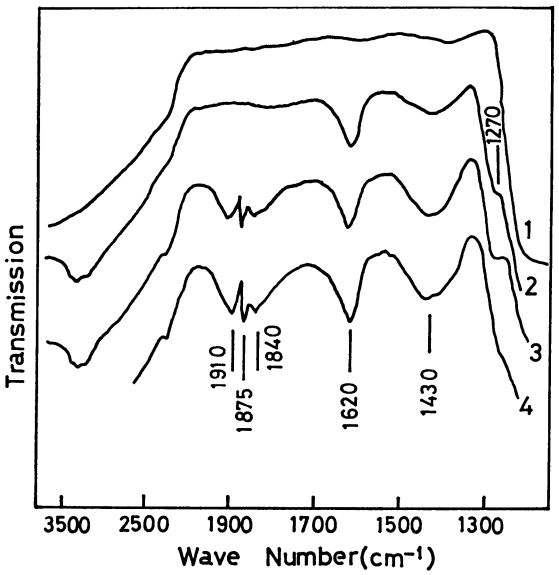

Fig. 5. Infrared spectra produced on introduction of NO over a Cu(II)NaY preadsorbing NH_3.
(1) Cu(II)NaY after evacuation at 400 °C for 4 h. (recorded at 25 °C). (2) Cu(II)NaY evacuated for 30 min after the adsorption of NH_3 (0.75 Torr) at 25 °C. (3) 60 min after the introduction of NO (64 Torr) to (2) at 25 °C. (4) After heating of (3) to 80 °C.

adsorbed NO, as first reported by Tarrit *et al.*[9] Bands at 1875 cm^{-1} are ascribable to gaseous NO. Gaseous NO shows a typical rotation-vibration spectrum with its Q branch centered at 1875 cm^{-1}, as exemplified by curve 2 or 3 in Fig. 5. A band at 2240 cm^{-1} is due to gaseous N_2O, mainly brought about as an impurity contained in NO gas. Curves 3, 4, and 5 in Fig. 4 were recorded 30, 60, and 180 min respectively after the addition of NH_3 (8 Torr). The band at 1910 cm^{-1} became weaker with the elapse of time while the intensities of the band at 1620 cm^{-1} and a broad one at 1430 cm^{-1} increased. A shoulder at 1270 cm^{-1} is a characteristic band due to the symmetric deformation vibration of NH_3 contained in $Cu(II)(NH_3)_4$.

NH_3 was adsorbed prior to the introduction of NO (Fig. 5). In curve 1, bands at 1270 and 1620 cm^{-1} and a broad band around 3300 cm^{-1} are ascribable to adsorbed NH_3, while a broad band around 1430 cm^{-1} is due to the deformation vibration of NH_4^+ formed. Major changes in the spectra caused by the introduction of gaseous NO (64 Torr) were the increase of the broad band centered at 1430 cm^{-1} and the slight increase of the band at 1620 cm^{-1}. Bands in 1910—1840 cm^{-1} of curves 2 and 3 are attributed to gaseous NO. Throughout Figs. 4 and 5, there is no evidence for the formation of nitrosyl ammine complex of Cu(II) ions. The NO adsorption is much weaker as compared with NH_3 adsorption. The adsorbed NO is easily replaced by NH_3. This makes the Langmuir-Hinshelwood type of reaction between adsorbed NO and adsorbed NH_3 (Eq. 2) less plausible. The reaction between NO and NH_3 gives rise to a remarkable increase in intensity of the broad band around 1430 cm^{-1}. It is probable that this band is in fact a composite of bands responsible for NH_4^+ and some other adsorbates. It seems that in this case the absorption of NO_2^- overlaps that for NH_4^+. NO_2^- shows absorption at 1430 and 1330 cm^{-1} in $[Co(NH_3)_nNO_2]^{2+}$, and at 1630, 1420, 1332, and 1260 cm^{-1} in $K_2Ba[Cu(NO_2)_6]$.[10,11]

Regeneration of Cu(II) from Cu(I). The bell-shaped dependence of the catalytic activity of Cu(II)-NaY catalysts implies that a reversible redox change occurs between Cu(II) and Cu(I) with the change in reaction temperature. Elucidation of the redox step is considered to contribute to the understanding of the catalytic reaction. A study was made on how the Cu(I) ions produced in the catalytic reaction at high temperature were reoxidized by lowering temperature in the same system. The experiments were performed in a flow system as well as in a pulse reactor. In the flow experiments, either a gas of NO (3%), NH_3 (2%), and He (95%) or a purge gas of He was allowed to flow (60 cm^3/min) over the catalyst bed. Cu(II)NaY with 60% cation exchange were first treated in a stream of the gas mixture at 300 °C for 4 h and then purged by He stream for 15 min. Almost all the Cu(II) ions were reduced to Cu(I) as revealed by ESR. The reduced sample was then cooled to the desired temperature and brough again into contact with the flow of the gas mixture. This caused a transient reaction to occur until a stationary catalytic reaction between NO and NH_3 was reached. The stationary state was reached

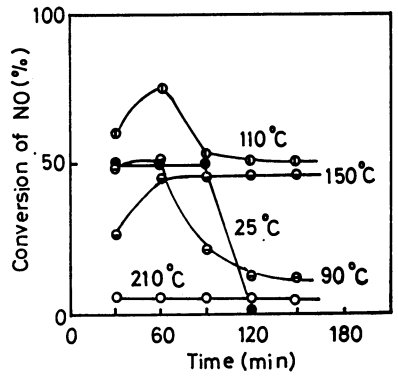

Fig. 6. Time course of NO conversion observed when gas mixture NO (3%)+NH_3 (2%) was contacted to reduced copper ion-exchanged Y zeolites at various temperatures.

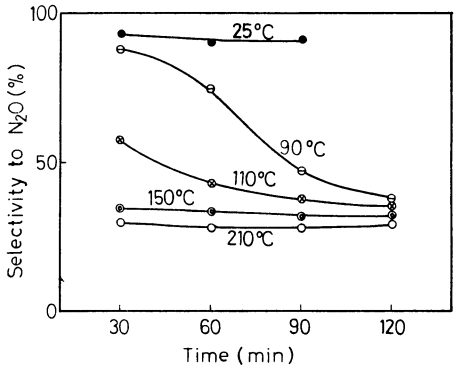

Fig. 7. Time course of the slectivity to N_2O, corresponding to Fig. 6.

within 60 min at 150 °C and above, while a period longer than 2 h was required at 90 °C and below.

The transients in conversion of NO and in selectivity for N_2O formation are shown in Figs. 6 and 7, respectively. The former transients are complicated. Selectivity for N_2O formation, on the contrary, showed monotonous decreases with time from the initial values to the stationary ones near 1/3 except for the case at 25 °C, where no stationary reaction proceeded at a

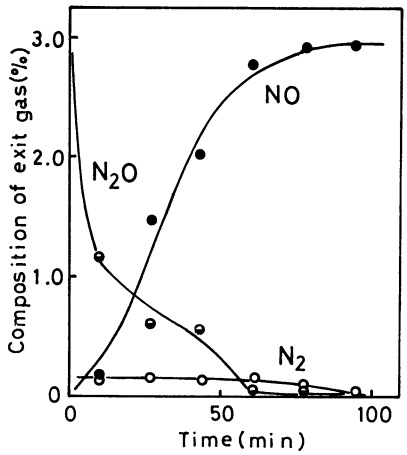

Fig. 8. Time course of N_2O and NO formation observed when NO (3%)+NH_3 (2%) was contacted to a reduced copper ion-exchanged 13X zeolites at 15 °C. Contact time; 1.0 g·s/cm^3.

significant rate. The high N_2O selectivity at the initial period, especially at lower temperatures, suggests that the transient reaction is connected to the reoxidation of Cu(I) to Cu(II). The transients at 15 °C are described in more detail in Fig. 8. In this case, Cu(II)Na 13X with 66% Cu(II) ion-exchanged was used after the reduction. The consumption of NO decreased rapidly with time until it ceased within *ca.* 1 h. A corresponding change took place in the evolution of N_2O, while N_2 formation in small quantities decreased more gradually over a longer reaction period. The color of the catalyst turned rapidly into pale greyish blue on contact with the gas mixture, and then gradually into blue developing from an upstream end of the catalyst bed to another. When the catalyst became entirely blue, N_2O formation stopped. The greyish blue might be due to the complex formation of a trace amount of unreduced Cu(II) ions with NH_3. The blue coloration is ascribable to the ammine complex of the Cu(II) ions regenerated.

The transient reaction at 15 °C was examined by a pulse reaction technique in order to obtain quantitative information. It was found that 2.7 mol of NO and 0.8 mol of N_2O are consumed and formed, respectively, to regenerate 1.0 mol of Cu(II). This strongly indicates the following disproportionation reaction.

$$Cu(I)(NH_3)_m \xrightarrow{+3NO} Cu(II)(NH_3)_mNO_2^- + N_2O \quad (4)$$

The reaction was found to proceed only in the presence of NH_3. After the completion of reaction, the catalyst, when heated at 150 °C in the same atmosphere, evolved a large amount of N_2 presumably by the following reaction.

$$Cu(II)(NH_3)_mNO_2^- + NH_4^+{}_{ad} \longrightarrow Cu(II)(NH_3)_m + N_2 + 2H_2O \quad (5)$$

Nitrite ion NO_2^- is known to react with NH_4^+ to produce N_2. Reaction (5) is considered to be slow at 25 °C, judging from the prolonged evolution of a small amount of N_2 (Fig. 8).

Discussion

From the results, we propose the following reaction path for the steady reaction between NO and NH_3 over Cu(II)NaY catalysts.

$$Cu(II)(NH_3)_n + NO \not\longrightarrow Cu(I)(NH_3)_m + N_2 + H_2O + (n-m-1)NH_3 + H^+{}_{ad} \quad (6)$$

$$H^+{}_{ad} + NH_3 \longrightarrow NH_4^+{}_{ad} \quad (7)$$

$$Cu(I)(NH_3)_m + 3NO \longrightarrow Cu(II)(NH_3)_mNO_2^- + N_2O \quad (8)$$

$$Cu(II)(NH_3)_mNO_2^- + NH_4^+{}_{ad} \longrightarrow Cu(II)(NH_3)_m + N_2 + 2H_2O \quad (9)$$

$$Cu(II)(NH_3)_m + (n-m)NH_3 \longrightarrow Cu(II)(NH_3)_n \quad (10)$$

$$4NO + 2NH_3 \longrightarrow 2N_2 + N_2O + 3H_2O \quad (11)$$

Here, n and m are the numbers of NH_3 molecules coordinating to a Cu(II) ion, probably 4 and 2, respectively, because of the complexes $Cu(II)(NH_3)_4$ and $Cu(I)(NH_3)_2$. Reaction (6), initiated between NO and coordinated NH_3, produces N_2, H_2O, and an atomic hydrogen, the last species of which reduces a Cu(II) ion to Cu(I) through a electron transfer. The H^+ produced is adsorbed on the framework oxygen of zeolite, being ammoniated to form NH_4^+ according to Reaction (7). Reactions (6) and (7) are supported by the result of IR study which shows that the band intensity of NH_4^+ at 1430 cm^{-1} for NH_3-preadsorbed Cu(II)-NaY increases on contact with NO. Reaction (8), which is identical with Reaction (4), is applied to regenerate Cu(II) ions. The NO_2^- produced then reacts with NH_4^+ by Reaction (9) to evolve N_2. The overall reaction is reduced to Reaction (11) which explains the observed N_2O selectivity at zero contact time.

The bell-shaped temperature dependence of catalytic activity is explained as follows. At temperatures lower than 120 °C, Reaction (6) is slow and rate-determining. Above 120 °C, on the other hand, it is presumed that Reaction (8) becomes less and less favored with an increase in temperature, causing the stationary Cu(II) concentration and therefore the steady reaction rate also to decrease with increasing temperature.

Reaction (8) can formally be separated into the following two reactions.

$$3NO \longrightarrow NO_2 + N_2O \quad (12)$$

$$Cu(I)(NH_3)_m + NO_2 \longrightarrow Cu(II)(NH_3)_mNO_2^- \quad (13)$$

The disproportionation reaction of NO on zeolites was first reported by Addison and Barrer.[12] They found that over unexchanged zeolites the reaction is fast at dry ice temperature or at 0 °C but very slow at 25 °C. Regarding Reaction(13), Kasai and Bishop reported that addition of NO_2 to Cu(I)NaY at room temperature restores the ESR signal of Cu(II) instantaneously.[13] The important result in the present study is that Reaction (8) proceeds only in the presence of NH_3. This implies that Reaction(8) can not be separated into Reactions(12) and (13). The crucial role of NH_3 for Reaction (8) may come from two possible effects.

(1) The redox potential between Cu(I) and Cu(II) is lowered by the formation of ammine complexes; it is 0.153 eV for $Cu(I) \rightarrow Cu(II) + e$, whereas −0.01 eV for $Cu(I)(NH_3)_2 + 2NH_3 \rightarrow Cu(II)(NH_3)_4 + e$.

(2) The location of copper ions in the zeolite framework is affected by the presence of NH_3. As a result of coordination, NH_3 pulls out copper ions from the sodalite cage or hexagonal prism toward the supercage in which the copper ion becomes more easily accessible for reactants.

Which of the two effects is more dominant can not be distinguished at present. However, the same effects can be operative for the depression of the reaction rate above 120 °C. The dissociation pressure of NH_3 for $CuSO_4 \cdot 4NH_3 \rightarrow CuSO_4 \cdot 2NH_3 + 2NH_3$ is 0.08 atm at 120 °C.[14]

It is of interest to compare the present reaction with the oxidation of ammonia with oxygen over Cu(II)NaY catalyst reported by Williamson *et al.*[15] In the latter reaction, the rate was found to show first and zero orders with respect to NH_3 and O_2, respectively, and was concluded to be solely determined by a step in which Cu(II) ions are reduced to Cu(I) by NH_3. There are several marked contrasts between the reactions of

NH_3–NO and NH_3–O_2.

(1) The dependence of the rate on the NH_3 partial pressure differs entirely for the two reaction. This reflects that, unlike the NH_3–O_2 reaction, the NH_3–NO reaction does not follow a simple redox mechanism.

(2) The NH_3–NO reaction is characterized by the bell-shaped temperature dependence, whereas the rate of the NH_3–O_2 reaction shows a normal increase with increasing temperature. This indicates that, at higher temperatures, the reoxidation of Cu(I) to Cu(II) is much slower in the former case. This would be important when the NH_3–NO reaction is carried out in the presence of oxygen.

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