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Kinetic Studies of Reduction of Nitric Oxide with Ammonia on Cu^{2+}-Exchanged Zeolites

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The selective catalytic reduction of nitric oxide with ammonia in the presence of oxygen has been studied on Cu^{2+} ion-exchanged zeolite catalysts. In the case of Cu^{2+}-exchanged ZSM-5, the reaction proceeded selectively at lower temperatures, where nitric oxide and ammonia reacted with one-to-one stoichiometry to produce nitrogen. At higher temperatures, an oxidation of ammonia with oxygen occurred concomitantly to reduce the conversion of nitric oxide. The formation rate of nitrogen was first-order with respect to the partial pressure of nitric oxide, nearly half-order to that of oxygen, and zero-order to that of ammonia. The apparent activation energies were almost the same for all Cu–ZSM-5 examined having different Cu^{2+}-exchange levels and Si/Al atomic ratios. The ideality of Cu^{2+}-exchange ascertained from the stoichiometry of ion-exchange for the exchange levels less than 200% suggested the atomic dispersion of copper species. The specific activity per Cu^{2+} ion increased with increasing ion-exchange level from 29 to 195% and also with decreasing the Si/Al atomic ratio from 71 to 23. The specific activities of various Cu–ZSM-5 were found to depend on the concentration of the Cu^{2+} ions; i.e., the higher the copper concentration, the higher the specific activity. The active copper species were proposed to be paired Cu^{2+} species in view of the relation between the specific activity and the copper concentration.

INTRODUCTION

Copper is one of the promising elements which have the ability to activate nitric oxide for the reduction with ammonia or hydrocarbons and also for the decomposition into nitrogen and oxygen. Seiyama *et al.* (1) have examined various transition metal cation exchanged Y zeolites for the selective catalytic reduction (SCR) of nitric oxide with ammonia in the absence of oxygen and found that Cu^{2+}–NaY is the most active catalyst. They also examined the effects of coexisting gases (2). The presence of oxygen enhanced the activity, while H_2O and SO_2 had poisoning effects. Cu^{2+}-exchanged mordenite has also been reported (3, 4) to be active for the SCR of nitric oxide with ammonia in the presence of oxygen. The activity was much higher than that of Fe^{3+}- or proton-exchanged mordenite. Iwamoto *et al.* (5) have found that Cu–NaY is also active for the decomposition of nitric oxide into nitrogen. The decomposition activity was very low for Cu–NaY with Cu^{2+}-exchange level less than 40%, but above 40% it increased markedly with Cu^{2+}-exchange level up to 73%.

ZSM-5 is an unique zeolite, that is, Cu^{2+} cations can be introduced by an ion-exchange method with the exchange level exceeding 100%, while a similar excess in the exchange level has been reported for Cu-Y (6). Although the definitive mechanism for the overexchange in ZSM-5 is not clarified yet, Cu^{2+}-exchanged ZSM-5 has been studied intensively as a catalyst for the removal of nitrogen oxides. Cu^{2+}-exchanged ZSM-5 zeolites were recently found to have the highest activity so far documented for the catalytic decomposition of nitric oxide into nitrogen and oxygen (7). The formation of nitrogen took place at the Cu^{2+}-exchange level of 40% or more and the yield of nitrogen increased with Cu^{2+}-exchange level even when the exchange level exceeded 100% (8). Li and Hall (9) have also measured the activity for the decomposition of nitric oxide on Cu–ZSM-5 having various Cu loadings and found that the turnover frequency calculated from the total amount of Cu increased with increasing the Cu^{2+}-exchange level from 72 to 114%. The same catalyst, Cu–ZSM-5, has been found to be active for the reduction of nitric oxide using hydrocarbons as reductants (10–15). When ethene was used as a reductant (12), the activity of Cu-ZSM-5 depended on the Cu^{2+}-exchange level; that is, the activity increased with increasing the exchange level, went through the maximum at around 100% exchange level, and then decreased, which was different from the dependence in the decomposition of nitric oxide

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as mentioned above. The reduction of nitric oxide with some oxygenate compounds, such as propanol and acetoaldehyde, was also studied on Cu–ZSM-5 catalysts (16).

We have reported (17) that H–ZSM-5 is acive for the selective reduction of nitric oxide with ammonia in the presence of an excess amount of oxygen, which is a similar result to the same reaction on H–mordenite reported earlier (18). In this study, we applied Cu^{2+}-exchanged zeolite catalysts to the same reaction. Our main purpose is to clarify the effect of copper concentration in zeolites on the activity for the selective reduction of nitric oxide based on the kinetic results.

EXPERIMENTAL

Catalysts

ZSM-5 zeolites were synthesized hydrothermally (19) to have Si/Al atomic ratios of 23, 45, and 71. They were transformed into H–ZSM-5 by the usual ion-exchange method using NH_4NO_3 aqueous solutions followed by the calcination in air at 773 K. Na–mordenite (Nippon Kagaku Kogyo, Si/Al = 6.4) and Na–Y (Tosoh, Si/Al = 3.6) were transformed into the proton forms by a similar ion-exchange method. Dealuminated H–mordenite (Tosoh, Si/Al = 67) was used as supplied. Cupric ions were loaded on these zeolites by the ion-exchange method using aqueous solutions (pH = 5) of copper acetate, $Cu(CH_3COO)_2$, followed by washing with pure water, drying in air at 403 K for 12 h, and calcination in air at 773 K for 4 h to obtain Cu–ZSM-5 (Cu–Z), Cu–mordenite (Cu–M), and Cu–Y. Cu^{2+}-loading was controlled by changing the temperature of the ion-exchange (298 or 343 K), the concentration of copper acetate (2.0×10^{-5} or 4.0×10^{-5} mol cm^{-3}), the number of exchange–decantation cycles and the exchange time. Though these procedures did not provide the strict reproducibility in the loading of copper, we varied the loading by trial and error from 0.29 to 2.0 wt% for Cu–Z, from 0.64 to 3.7 wt% for Cu–M, and from 1.4 to 5.2 wt% for Cu–Y. These loadings correspond to the Cu^{2+}-exchange levels of 29–195% (Cu–Z), 56–136% (Cu–M), and 17–65% (Cu–Y), respectively. Omitting the washing after Cu^{2+} ion-exchange from the procedure above, which was a kind of impregnation, resulted in higher copper loadings on ZSM-5 up to 2.8 wt%, corresponding to 275% apparent exchange level. The concentrations of copper and aluminum in zeolites were determined by atomic absorption spectrophotometry. The catalysts were pressed and broken into grains of 20–28 mesh. We express the catalysts as Cu(x)–Z(y), Cu(x)–M(y), and Cu(x)–Y(y), where x and y represent the percentage degree of Cu^{2+}ion-exchange and the Si/Al atomic ratio of zeolites, respectively.

Procedure

The reduction of nitric oxide with ammonia was carried out using a conventional flow reaction system under atmospheric pressure with a quartz reactor of 17-mm i.d. A specific amount of catalyst put in the reactor was heated in flowing helium from 298 to 773 K in 1 h and kept at the temperature for 1 h to remove adsorbed water. Then a mixture of NO, NH_3, and O_2 was fed with helium carrier onto the catalyst at a specific reaction temperature. The standard concentrations of reactants were 0.10% for both NO and NH_3 and 2.0% for O_2. The weight of catalyst (0.027–0.76 g) and the total flow rate (2.1×10^4–4.0×10^4 cm^3 h^{-1} were adjusted to get W/F of 1.0×10^{-6}–2.5×10^{-5} g h cm^{-3} (GHSV of 2.9×10^4–7.1×10^5 h^{-1}). The effluent gas was analyzed by GC (Tyran M-200) with Molecular Sieve 5A and Plot Q columns for N_2, N_2O, and O_2, by an NO_x analyzer (Yanaco ECL-77A) with a chemiluminescent detector for NO and NO_2, and by colorimetry using Nessler's reagent for ammonia. Unreacted ammonia was collected by passing the effluent through 2×10^{-5} mol cm^{-3} hydrochloric acid before it was introduced into the NO_x analyzer.

RESULTS AND DISCUSSION

We carried out the reaction on various Cu^{2+}-exchanged zeolites. To study the effect of copper concentration, ZSM-5 is an useful zeolite because the aluminum concentration can be varied widely by the hydrothermal synthesis without any severe dealumination treatments and because the apparent Cu^{2+}-exchange level can be varied up to 200%. Therefore, we first concentrated on the results obtained for Cu–ZSM-5. The reaction was carried out on Cu–Z having various Cu^{2+}-exchange levels and various Si/Al ratios at temperatures of 373–873 K. At these temperatures, the activity and selectivity of these catalysts did not change for more than 48 h of process time. Reaction products containing an N-atom were N_2, NO_2, and N_2O. The amount of NO_2 was negligibly small for all the catalysts. Figures 1a and 1b show the effect of the reaction temperature for Cu(79)–Z(45) and Cu(147)–Z(45), respectively, obtained at W/F of 3.3×10^{-6} g h cm^{-3}. Though these catalysts had different Cu^{2+}-exchange levels, below and above 100%, the curves showed a similar dependence on the reaction temperature. Figure 1c shows the results obtained on H–ZSM-5 (Si/Al = 45). The conversion of nitric oxide was much lower than that on the Cu–Z catalysts. It is clear that the reduction of nitric oxide on Cu–ZSM-5 was catalyzed by the copper ions exchanged into ZSM-5. Protons themselves and a trace amount of iron impurity, if any, are not responsible for the activity of Cu–ZSM-5. A possibility for the protons to affect the activity of copper ions was examined by comparing the

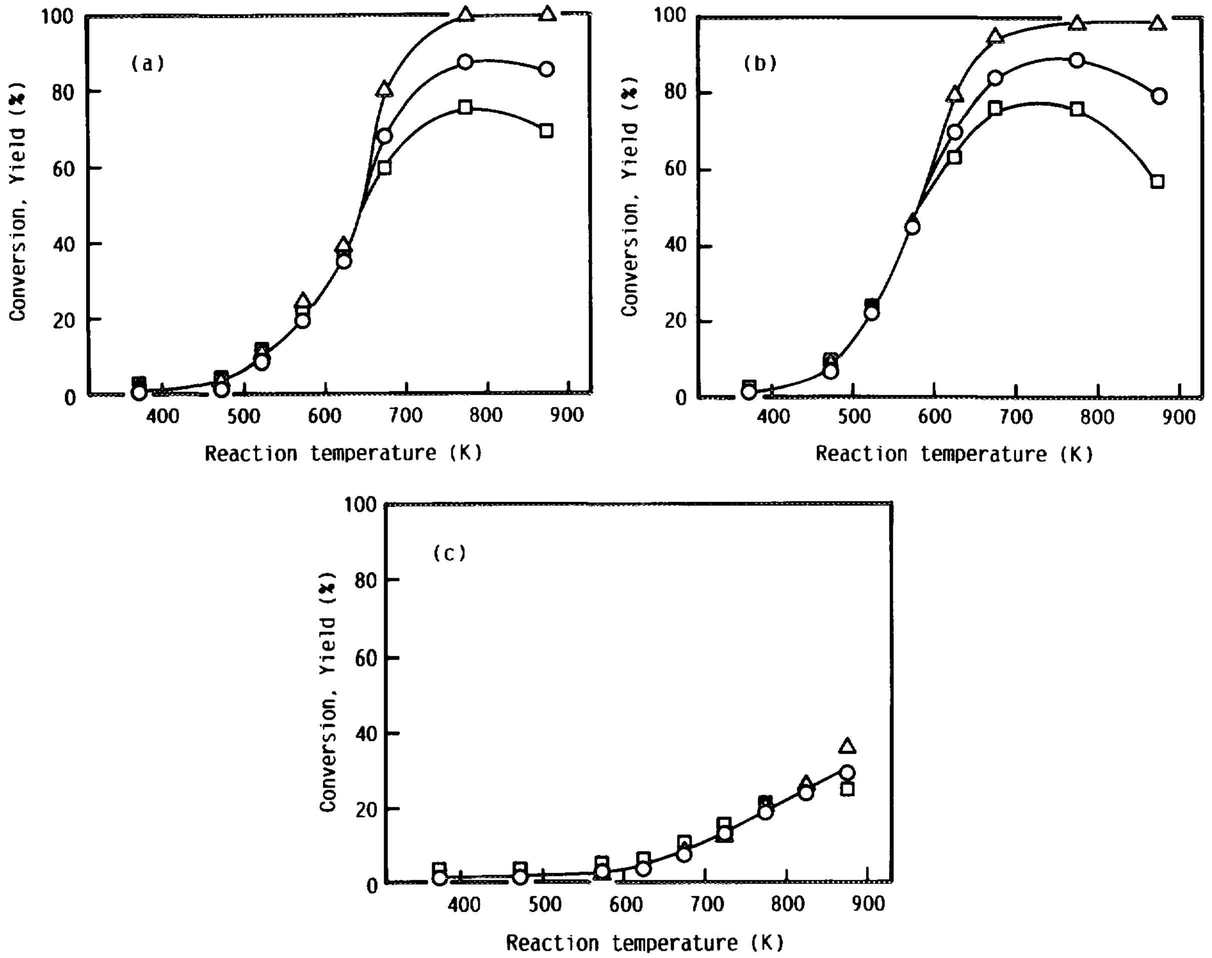

FIG. 1. Reduction of nitric oxide with ammonia in the presence of oxygen on Cu(79)–Z(45) (a), Cu(147)–Z(45) (b), and H–Z(45) (c). Conversion of nitric oxide (□) and ammonia (△) and yield of nitrogen (○) were measured at $W/F = 3.3 \times 10^{-6}$ g h cm^{-3}. Concentrations of reactants were 0.10% (both NO and NH$_3$) and 2.0% (O$_2$) in He carrier.

activity of Cu^{2+}(99%)-exchanged H–ZSM-5 (Si/Al = 45) with that of Cu^{2+}(100%)-exchanged Na–ZSM-5 (Si/Al = 45). NO-conversions and N$_2$-yields were 32.4 and 34.9% for the former and 35.5 and 34.0% for the latter, indicating that the protons on the cation sites do not have any significant effect on the reduction of nitric oxide catalyzed by the copper ions.

The possibility for the decomposition of nitric oxide into nitrogen and oxygen was examined under the same reaction conditions as used in the SCR of nitric oxide without feeding ammonia on the same Cu–Z catalysts used in Figs. 1a and 1b. Nitric oxide reacted with oxygen at 473 K and above. The conversion of nitric oxide increased with the temperature and reached the maximum at 673 K, then decreased at higher temperatures because of the equilibrium of the oxidation of NO into NO$_2$ (20). The maximum conversions on these catalysts were about 25%. The N-containing product was almost exclusively NO$_2$; N$_2$ was only detected in a negligible amount at any temperature. Iwamoto *et al.* (8) studied the effect of coexisting oxygen on the decomposition of nitric oxide using Cu–ZSM-5 catalysts with various Cu^{2+}-exchange levels. They found that the decomposition was inhibited by oxygen and that the conversion of nitric oxide into N$_2$ was only 5% on Cu–ZSM-5 of 152% ion-exchange level under the following reaction conditions: $T = 773$ K; NO, 0.10%; O$_2$, 0.50%; $W/F = 8.3 \times 10^{-5}$ g h cm^{-3}. In our case, W/F was one order of magnitude smaller and the partial pressure of O$_2$ was four times higher. Therefore, it is reasonable that the decomposition of nitric oxide on Cu–ZSM-5 could be neglected under our reaction conditions. Kinetic studies by Li and Hall (9) also revealed the inhibiting effect of oxygen on the decomposition of nitric oxide on Cu(166%)–ZSM-5. They found that the rate of decomposition fell off at the inverse of $(1 + K[O_2]^{1/2})$, where K, the equilibrium constant for O$_2$ adsorption, increased with decreasing reaction temperature. This again supports the idea that, in our case, the inhibition by oxygen is serious at as low as 573 K to observe the negligible decomposition.

In the case of the reduction of nitric oxide with ammonia on Cu(79)–Z(45), the amount of N_2O formed as well as that of NO_2 were negligible. The lack of N_2O formation is in contrast with the results obtained with platinum foil catalysts (21), where N_2O was produced in a N_2/N_2O ratio of about 2 at 573 K from the mixture of NO, NH_3, and O_2. As shown in Fig. 1a, the conversion of NO, the conversion of NH_3, and the yield of N_2 gave almost the same values at 623 K or lower. These observations indicate that the reduction of nitric oxide occurs selectively at the lower temperatures with the following overall stoichiometry:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O. \qquad [1]$$

This is the same reaction stoichiometry that has been proposed for the SCR of nitric oxide on vanadia–titania (22), H–mordenite (3), and Cu–NaY (2).

As shown in Figs. 1a and 1b, NO-conversion, NH_3-conversion, and N_2-yield were different from each other at higher temperatures. The NH_3-conversion was the highest, reaching almost 100% at above 700 K, while the NO-conversion was the lowest. Therefore, the selectivity for the formation of nitrogen, Eq. [1], decreased at higher temperatures. This could be explained by side reactions between NH_3 and O_2:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O, \qquad [2]$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O. \qquad [3]$$

These side reactions lead to the difference in the conversions and yield, i.e., the high NH_3-conversion and the low NO-conversion compared with the N_2-yield. In order to confirm the contribution of these reactions, the oxidation of ammonia with oxygen was carried out under the same reaction conditions as for the SCR without adding nitric oxide in the feed gas. Figure 2 shows the change in NH_3-conversion with the reaction temperature obtained on Cu(79)–Z(45), Cu(147)–Z(45), and Cu(178)–Z(45). In all cases, N-containing products were N_2, NO, and N_2O. As the yields of both NO and N_2O were less than 1%, the conversion curves in Fig. 2 represent the yields of N_2. Therefore, it is confirmed that the oxidation reaction, Eq. [2], is catalyzed by Cu–ZSM-5 and that it decreases the selectivity for the formation of nitrogen, Eq. [1]. If the two reactions, Eqs. [1] and [2], take place simultaneously, the difference between NH_3-conversion and NO-conversion should correspond to the amount of consumed ammonia by reaction [2], where two molecules of N_2 are produced from four molecules of NH_3. Therefore, the yield of N_2 should be at the middle of the two conversion values. The results in Fig. 1 at higher temperatures roughly followed this relation, which indicates the concomitant oxidation of ammonia into nitrogen, Eq. [2].

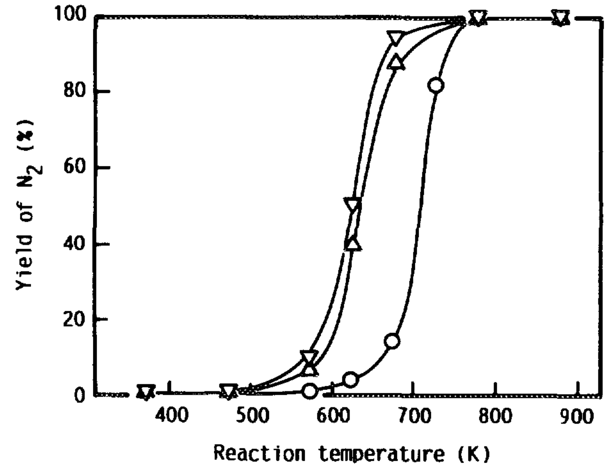

FIG. 2. Oxidation of ammonia on Cu(79)–Z(45) (○), Cu(147)–Z(45) (△), and Cu(178)–Z(45) (▽). A mixture of ammonia (0.10%) and oxygen (2.0%) was fed with helium carrier at $W/F = 3.3 \times 10^{-6}$ g h cm^{-3}.

From Figs. 1 and 2; it is clear that the activities of Cu(147)–Z(45) both for the SCR of nitric oxide ($T \leqq 573$ K) and for the oxidation of ammonia were higher than those of Cu(79)–Z(45). Higher activities of the excessively Cu^{2+}-exchanged (>100%) ZSM-5 were also reported for the decomposition of nitric oxide (8, 9). In order to clarify the effect of the extent of Cu^{2+}-exchange on the SCR activity, kinetic studies were carried out. Figure 3 shows the effect of the concentration of reactants on the rate of N_2 formation on Cu(147)–Z(45) measured at 573 K. At this temperature, the rate of N_2 formation represents the rate of the SCR of nitric oxide, Eq. [1], because NO-conversion and NH_3-conversion were almost the same as shown in Fig. 1b. The concentration of the specific reactant was varied while keeping those of other reactants equal to the standard values (NO, 0.10%; NH_3, 0.10%; and O_2, 2.0%). From Fig. 3, it is apparent that the reaction rate depended positively on the concentration of nitric oxide (a) and oxygen (c). On the other hand, the concentration of ammonia exhibited a different effect, that is, the rate depended on NH_3-concentration only at very low concentrations. At around the standard concentration (0.10%), the rate was almost independent of NH_3-concentration, which indicates that the rate is zeroth-order in NH_3-concentration. This suggests that most of the surface of Cu–ZSM-5 is covered with ammonia under the standard conditions.

The change in O_2-concentration before and after the passage through the catalyst bed must be negligibly small under the standard conditions because the reactant mixture contains an excess amount of oxygen compared with nitric oxide and ammonia. Therefore, the reaction rate can be expressed only by the partial pressure of nitric oxide. Figure 4 shows the change in N_2-yields with W/F measured at 573 K with Cu–Z having various Cu^{2+}-

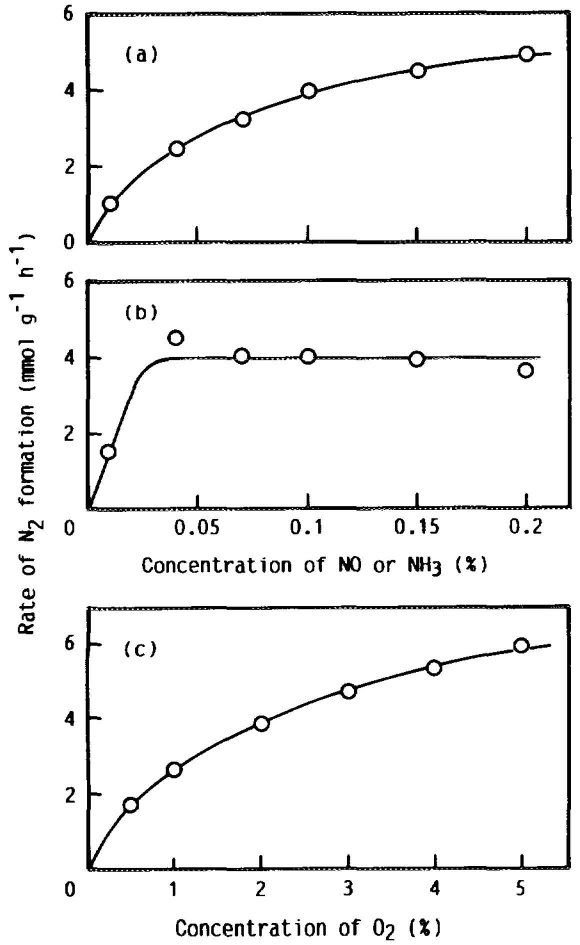

FIG. 3. Effects of the concentrations of nitric oxide (a), ammonia (b), and oxygen (c) on the rate of nitrogen formation measured with Cu(147)-Z(45) at 573 K and $W/F = 3.3 \times 10^{-6}$ g h cm^{-3}. Concentration of a specific reactant was varied keeping the others constant at 0.10% (NO or NH_3) or 2.0% (O_2).

exchange levels and Si/Al ratios. W/F was varied by changing the weight of catalyst (0.044–0.76 g) and the total flow rate (2.1×10^4–4.0×10^4 cm^3 h^{-1}). Curvatures were found for most of the catalysts, indicating that the reaction took place out of the differential conditions. The results were then treated assuming that the reaction rate had first-order dependence on the concentration of nitric oxide. The first-order plots using an integrated equation are shown in Fig. 5. Linear relations were obtained for all the catalysts, which confirms that the SCR of nitric oxide with ammonia in the presence of excess oxygen is the first-order reaction with respect to the concentration of nitric oxide under our reaction conditions. The first-order dependence on NO-concentration has been also reported (23) for the SCR of nitric oxide with ammonia on Cu^{2+}-exchanged mordenite.

The reaction order with respect to the pressure of oxygen was treated as follows. From the above results, the reaction rate (r) can be expressed as

$$r = k[\mathrm{NO}] = k'[\mathrm{O_2}]^m[\mathrm{NO}], \qquad [4]$$

where k and k' are the rate constants. The value of k can be obtained from the slope of the first-order plot (Fig. 5). A similar first-order plot with respect to NO-concentration was obtained for each data in Fig. 3c. Though each plot only had one point, the good linearity shown in Fig. 5 made it reasonable to elucidate the k value from each slope. As the relation between k and k' is simply expressed as

$$k = k'[\mathrm{O_2}]^m, \qquad [5]$$

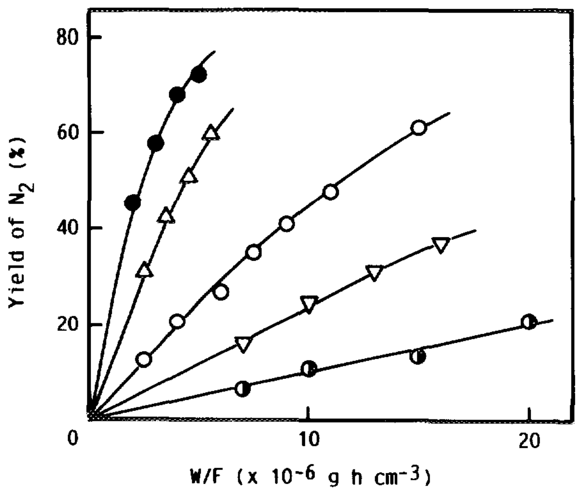

FIG. 4. Change in the yield of nitrogen with W/F on Cu(29)-Z(45) (◑), Cu(120)-Z(71) (▽), Cu(79)-Z(45) (○), Cu(79)-Z(23) (△), and Cu(178)-Z(45) (●) measured at 573 K with the reactant containing NO (0.10%), NH_3 (0.10%), and O_2 (2.0%).

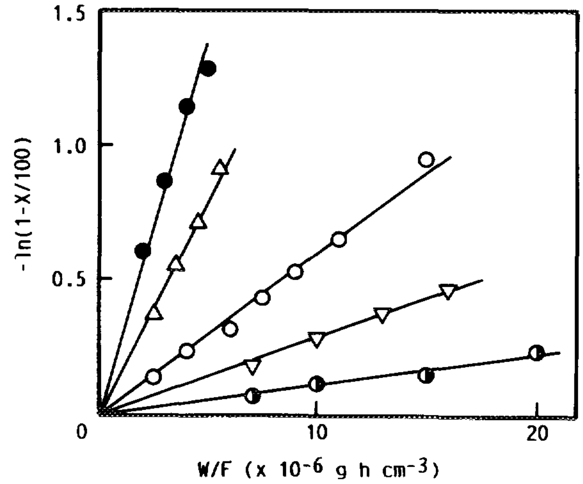

FIG. 5. First-order plot for the data of Fig. 4. Symbols represent the same catalysts as in Fig. 4.

we can estimate the reaction order, m, with respect to O_2-concentration from the slope of the ln k vs ln $[O_2]$ plot (Fig. 6). The slope of this line was 0.60, which suggests that the SCR of nitric oxide is roughly half order with respect to the partial pressure of oxygen. In the case of the same reaction on V_2O_5 (24), the reaction rate increased with O_2 concentration similarly to Fig. 3c except for the negligible increase at above 1% of O_2 and the rate was zero order with respect to NH_3-concentration and first order in NO-concentration. Arakawa *et al.* (25) have studied the reduction of nitric oxide with ammonia in the absence of oxygen on Cu^{2+}-exchanged NaY at 383 and 413 K. They found that the reaction rate was first-order in NO-concentration and nearly half-order in NH_3-concentration. Their results were obtained at lower temperatures and higher W/F than those used in our work. Therefore, the reaction mechanism may not be the same, which results in the different reaction order with respect to NH_3-concentration.

From the slope of each line in Fig. 5, the first-order rate constant, k, was obtained for each Cu–Z at 573 K. Apparent activation energies at 543–603 K were calculated from Arrhenius plots using the k values obtained in a similar manner. Figure 7 shows the relation between the apparent activation energy and the Cu^{2+}-exchange level for Cu–Z with various Si/Al ratios. Although some variations existed in the activation energies, they did not show any significant dependence on the exchange level or on the Si/Al ratio of ZSM-5 expressed by the different symbols. It is suggested that the catalytic property of an individual active site is almost the same for all the Cu–Z catalysts tested. As shown in Figs. 1a and 1b, the maximum conversion of nitric oxide was the same for Cu(79)–Z(45) and Cu(147)–Z(45) with a shift of the temperature at the maximum conversion. This may be explained by the similarity in the nature of active species between these two catalysts with the only difference in number or concentration of the active sites. A similar activation energy (49 kJ mol^{-1}) was reported for the SCR of nitric oxide with ammonia in the presence of oxygen on the V_2O_5 catalyst (24), where $V^{5+}{=}O$ species on V_2O_5 was responsible for the reduction activity. In the case of copper catalysts, Cu=O species can hardly generate at the exchange site of zeolites or on the surface of copper oxide particles. Therefore, the reaction mechanism probably is different from that on the V_2O_5 catalyst though the activation energies were nearly the same.

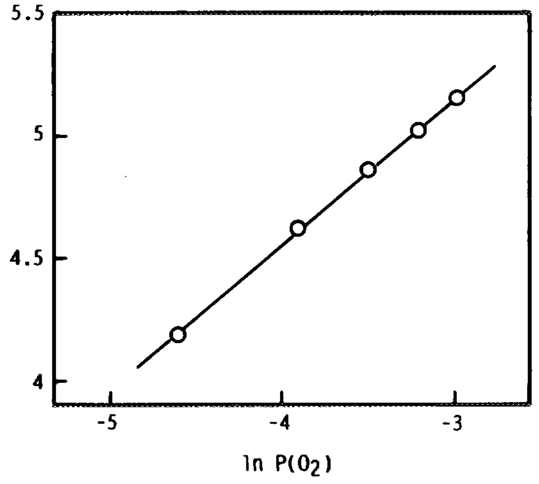

FIG. 6. Relation between ln k and ln $P(O_2)$ measured with Cu(147)–Z(45) at 573 K and W/F = 3.3 × 10^{-6} g h cm^{-3}.

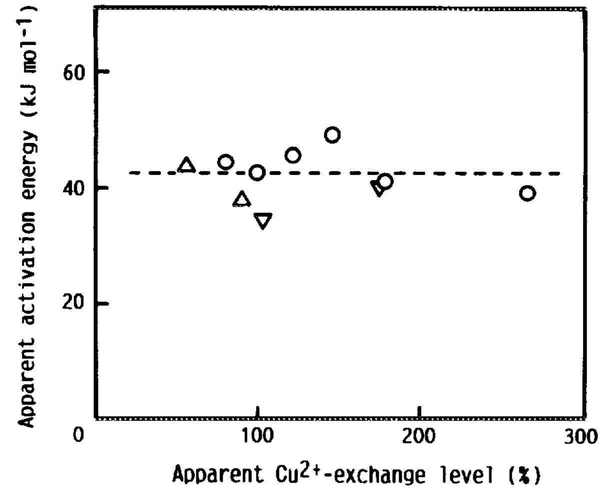

FIG. 7. Relation between the apparent activation energy and Cu^{2+}-exchange level for Cu–Z(23) (△), Cu–Z(45) (○), and Cu–Z(71) (▽).

The homogeneous nature of the active site of various Cu–Z indicated by the similarity in the activation energy may result from the homogeneity in the Cu^{2+}-exchange behavior even above 100% exchange levels. We studied on the details of Cu^{2+}-exchange first by exchanging Na^+ in ZSM-5 by Cu^{2+}. The ion-exchange was carried out for Na–ZSM-5(Si/Al = 46) at 303 K using 1.7 × 10^{-5} mol cm^{-3} aqueous solution of copper acetate (pH = 5) with varying the exchange period to get various copper loadings. Figure 8a shows the relation between the amount of incorporated Cu^{2+} and that of remaining Na^+ in ZSM-5, both expressed by the atomic ratio based on the amount of aluminum. The amount of Na^+ (Na^+/Al) decreased almost linearly with increasing the amount of Cu^{2+} ($2Cu^{2+}$/Al) with a slope of −1 (dotted line) up to $2Cu^{2+}$/Al = 0.7. This may be explained by the simple exchange between two Na^+ ions and one Cu^{2+} ion and also by that between two Na^+ and a pair of $Cu(OH)^+$ and H^+. The latter ion-exchange has been suggested for Cu–ZSM-5 (8, 26) and Cu–Y (27–29). Further incorporation of Cu^{2+} took place without a large decrease in Na^+/Al, which did not change significantly above $2Cu^{2+}$/Al = 1.3. This phenomena can be explained by the exchange between one H^+

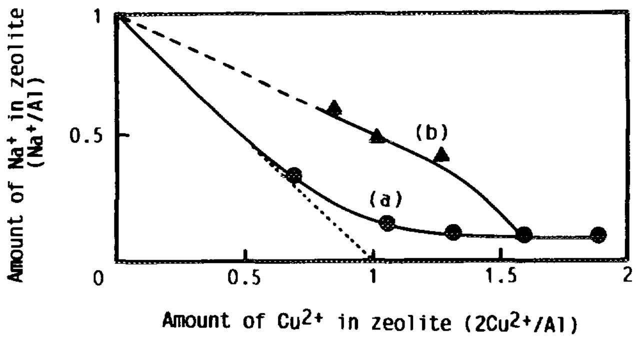

FIG. 8. Ion-exchange behavior of ZSM-5 in the forward exchange of Na–Z(46) by Cu^{2+} (a) and the reverse exchange of Cu(161)–Z(46) by Na^+ (b). Exchange was carried out at 303 K with 1.7×10^{-5} mol cm^{-3} solutions of copper acetate (a) and sodium chloride (b).

and one $Cu(OH)^+$, where H^+ has already been incorporated into ZSM-5 at the initial stage of the ion-exchange. Therefore, the exchange between two Na^+ and a pair of $Cu(OH)^+$ and H^+ should occur at the initial stage.

To ascertain the ideality of this exchange and to check the formation of unexchangeable copper aggregates, the reverse exchange was carried out with Cu(161)–Z(46) and an aqueous solution of sodium chloride (1.7×10^{-5} mol cm^{-3}) in a similar manner to the forward exchange mentioned above. In Fig. 8, the relation between the amount of remaining Cu^{2+} ($2Cu^{2+}/Al$) and that of incorporated Na^+ (Na^+/Al) in ZSM-5 is also shown. Na^+/Al increased with decreasing $2Cu^{2+}/Al$, finally following the broken line with a slope of -0.5. This broken line may represent the exchange between one Na^+ and one $Cu(OH)^+$ approaching the complete exchange into Na-ZSM-5. The relatively steep increase in Na^+/Al at the initial stage of the reverse exchange ($2Cu^{2+}/Al$ from 1.6 to 1.3) may be explained by the exchange between two Na^+ and a pair of $Cu(OH)^+$ and H^+; this exchange apparently corresponds to the stoichiometric exchange between two Na^+ and a Cu^{2+}. We do not know the reason why this exchange takes place preferably to the one-to-one exchange indicated by the broken line. There should be no exchangeable protons remaining when the forward exchange has been achieved completely to get 200% exchange level. In the case of Cu(161)–Z(46) used here, however, there could remain the exchangeable H^+ in the amount corresponding to ca. 40% exchange level. Although the reverse exchange did not proceed inversely through the same path as that of the forward exchange, the above results indicate that all the copper ions exist in Cu–Z as exchangeable counter cations. Therefore, copper species in the excessively exchanged Cu–Z are dispersed atomically and would not form aggregates within the loading of $2Cu^{2+}/Al < 2$. The X-ray diffraction patterns of Cu–Z after the calcination, in fact, did not show the presence of large CuO particles.

In order to clarify the active copper species for the SCR of nitric oxide, the effect of copper concentration on the activity of Cu^{2+} ions was investigated. The specific activity, k(Cu), was calculated by dividing the rate constant, k, obtained from the first-order plot (Fig. 5) by the total number of Cu ions in the catalyst. Figure 9 shows the relation between k(Cu) and the copper loading expressed by the corresponding Cu^{2+}-exchange level. In the case of Cu–Z having the same Si/Al ratio, k(Cu) increased with increasing Cu^{2+}-exchange level up to 200%, as indicated by three curves. The increase in k(Cu) was the most remarkable for Cu–Z(23), where k(Cu) increased from 0.5×10^{-15} to 3.2×10^{-15} cm^3 h^{-1} (Cu-atom)$^{-1}$ within a 110% increase in the exchange level. It should be noted that k(Cu) increased monotonously above the exchange level of 100% for Cu–Z(45) and Cu–Z(71) up to 200%. In the case of Cu–NaY, Williamson and Lunsford (30) have studied the effect of Cu^{2+}-exchange level on the reduction of nitric oxide with ammonia in the absence of oxygen. They found that the activity increased linearly with the exchange level from 6.5 to 44%, indicating that the specific activity per Cu^{2+} did not change. Seiyama *et al.* (1) have also studied the same reaction system and obtained a linear relation between the conversion of nitric oxide and the Cu^{2+}-exchange level from 7 to 79%. This is consistent with the results of Williamson and Lunsford (30) mentioned above. The reason why the dependence of the specific activity in our system on the Cu^{2+}-exchange level was different from that in their system may be the difference in the parent zeolites or the presence of oxygen in our system.

In the case of Cu-ZSM-5, Iwamoto *et al.* have also reported the effect of Cu^{2+}-exchange level on the decomposition of nitric oxide (8) and on the reduction of nitric oxide with ethene (12). In the former reaction, the conversion of nitric oxide gave S-shaped dependence, where the

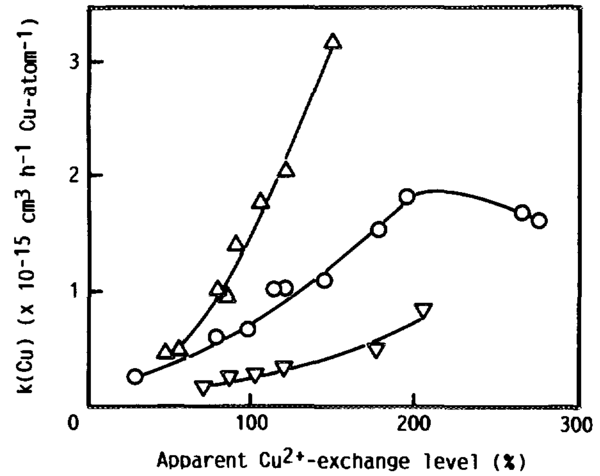

FIG. 9. Effect of Cu^{2+}-exchange level on the specific activity of Cu^{2+}. The activity was measured at 573 K on Cu–Z(23) (△), Cu–Z(45) (○), and Cu–Z(71) (▽) with the reactant mixture of NO (0.10%), NH_3 (0.10%), and O_2 (2.0%).

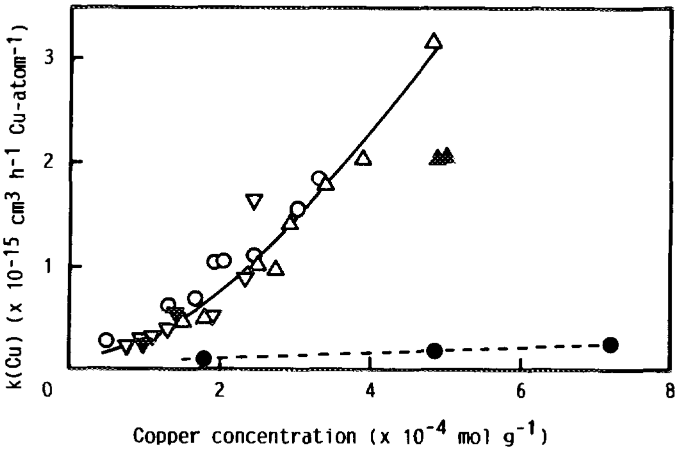

FIG. 10. Effect of copper concentration on the specific activity of Cu^{2+}. The activity was measured at 573 K on Cu–Z(23) (△), Cu–Z(45) (○), Cu–Z(71) (▽), Cu–M(6.4) (▲), Cu–M(67) (▼), and Cu–Y(3.6) (●).

conversion of nitric oxide increased sharply above the exchange level of 40%. Though the increase in activity at the exchange level above 70% was not clear because the conversion approached 100%, at least in the lower exchange levels, specific activity of Cu ions for the decomposition of nitric oxide increased with increasing the exchange level. Li and Hall (9) also reported that the specific activity (expressed by turnover frequency) for the decomposition of nitric oxide increased with copper exchange level from 72 to 114% on Cu–ZSM-5. These are similar phenomena as observed in our system. In the case of the reduction of nitric oxide with ethene (12), the conversion into nitrogen increased with Cu^{2+}-exchange level, but reached the maximum at around the exchange level of 100%. The cause of this difference in the effect of Cu loading on the two reactions is not clear so far and needs further investigation.

As shown in Fig. 9, when the Cu^{2+}-exchange level exceeded 200%, the specific activity of Cu–Z(45) decreased significantly. Above 200% exchange level, Cu^{2+} ions could not be located as countercations on cation exchange sites. These excess Cu^{2+} ions may form an aggregate such as a small particle of CuO. The decrease in specific activity indicates that copper species in such an aggregate are inactive or much less active than Cu^{2+} present as a counter cation. In addition, such CuO species may block the pores of ZSM-5, which may also result in the decrease in activity.

It is obvious from Fig. 9 that there is another factor which affected the activity; it is the Si/Al ratio. At the same exchange level, the lower the Si/Al ratio, the higher the specific activity. The lower Si/Al ratio corresponds to the higher aluminum concentration and also to the higher concentration of copper ions at the same Cu^{2+}-exchange level. Therefore, we considered the concentration of copper ions to be a critical factor which governs the specific activity. As shown by the open symbols in Fig. 10, the *k*(Cu) values in Fig. 9 were plotted against the concentration of copper ions in Cu–Z except for Cu(265)–Z(45) and Cu(275)–Z(45), which could contain the aggregated copper species as mentioned above. In contrast with the results in Fig. 9, all the *k*(Cu) values followed the same relation independent of the Si/Al ratio, which was roughly expressed by a single curve in Fig. 10. Accordingly, it is concluded that the specific activity is governed by the concentration of copper ions in Cu–ZSM-5.

Next, we examined the catalytic properties of Cu^{2+}-exchanged mordenite and Y-zeolite to clarify the effect of zeolite structure on the specific activity of Cu^{2+}. Figure 11 shows the effect of reaction temperature on the SCR of nitric oxide with ammonia using Cu(95)–M(67) (a) and Cu(17)–Y(3.6) (b) as catalysts at *W*/*F* of 7.0×10^{-6} and 6.0×10^{-6} g h cm^{-3}, respectively. In the case of Cu(95)–M(67), the activity arose above 500 K and increased drastically at around 600 K. Above 623 K, NH_3-conversion, N_2-yield, and NO-conversion were different from each other, indicating that the reaction between NH_3 and O_2 occurred concomitantly as in the case of Cu–Z mentioned earlier (see Fig. 1). At higher temperatures, the selectivity for the SCR, Eq. [1], was low compared with Cu–Z. On the other hand, Fig. 11b shows that Cu(17)–Y(3.6) had much higher selectivity than Cu–Z; the selectivity was almost 100% even at higher temperatures. Though the activity of Cu(17)–Y(3.6) was low at above 573 K compared with Cu–Z and Cu–M, it should be noted that Cu(17)–Y(3.6) exhibited a significant activity at 373 K, where Cu–Z and Cu–M were almost inactive. This low-temperature activity of Cu–Y has already been reported for the SCR of nitric oxide with ammonia in the absence of oxygen (1) and also in the presence of oxygen (2). The active sites of Cu–Y effective at the low temperatures should give much lower activation energy than that obtained for Cu–Z (Fig. 7) because the conversion increased only slightly from 373 K to 473 K. Therefore, the active sites and/or the reaction mechanism could change with reaction temperature on Cu–Y.

As shown in Fig. 11, the SCR of nitric oxide, Eq. [1], took place almost selectively at 573 K on both Cu–M and Cu–Y. At this temperature the first-order rate constant, *k*, was obtained in a similar manner as in the case of Cu–Z. Then the specific activity per Cu^{2+} ion, *k*(Cu), was also obtained and plotted against the concentration of Cu^{2+} as indicated by solid symbols in Fig. 10. For Cu–M, the specific activity also increased with the concentration of Cu^{2+} and its value was roughly equal to that for Cu–Z having the same concentration. However, the specific activity of Cu–Y was very low compared with Cu–Z and Cu–M.

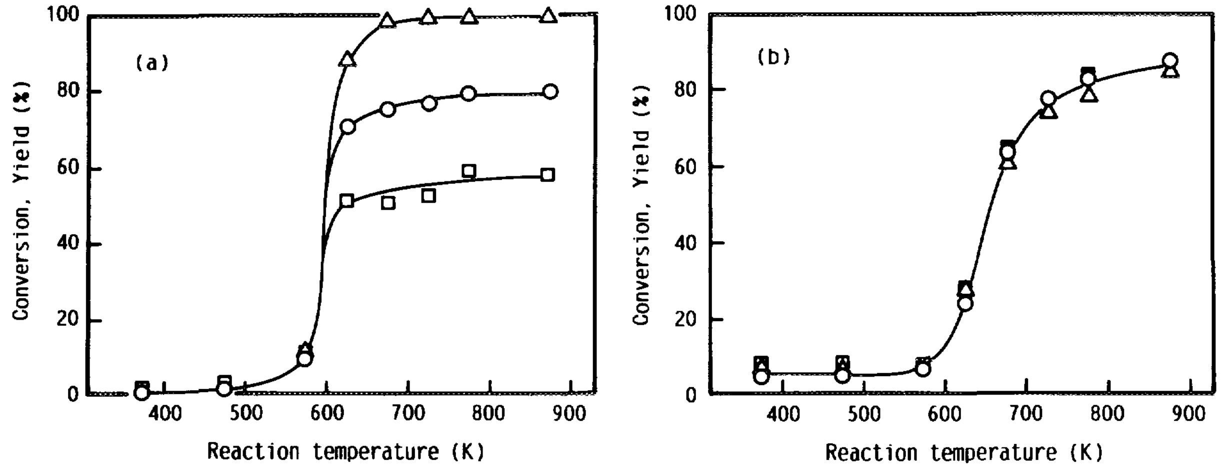

FIG. 11. Reduction of nitric oxide with ammonia in the presence of oxygen on Cu(95)–M(67) (a) and Cu(17)–Y(3.6) (b). Conversion of nitric oxide (□) and ammonia (△) and yield of nitrogen (○) were measured at $W/F = 7.0 \times 10^{-6}$ (a) and 6.0×10^{-6} g h cm^{-3} (b), respectively. Concentrations of reactants were 0.10% (NO and NH_3) and 2.0% (O_2).

In the case of Cu–Z and Cu–M, the increase in k(Cu) was almost one order of magnitude over the copper concentration examined. As described above, the catalytic property of the individual active site should be equal for Cu–Z with different ion-exchange levels and different Si/Al ratios, because the apparent activation energies did not change significantly with these factors. Therefore, the change in k(Cu) shown in Fig. 10 could be explained by the change in the number of active species; i.e., the higher the copper concentration, the higher the proportion of the active copper ions to the total copper ions. An idea that ZSM-5 has two different exchange sites, one for the formation of active Cu species and the other for inactive ones, could not be adopted, because k(Cu) was not the function of the ion-exchange level but that of the copper concentration. Another explanation for the change in the proportion of the active species is that two adjacent Cu ions are necessary to form an active species. The proportion of such active species should increase with increasing the copper concentration if Cu ions are located at random into the cation sites. A similar adjacent copper species was considered by Iwamoto *et al.* (8, 31) to be the active species of Cu–ZSM-5 for the decomposition of nitric oxide. They proposed a $Cu^{2+}–O^{2-}–Cu^{2+}$ species as a possible active site which was formed by the dimerization of $Cu(OH)^+$ species during the high-temperature evacuation. This dimer species in Cu–ZSM-5 has also been discussed in view of the redox property of copper species (9) and of the extralattice oxygen (26) in the decomposition of nitric oxide. The TPD/TPR study (32) has supported the existence of the dimer species in the excessively ion-exchanged Cu–ZSM-5 though CuO particles have also been suggested to coexist.

We propose a possible reaction scheme, shown in Fig. 12, taking account of the kinetic results and the proposed active dimer species discussed above, though the characterization work on the dimer species was poor. The active dimer species (a) has NH_3 ligands on each Cu^{2+} and one bridging oxygen and is located on two adjacent cation sites of zeolite. The number of NH_3 ligands, n, may be 3 taking account of four NH_3 ligands on an isolated Cu^{2+} in Cu–Y (30). On the aluminum poor zeolite, the dimer may be in the middle of two remote cation sites or one copper may be on the cation site and the other far from the other site.

A molecule of NO and a dissociated oxygen react with the bridging oxygen, which results in the formation of an bridging NO_3 species (b). From the kinetic results that the reaction rate is first-order in NO-concentration and half-order in O_2-concentration, this step from (a) to (b) is the rate-determining step. Another molecule of NO attacks the NO_3 species to form two NO_2, one on each copper (c). The adsorption of nitric oxide on Cu–ZSM-5 has been studied by IR (31, 33–35), ESR (34) and TPD (36). The IR spectra revealed the presence of NO_2 species at 1448 cm^{-1} (35), around 1630 cm^{-1} (33, 34) and 2125 cm^{-1} (31, 33, 34) as well as several NO species. From the TPD study, Li and Armor (36) also indicated the presence of adsorbed NO_2 species. In the case of NO decomposition on Cu–ZSM-5, the reactive intermediate was proposed to be NO species (9, 31, 36) or NO_2 species (33, 35). In our case, an excess amount of oxygen could result in the formation of NO_2 species instead of NO species. Adsorbed NO_2 species has already proposed to be the reaction intermediate for the NO–NH_3–O_2 reaction on V_2O_5 catalysts from IR studies (37). The reactive NO_2 and one of the NH_3 ligands bound to the same Cu ion react to produce N_2 and H_2O leaving an OH group and a coordinatively unsaturated site on each Cu (d). NH_3 can occupy readily the coordinatively unsaturated site, while

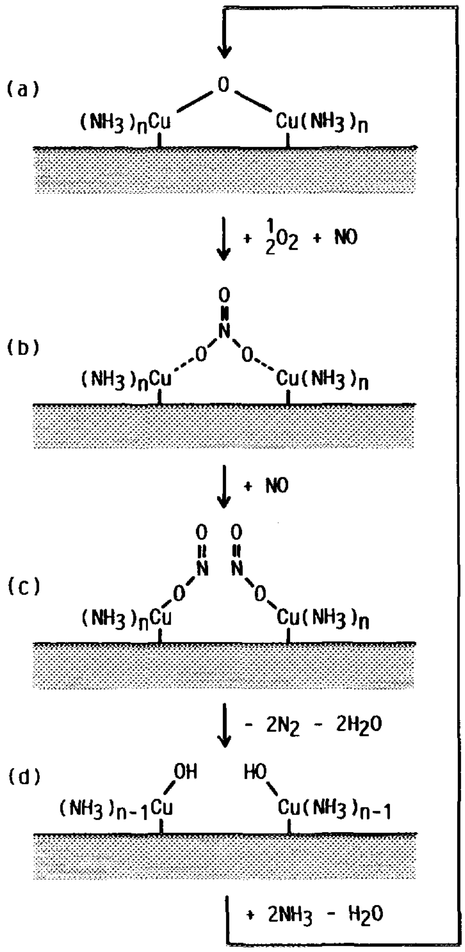

FIG. 12. Reaction scheme of the SCR of nitric oxide with ammonia in the presence of oxygen on the active copper dimer.

dehydration from the two OH groups regenerates the initial dimer species (a).

When a Cu^{2+} ion is isolated on the cation site of zeolites without forming the dimer, four NH_3 ligands may surround the Cu^{2+} ion (30). To form the reactive Cu-NO_2 species, the bond between Cu and NH_3 is thought to be too strong compared with the bridging bond between Cu and O in the dimer species, because the reaction rate did not depend positively on NH_3-concentration. Therefore, the activity of the dimer species is much higher than that of the isolated Cu ion. In the case of Cu–Y, the Cu–O–Cu species were formed by the dehydration and located within the β-cages of the framework structure (28, 38). Therefore, the inaccessibility of NO molecules to the Cu–O–Cu species may result in the low activity of Cu–Y. A similar inaccessibility has been used to explain the low activity of Cu–Y for the decomposition of nitric oxide (5).

CONCLUSIONS

Cu^{2+}-exchanged ZSM-5 zeolites are active catalysts for the reduction of nitric oxide with ammonia in the presence of oxygen. The formation of nitrogen proceeds almost selectively except that the oxidation of ammonia with oxygen occurs concomitantly at higher temperatures than 573 K. Copper ions are dispersed atomically as exchangeable countercations when copper loadings are lower than those corresponding to an exchange level of 200%. The specific activity per copper ions for the formation of nitrogen increases with increasing concentration of copper ions, while the apparent activation energies do not change significantly. The specific activity of Cu^{2+} in Cu–mordenite is comparable to that of Cu^{2+} in Cu–ZSM-5, while Cu–Y has much less specific activity. The active species in Cu–ZSM-5 consists of a pair of copper ions connected with each other by a bridging oxygen. The proportion of such an active species to the total copper ions increases with copper concentration, resulting in the increase in specific activity.

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