

Kinetic Studies of Reduction of Nitric Oxide with Ammonia on Cu²⁺-Exchanged Zeolites

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Received May 17, 1993; revised April 18, 1994

The selective catalytic reduction of nitric oxide with ammonia in the presence of oxygen has been studied on Cu²⁺ ion-exchanged zeolite catalysts. In the case of Cu²⁺-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 Cu²⁺-exchange levels and Si/Al atomic ratios. The ideality of Cu²⁺-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 Cu²⁺ 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 Cu²⁺ ions; i.e., the higher the copper concentration, the higher the specific activity. The active copper species were proposed to be paired Cu²⁺ species in view of the relation between the specific activity and the copper concentration. © 1994 Academic Press, Inc.

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 Cu²⁺-NaY is the most active catalyst. They also exam-

ined the effects of coexisting gases (2). The presence of oxygen enhanced the activity, while H₂O and SO₂ had poisoning effects. Cu²⁺-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 Fe³⁺- 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 Cu²⁺-exchange level less than 40%, but above 40% it increased markedly with Cu²⁺-exchange level up to 73%.

ZSM-5 is a unique zeolite, that is, Cu²⁺ 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, Cu²⁺-exchanged ZSM-5 has been studied intensively as a catalyst for the removal of nitrogen oxides. Cu²⁺-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 Cu²⁺-exchange level of 40% or more and the yield of nitrogen increased with Cu²⁺-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 Cu²⁺-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 Cu²⁺-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 acetaldehyde, was also studied on Cu-ZSM-5 catalysts (16).

We have reported (17) that H-ZSM-5 is active 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 Cu²⁺-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 NH₄NO₃ 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(CH₃COO)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. Cu²⁺-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 Cu²⁺-exchange levels of 29–195% (Cu-Z), 56–136% (Cu-M), and 17–65% (Cu-Y), respectively. Omitting the washing after Cu²⁺ 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 Cu²⁺ 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, NH₃, and O₂ 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 NH₃ and 2.0% for O₂. The weight of catalyst (0.027–0.76 g) and the total flow rate (2.1 × 10⁴–4.0 × 10⁴ cm³ 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 × 10⁴–7.1 × 10⁵ h⁻¹). The effluent gas was analyzed by GC (Tyran M-200) with Molecular Sieve 5A and Plot Q columns for N₂, N₂O, and O₂, by an NO_x analyzer (Yanaco ECL-77A) with a chemiluminescent detector for NO and NO₂, 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 Cu²⁺-exchanged zeolites. To study the effect of copper concentration, ZSM-5 is a useful zeolite because the aluminum concentration can be varied widely by the hydrothermal synthesis without any severe dealumination treatments and because the apparent Cu²⁺-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 Cu²⁺-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 N₂, NO₂, and N₂O. The amount of NO₂ 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 Cu²⁺-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

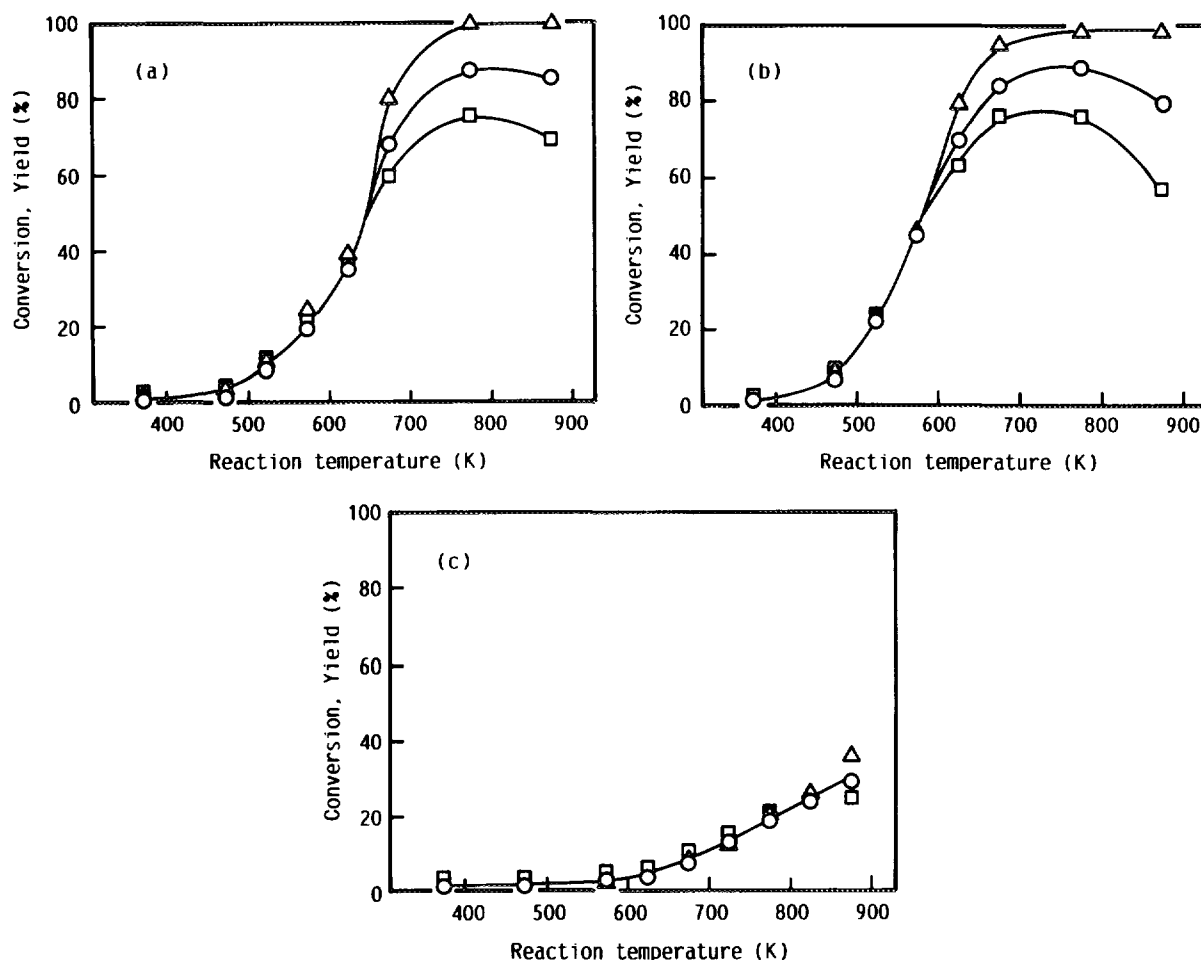


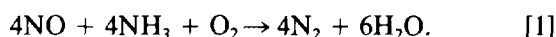
FIG. 1. Reduction of nitric oxide with ammonia in the presence of oxygen on Cu(79)-Z(45) (a), Cu(147)-Z(45) (b), and H-Z(45) (c). Conversion of nitric oxide (□) and ammonia (Δ) and yield of nitrogen (○) were measured at $W/F = 3.3 \times 10^{-6} \text{ g h cm}^{-3}$. Concentrations of reactants were 0.10% (both NO and NH₃) and 2.0% (O₂) in He carrier.

activity of Cu²⁺ (99%)-exchanged H-ZSM-5 (Si/Al = 45) with that of Cu²⁺ (100%)-exchanged Na-ZSM-5 (Si/Al = 45). NO-conversions and N₂-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 NO₂ (20). The maximum conversions on these catalysts were about 25%. The N-containing product was almost exclusively NO₂; N₂ was only detected in a negligible amount at any temperature. Iwamoto *et al.* (8) studied the effect of coex-

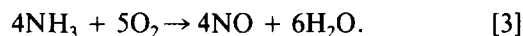
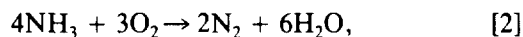
isting oxygen on the decomposition of nitric oxide using Cu-ZSM-5 catalysts with various Cu²⁺-exchange levels. They found that the decomposition was inhibited by oxygen and that the conversion of nitric oxide into N₂ was only 5% on Cu-ZSM-5 of 152% ion-exchange level under the following reaction conditions: $T = 773 \text{ K}$; NO, 0.10%; O₂, 0.50%; $W/F = 8.3 \times 10^{-5} \text{ g h cm}^{-3}$. In our case, W/F was one order of magnitude smaller and the partial pressure of O₂ 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 $(1 + K[\text{O}_2]^{1/2})$, where K , the equilibrium constant for O₂ 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 N₂O formed as well as that of NO₂ were negligible. The lack of N₂O formation is in contrast with the results obtained with platinum foil catalysts (21), where N₂O was produced in a N₂/N₂O ratio of about 2 at 573 K from the mixture of NO, NH₃, and O₂. As shown in Fig. 1a, the conversion of NO, the conversion of NH₃, and the yield of N₂ 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:



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, NH₃-conversion, and N₂-yield were different from each other at higher temperatures. The NH₃-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 NH₃ and O₂:



These side reactions lead to the difference in the conversions and yield, i.e., the high NH₃-conversion and the low NO-conversion compared with the N₂-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 NH₃-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 N₂, NO, and N₂O. As the yields of both NO and N₂O were less than 1%, the conversion curves in Fig. 2 represent the yields of N₂. 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 NH₃-conversion and NO-conversion should correspond to the amount of consumed ammonia by reaction [2], where two molecules of N₂ are produced from four molecules of NH₃. Therefore, the yield of N₂ 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].

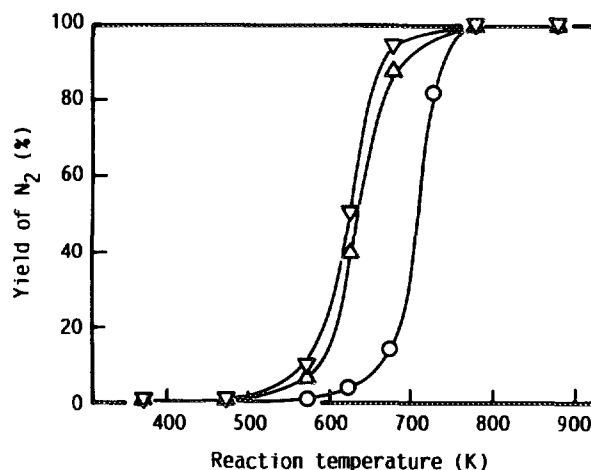


FIG. 2. Oxidation of ammonia on Cu(79)-Z(45) (○), Cu(147)-Z(45) (△), and Cu(178)-Z(45) (▽). A mixture of ammonia (0.10%) and oxygen (2.0%) was fed with helium carrier at $W/F = 3.3 \times 10^{-6} \text{ g h cm}^{-3}$.

From Figs. 1 and 2; it is clear that the activities of Cu(147)-Z(45) both for the SCR of nitric oxide ($T \leq 573 \text{ K}$) and for the oxidation of ammonia were higher than those of Cu(79)-Z(45). Higher activities of the excessively Cu²⁺-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 Cu²⁺-exchange on the SCR activity, kinetic studies were carried out. Figure 3 shows the effect of the concentration of reactants on the rate of N₂ formation on Cu(147)-Z(45) measured at 573 K. At this temperature, the rate of N₂ formation represents the rate of the SCR of nitric oxide, Eq. [1], because NO-conversion and NH₃-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%; NH₃, 0.10%; and O₂, 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 NH₃-concentration only at very low concentrations. At around the standard concentration (0.10%), the rate was almost independent of NH₃-concentration, which indicates that the rate is zeroth-order in NH₃-concentration. This suggests that most of the surface of Cu-ZSM-5 is covered with ammonia under the standard conditions.

The change in O₂-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 N₂-yields with W/F measured at 573 K with Cu-Z having various Cu²⁺-

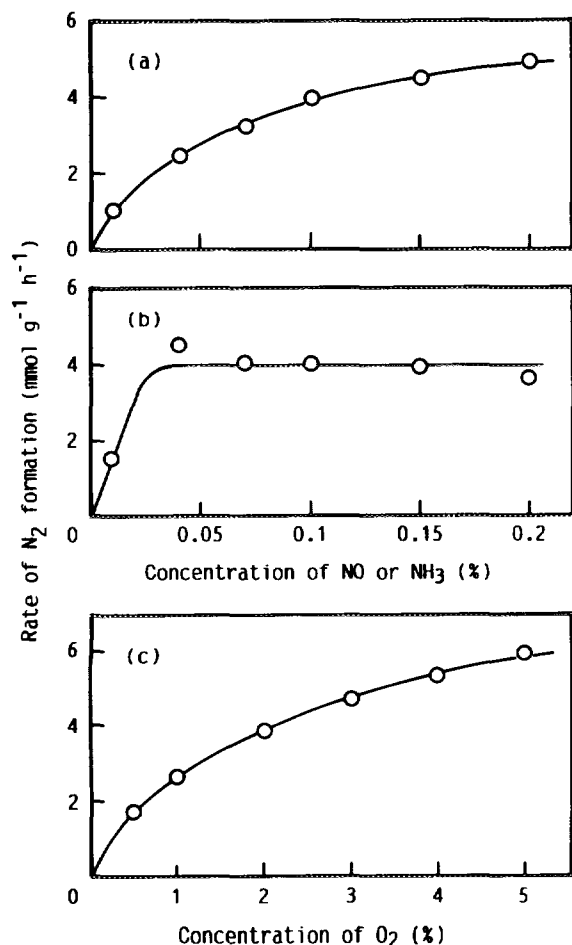


FIG. 3. Effects of the concentrations of nitric oxide (a), ammonia (b), and oxygen (c) on the rate of nitrogen formation measured with Cu(147)-Z(45) at 573 K and $W/F = 3.3 \times 10^{-6} \text{ g h cm}^{-3}$. Concentration of a specific reactant was varied keeping the others constant at 0.10% (NO or NH₃) or 2.0% (O₂).

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 – $4.0 \times 10^4 \text{ cm}^3 \text{ h}^{-1}$). 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 Cu²⁺-exchanged mordenite.

The reaction order with respect to the pressure of oxygen was treated as follows. From the above results, the

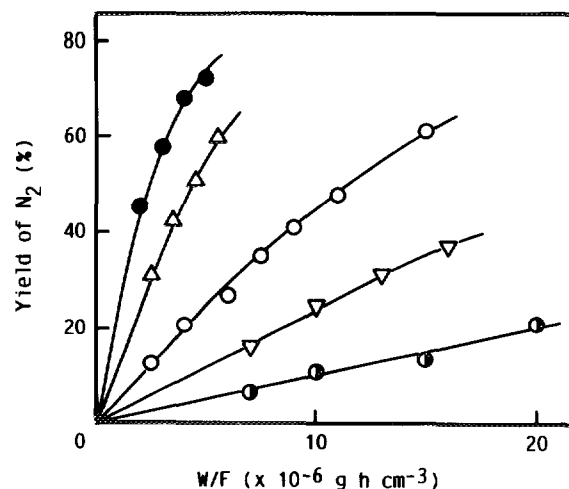


FIG. 4. Change in the yield of nitrogen with W/F on Cu(29)-Z(45) (●), Cu(120)-Z(71) (▽), Cu(79)-Z(45) (○), Cu(79)-Z(23) (△), and Cu(178)-Z(45) (●) measured at 573 K with the reactant containing NO (0.10%), NH₃ (0.10%), and O₂ (2.0%).

reaction rate (r) can be expressed as

$$r = k[\text{NO}] = k'[\text{O}_2]^m[\text{NO}], \quad [4]$$

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

$$k = k'[\text{O}_2]^m, \quad [5]$$

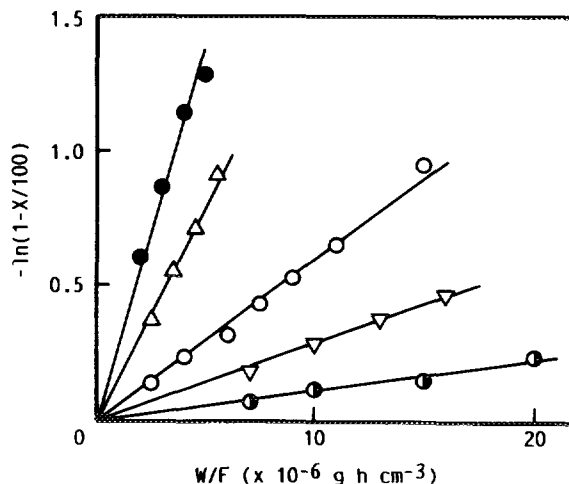


FIG. 5. First-order plot for the data of Fig. 4. Symbols represent the same catalysts as in Fig. 4.

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