

Catalytic Decomposition of Nitric Oxide over Cu-Zeolites

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Cu-exchanged zeolites have been under investigation as catalysts for NO decomposition. Among the zeolites tested Cu-ZSM-5 had the highest turnover frequency. The Arrhenius plots for all the catalysts leveled off or inverted near 773 K, and these curves were entirely reversible on decreasing the temperature. The NO decomposition rate was first order in NO pressure and was inhibited by O₂. The kinetics could be described in the Langmuir–Hinshelwood form, with the inhibition being half order in O₂ pressure. The redox capacities of Cu-ZSM-5 measured in microbalance experiments were near 0.5 O/Cu, i.e., 1 e⁻/Cu. Interestingly, O₂ could be desorbed isothermally from an initially oxidized catalyst upon flushing the catalyst with He. ESR spectra confirmed that the Cu²⁺ in the catalysts was being reduced to Cu¹⁺ during the spontaneous desorption of a corresponding amount of O₂. This spontaneous desorption of O₂ was also observed when pure O₂ in the microbalance was replaced by an O₂/He mixture, i.e., when the partial pressure of O₂ over the catalyst was lowered. This phenomenon is regarded as a key requirement for a sustained NO decomposition activity. An interpretation of the kinetics in light of these findings is presented. © 1991 Academic Press, Inc.

INTRODUCTION

Except at very high temperatures, the catalytic decomposition of NO into N₂ and O₂ is thermodynamically favorable. However, as Hightower and Van Leirsburg (1) have pointed out, as of 1974 a suitable catalyst had not been found. A number of catalysts, e.g., Pt, Rh, Ru, Co₃O₄, NiO, CuO, ZrO, etc., had been tried and were found to decompose NO, but none of these had sufficiently high activity to be of practical interest. The reduced forms were rapidly oxidized by NO with release of N₂, but not O₂. Thus, the catalysts became oxidized and reducing agents were required to restore them back to their initial states. The redox process could be stepwise or catalytic. With the Fe-zeolites the catalytic cycle could be adequately described by this two-step process with the rate of the reaction being limited either by the rate of reduction, or by the rate of the oxidation (2). Not only were the kinetics consistent with this mechanism, but

also the resulting pressure dependencies properly reflected the average valence state of the altermvalent cations in the steady-state reaction. N₂O decomposition was catalytic, but NO simply oxidized the catalysts at temperatures up to 1000 K and further decomposition became immeasurably slow (3).

Amirnazmi *et al.* (4) investigated NO decomposition over Pt and the oxides of Fe, Co, Ni, Cu, and Zr at temperatures up to 1270 K. They reported that the kinetics were of the Langmuir–Hinshelwood form with oxygen inhibition of the first order. More recently, Iwamoto and co-workers found that Cu-exchanged zeolites catalyzed the decomposition reaction (5), and reported that Cu-ZSM-5 was the most active catalyst so far known (6–9). However, their data showed that the N₂ formed was significantly less than the equivalent NO which had disappeared, and that the O₂ deficiency was even greater. These findings were confirmed by Li and Hall (10) who obtained a complete mass balance and reported that the discrepancies could be quantitatively accounted for by the NO₂ which appeared in

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TABLE 1
Catalyst Information

Catalyst	Si/Al	Cu/Al	Na/Al	(2Cu + Na)/Al	Cu loading mmol/g
Cu-Z-21-114 ^a	21	0.57	0.09, (1.41) ^b	1.23	0.42
Cu-Z-21-86	21	0.43	0.29, (1.41)	1.15	0.32
Cu-Z-21-72	21	0.36	0.51, (1.41)	1.23	0.26
Cu-Z-26-166	26	0.83	0.38, (1.65)	2.04	0.49
Cu-Z-24-76	24	0.38	0.66, (1.38)	1.42	0.25
Cu-Z-12-140	12	0.70	0.03, (0.99)	1.43	0.82
Cu-Z-14-96	14	0.48	0.00, (1.00)	0.96	0.51
Cu-M-5-64	5	0.32	0.25, (0.96)	0.89	0.79
Cu-β-14-300 ^c	14	1.50	— ^d	—	1.65
Cu-Y-2.4-80	2.4	0.40	0.19, (0.93)	0.99	1.72
Cu-Y-2.5-74	2.5	0.37	0.26, (1.0)	1.00	1.56
Cu-Y-6.6-82	6.6	0.41	— (1.0)	—	0.84

^a Z represents ZSM-5.

^b The values in parenthesis are the Na/Al ratios of their parent zeolites.

^c Cu²⁺ was exchanged (?) into the H-zeolite.

^d Samples were not analyzed for Na.

the products. It was further established that NO₂ was formed in a homogeneous reaction of the product O₂ with the undecomposed NO at low temperatures downstream from the reactor. Thus, the catalytic decomposition of NO over Cu-ZSM-5 is intrinsically stoichiometric. These facts lead to some interesting questions. How will the observations be reflected in the kinetics? And will the latter be comparable with those of Amirnazmi *et al.* for bulk oxides? Is the rate of the reaction limited by the rate of O₂ desorption? Is this the rate-determining step? These questions are considered herein.

EXPERIMENTAL

Catalyst preparation. Cu²⁺ was introduced into various zeolite preparations using conventional base-exchange procedures. They are identified in the following fashion: cation type of zeolite-Si/Al ratio-Cu exchange level in percentage, e.g., Cu-ZSM-5-26-166. The available information about these catalysts is given in Table 1. The elemental analyses were provided by Air Products & Chemicals Inc. and by Galbraith Laboratories. Note that some of the catalysts contained more than the stoichiometric amount of Cu²⁺ required to satisfy the base-exchange capacity of the zeo-

lite (stoichiometric exchange occurs when one Cu²⁺ replaces two Na⁺ and the molar ratio Cu/Al = 0.5). As shown in Table 1, most of the ZSM-5 (parent zeolites) contained more than the stoichiometric amount of Na (Na/Al > 1), whereas the Y-zeolites did not. For some of the former the values of (2Cu + Na)/Al were close to those of the Na/Al of their parent zeolites. This phenomenon has been noted previously (8, 11). Woolery *et al.* (12) investigated a series of ZSM-5 samples using FTIR and MASNMR, and reported that internal silanols were found in highly siliceous ZSM-5 and that these were believed to be responsible for the phenomenon of excess cation exchange.

The starting materials were the Na⁺ form of zeolites except where specifically noted. Most of the parent zeolites were synthesized by T. R. Gaffney of Air Products and Chemicals, Inc., but several were obtained from commercial sources. The ZSM-5-zeolites were made using a template-free preparation method (13). Dilute aqueous solutions of cupric acetate or nitrate were used for the ion exchanges. The concentrations of the cupric ion in the solutions and the number of times the exchange was repeated were adjusted to obtain various exchange levels. All the ion-exchange steps were made at 298 K, and the preparations were thoroughly washed with distilled water at the same temperature before drying. The final catalysts were analyzed for Si, Al, Cu, and Na. Some examples of these techniques have been reported previously (10).

Activity measurements and kinetic studies. The activity measurements and kinetic studies were made at atmospheric pressure using 4% NO in He in a microcatalytic reactor in a steady-state flow mode. The reactor was a 4-mm-i.d. Pyrex glass U-tube. The detailed experimental conditions and the procedures for the gas chromatographic analysis were the same as those used earlier (10). Samples weighing 20–50 mg were used for the kinetic studies and the measurements of turnover frequencies. NO consumption is not a true measure of the degree of the

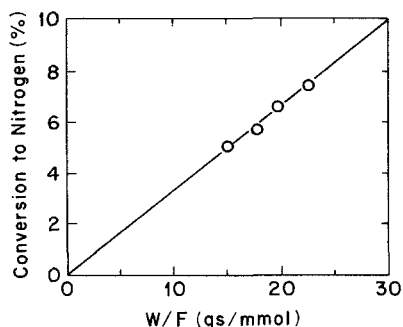


FIG. 1. Conversion- W/F plot for the NO decomposition reaction over Cu-ZSM-5-26-166 at 773 K. The inlet concentration of NO was 4% in He.

NO decomposition because of the secondary homogeneous oxidation of undecomposed NO to NO_2 as described previously (10). Therefore, the turnover frequencies of NO decomposition were expressed as twice the number of N_2 molecules produced per Cu ion per second. The conversions were also referred to N_2 formation. In the kinetic studies, the conversions were kept below 10% to ensure the reaction rates were not diffusion limited. As shown in Fig. 1, the straight line plot of conversion vs W/F indicates that the data were obtained in the differential region. Here W is the catalyst weight and F the flow rate in millimoles per second and the slope is the millimoles converted per gram per second. The standard catalyst pretreatment was drying in He at 823 K for 2 h before cooling to the reaction temperatures.

For the determination of the reaction orders, a power rate law was assumed; this was written as

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

where $[\text{NO}]$ was the concentration of NO in the feed, $[\text{O}_2]$ was the concentration of O_2 (when O_2 was added), n was the reaction order in NO, and m the reaction order in O_2 . Thus, to determine the reaction order for NO, values of $\ln(r)$ were plotted vs $\ln[\text{NO}]$. The concentration was varied in the feed while keeping the total flow rate constant.

Similarly, to determine the order for O_2 , streams of NO/He and O_2 /He were mixed inside the furnace and near the catalyst bed. The values of $\ln(r)$ were plotted against $\ln[\text{O}_2]$ while keeping the total flow and the partial pressure of NO in the mixed NO/ O_2 /He stream constant.

The reaction system was also operated in the pulse mode for transient studies. In this case, pulses of a NO/He mixture were sent to a pretreated catalyst, and the mixture leaving the catalyst was analyzed by gas chromatography. Samples were reduced with 4% CO in He or oxidized with pure O_2 at 773 K in a flow mode before the pulse studies were made.

Microbalance experiments. A Cahn microbalance (Model RG-2000) was used for the redox experiments in a flow mode. Samples weighing about 200 mg were placed in a quartz bucket. The temperature of the system was maintained constant and measured by a thermocouple placed near the bucket. Two channels of gases flowed through the system simultaneously. The inert gas, purified He (Ar when NO was used), flowed through the balance chamber to protect the weighing mechanism. A second stream of gas (O_2 , CO or NO in He) flowed through the heated sample chamber surrounding the hanging bucket. The two channels of gases exited via a common outlet above the bucket. Before recording the catalyst weight, the system was flushed with He in both channels to eliminate weakly held CO on the sample and to minimize buoyancy effects. The concentrations of CO and NO were 4% in He. Pure O_2 was used as an oxidizing agent in some of the redox experiments. However, O_2 /He mixtures were also used to study the pressure dependence of the weight changes. Blank tests were made using Na-zeolites under identical conditions, but no weight change could be detected. Given the Cu loadings from elemental analysis of the sample, weight changes due to the redox process could be expressed in units of number of oxygen atoms per Cu atom. The typical absolute uncertainty for

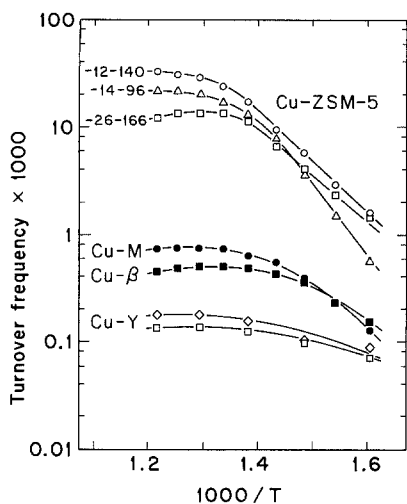


FIG. 2. Arrhenius plots for NO decomposition over Cu-zeolites. The inlet concentration of NO was 4% in He. The total pressure was 1 atm. The turnover frequency is defined as the number of NO molecules converted to N_2 per second per Cu ion.

a weight measurement was 20 μg (peak-to-peak noise), while the weight change due to the redox process was typically 1 to 2 mg.

Electron spin resonance spectroscopy (ESR). ESR spectra were obtained using a Varian E-4 spectrometer at X-band frequency (9.1 GHz). Spectra were recorded at sample temperatures of about 297 K. Because the curves compared were identical in shape, the relative concentrations of Cu^{2+} could be obtained directly from the integrated intensities of the derivative spectra. The estimated error was $\pm 5\%$ on a relative scale of 100. Before recording ESR spectra, samples were pretreated in a BET system. The oxidation or reduction was usually carried out at 773 K in 500 Torr of O_2 or in 400 Torr of CO for various times.

RESULTS

Reaction studies. The turnover frequencies for NO decomposition over various Cu-exchanged zeolites are compared in Fig. 2 in the form of Arrhenius plots. Cu-ZSM-5 was more active than the other zeolite struc-

tures tested. Although Y-zeolite has the largest pore size and highest Cu loading, it was the least active. Its turnover frequencies were from 1 to 2 orders of magnitude lower than those of Cu-ZSM-5. The dealuminated Cu-Y had activities similar to those of the normal Cu-Y, suggesting that the Si/Al ratio of a zeolite is not a controlling factor of its catalytic activity. The turnover frequencies for Cu-mordenite and Cu-Beta were comparable and lay between those of Cu-ZSM-5 and Cu-Y. All of the Arrhenius plots tended to bend over or to level off at temperatures higher than 773 K ($1000/T = 1.3$), and the data were reversible on decreasing the temperature. The Arrhenius plots for some samples, e.g., Cu-ZSM-5-26-166, were measured several times with varied external variables, e.g., flow rate of the feed and reactant partial pressure, but essentially identical plots were obtained. Similar results have been reported by Iwamoto *et al.* for Cu-ZSM-5 catalysts at higher conversions and over a broader temperature range, 673 to 973 K (8). The rates of N_2 formation over various catalysts are given in Table 2. In a practical sense, Cu-ZSM-5

TABLE 2

Rates^a for Nitric Oxide Decomposition at 773 K and Activation Energies

Catalyst	Rate ^b (mol · NO/g-min)	Cu loading (mol · Cu/g)	TOF × 1000	E_a^c kcal/mol
Cu-Z-12-140	1.39×10^{-3}	8.2×10^{-4}	28.2	22
Cu-Z-14-96	6.15×10^{-4}	5.1×10^{-4}	20.1	29
Cu-Z-21-114	5.39×10^{-4}	4.2×10^{-4}	21.4	26
Cu-Z-26-166	3.91×10^{-4}	4.9×10^{-4}	13.3	17
Cu-Z-24-76	1.66×10^{-4}	2.5×10^{-4}	5.66	17
Cu-M-5-62	3.52×10^{-5}	7.9×10^{-4}	0.74	17
Cu-Y-2.5-74	1.62×10^{-5}	1.56×10^{-3}	0.17	5
Bulk Co_3O_4^d	3.05×10^{-6}	—	—	28
Bulk CuO^e	—	—	0.25	8

^a The inlet pressure for NO was 4% of an atmosphere.

^b Moles of NO which have been converted to N_2 , i.e., decomposition rates.

^c The apparent activation energies are for the linear parts of the Arrhenius plots for the lower temperature region.

^d Data taken from Ref. (14) and the inlet pressure of NO was extrapolated to 4% of an atmosphere with the assumption that the reaction was first order to NO.

^e Data taken from Ref. (4). The reaction temperature was 873 K, and the inlet pressure of NO was extrapolated to 4% of an atmosphere based on the first order of NO pressure dependence. Z represents ZSM-5.

was a much better catalyst than any others tested; both the TOF and the specific rates were higher than those obtained from the other zeolite structures.

Typically for a specific type of zeolite, the higher the Cu loading, the higher is the specific catalytic activity. This is demonstrated in Fig. 3 where three Cu-ZSM-5 samples, prepared from the same parent zeolite (ZSM-5-21) but having different Cu loadings, are compared. The activity differences among the samples were greatest at the highest temperatures. A similar phenomenon was observed with Cu-ZSM-5-26-166 and Cu-ZSM-5-24-76 and with Cu-Y catalysts with various Cu loadings.

The effect of redox pretreatment on the catalytic activity for NO decomposition was checked, and the results are shown in Fig. 4. Various pretreatments were applied to the same sample (100 mg of Cu-ZSM-5-26-166), and the catalytic activities for the steady-state NO decomposition were determined following each successive treatment. Identical conditions were used in all these measurements. Reduction in 4% of CO in He

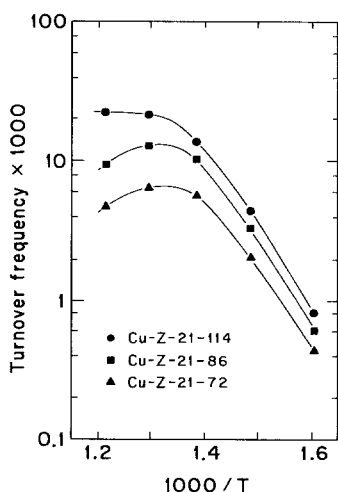


FIG. 3. The effect of Cu-exchanged level on the specific catalytic activity (turnover frequency) for NO decomposition. These three samples were prepared from the same starting zeolite, ZSM-5-21. TOF is defined as in Fig. 2.

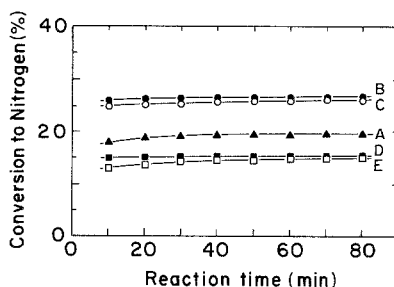


FIG. 4. Effects of the redox pretreatment on NO decomposition activity over Cu-ZSM-5-26-166. The reaction was run at 773 K, (A) after an oxidation in pure O₂ overnight; (B) after a reduction by a mixture of 4% CO in He for 2 h; (C) following B after reoxidation in O₂ for 1.5 h; (D) after a reduction by the CO/He mixture overnight; (E) following D after an oxidation in pure O₂ for 1.5 h. The pretreatment temperature was 773 K.

for 2 h modestly increased the steady-state conversion from that of the fresh sample, 20% (A), to 27% (B). This enhancement of catalytic activity was not affected further by reoxidation (C). However, severe reduction of the sample (overnight) resulted in a lower steady-state conversion (D), 15%, compared to the original conversion (A). Reoxidation of this sample (E) had essentially no effect on the conversion (D). The activities were measured over time periods of 15 to 80 min. All the conversions were in the steady state, and they did not decay for hours. The changes which were observed may have corresponded to redistribution of Cu ions.

The transient behavior of the catalyst, Cu-ZSM-5-26-166, was studied using pulse experiments. The catalyst was reduced in CO or oxidized by O₂ at 773 K before NO/He mixtures were pulsed to the reactor, and the N₂ and NO product was determined at the outlet. Some results obtained at 773 K are shown in Fig. 5. On the reduced sample, the NO conversions decreased with the passage of successive pulses duplicating exactly the NO conversion to N₂. These data were identical for each pulse for the first five pulses from which no O₂ was released by the catalyst. Beginning with the sixth pulse, the NO consumption suddenly increased with the number of the pulses while the N₂

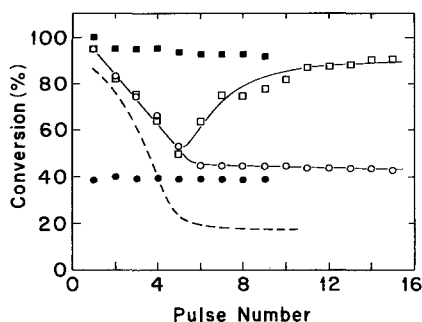


FIG. 5. Pulsed experiments for NO decomposition over Cu-ZSM-5-26-166. (□) represents the conversion of NO (the disappearance of NO) over a reduced sample pulsed at 773 K, (○) the conversion to N₂ over the reduced sample pulsed at 773 K, (■) the conversion of NO over an oxidized sample pulsed at 773 K, and (●) the conversion to N₂ over the oxidized sample pulsed at 773 K. The dashed line shows the conversion to N₂ over the reduced sample when pulsed at 623 K.

formation quickly reached a final constant value. Now, the NO consumption increased to about 90% while the conversion to N₂ leveled at about 45%. This difference resulted from reaction of the O₂ released with the unreacted NO to form NO₂ (10). After the same catalyst was oxidized at 773 K overnight, however, the conversions reached nearly the same final levels immediately following the first pulse. In neither case was any O₂ detected, demonstrating the high efficiency of the secondary reaction. It is probable that on the reduced catalyst, NO molecules were stoichiometrically decomposed to N₂ molecules and O atoms, and that the latter were used for reoxidation of the catalyst to its final (stabilized) oxidation state. When the O atoms have nearly saturated the catalyst, those produced from further decomposition of NO desorbed as O₂ molecules which very efficiently reacted with the residual NO left from the reaction to form NO₂ in the exit line (10). The oxidized catalyst on the other hand was already saturated with oxygen. The reaction, therefore, immediately produced constant values. These data demonstrate that a sharp cut-off exists (oxidation state) below which spontaneous desorption of O₂ cannot occur;

but of course this is in all probability a function of temperature. This will become important in considering the interpretation of the gross kinetics, *vide infra*.

Interestingly, as shown in Fig. 5, when the same sample in reduced form was pulsed at 623 K (dashed line), the initial conversion (the first pulse) for N₂ formation was fairly high, 84%, i.e., close to that at 773 K, 95%. However, the stabilized conversions in the pulse mode at 623 K were only about half of those at 773 K. This emphasizes the distinction between reaction of NO to reoxidize the reduced catalyst and its decomposition rate.

Kinetic studies. The dependence of the NO decomposition rate on the partial pressures of NO and O₂ were investigated over Cu-ZSM-5-26-166 at different temperatures. Some results are shown in Figs. 6 and 7. The NO decomposition is close to first order in NO concentration in the temperature range of 623 to 823 K (NO concentrations varied from 1 to 4%). The reaction order for O₂ was negative and temperature dependent. Interestingly, the sensitivity to O₂ decreased with increasing temperature in the range where the Arrhenius plots changed slope. The O₂ concentrations were varied between 0.5 to 1%. A more detailed examination of these phenomena is warranted.

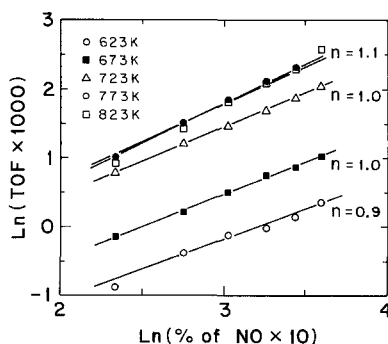


FIG. 6. The dependence of the NO decomposition rate (turnover frequency) on the pressure of NO over Cu-ZSM-5-26-166. The total pressure (1 atm) and the flow rate (42 cm³/min) were kept constant while the NO concentration of the feed was varied.

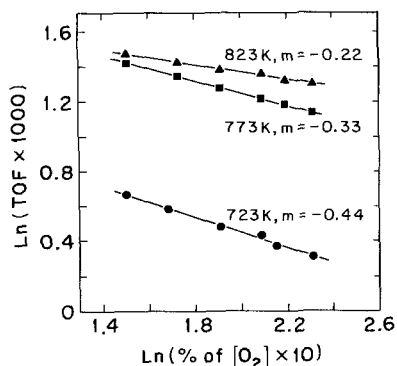


FIG. 7. The dependence of the decomposition rate on the pressure of O_2 for Cu-ZSM-5-26-166. The total pressure (1 atm), total flow rate ($38 \text{ cm}^3/\text{min}$) and the concentration of NO (2%) were kept constant while the concentration of the O_2 in the feed was varied. To avoid formation of NO_2 the NO/He and O_2 /He streams were joined and mixed in the preheater section (inside the furnace) a few cm upstream from the catalyst bed.

As shown in Fig. 8, the reciprocal of the rates increased linearly with the square root of the oxygen partial pressure. Based on these results, the rate equation for the NO decomposition reaction on Cu-ZSM-5-26-166 can be written as

$$r = \frac{d[N_2]}{d\tau} = \frac{k[NO]}{1 + K[O_2]^{1/2}}, \quad (1)$$

where conventionally, r is turnover rate in units of $[\text{s}^{-1} \cdot \text{site}^{-1}]$, k is the rate constant

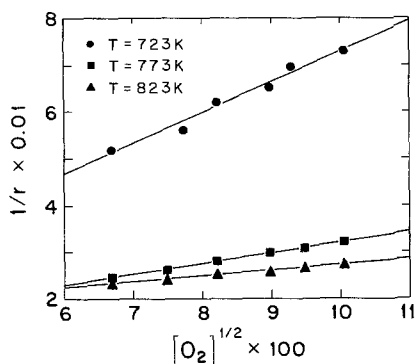


FIG. 8. The relationship between the reciprocal rate and the square root of oxygen concentration for Cu-ZSM-5-26-166. Data were taken from Fig. 7.

TABLE 3

The Rates and Adsorption Equilibrium Constants^a

T/K	k^b	K^c
623	0.95	—
673	1.91	—
723	5.03	157.5
773	7.58	84.2
823	7.43	53.0

^a The data were obtained on Cu-ZSM-5-26-166, and the $[O_2]$ and $[NO]$ were in units of mol/liter.

^b k in units of $[\text{s}^{-1} \cdot \text{site}^{-1} \cdot (\text{mol} \cdot \text{liter})^{-1}]$.

^c In units of $(\text{mol}/\text{liter})^{-1/2}$.

in units of $[\text{s}^{-1} \cdot \text{site}^{-1} \cdot (\text{mol} \cdot \text{liter})^{-1}]$, and K is the equilibrium constant for O_2 adsorption on the catalytic sites in units of $(\text{mol}/\text{l})^{-1/2}$. The concentrations of NO and O_2 are in units of mol/liter. The rate constants and the equilibrium constants listed in Table 3 are the results of our experimental determinations over Cu-ZSM-5-26-166. The O_2 adsorption equilibrium constant is an important term in the rate equation.

Redox properties of the catalysts. The redox studies were made using a flow microbalance with Cu-ZSM-5-26-166 at 773 K. The results of some CO/ O_2 cycles are summarized in Fig. 9, where the nearly invariant weights reached in the indicated times are shown by the horizontal bars. Following an initial oxidation in pure O_2 overnight the

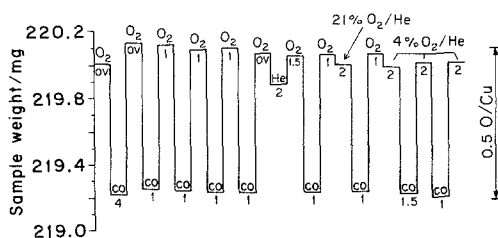


FIG. 9. Redox cycles (CO/ O_2) at 773 K over Cu-ZSM-5-26-166 in a microbalance. Pure O_2 was used as the oxidizing agent except where indicated otherwise, and a mixture of 4% CO in He was used as the reducing agent. The numbers under bars represent time in hours, ov = overnight.

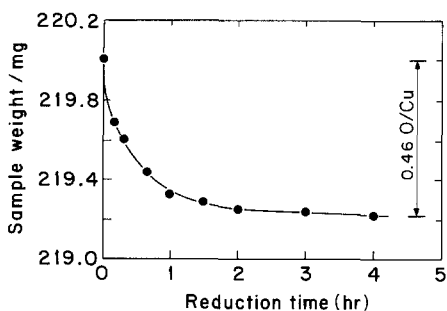


FIG. 10. Sample weight loss as a function of reduction time for Cu-ZSM-5-26-166 at 773 K. The sample had been previously oxidized by pure O_2 at 773 K overnight.

sample was reduced in 4% of CO in He for 4 h. In the following cycles, the sample weights for the reduced and oxidized states were stable, and redox capacities were nearly 0.5 O/Cu. Interestingly, it was found that the stable sample weight in the oxidized state was dependent on the partial pressure of O_2 . Replacing pure O_2 by pure He resulted in a sample weight decrease equivalent to 0.11 O/Cu in 2 h. Replacing pure O_2 by 21% and 4% O_2 /He mixtures effected more modest weight losses in 1 h equivalent to 0.035 and 0.046 O/Cu, respectively. Obviously, spontaneous reduction of the material occurs. Certain O atoms in the zeolite are not stable and desorb as molecular O_2 at 773 K when the O_2 partial pressure is lowered. This is the important feature of the catalyst which makes NO decomposition possible. It may also be an indication that a dynamic equilibrium is being maintained even in the presence of 1 atm of O_2 , i.e., that the catalyst may be almost, but never completely oxidized.

The initial reduction time of 4 h was justified by the recorder plot of the microbalance data shown in Fig. 10. The equivalent of 70% of Cu^{2+} ions was reduced to Cu^{1+} in 40 min by CO at 773 K and 100% was approached after 2 h when the weight became fairly stable. In this state, the sample weight loss due to reduction was equivalent to nearly 0.5 O/Cu. This was consistent with

what was found by ESR techniques, *vide infra*.

The CO/NO redox cycles at 773 K for the same catalyst are shown in Fig. 11. The redox capacities of CO/NO cycles on the sample were similar to those of CO/ O_2 cycles, i.e., about 0.5 O/Cu. The sample weights for the NO oxidized state (where NO decomposition was occurring concomitantly) were a little higher than those in 1 atm of O_2 , i.e., by about 0.03 NO/Cu. But after flushing the system with He for 1 h, the sample weights became almost identical. The weight loss on removal of the ambient O_2 by flowing He for 1 h amounted to about 0.1 O/Cu. Evidently, during steady-state NO decomposition most of the Cu sites were occupied. Thus, the oxidation state of most of the Cu ions in the steady state was Cu^{2+} . Figure 12 shows the details of the transient weight loss of an NO oxidized sample upon He flushing, along with that of an O_2 oxidized sample. The two distinct initial rates of weight loss suggest that two distinct species are being released from the sample. After the desorption of the nitrogen-containing species, weight loss rates for the two experiments became practically identical. The adsorption of molecular NO would be expected to be extremely unstable at such high temperatures, and thus the most surprising thing revealed by Fig. 12 is the amount of NO molecules desorbed (0.04/Cu) in the precipitous decrease during the first minute. These data suggest that in

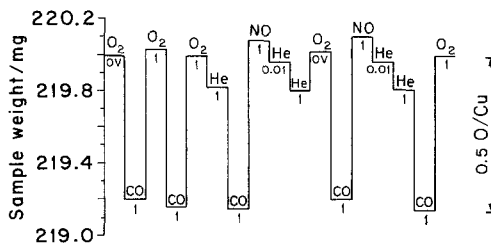


FIG. 11. Redox cycles (CO/ O_2 and CO/NO) over Cu-ZSM-5-26-166 at 773 K. Pure O_2 , 4% CO in He, and 4% NO in He were used for this experiment. The numbers under bars represent time in hours.

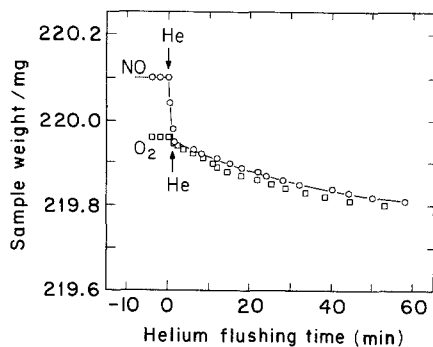


FIG. 12. Sample weight loss as functions of He flushing time at 773 K for Cu-ZSM-5-26-166. (○) the sample had been oxidized in a 4% NO/He mixture at 773 K before flushing, (□) the sample had been oxidized in pure O₂ at 773 K.

the steady state a minimum of a few percent of the Cu centers are occupied and thus may be amenable to spectroscopic observation. The slower rate of weight loss which followed is undoubtedly due to O₂ desorption from the sample, since it is essentially identical to that produced when O₂ was used as an oxidizing agent. What remains unknown is the extent of oxygen vacancies maintained in the steady-state reaction.

Isolated Cu²⁺ is paramagnetic. Therefore, electron spin resonance spectroscopy can be used to follow the Cu²⁺ in a zeolite during a redox process (Fig. 13). Reduction

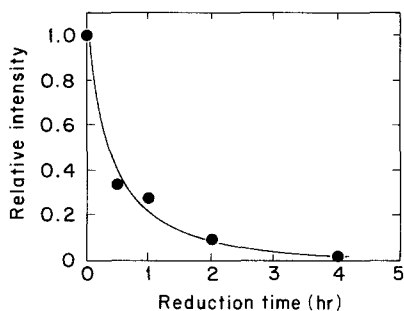


FIG. 13. The relative intensity of the Cu(II) signal detected by ESR as a function of reduction time. The sample, Cu-ZSM-5-26-166, was reduced in 400 Torr of CO at 773 K. The ESR signal was normalized based on the signal of the unreduced sample.

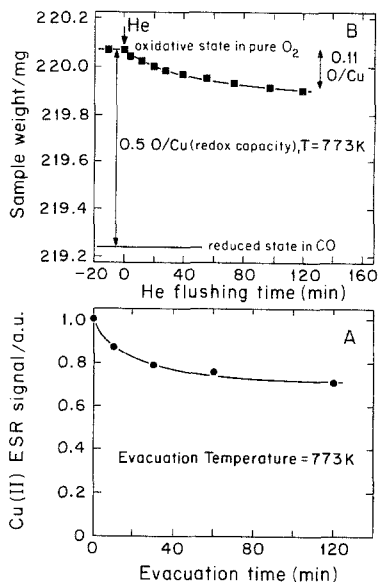


FIG. 14. (A) Relative Cu(II) ESR intensity as a function of evacuation time. The sample (Cu-ZSM-5-26-166) was evacuated at 773 K for various times. Each evacuation was preceded by an oxidation treatment at 773 K in 500 Torr of O₂ for 2 h; (B) Spontaneous O₂ desorption from Cu-ZSM-5-26-166 in He at 773 K measured by a microbalance.

of an oxidized sample (Cu-ZSM-5-26-166) resulted in a significant decrease in the ESR signal intensity when compared with the original oxidized sample. These data should be compared with the microbalance data shown in Fig. 10 to see the quantitative relation between the ESR signal of Cu²⁺ and the stoichiometric determinations. Note that the ESR signal was nearly gone after reduction in 400 Torr of CO at 773 K for 4 h, but the signal was restored to its original level when this sample was reoxidized by 400 Torr of O₂ overnight at 773 K.

The spontaneous desorption of O₂ from the Cu-ZSM-5 catalysts in He at high temperatures must accompany a reduction of Cu²⁺ to Cu⁺. This was verified by the ESR experiments. Figure 14A shows the relative ESR intensities of the Cu²⁺ signal at various evacuation times at 773 K. (Evacuation of a catalyst may be considered equivalent to flowing He through the sample for the same

amount of time.) The relative intensity decreased monotonically with evacuation time to about 75% of its original value (before evacuation at 773 K). These observations were in fair agreement with the microbalance data corresponding to the spontaneous removal of an about equivalent amount of oxygen (Fig. 14B).

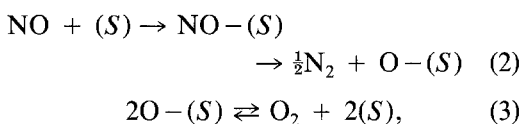
DISCUSSION

The most active catalyst for NO decomposition reported prior to 1974 (1) was bulk Co_3O_4 (14). Even with this catalyst the rate was very low (Table 2). It became generally believed that the rate of removal of the strongly adsorbed product oxygen from the surface limits the NO decomposition on most catalysts. Therefore, the sustained relative high activity of Cu-ZSM-5 catalyst can be best understood from the fact that the product oxygen is continuously desorbed from the active sites in the steady-state reaction. The microbalance experiments (Figs. 9–12, 14) support these arguments. The Cu-ZSM-5 sample underwent self reduction when the O_2 stream was replaced by He or O_2/He mixtures (Fig. 9) and this effected the spontaneous reduction of Cu^{+2} to Cu^{+1} as evidenced by the decrease of ESR signal (Figs. 12, 14).

In view of the forgoing comments the observed kinetics, represented by Eq. (1), at first sight seem surprising. A first-order dependence on the NO pressure (the oxidizing agent) would not ordinarily be expected for a system limited by the rate of reduction. The situation here is reminiscent of the NH_3 synthesis where the rate of the reaction depends on the rate of dissociative chemisorption of N_2 even though the surface is heavily covered with strongly chemisorbed N atoms (the MASI) which must be removed by reduction with H_2 . In the present situation the catalyst is almost completely oxidized in the steady-state reaction and the concentration of surface vacancies (reduced sites) is controlled by the rate of spontaneous desorption of O_2 (reduction) and the reversal of this process (which is the origin of the observed

inhibition by the ambient O_2 pressure). A self-consistent interpretation can be generated in an analogous fashion.

Presently we know essentially nothing about the surface intermediates involved in the reaction except that under reaction conditions the nitrogen-containing species is weakly chemisorbed (Figs. 11 and 12). Consequently in the formation of the N–N bond, we write only the simplest chemistry required to obtain Eq. (1), i.e.,



where (S) represents surface vacancies; $\text{NO}-(S)$ and $\text{O}-(S)$ represent adsorbed NO and oxygenation atom sites, respectively. In the steady state, a flux of $\text{O}-(S)$ is generated directly or indirectly via Eq. (2) and this is balanced and limited by the desorption of O_2 . If it is assumed that the ambient gas phase of O_2 maintains an equilibrium with the oxygen atoms held by the catalyst, a supply of vacant sites will be maintained. Thus, it follows from Eq. (3) that

$$K = [\text{O}_2][[S)]^2/[\text{O}-(S)]^2 \quad (4a)$$

or

$$[\text{O}-(S)] = [\text{O}_2]^{1/2}[[S)]/K^{1/2} \quad (4b)$$

Further, the conservation of surface sites, populated or not, gives

$$\begin{aligned} [[S)] + [\text{NO}-(S)] \\ + [\text{O}-(S)] = C \quad (5) \end{aligned}$$

where C is a constant. Since the reaction proceeds with catalyst in nearly the completely oxidized state (e.g., see Fig. 5), it may be assumed that $[\text{NO}-(S)]$ is small compared with $[\text{O}-(S)]$ and may be neglected. Thus, combining Eqs. (4) and (5) yields

$$\begin{aligned} [[S)] = C/\{1 + [\text{O}_2]^{1/2}/K^{1/2}\} \\ = C'\{1 + K'[\text{O}_2]^{1/2}\} \quad (6) \end{aligned}$$

where $K' = 1/K^{1/2}$. Under steady-state con-

ditions, the overall decomposition rate is equal to the rate of each elementary step; i.e., the flux of products ($O_2 + N_2$) from the surface must stoichiometrically balance the net flux of NO to the surface. The latter is the net rate of adsorption of NO (Eq. (2)) which may be written

$$r = k[NO][S]. \quad (7)$$

Substitution of Eq. (6) into Eq. (7) yields

$$r = k'[NO]/\{1 + K'[O_2]^{1/2}\}, \quad (8)$$

where $k' = kC$.

Kinetics can never establish a mechanism. Consequently the picture presented above may require adjustment as further studies are carried out. Nevertheless we think its main features are correct. It affords an explanation for the first-order dependence on the concentration of NO while the rate of the reaction is limited by the self-reduction of the catalytic sites by desorption of O_2 . Moreover, it emphasizes two areas where further research is needed, viz., on the oxidation step where N-N bonds are formed, and on the self-reduction step where reduced sites (S) are created, especially on the kinetics of this process (the dependence on the external variables and on the extent of reduction). With respect to the former, the involvement of dinitrosyl species seems likely. These were observed on Fe-Y at room temperature (15) and the rationale for their probable involvement in the formation of N_2 has been discussed by Casewit and Rappé (16). In this case, N_2O must be formed as a transient intermediate. Hence, it is really not known what is desorbed during the precipitous drop in weight shown in Fig. 12 when the steady-state system was flushed with He (let alone what surface species were present). All that can be said at present is that the nitrogen-containing species is facile to decomposition and that the observed pressure dependence is the requirement necessary to maintain its steady-state concentration which in turn is limited by the pseudoequilibrium expressed by Eq. (3).

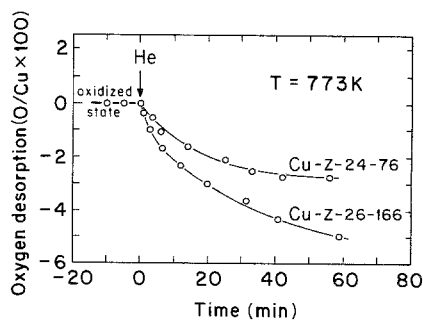


FIG. 15. Isothermal desorption of O_2 from two Cu-ZSM-5 catalysts of different Cu loadings into a He stream.

Amirnazmi *et al.* (4) studied the kinetics of NO decomposition over metal oxides and Pt at temperatures above 873 K and deduced a rate equation to describe the reaction, viz.,

$$r = (\text{molecules NO/cm}^2 \text{ s}) \\ = kN[NO]/\{1 + \alpha K[O_2]\}, \quad (9)$$

where N is Avogadro's number, k is the reaction rate constant in cm/s, K is an adsorption equilibrium constant for O_2 in atm^{-1} , α is a conversion factor (in $\text{atm} \cdot \text{cm}^3/\text{mol}$) required to render this term dimensionless when the concentration of NO and O_2 are in mol/cm^3 . Formally the only difference between our findings and theirs is the order in $[O_2]$ in the denominator term, with ours being $\frac{1}{2}$ and theirs unity. Perhaps, this reflects the much higher temperature required for their much less active catalysts. The half order of the $[O_2]$ term in our model suggests that O_2 molecules were formed by combination of two adsorbed oxygen atoms and that it is the atomically adsorbed oxygen which inhibits the NO decomposition. A special assumption was required to explain their observed first-order dependence (4), viz., the reaction of two forms of atomic oxygen, one surface mobile and the other rigidly held by the lattice.

The spontaneous desorption of O_2 from the catalyst at high temperatures (Eq. (5)) is closely related to its steady-state NO decomposition activity. As shown in Fig. 15,

TABLE 4

O₂ Desorption Rates^a (r_d) and NO Decomposition Rates (TOF) over Cu-ZSM-5-26-166

T/K	$r_d \times 10^5$ (O/Cu-s)	TOF $\times 10^3$ (s ⁻¹ · site ⁻¹)
623	1.9	1.6
673	3.7	4.8
723	6.3	11.0
773	10.5	13.3
823	15.0	11.7

^a The O₂ desorption rates were obtained isothermally by flushing He through the preoxidized sample (the sample was preoxidized in flowing 4% O₂ in He at the same temperatures), and only the initial rates are given in this table.

the O₂ desorption rate for Cu-ZSM-5-26-166 is higher and more extensive than that of Cu-ZSM-5-24-76 at 773 K, and the turnover frequency of the former is twice that of the latter (Table 2). Moreover, the initial rate of O₂ desorption from Cu-ZSM-5-26-166 at various temperatures (obtained from the initial slopes of curves similar to the one shown in Fig. 15) were, within experimental error, proportional to steady-state activities at the same temperatures (Table 4). This may be anticipated from Eq. (7) if (S) is proportional to the oxygen desorption rate. An alternative way of viewing the system would be to recognize O-(S) as the MASS (most abundant surface species) whose presence automatically limits the rate by controlling (S).

The data presented in Fig. 5 are generally supported by the microbalance results (Fig. 9). The working catalysts probably consist of a relatively small number of Cu⁺ centers (or adjacent Cu⁺ pairs) maintained in a steady state by balance of the rate of oxidation with the rate of O₂ desorption. Conceivably, the active sites for the decomposition in steady-state conditions are Cu⁺ ions amounting to less than 10% of the total Cu. Therefore, the oxidation of the reduced Cu species and spontaneous reduction of the oxidized Cu species are essential steps in

the mechanism for the steady-state NO decomposition.

Our microbalance data showed that about 0.5 O/Cu are present on Cu-ZSM-5-26-166 after the initial oxidation–reduction cycles, suggesting that adjacent Cu ions are bridged by an oxygen atom. Low Cu-loading catalysts have low O₂ desorption rates (on a per Cu atom basis) and low turnover frequencies for NO decomposition. Evidently, the longer the mean distance between Cu ions in the zeolite (as a result of lower loading) the slower the formation of oxygen molecules for a given zeolite structure.

It has been reported previously (2, 17–20) that transition metal ions in zeolite act as oxygen carriers and that two-step redox processes can be reversibly carried out. According to Garten *et al.* (21), the oxygen atoms added to Fe(II)Y when it is converted to Fe(III)Y are held as bridges between two ions inside the cuboctahedra. On the other hand, Hall and co-workers have noted that these ions may simply act as reversible electron sinks that permit oxygen atoms to be added to, or removed from, the lattice. Jacobs and Beyer (22) proposed a model for redox cycles on Cu–Y: Cu(I) and (AlO)⁺ are formed by reduction of Cu(II)–Y with CO; upon reoxidation the concentration of (AlO)⁺ remains unchanged, while Cu(I) ions are transformed into the Cu²⁺–O–Cu²⁺ species.

It is not difficult to visualize the oxygen bridge between two transition metal ions in Y-zeolite, where the metal ions are relatively close together because of the relatively high Al content. On ZSM-5 zeolite, the Cu ions are sparse because of fewer Al ions present (high Si/Al ratios). This leads to some critical unanswered questions about ZSM-5 zeolite. Why are these preparations more active than Y-zeolites? How can two Cu ions be bridged when they are far apart? When O₂ is used as an oxidizing agent, how is it dissociated? How do two O atoms combine to form O₂ molecules? Is lattice oxygen involved in the formation of O₂ molecules? These questions are not answered by the

present experimental results, but remain a challenge for further research.

The nature of the active centers is not defined by the present work. However, it is probable that they are the same or closely similar to those required for NO reduction. Moreover, the active sites may consist of a multiplet which includes a pair of Cu ions with chemically altered coordination. Our study on the effects of pretreatment on the NO decomposition rate suggests that a redistribution of active centers occurs in the zeolite during the reduction process.

According to Iwamoto *et al.* (23), formation of Cu^+ was observed upon evacuation of a Cu-ZSM-5 sample. Their fluorescence spectra reportedly indicated that Cu^+-Cu^+ dimers were present in their evacuated sample. It was further suggested that $\text{Cu}^{\delta+}-\text{O}^{\delta-}-\text{Cu}^{\delta+}$ species were the active sites for the NO decomposition. These ideas are consistent with the present findings.

The EXAFS studies of Hamada *et al.* (24) over a 3.6 wt% Cu loading ($\text{Cu}/\text{Al} = 1.2$) Cu-ZSM-5 revealed, besides the major peak at 2.01 Å in their Fourier transforms due to Cu–O bonding, a minor peak at 3.13 Å (phase shifts were corrected). However, the latter was not found on a 1.4% loading ($\text{Cu}/\text{Al} = 0.48$) Cu-ZSM-5 sample. These data suggested that Cu–Cu bonding may exist in ZSM-5. Similar EXAFS data were reported by Kuroda *et al.* (25) for series Cu–mordenite samples.

The leveling-off or bending-over of the Arrhenius plots with all the catalysts studied is curious. These plots were obtained repeatedly using different experimental conditions. In all cases the activation energy became low and passed through zero before becoming negative, as also observed by Iwamoto *et al.* (8). Hence, diffusion control alone cannot account for these observations. The complete reversibility suggested that no structural damage occurred even at the highest temperature 823 K. Hence, this behavior appears to be kinetic

in origin. A classical explanation of this would be that the rate becomes limited by the concentration of adsorbed NO at high temperatures.

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