Comparison of Catalytic Decomposition of Dinitrogen Oxide and Nitrogen Monoxide over Cu/ZSM-5 and Cu/Y Zeolites

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(Received October 20, 1997)

A comparative study of NO and N_2O decomposition over Cu/ZSM-5 and Cu/Y zeolites with various Cu loading levels has been carried out at 523—823 K. The Arrenhius plot of NO decomposition tended to level off above 773 K, as reported in the literature, while that of N_2O decomposition was linear. It was noted that the reactivity of N_2O decomposition rose much more sharply than that of NO decomposition with an increase in the level of the copper-ion exchange. The implications of these results on the reaction mechanism were discussed. In addition, the adsorption of NO on Cu/ZSM-5 and Cu/Y was measured by IR at 173—373 K and the results were compared with the catalytic decomposition results.

N_2O and NO are both pollutants which need to be abated. The ideal method for the abatement of N_2O and NO is the direct decomposition into molecular nitrogen and oxygen. It is known that Cu/ZSM-5 zeolite is an active catalyst for both N_2O and NO decomposition.[1,2] It has been shown that Cu/ZSM-5 is much more active than Cu/Y zeolite, even though the reason for this superiority of Cu/ZSM-5 is not fully understood.[2,3] Yasuda et al.[4] have compared the decomposition of N_2O and NO over perovskite mixed oxides and indicated that desorption of oxygen, a common step of both reactions, is not the rate-determination step, and the oxygen adsorbed is in equilibrium with the oxygen in the gas phase.

With the idea that a better understanding of catalytic reactions would lead to discovery of possible means of future improvement, many studies have been carried out to identify the nature of the active sites and the mechanism of the NO and N_2O decompositions. Investigations of the catalyst structure have focused on determining the copper dispersion over zeolite and the oxidation state of the copper. ESR spectra of Cu/ZSM-5 showed that copper ions in ZSM-5 after the ion-exchange are present mainly as Cu^{2+}, but heating in a helium stream or in vacuum results in the reduction of Cu^{2+} to Cu^+.[5—7] The amount of Cu^+ evaluated by the adsorption of CO[8] increased sharply when the copper ion-exchange level exceeded 80—100%. IR results of NO adsorption have shown that nitrosyl complexes are formed on Cu^{2+} and Cu^+ ions.[5,9—12] The results of EXAFS[13] and photoluminescence[8] suggested that $[Cu–O–Cu]^{2+}$ pair species are present in the excessively ion-exchanged Cu/ZSM-5. It was also indicated that the number of Al ions near the Cu site influences the reactivity.[14]

Taking account of the catalytic effectiveness factor, we previously compared the intrinsic catalytic activities of several Cu catalysts for N_2O decomposition on the basis of the surface copper atom, turnover frequency, TOF.[15] The catalysts examined were copper ion-exchanged ZSM-5, mordenite, and Y zeolite; and cupric oxide supported γ-alumina and perovskite-related $La_{1.5}Sr_{0.5}CuO_4$ for which the surface Cu was measured by the adsorption of NO and the oxidation of N_2O. In the case of ZSM-5, the TOF of the N_2O decomposition increased greatly with an increase in the copper content. In contrast, the catalytic activities increased moderately for mordenite, Y zeolite and γ-alumina. Thus, while the TOF's were comparable at low loading levels of Cu, the TOF of ZSM-5 was about 100-fold higher than mordenite and γ-alumina at the copper contents of 5 wt%.

Hence, it is interesting to examine the dependencies on the ion-exchange level of the TOF for NO decomposition. The dependencies of the intrinsic catalytic activities for the NO decomposition on the Cu ion exchange level have never been reported, since the conversions reached ca. 90% and were saturated in Ref. 8. The comparison of the results with those for N_2O decomposition by using the same catalysts is also meaningful in order to examine the hypothesis suggested by several groups that the NO decomposition proceeds via N_2O.[11,16] In the present study, the NO and N_2O decomposition over Cu ion-exchanged ZSM-5 and Y zeolite having different exchange levels are compared, and discussed in relation to the reaction mechanism. IR studies of NO adsorption were carried out to examine the redox properties of Cu ions on Cu/ZSM-5 and Cu/Y.

Experimental

1. Catalysis. Na/ZSM-5 ($SiO_2/Al_2O_3 = 23.8$) was supplied by Tosoh Co. Na/Y zeolite (JRC-Z-Y5.6) was a reference catalyst of the Catalysis Society of Japan. Cu/zeolites were prepared in the same way as in the previous work,[15] that is, by repeated ion-

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exchange of these Na/zeolites with the solution of 0.02 M cupric acetate (1 M = 1 mol dm^{-3}), until the desired exchange levels were achieved. The copper contents were determined by atomic absorption spectroscopy.

2. Catalytic Tests. The decompositions of N_2O and NO were carried out in a fix-bed flow reactor made of quartz at atmospheric pressure, as described previously.[15] In the standard pretreatment, the catalysts were heated in a stream of helium at 773 K for 2 h. Reaction gases were 0.1% N_2O or 1.0% NO in helium. Usually the conversion was kept below 10% by adjusting the weight of catalyst and the flow rate. The rates of reaction are calculated from the following equations:

$$r_{N_2O} = \%\ \text{conversion of } N_2O \text{ into } N_2/(W/F_{N_2O}) \qquad (1)$$

$$r_{NO} = 2x\%\ \text{conversion of NO into } N_2\%/(W/F_{NO}) \qquad (2)$$

Here, W is the weight of catalyst, and F_{N_2O} and F_{NO} are the flow rates of N_2O and NO, respectively. The gas composition was analyzed by gas chromatography and a NO_x meter as described before.[15]

3. FTIR Measurements. The IR spectra were measured in an in-situ IR cell as illustrated in Fig. 1.[17] The cell, made of quartz, was surrounded by a stainless pipe through which liquid nitrogen was flowed and by an electric heating ribbon, so that it can be cooled to as low as 170 K and heated to as high as 773 K. The temperature was measured with a chromel–alumel thermocouple inserted near the catalyst wafer. A self-supporting wafer (about 0.1 g, 2.0 cm in diameter) was made by pressing at 200 kg cm^{-3} and fixed to a quartz holder in the IR cell. Then CaF_2 optical windows were sealed tightly to the cell by two flanges with rubber O-rings. A Pyrex-made vacuum line was connected to the cell. IR spectra were recorded on a spectrophotometer (JASCO FT/IR-550) by accumulating 40 scans from 2500 to 1000 cm^{-1} at a resolution of 2 cm^{-1}.

The general procedures of the IR measurement are as follows: The wafer was pretreated in-situ, first in 100 Torr O_2 at 673 K for 1 h, (1 Torr=133.322 Pa), then in vacuum at 773 K for 2 h. After the cell was cooled to 173 K, the spectrum of the pretreated sample was measured at 173 K and this was used as a background spectrum. NO was dosed incrementally at 173 K, and the spectrum was measured after each dose (spectra a and b in Figs. 7, 8, 9, 10, and 11). Then the evacuation and addition of NO was carried out repeatedly and the spectrum was taken at each interval. Then, the temperature was raised to 298 K in about 30 min and held at 298 K for about 1 h. The spectra c and d were recorded at 298 K before and after evacuation for 30 min, respectively. Before the temperature was elevated to 373 K, NO was dosed again and the spectrum e was recorded. After the temperature was held for 30 min at 373 K, the spectrum f then after evacuating for 30 min the spectrum g were recorded. The pressure of NO remaining in gas phase was measured at each step.

Results

1. Properties of Catalysts. The basic properties of the catalysts used are listed in Table 1. Here the catalysts are abbreviated by "Cu/zeolite-Cu exchange level". For example, Cu/Z-142 and Cu/Y-80 mean ZSM-5 and Y zeolite of which the Cu ion-exchange levels, 2Cu/Al, are 142 and 80%, respectively. For Cu/Z-142 and Cu/Z-89, the values of

Table 1. List of Catalysts

Catalyst	Cu/Al	Na/Al	Cu loading wt/%	Ratio of number of Cu on the surface to that loaded[a]
Cu/Z-142[b]	0.71	0.01	5.3	0.81
Cu/Z-89	0.45	0.16	3.3	0.85
Cu/Z-60	0.30	0.39	2.1	0.85
Cu/Z-30	0.15	0.68	1.1	0.91
Cu/Y-80	0.40	0.21	5.0	0.14
Cu/Y-52	0.26	0.42	3.3	0.11
Cu/Y-19	0.10	0.79	1.2	0.05

a) Irreversible adsorption of NO at 273 K. b) Z represents ZSM-5.

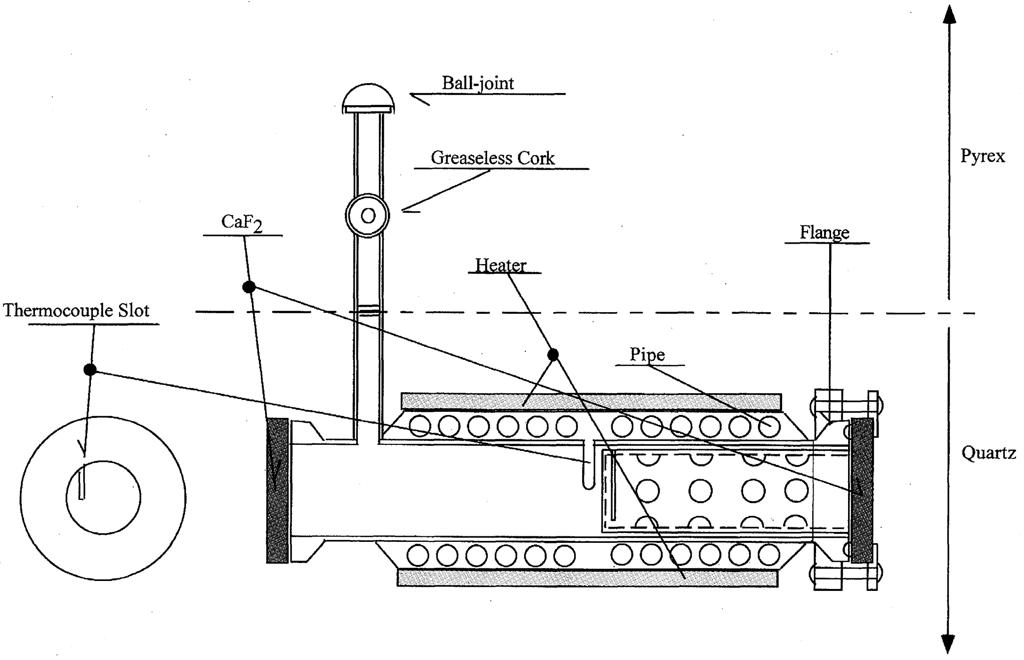

Fig. 1. Low temperature in-situ infrared cell.

(2Cu+Na)/Al were greater than unity, while the values were approximately unity for the rest. In spite of the repeated ion-exchange, the highest Cu ion-exchange level obtained for Y zeolite was about 80%. Excessively ion-exchanged Cu/Y could be obtained by adjusting the pH of the solution, as reported in the literature.[8] However, in this case the precipitation of Cu hydroxide would be inevitable. The ratio of the surface Cu to the total Cu supported was determined by the irreversible adsorption of NO at 273 K, as described previously.[15]

2. The Decomposition of N_2O and NO. N_2 and O_2 were the only products in N_2O decomposition, while, in addition to N_2 and O_2, small amounts of N_2O and NO_2 were also produced in NO decomposition. The steady state was usually reached in about 3 h for both reactions as, shown in Fig. 2. Similar time courses were observed for the catalysts used and the catalytic activities were calculated by using the steady state conversions.

The dependences on the contact time were investigated for both reactions. A linear relation was achieved between W/F (W: catalyst weight; F: flow rate) and % conversion for N_2O decomposition, as reported previously.[15] As for the NO decomposition over Cu/Z-142, the composition of products changed with W/F and temperature as shown in Fig. 3. The formation of N_2O showed a maximum at around 573 K for W/F=2.0 g s cm^{-3} and 623 K for W/F=0.12 g s cm^{-3}. When the conversion was below 10%, a linear relation between the rate of NO decomposition into N_2 and the contact time was also confirmed, as shown in Fig. 4.

Arrhenius plots for the rates of NO and N_2O decomposition into N_2 are shown in Fig. 5. All the rates were measured at the steady state, by changing the reaction temperature step by step both in higher and lower directions. The variations of the rates with temperature were reversible. The Arrhenius plots for NO decomposition tended to be leveled off at tem-

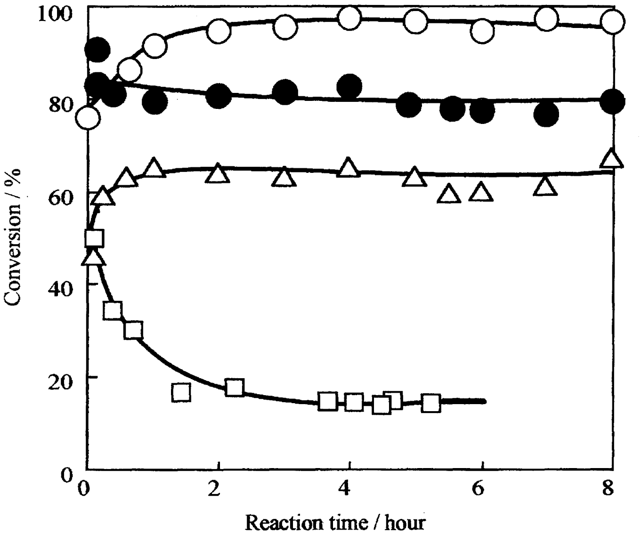

Fig. 2. Time courses of NO and N_2O decomposition catalyzed by Cu/Z-142. ○, NO; ●, NO into N_2; △, NO into O_2; W/F=4.0 g s cm^{-3}; T=723 K; □, N_2O into N_2; W/F=0.01 g s cm^{-3}; T=623 K.

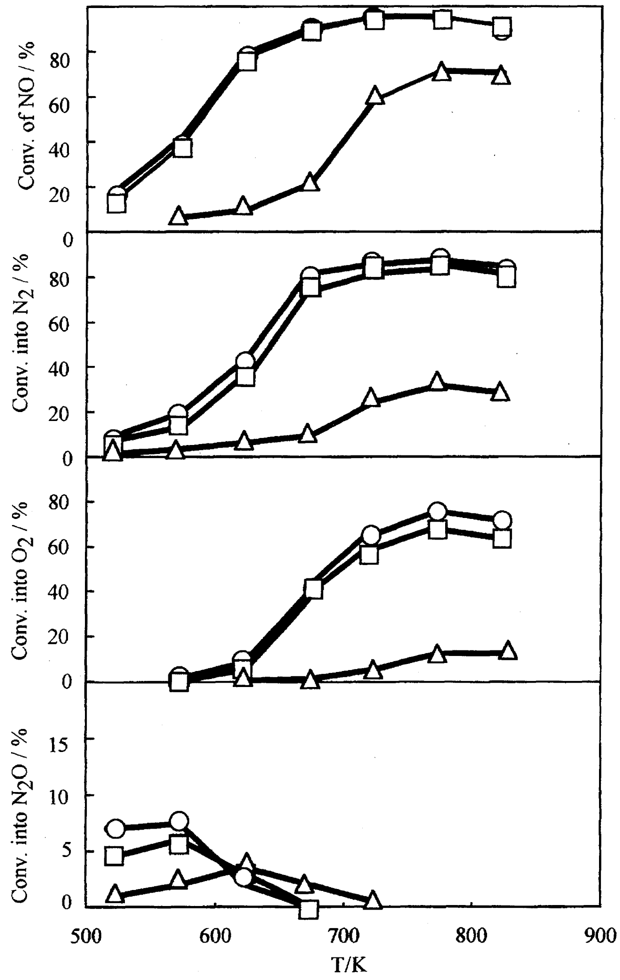

Fig. 3. Temperature dependences of the conversions of NO and into N_2, O_2, and N_2O for NO decomposition catalyzed by Cu/Z-142. ○, W/F=4.0 g s cm^{-3}; □, W/F=2.0 g s cm^{-3}; △, W/F=0.12 g s cm^{-3}.

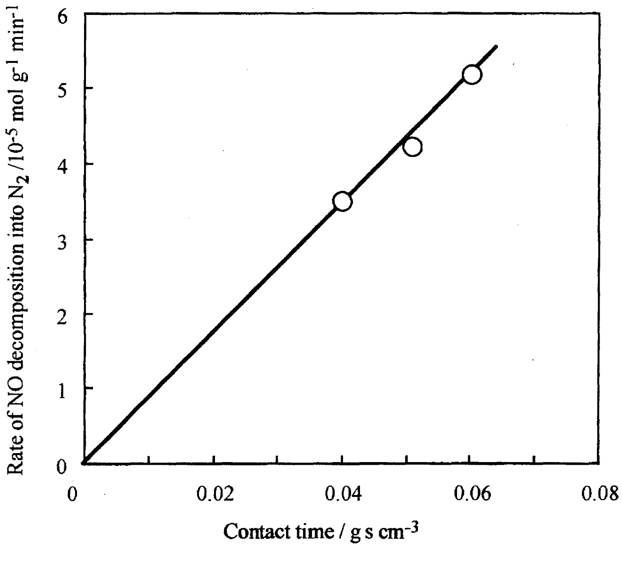

Fig. 4. Dependence of the rate of NO decomposition into N_2 on contact time at 723 K for Cu/Z-142. The conversion was kept below 10%.

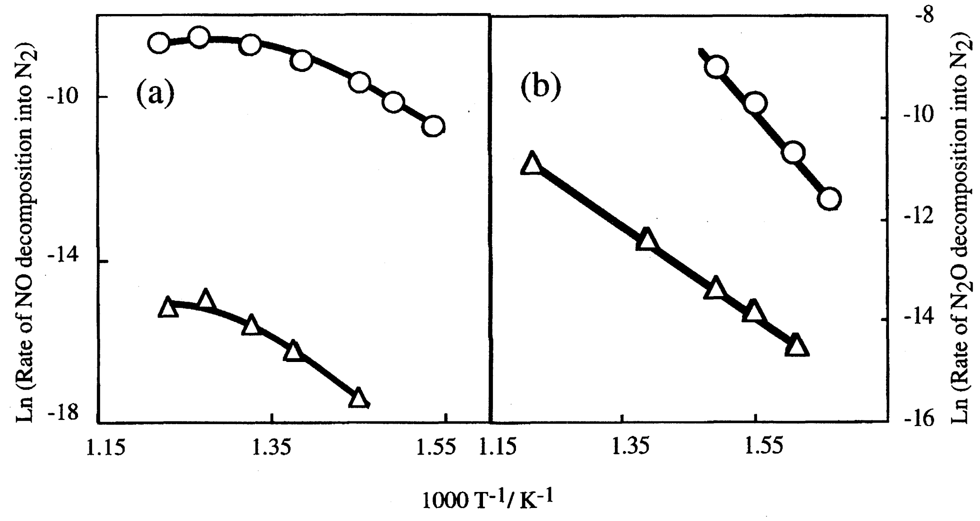

Fig. 5. Arrhenius plots for the decompositions of NO (a) and N_2O (b). Pretreatment, 773 K in helium for 2 h; reaction gas, 1.0% NO in helium. ○, Cu/Z-142; △, Cu/Y-80.

peratures above 773 K (Fig. 5a) as in the previous works.[15] On the other hand, Arrhenius plots for N_2O decomposition were linear (Fig. 5b).

The dependences of the rates of NO and N_2O decomposition on the exchange level of Cu ion are presented comparatively in Fig. 6, in which the ordinate is TOF. TOF is the reaction rate normalized to the surface Cu shown in Table 1. For Cu/Z with a low Cu ion-exchange level, that is, Cu/Z-30, the TOF of NO decomposition was in the same order as the TOF of Cu/Y catalyst, just like in the case of N_2O decomposition.[15] The TOF of NO decomposition increased sharply as the Cu ion-exchange level increased to 90%, but it tended to be saturated as the Cu ion-exchange level exceeded 90%. This tendency noted for NO decomposition (Fig. 6a) was clearly different from that for N_2O decomposition reported previously[15] (Fig. 6b).

3. IR Study of NO Adsorption. **(1) Adsorption of NO on Na/Y Catalysts.** The spectra of adsorption of NO on Na/Y are shown in Fig. 7. The admission of (equilibrium pressure of NO (denoted by Pe), 0.1 Torr) at 173 K (spectrum a) gave three bands at 1930, 1550, and 1297 cm^{-1}, which have been assigned to N_2O_3.[18,19] Increasing Pe to 0.2 Torr increased the band intensities (spectrum b). When the temperature was raised to 298 K, the intensities of these three bands decreased and new bands appeared around 2100 and 1400 cm^{-1}, which are assignable to NO_2 and NO_3, respectively, according to the literature.[19,20] The band intensities did not much decrease by the evacuation at 298 and 373 K. All these data were consistent with those reported by Chao and Lunsford.[19]

(2) Adsorption of NO onto Cu/Y-80. Figure 8 shows the spectra of NO adsorption on Cu/Y-80. Upon the admission of NO (Pe, 0.1 Torr) several bands were observed (spectrum a). The bands at 1949, 1925, and 1893 cm^{-1} are assigned to

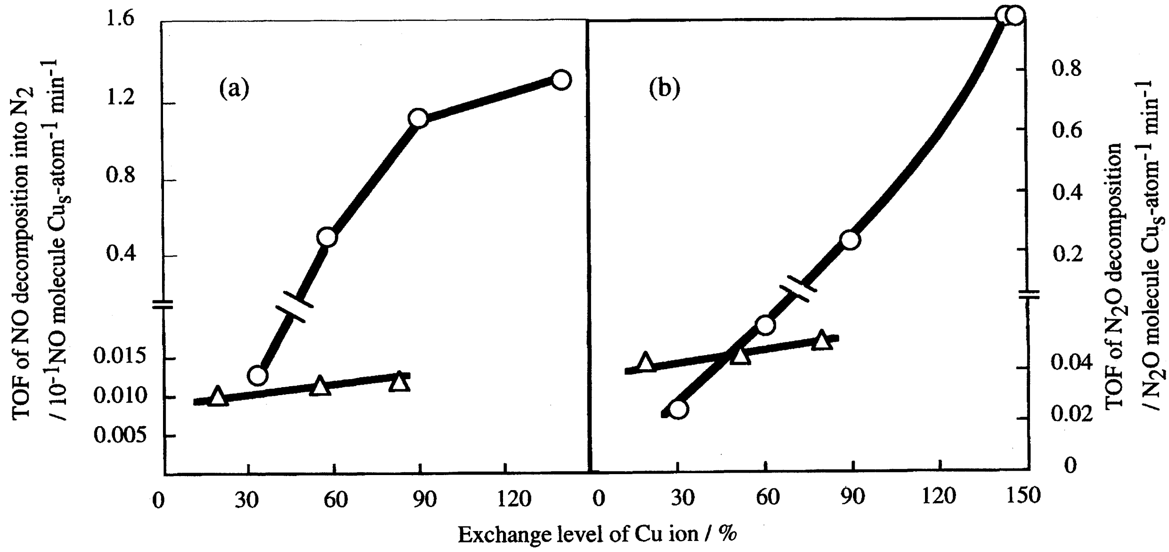

Fig. 6. Dependences of turnover frequency (TOF) of N_2O (a) and NO (b) decompositions into N_2 on the Cu ion exchange level at 723 K. ○, Cu/Z; △, Cu/Y.

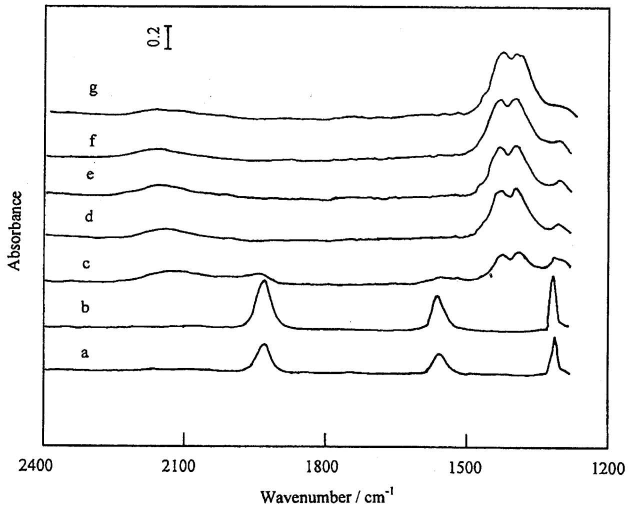

Fig. 7. IR spectra of NO adsorbed on Na/Y. (a) 0.1 Torr NO at 173 K; (b) 0.2 Torr at 173 K; (c) 0.4 Torr at 298 K; (d) evacuated at 298 K for 30 min; (e) 2.6 Torr at 298 K; (f) 2.9 Torr at 373 K; (g) evacuated at 373 K for 30 min.

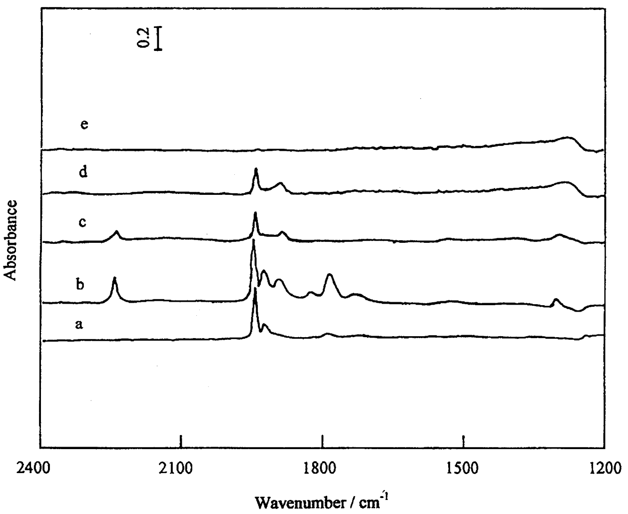

Fig. 8. IR spectra of NO adsorbed on Cu/Y-80. (a) 0.1 Torr NO at 173 K; (b) 2.1 Torr at 173 K; (c) evacuated at 173 K for 30 min; (d) 2.8 Torr at 298 K; (e) evacuated at 298 K for 30 min.

nitrosyl species on Cu^{2+}.[9,11] The band at 1785 cm^{-1} is due to nitrosyl species on Cu^+.[9] The weaker bands at 1826 and 1726 cm^{-1} are of dinitrosyl species on Cu^+.[9] By increasing Pe, these bands became more intense and a new peak appeared at 2243 cm^{-1}, which has been assigned to N_2O.[8,9] By the evacuation at 173 K, the bands due to dinitrosyl and nitrosyl species on Cu^+ and N_2O disappeared, while nitrosyl species on Cu^{2+} were still observed (spectrum c). The nitrosyl species on Cu^{2+} were observed at 298 K (spectrum d), disappeared by the evacuation (spectrum e).

(3) Adsorption of NO on Na/Z. Figure 9 shows the spectra of NO adsorption on Na/Z. At Pe=0.1 Torr and 173 K, a very weak band was observed at 1900 cm^{-1}, which can be assigned to nitrosyl species. Increasing Pe to 2.0 Torr increased the band intensity and new bands appeared at 2280,

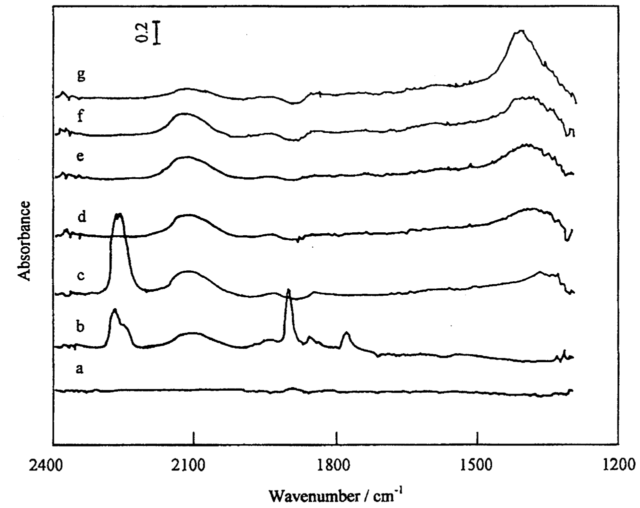

Fig. 9. IR spectra of NO adsorbed on Na/Z. (a) 0.1 Torr NO at 173 K; (b) 2 Torr at 173 K; (c) 8 Torr at 298 K; (d) evacuated at 298 K for 30 min; (e) 2.5 Torr at 298 K; (f) 2.9 Torr at 373 K; (g) evacuated at 373 K for 30 min.

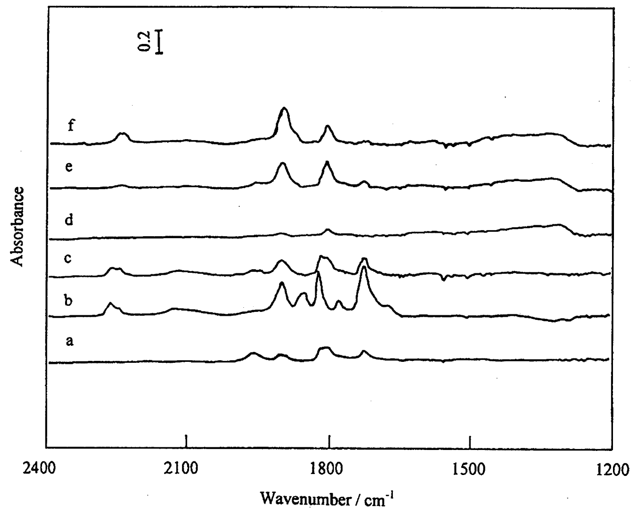

Fig. 10. IR spectra of NO adsorbed on Cu/Z-30. (a) 0.1 Torr NO at 173 K; (b) 2.0 Torr at 173 K; (c) evacuated at 173 K for 30 min; (d) evacuated at 298 K for 35 min; (e) 3.1 Torr at 298 K for 60 min; (g) 3.1 Torr at 298 K for 120 min.

2270, 2100, 1860, and 1760 cm^{-1}, as shown in spectrum b. The last two bands can be attributed to dinitrosyl species.[19] 2280—2270 cm^{-1} bands are assignable to N_2O and 2100 cm^{-1} to NO_2.[20] When the temperature was raised to 298 K, the bands due to dinitrosyl and nitrosyl species disappeared and the intensities of the bands due to N_2O and NO_2 increased with the appearance of NO_3 bands. The intensities of bands due to NO_2 and NO_3 changed little by the evacuation at 298 and 373 K.

(4) Adsorption of NO on Cu/Z-30 and Cu/Z-142. Figure 10 shows the spectra of NO adsorption on Cu/Z-30. At Pe=0.1 Torr and 173 K, five bands were observed at 1960, 1906, 1830, 1810, and 1732 cm^{-1}. The former two bands can be assigned to nitrosyl species on Cu^{2+}, 1810 cm^{-1} to nitrosyl on Cu^+, and 1830 and 1732 cm^{-1} to dinitrosyl

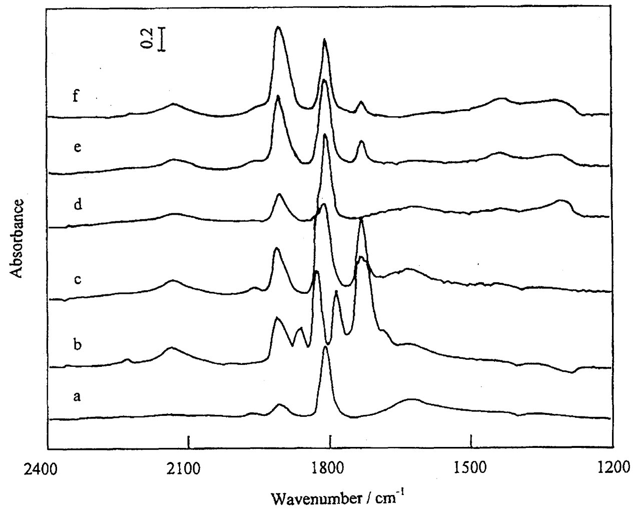

Fig. 11. IR spectra of NO adsorbed on Cu/Z-142. (a) 0.1 Torr NO at 173 K; (b) 2.0 Torr at 173 K; (c) evacuated at 173 K for 30 min; (d) evacuated at 298 K for 35 min; (e) 2.8 Torr at 298 K for 60 min; (g) 2.8 Torr at 298 K for 120 min.

species on Cu^{2+}. Increasing Pe to 0.5 Torr increased these band intensities with the appearance of two peaks around 2230 and 2100 cm^{-1}, which are assigned to N_2O and NO_2, respectively.[20] All bands were still observed by the evacuation at 173 K (spectrum c). Only the bands due to nitrosyl species on Cu^+ and Cu^{2+} were observed by the evacuation at 298 K (spectrum d). When NO was introduced at 298 K, the bands due to nitrosyl and dinitrosyl species Cu^+ and Cu^{2+} were observed and the intensities changed with time (spectra e and f). Similar bands were observed for Cu/Z-142 and the relative intensities changed (Fig. 11). IR adsorption peaks and their assignments are summarized in Table 2.

Discussion

1. Comparison of the Effects of Cu Ion-Exchange Level between ZSM-5 and Y Zeolite and between the Decomposition of NO and N_2O.

TOF of Cu/ZSM-5 for NO decomposition increased sharply with an increase in Cu ion exchange level and tended to be saturated above 90%. The variation was similar to that reported by Iwamoto et al.[8] except that saturation was observed at higher Cu ion exchange level. This correlation was confirmed independently by several other groups.[3,22] This phenomenon was usually interpreted as follows: There are two or more kinds of ion-exchange sites with different catalytic activities and the proportion of the more active sites increases with the exchange level of ZSM-5.

For example, it was proposed that Cu–Cu ion pair sites are more active. One possible reason is that the reduction-oxidation between Cu^{2+} and Cu^+ proceeds more easily for the pair sites or that NO decomposes efficiently with cooperation of two adjacent active sites, facilitating the formation of N–N bond.[8] If the latter is the case, and if one assumes that the O_2 formation is easy, it is expected that the catalytic activity for NO decomposition should depend much more on the exchange level than that for N_2O decomposition, since for N_2O decomposition there is no need of the formation of N–N bond. However, as seen in Fig. 6, the present results contradict this expectation. The catalytic activity of Cu/ZSM-5 for N_2O decomposition increased more with an increase in the Cu ion-exchange level than that for NO decomposition. Therefore, the latter possibility is excluded.

As for the reaction mechanism of NO decomposition, it has been proposed by Pirone et al.[23] and Aylor et al.[16] that NO decomposition proceeds in the following consecutive reaction steps:

$$NO \rightarrow N_2O \rightarrow N_2 \quad (3)$$

Here the second step is not the rate-determining step, as N_2O decomposition is usually much faster than NO decomposition. This is also indicated by the present observation that NO and N_2O decomposition exhibited different dependency on the Cu loading level for Cu/Z (Fig. 6). It is also probable that the main path of NO decomposition does not

Table 2. IR Absorption Peaks (cm^{-1}) and Their Tentative Assignment for Surface Species Formed from NO on Na- and Cu-Zeolite

Species	Cu/Z	Na/Z	Cu/Y	Na/Y	Note	Reference
N_2O	2230/2247	2250/2260	2240	—		8, 9
NO_2	2131	2140	2180		Broad and adsorbed on framework	21
					Hydroxyl	
	1960				Weak	8
NO			1948		Strongly on Cu^{2+}	9, 11
N_2O_3			1930	1930	together with peaks at 1570 and 1310	18, 19
NO	1906—1920		1892		Cu^{2+}	8, 9
NO		1902			Weak	19
N_2O_3	1860					16
$(NO)_2$	1823—1830				Dinitrosyl on Cu^+ (asym)	8, 9
NO	1810—1815				on Cu^+	8, 9
$(NO)_2$		1780			Weak	20
NO			1785		Cu^+	9
$(NO)_2$	1730		1728		Dinitrosyl on Cu^+ (sym)	8, 9
N_2O_3				1570		19
N_2O_3				1310		19

involve N_2O formation.

Li and Hall,[3)] Iwamoto et al.,[5)] and Schay and Guczi[24)] have suggested a redox mechanism in which the desorption of oxygen is the rate-limiting step. The redox mechanism was consistent with the rate equation.[4)] A similar mechanism was also proposed for N_2O decomposition by Kobayashi and Kobayashi.[25)] If the rate-determining step is the desorption of surface oxygen, the catalytic activities for NO and N_2O decomposition should depend on the Cu ion exchange level and the reaction temperature in a very similar way, as the desorption of surface oxygen is the common step for the two reactions. The effects of reaction temperature and the effect of Cu ion exchange level observed in the present study were different from this expectation. Therefore, the common step, the desorption of oxygen, is not the rate-determing step as in the case of Cu-containing perovskites.[4)] This is one of the reasons why the dependency of the catalytic activity for the NO decomposition on the Cu ion exchange level is different from that for the N_2O decomposition.

As shown in Fig. 6, the catalytic activity of ZSM-5 for the decompositions of NO and N_2O increased much more with an increase in the exchange level of Cu ion than those of Cu/Y zeolite, and hence the activities at high Cu ion exchange levels of Cu/ZSM-5 were much greater than that of Cu/Y. The reasons for the difference may be complex and are not clear yet. One of the possible reasons is that the state of Cu ions and their affinity towards NO molecule are different between Cu/ZSM-5 and Cu/Y, as shown by IR spectra. This will be discussed in the next section.

2. IR Results Relevant to the Reaction Mechanism. Even with the repetition of adsorption of NO and the subsequent evacuation at 173 K, the IR spectra of all samples little changed. On the other hand, the spectra changed with time at 298 K, as shown in Figs. 10 and 11. Therefore, the spectra c (evacuated at 173 K) reflect the actual numbers of Cu^+ and Cu^{2+}. Only nitrosyl species on Cu^{2+} were observed for the spectrum e in Fig. 8, suggesting that copper in Cu/Y-80 is Cu^{2+}. On the other hand, for spectra c in Figs. 10 and 11, the intense bands due to nitrosyl and dinitrosyl species on Cu^+ were observed. At 298 K, similar results were observed by the comparison of the spectra c or d in Figs. 8, 10, and 11, showing the reflection of the amount and the stability of Cu^+ at elevated temperatures. These facts suggest that Cu/Z zeolites contain much larger amount of Cu^+ than Cu/Y zeolites do. In addition, the band intensity ratio of NO/Cu^+ to NO/Cu^{2+} for Cu/Z-142 was higher than that for Cu/Z-30. This fact suggests that Cu^+ in Cu/Z-142 is more stable than Cu/Z-30. The amount and stability of Cu^+ may be related to the catalytic activity for the decomposition of NO and N_2O. Thus, zeolite structure apparently plays an important role in determining of the state of metal cations.

In spectrum b of Fig. 9, an intense peak of N_2O, which is produced by NO disproportionation, was observed for Na/Z. In contrast, no N_2O was observed for Na/Y, but N_2O_3 was found in spectrum b of Fig. 7. These facts show that the activity of Na/Z for the disproportionation of NO is higher than that of Na/Y. It is likely that the difference of activity for disproportionation of NO also results from that of zeolite structure.

Trout and coworkers have shown that a plausible pathway for NO decomposition is the reaction on Cu cations associated with single Al sites on the basis of quantum mechanical calculations.[26)] It is possible that a highly siliceous Cu/ZSM-5 contains more isolated Cu ions associated with a single framework Al atoms. Therefore, the ration of Si/Al of zeolites may also play a role in the catalytic activity.

Conclusions

The catalytic activities of NO and N_2O decomposition of Cu ion-exchanged ZSM-5 and Y zeolites with various Cu loading levels were compared. It was found that (1) the catalytic activity of Cu/ZSM-5 increased remarkably with the Cu loading level, while the increase was not much for Cu/Y, the activity of Cu/Z-142 being very high; and (2) the activity for N_2O decomposition increased with the Cu ion-exchange level much more than that for NO decomposition. Based on these facts, it was concluded that the rate-determining step is not the desorption of oxygen. The study of IR of NO adsorption showed that the disproportionation of NO occurs much more rapidly on Na/ZSM-5 than on Na/Y and the concentration of Cu^+ on Cu/ZSM-5 is much higher and more stable than that on Cu/Y. Besides, NO is more strongly adsorbed on Cu ions on Cu/ZSM-5 than on Cu/Y. These are reasons suggested for the differences observed between Cu/Z and Cu/Y.

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