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Temperature programmed desorption study of adsorbed species formed by the decomposition of N_2O on ion-exchanged copper zeolite catalysts

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Abstract

The nature of the adsorbed species on Cu-ZSM-5 (Cu-Z), Cu-Mordenite (Cu-M), and Cu-Y-zeolite (Cu-Y) was investigated by means of temperature programmed desorption (TPD). When dinitrogen monoxide (N_2O) came into contact with Cu-zeolites above 573 K, the decomposition of N_2O occurred accompanied by the formation of adsorbed oxygen species and adsorbed nitrogen oxide species. In the TPD runs, three O_2 desorption peaks appeared at temperatures of 623, 673, and 753 K and were named α-, β-, and γ-peaks, respectively. The O_2 desorption at the α- and γ-peaks became quickly saturated after contacting N_2O at 598 K, while the amount of O_2 desorbed at the β-peak increased with time, not reaching a constant level until 120 min of exposure. The activity for the decomposition of N_2O decreased with the accumulation of β-oxygen over the catalyst. The rate of N_2O decomposition depended upon the nature and amount of the copper zeolite catalysts available, as determined by the formation of α- and/or β-oxygen. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Cu-zeolite; Dinitrogen monoxide; Direct decomposition; Characterization; TPD

1. Introduction

Nitrous oxide (N_2O) has been identified as a greenhouse gas and a contributor to the destruction of ozone in the stratosphere. The decomposition of N_2O over solid catalysts has been studied by a number of investigators [1]. These catalysts include metals, pure and mixed metal oxides, and zeolite systems. The transition metal ion-exchanged zeolites have been shown to exhibit high activities for the decomposition of N_2O [2–10]. Li and Armor [5,6] have reported that Co- and Cu-ion exchanged ZSM-5 zeolites are highly active catalysts for the decomposition of N_2O into its elements under mild conditions. Kapteijin et al. [10] have shown that the decomposition is first order in the N_2O pressure over Fe- and Co-ZSM-5 but has a slightly lower order over Cu-ZSM-5. In addition, the inhibition of O_2 observed for Cu-ZSM-5 is absent for Co- and for Fe-ZSM-5 at lower temperature. In the kinetic model, N_2O oxidizes an active site and removes it in a second step, thereby forming O_2. This second step appears to be the most difficult in all cases.

In the present study, the desorption behavior of adsorbed oxygen species formed on Cu-zeolite catalysts is studied by means of a thermal desorption method. Involvement of the adsorbed oxygen species

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in the decomposition of N_2O over Cu-zeolites is discussed.

2. Experimental

Cu-ZSM-5 (Cu-Z), Cu-Mordenite (Cu-M), and Cu-Y-zeolite (Cu-Y) were prepared by an ion-exchange method in an aqueous solution of copper prepared from copper(II) acetate and an aqueous solution of ammonia. The ion-exchanged zeolites were filtered out, washed with distilled water, and dried at 383 K for 12 h, and were then further calcined in air for 3 h at 773 K. The zeolites used were supplied from Tohso. Copper loadings were 1.1–5.6 wt%, and the ion-exchange levels were 12–125%. The samples identified are given by zeolite type, percent copper loading, and percent exchanged, e.g., Cu-Z-3.9-103. The copper-loading percentages were calculated from the difference in copper(II) concentrations of the solutions before and after ion-exchange. The valence state of the copper was inspected by UV/Vis/NIR diffuse reflectance spectroscopy. The spectra were recorded on a UV/Vis/NIR spectrophotometer (Hitachi model 330) with a diffuse reflectance attachment.

The reactant gas used was 4 vol% N_2O diluted with helium (Sumitomo Seika). The reaction was carried out in a conventional flow reactor at W/F of 0.6 g s cm^{-3} and at 523–773 K. The reactor was made of 12 mm diameter quartz tubing in which the catalyst sample (0.5 g) was mounted on loosely packed quartz wool. The concentrations of N_2O, NO, N_2, and O_2 in the outflow gas were determined by the use of gas chromatographs with porapak Q and molecular sieve 5A columns. The concentration of NO_2 was monitored by means of a UV/Vis spectrophotometer.

The TPD experiment was carried out in the same reactor as that used for the reaction. Prior to the TPD runs, the catalysts were treated in the reactor at 773 K for 3 h and cooled to room temperature in a stream of He. Four vol% NO diluted with He was then fed over a catalyst at room temperature for given periods of time and was purged by switching to a pure He stream until no NO was detected in the outflow. Programmed heating was started from room temperature to 773 K at a rate of 10 K/min. The amounts of the gases desorbed were estimated from the peak areas of the TPD.

Infrared spectra of surface nitrogen oxide and oxygen species were recorded by means of a Fourier transform-infrared (FT-IR) spectrophotometer (Nihon Bunko FT-IR5M) with a diffuse reflectance attachment (Nihon Bunko DG-500/H). The powdered catalyst was placed on the sample cell in the diffuse reflectance attachment. Four vol% N_2O diluted with He was fed over the catalyst at 598 K for given periods of time and was purged by switching to a pure He stream at temperatures between 598 and 673 K. The IR measurement of adsorbed species was then carried out at the same temperature used for adsorption or at room temperature.

3. Results and discussion

3.1. *The decomposition of N_2O over Cu-zeolite in a steady state*

Fig. 1 illustrates typical results for the partial pressures of N_2, O_2, and NO_2 in the effluent as functions of the reaction time in the decomposition of 4% N_2O over Cu-Z-3.9-103 at 598 K. When 4% N_2O was introduced on the catalyst treated in a stream of He at 773 K, the partial pressure of N_2 in the effluent overshot rapidly and then decreased to a steady state value within 120 min, whereas that of O_2 grew rapidly and then decreased to a steady state value. Under the transient state of the reaction, the partial pressure of O_2 was lower than that expected from the stoichiometry of the decomposition ($N_2O \rightarrow N_2 + \frac{1}{2}O_2$). The values estimated from the partial pressure of N_2 are

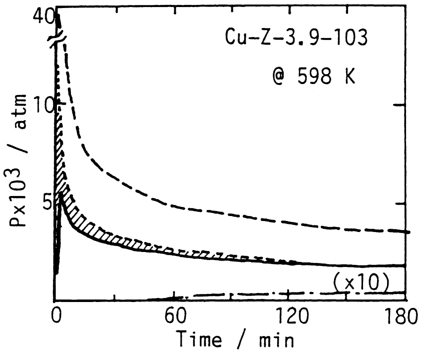

Fig. 1. Partial pressures of N_2, O_2, and NO_2 in the effluent as functions of the reaction time in the decomposition of 4% N_2O over Cu-Z-3.9-103 at 598 K. (– – –) N_2; (- - -) $\frac{1}{2}N_2$; (———) O_2; (— — —) NO_2.

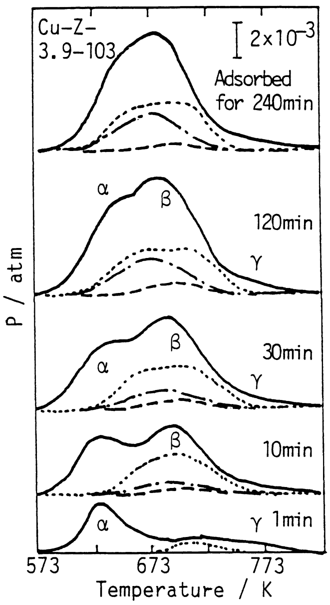

Fig. 2. TPD curves of the adsorbed species formed on Cu-Z-3.9-103 by the decomposition of N_2O at 598 K. (———) O_2; (- - -) NO; (— — —) NO_2; (— – —) N_2.

indicated by a dotted line in Fig. 1. This strongly suggests that the adsorbed oxygen species were appreciably formed on Cu-Z in the course of the decomposition of N_2O. The evolution of NO_2 in mere trace amounts took place in the decomposition of N_2O over Cu-Z-3.9-103 from 50 min and then increased to a steady state value within 120 min. The formation of small amounts of NO_x has been observed during N_2O decomposition over Cu-ZSM-5 and various metal oxide catalysts [9–11]. Most probably, NO is formed by the decomposition of N_2O, $2N_2O \rightarrow 2NO+N_2$, and thus NO_2 is produced by the oxidation of NO [9].

3.2. *The desorption behavior of adsorbed species formed on Cu-zeolites*

Fig. 2 illustrates the TPD curves of the adsorbed species formed on Cu-Z-3.9-103 by the decomposition of N_2O at 598 K for 1, 10, 30, 120, and 240 min. The peaks occurring in the temperature ranges of 623, 673, and 753 K are henceforth named as α-, β-, and γ-peaks, respectively. The evolution of NO, NO_2, and N_2 was also observed in the β- and γ-peak regions. In our previous paper [12], it was reported that NO_3-type adsorbed species are formed by the adsorption of NO over Cu-Z and are desorbed as NO, NO_2, and O_2 in TPD runs at 673–723 K. By FT-IR spectroscopy, it was confirmed that the absorption bands for the NO_3-type species (1570–1630 cm^{-1}) were formed by the decomposition of N_2O at 598 K on Cu-Z-3.9-103 and disappeared above 723 K. This suggests that NO_3-type adsorbed species are formed by the adsorption of NO and/or NO_2. These NO_x were produced by the decomposition of N_2O. On the basis of the results shown in Fig. 2, it can be seen that after exposure to a stream of N_2O at 598 K for 1 min, α- and γ-O_2 peaks were observed, while the amount of O_2 desorbed at these peaks was unchanged by further exposure to a stream of N_2O. The amount of O_2 desorbed at the β-peak increased with increases in the exposure time and then reached a constant level at 120 min. The activity for the decomposition of N_2O decreased with the accumulation of β-oxygen over the catalyst. The surface oxygen, which was formed by the adsorption of O_2 at 773 K, desorbed at only the γ-peak. The differences in amounts between the oxygen evolved at an initial transient state and that expected from the stoichiometry of the N_2O decomposition correspond to the amounts of oxygen desorbed at the α- and β-peaks. This is indicated by the shaded area in Fig. 1. These findings suggest that the surface sites on which α- and β-oxygen are adsorbed are active sites for N_2O decomposition.

Fig. 3(A) and (B) illustrate the TPD curves of the adsorbed species formed on Cu-M-3.0-67 and Cu-Y-3.0-24 by the decomposition of 4% N_2O at 598 K for 1, 10, 30, 60, and 120 min. It can be seen that β- and γ-oxygen species were formed on Cu-M, whereas only β-oxygen species were formed on Cu-Y. It is shown that the amount of the β-oxygen species adsorbed on these catalysts increased with increases in the time of exposure to a stream of N_2O. No desorption peak of NO, NO_2, N_2, or α-O_2 appeared in the decomposition of 4% N_2O over both catalysts at 598 K for 120 min.

3.3. *The desorption of adsorbed species formed on various Cu-zeolites with different copper exchange levels*

Fig. 4 illustrates the TPD curves of the adsorbed species formed on Cu-Z-2.0-51, -3.0-77, -3.9-103, and -4.6-125 by the decomposition of N_2O at 598 K for 120 min. It is seen that α-, β-, and γ-peaks were

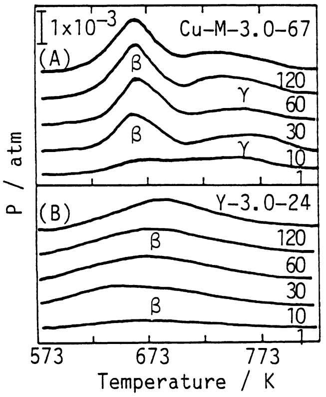

Fig. 3. TPD curves of the adsorbed species formed on Cu-M-3.0-67 and Cu-Y-3.0-24 by the decomposition of N_2O at 598 K. (———) O_2.

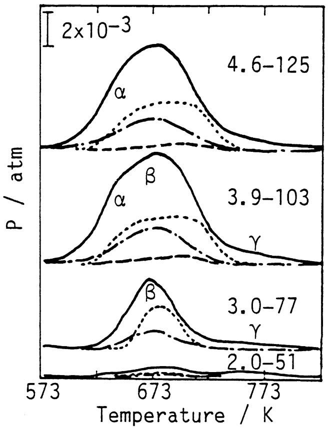

Fig. 4. TPD curves of the adsorbed species formed on Cu-Z by the decomposition of N_2O at 598 K for 120 min. (———) O_2; (- - -) NO; (— — —) NO_2; (– – –) N_2.

observed over the catalysts with copper exchange levels above 100%, whereas β- and γ- peaks were observed over those below 77%. Fig. 5(A) and (B) illustrate the TPD curves of the adsorbed species formed on Cu-M-1.1-23, -2.2-50, -3.0-67, and -3.7-83 and on Cu-Y-1.5-12, -3.0-24, -4.4-36, and -5.6-47, respectively. These oxygen species were formed by the decomposition of 4% N_2O at 598 K for 120 min. For extensive ion-exchange levels over both catalysts, it can be seen that β- and γ-peaks were formed on Cu-M, whereas only the β-oxygen species was formed on Cu-Y. No α-oxygen species was observed on Cu-M and Cu-Y with copper ion exchange levels below 83%.

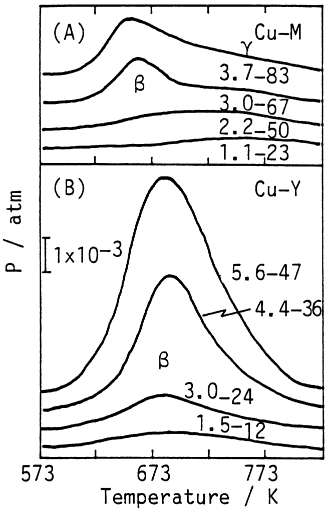

Fig. 5. TPD curves of the adsorbed species formed on Cu-M and Cu-Y by the decomposition of N_2O at 598 K for 120 min. (———) O_2.

The precursor structures of copper on Cu-zeolites with various ion exchange levels were investigated by means of diffuse reflectance UV/Vis spectroscopy. The absorption band which appeared at 270 nm can be ascribed to the charge transfer between the surface oxygen and the isolated Cu^{2+} ion in octahedral co-ordination [13]. The reflectivity at 270 nm is thus

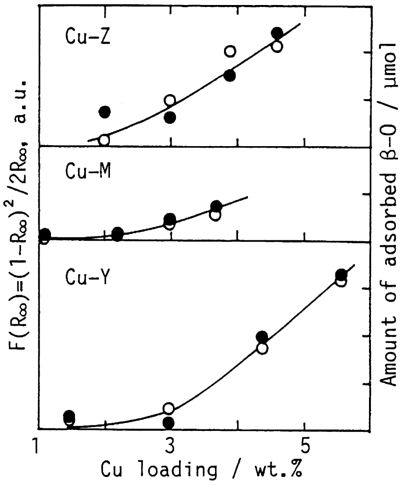

Fig. 6. Relationship between the reflectivity $F(R_\infty) = (1-R_\infty)^2/2R_\infty$ ascribed to the Cu^{2+} ion in octahedral co-ordination or the amount of β-oxygen and the amount of copper loading on Cu-zeolite. (●) isolated Cu^{2+}; (○) adsorbed β-oxygen.

proportional to the concentration of the isolated surface cupric ion over Cu-zeolite. In Fig. 6, the reflectivity $F(R_\infty)=(1-R_\infty)^2/2R_\infty$ at 270 nm estimated by the Kubelka–Munk equation and the amount of β-oxygen adsorbed on the site at steady states of N_2O decomposition are plotted against the amount of copper loadings over Cu-zeolites. A good relationship exists between these parameters. This suggests that the β-oxygen is formed by the decomposition of N_2O over the isolated cupric species in octahedral co-ordination. It is concluded that the isolated surface cupric ions play a pivotal role in the decomposition of N_2O as active sites.

3.4. The relationship between the rate of N_2O decomposition and/or O_2 desorption and the amount of adsorbed oxygen species

The correlation between the catalytic activity of Cu-Z, Cu-M, and Cu-Y at 598 K and the amount of copper loading is depicted in Fig. 7. It can be seen that the catalytic activity for the decomposition of N_2O increased with an increase in copper loading, and the activity order is Cu-Z>Cu-M>Cu-Y. For Cu-Z with copper loadings above 3.9 wt% (ion exchange levels above 103%), the catalytic activity increased sharply.

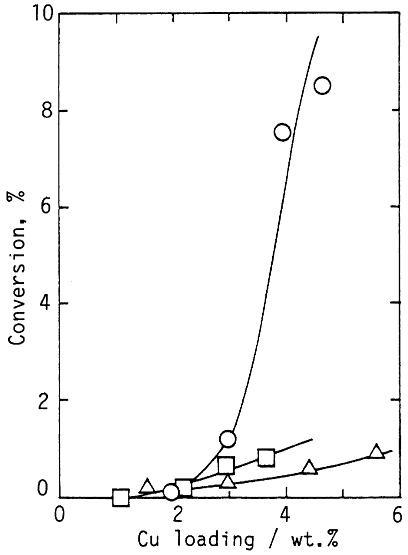

Fig. 7. Relationship between the conversion of N_2O decomposition over Cu-zeolites and the amount of copper loading. (○) Cu-Z; (□) Cu-M; (△) Cu-Y.

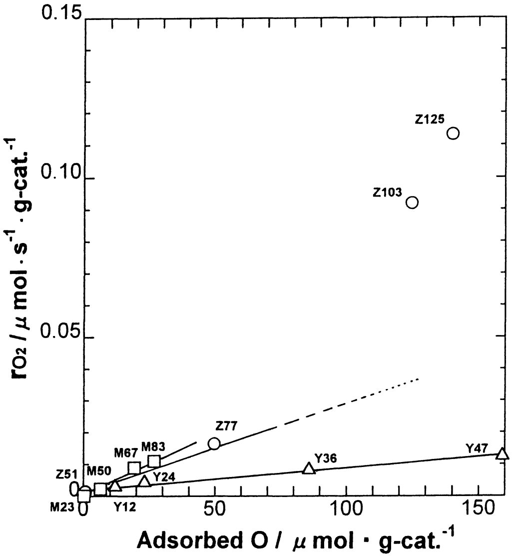

Fig. 8. Relationship between the rate of O_2 formation and the amount of α- and β-oxygen adsorbed at the steady state of N_2O decomposition at 598 K over Cu-zeolites. (○) Cu-Z; (□) Cu-M; (△) Cu-Y.

Fig. 8 shows the relationship between the rate of O_2 formation and the amount of α- and β-oxygen adsorbed at the steady state of N_2O decomposition at 598 K over Cu-zeolites. α-oxygen was observed over Cu-Z with ion-exchange levels above 103%. For the catalysts with copper ion exchange levels below 80%, a good linear relationship exists between these parameters. This suggests that the rate of N_2O decomposition is proportional to the amount of the surface site, the isolated surface cupric ion, for the formation of β-oxygen. The differences in the activity of the catalysts with copper ion-exchange levels below 80% depended upon the nature of the surface site of the zeolites (Cu-M>Cu-Z>Cu-Y). On the other hand, over Cu-Z with a copper ion-exchange level above 100%, the plots of the activity deviate greatly from the linear relationship between the rate of N_2O decomposition and the amount of oxygen adsorbed. The pronounced catalytic activity of Cu-Z with copper ion-exchange level above 100% could be explained by the role of the surface specific site on which the α-oxygen is adsorbed.

4. Conclusions

In the TPD runs, the evolution of adsorbed oxygen formed by the decomposition of N_2O takes place at temperatures of 623, 673, and 753 K as α-, β-, and γ-peaks, respectively. The O_2 desorption at the α- and γ-peaks was rapidly saturated after contacting N_2O at 598 K, while the amount of oxygen desorbed at the β-peak increased with an increase in the time of exposure. The activity for the decomposition of N_2O depends upon the nature and the amount of the site for the formation of α- and/or β-oxygen.

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