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N_2O AND NO_2 FORMATION IN THE DISPROPORTIONATION OF NO OVER ION EXCHANGED Cu-ZSM-5 AT LOWER TEMPERATURE

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Abstract

NO_3-type and NO_2-type adsorbed species are formed on Cu-ZSM-5 together with adsorbed O species at 523 K in the decomposition of NO accompanied by the evolution of N_2, N_2O, and NO_2.

Keywords: Cu-ZSM-5, NO decomposition, NO_x-type adsorbed species

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INTRODUCTION

Numerous papers concerning the catalytic decomposition of NO have recently been published. Copper ion-exchanged ZSM-5 (Cu-Z) has been repeatedly shown to be a highly active and selective catalyst [1-8]. Over Cu-ZSM-5 catalysts, it has been reported [3-5] that various adsorbed species, including $Cu^+(NO)$, $Cu^+(NO)_2$, $Cu^{2+}(NO)$, $Cu^{2+}O^-(NO)$, N_2O, NO_2, N_2O_3, and NO_3^-, are formed by adsorption of NO at room temperature. Recently, it was shown that only small concentrations of $Cu^+(NO)$, $Cu^{2+}O^-(NO)$, NO_2, and NO_3^- are detected by *in situ* observation at temperatures between 673 and 773 K. Trout *et al.* [5] have been proposed that the mechanism of NO decomposition through $Cu^+(NO)_2$ or $Cu^{2+}(NO_2^-)(NO)$ as an intermediate. However, few reports have focused on the mechanism of the formation of N_2O and NO_2 in the NO decomposition over Cu-zeolites at lower temperatures below 573 K, at which no N_2 formation is observed in the steady state of NO decomposition.

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In our previous reports [9,10], the nature of the surface species formed upon adsorption of NO on copper ion-exchanged mordenite and Y-type zeolite was investigated. The NO_x-type adsorbed species, which desorbed as NO, NO_2, and O_2 in He at 653-673 K, may have formed by the reaction between NO and the adsorbed oxygen species (Os). In the present study, the structures and desorption behavior of NO_x species formed on Cu-ZSM-5 catalysts below 523 K with different ion-exchange levels were studied by means of a thermal desorption method. The sites for the formation of NO_x species below 523 K will be discussed.

EXPERIMENTAL

Cu-ZSM-5 catalysts were prepared by a conventional ion-exchange method [9,10]. Na-ZSM-5 (Si/Al =11.9) was supplied from Tohso Co. Copper ion exchange levels were 27, 57, 72, 92, and 116%. The sample identification is based on the percent of copper exchanged, *e.g.*, Cu-Z-116.

The reactant gas used was 4 vol.% NO diluted with helium. The reaction was carried out in a conventional flow reactor at W/F of 0.6 g s cm^{-3} and at 523 K. Prior to the reactions, the catalysts were treated in the reactor at 773 K for 2 h then cooled to reaction temperature in a stream of He. For preadsorption of NO, NO was fed over a catalyst at reaction temperature for a given period of time, then the NO stream was switched to helium at the same temperature for 30 min. After flushing the catalyst in a stream of He, NO was again fed over the catalyst at the same temperature for a given period of time. Programmed heating was started at a rate of 10 K min^{-1}. The concentrations of NO, N_2O, N_2, and O_2 in the outflow gas were determined by gas-chromatography. The concentration of NO_2 was monitored by means of a UV/VIS spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows the typical results for changes in the partial pressure of the products in the effluent in the decomposition of 4 vol.% NO over Cu-Z-116 measured at 523 K. These catalysts, shown in Fig. 1 (1)-(6), were previously treated in the stream of 4 vol.% NO for 0, 3, 4, 15, 30, and 60 min at 523 K. Figure 1 (1) shows the results for NO decomposition over Cu-Z-116 previously treated in a stream of helium. When NO was introduced over the catalyst treated in helium, the partial pressure of N_2O in the effluent overshot rapidly then decreased toward a steady state value, whereas that of NO_2 grew to a steady state value in a monotonic manner. It was found that the excess amount of N_2O predicted by the stoichiometric reaction (3NO –> N_2O + NO_2) is evolved at the initial stage of the decomposition of NO, and that the steady state value of N_2O is precisely identical to that of NO_2. On the other hand, the partial pressure of N_2 overshot rapidly and disappeared within 4 min. When NO was fed over the catalyst previously treated in 4 vol.% NO for 3 min [Fig. 1 (2)], the amount of excess N_2O evolved at the initial stage of the second contact decreased apparently, and N_2 evolution almost disappeared. As shown in Fig. 1 (3)-(5), the amount of excess N_2O decreased with an increase in the time interval of NO pretreatment. When the catalyst had been pretreated in 4 vol.% NO for 60 min [Fig. 1 (6)], the excess N_2O was not detectable and the steady state values of N_2O and NO_2 were evolved immediately after the introduction of NO.

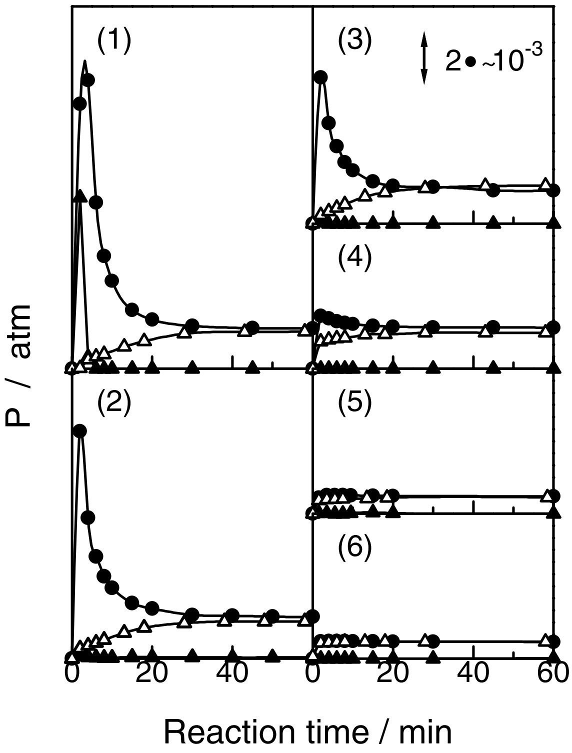

Fig. 1. Partial pressure of products in the effluent for the decomposition of 4 vol.% NO over Cu-Z-116 pretreated in a stream of 4 vol.% NO for various time intervals at 523 K. (1) 0 min, (2) 3 min, (3) 4 min, (4) 15 min, (5) 30 min, (6) 60 min (▲) N_2, (●) N_2O, (Δ) NO_2

In Fig. 2, the amount of N_2 and excess N_2O evolved at the second contact (shown in Fig. 1) are plotted by a dashed line against the time interval of the first contact (the pretreatment time) of 4 vol.% NO over the catalyst. In this figure, the sum of N_2 and excess N_2O evolved at the first and the second contacts are plotted by a solid line against the time interval of the first dose. It can be seen that the amount of N_2 and excess N_2O evolved at the second contact decreased with an increase in the time interval of the first dose, while the sum of N_2 and that of excess N_2O were truly constant, independently of any difference in the time interval of the first dose. When the experiments for the decomposition of N_2O were carried out at various NO partial pressures between 0.5 vol.% and 12 vol.%, the amounts of N_2 and N_2O evolved were constant above 2 vol.% NO. This finding strongly suggests that the active site for the formation of N_2 is occupied by the adsorbed species upon pretreatment in 4 vol.% NO for 4 min, and that the species adsorbed on the active site for the formation of N_2O attains the stationary state within 60 min upon pretreatment in 4 vol.% NO.

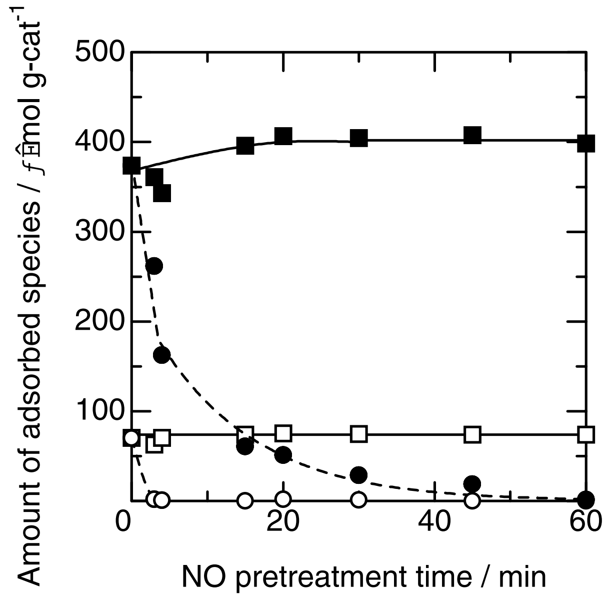

Fig. 2. Relationship between the amount of N_2 and excess N_2O evolved and the time interval of the first contact (the pretreatment time) of 4 vol.% NO with the catalyst. (○) N_2 evolved at second contact, (●) excess N_2O evolved at second contact, (□) total evolution of N_2, (■) total evolution of excess N_2O

Figure 3 (1), (2), (3), and (4) illustrate the TPD curves for the NO_x species adsorbed on Cu-Z with copper ion exchange levels of 116, 92, 72, and 57%, respectively. After attainment of a steady state of 4 vol.% NO decomposition over the catalysts at 523 K for 60 min, the stream of NO was switched to helium at the same temperature for 30 min then programmed heating was started from 523 K. When the 4 vol.% NO was switched to a helium stream, only NO desorbed from the catalyst, while various desorption peaks appeared at elevated temperatures. The desorption peaks of O_2, NO, and NO_2 were observed around 673 K. In our previous reports [9,10], it was shown by TPD and IR measurements that NO_3-type and/or NO_2-type adsorbed species were formed by the reaction between the adsorbed oxygen species and NO in the decomposition of NO and were desorbed independently at elevated temperatures as (NO + O_2) and/or NO_2, respectively.

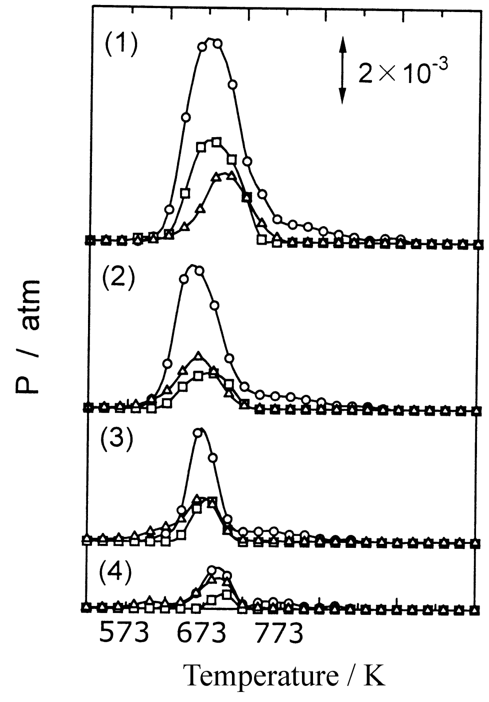

Fig. 3. TPD curves of the adsorbed species formed on Cu-Z in the decomposition of 4% NO at 523 K for 60 min (1) Cu-Z-116, (2) Cu-Z-92, (3) Cu-Z-72, (4) Cu-Z-57. (○) O_2, (□) NO, (Δ) NO_2

In the infrared spectra of NO_x species formed by the decomposition of 4 vol.% NO at 523 for 60 min on Cu-zeolite [9,10], absorptions ascribed to adsorbed NO_x-type species (1570, 1610, 1630 cm^{-1}) are observed. This suggests that NO_2-type and NO_3-type species adsorbed at the temperature of NO decomposition do occur. In the TPD experiment (Fig. 3), the peak area of O_2 desorbed at 673 K was much larger than that of NO appearing at the same temperature. This finding suggests that O_2 desorbed at 673 K is provided by both the decomposition of NO_3-type adsorbed species and the desorption of adsorbed oxygen species.

In conclusion, our results suggest that the N_2 produced is accompanied by the formation of NO_3-type adsorbed species in the decomposition of NO according to the reactions: $2NO \rightarrow N_2 + 2Os_1$ (1), $2Os_1 + NO \rightarrow NO_3s_1$ (2), while the N_2O produced is accompanied by the formation of both NO_2-type adsorbed species and adsorbed O species according to the following reactions at another site: $2NO \rightarrow N_2O + Os_2$ (3), $Os_2 + NO \rightarrow NO_2s_2$ (4), $NO_2s_2 \rightarrow NO_2 + s_2$ (5). The disproportionation of NO, $3NO \rightarrow N_2O + NO_2$ thus proceeded steadily over the N_2O formation site s_2, whereas the formation of N_2 was prevented by blocking the site s_1 by NO_3-type adsorbed species at temperatures below 523 K.

In order to verify the validity of the mechanism deduced from these equations, the amounts of evolved components at the initial stage of NO introduction were plotted against the amount of NO_x-type adsorbed species derived by TPD measurements. In Fig. 4 (1), the amount of NO_3-type adsorbed species is plotted against the amount of N_2 evolved at the initial stage of NO introduction over the catalysts treated in a stream of helium. The amount of NO_3-type adsorbed species was calculated on the basis of the amount of NO desorbed at 673 K. In Fig. 4 (2), the amounts of NO_2-type adsorbed species and adsorbed oxygen species are plotted against the amount of excess N_2O overshot at the initial stage of NO introduction over the catalysts treated in helium. The amount of adsorbed oxygen species corresponds to the difference of oxygen atoms desorbed at 673 K and the amount of oxygen atoms contained in the NO_3-type adsorbed species derived from the amount of NO desorbed at 673 K. In this figure, a black square indicates the sum of the amount of adsorbed oxygen species and the amount of NO_2-type adsorbed species, which correspond to net surface oxygen atoms formed during the disproportionation of NO over the catalyst. A good linear relationship is observed between the amounts of N_2 and N_2O evolved and the amounts of NO_3-type adsorbed species and surface oxygen atoms, respectively. These findings strongly suggest that the sites for the formation of NO_3-type and NO_2-type adsorbed species are identified as the sites for the formation of N_2 and N_2O, respectively.

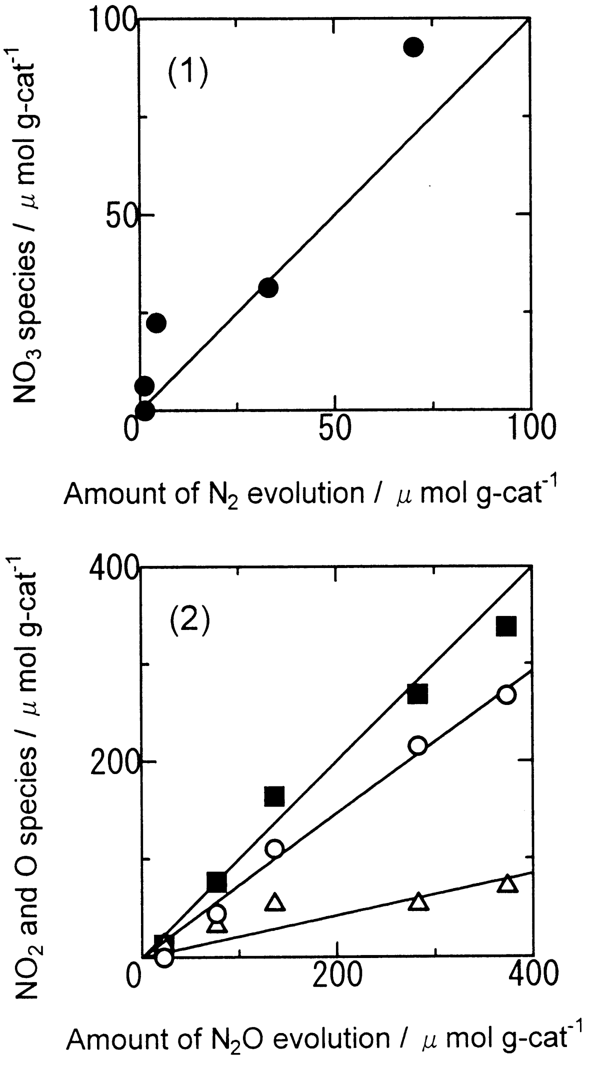

Fig. 4. (1) Relationship between the amount of NO_3-type adsorbed species and the amount of N_2 evolved at the initial stage of NO introduction over the catalysts treated in helium. (2) The relationship between the amounts of NO_2-type adsorbed species and adsorbed oxygen species and the amount of excess N_2O overshot at the initial stage of NO introduction over the catalysts treated in helium. (●) NO_3-type adsorbed species, (■) sum of NO_2-type adsorbed species and adsorbed oxygen species, (○) adsorbed oxygen species, (Δ) NO_2-type adsorbed species

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