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Evidence for the Role of Monovalent Copper Ions in the Photocatalytic N_2O Decomposition on Excessively Copper Ion-Containing ZSM-5 Zeolite

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Synopsis. The activity of the photocatalytic N_2O decomposition into N_2 and O_2 on a degassed Cu-containing ZSM-5 zeolite (percent exchange, 145%) corresponded well to the amount of monovalent copper (Cu^+) present on the Cu/ZSM-5, which was titrated by the irreversibly adsorbed CO at 273 K.

The decomposition of dinitrogen monoxide (N_2O) is an important reaction for reducing the grobal air pollution, because of its contributions to stratospheric ozone destruction and greenhouse effect. Recently, Li and Armor reported that one of the most active catalysts for N_2O decomposition is Cu-containing ZSM-5 zeolite (Cu/ZSM-5, Cu content=3.7wt%),[1] which is well known as an active catalyst for the thermal-[2,3] and photo-[4] decomposition of nitrogen monoxide. However, N_2O decomposition on the Cu/ZSM-5 requires a high reaction temperature (>573 K). We found that Cu/ZSM-5 acts as a photocatalyst for N_2O decomposition at 278 K.[5] In our previous paper[5] the role of monovalent copper ions (Cu^+) in the photocatalytic decomposition of N_2O on Cu/ZSM-5 was qualitatively suggested by the use of diffuse reflectance spectroscopy (DRS). In this communication, the authors wish to report on quantitative evidence which supports the important role of Cu^+ in the photocatalytic N_2O decomposition on Cu/ZSM-5 catalyst. The N_2O decomposition rates were measured on the Cu/ZSM-5 degassed at 583—823 K, since it has been reported that the amount of Cu^+ can be controlled by the degassing temperature of the Cu-ZSM-5 zeolite.[6] The amount of Cu^+ on the degassed Cu/ZSM-5 was volumetrically titrated by the irreversible adsorption of carbon monoxide (CO) at 273 K.

Experimental

Na-ZSM-5 (Si/Al=41), prepared by the procedure proposed by Yoshimura et al.,[7] was ion-exchanged at 353 K for 12 h in an aqueous $Cu(NO_3)_2$ solution of 0.1 equiv, washed with distilled water several times, and dried at 383 K for 24 h, followed by calcination at 773 K for 5 h. The content of copper in the Cu exchanged-ZSM-5 zeolite (Cu/ZSM-5), thus prepared, was analyzed to be 1.74wt% (percent exchanged, 145%) by atomic absorption spectrometry. The Cu/ZSM-5 was degassed ($<1.33\times10^{-2}$ Pa) at the desired temperature for 2 h prior to the reaction. The reaction of N_2O (99.8% purity) of 0.67 kPa diluted by 6.25 kPa of He was carried out at 278 K in a closed gas-circulating system. The detail reaction procedure has been described elsewhere.[5] The amount of irreversibly adsorbed CO at 273 K was determined from the difference between the first adsorption isotherm and the second isotherm obtained after degassing the CO covered-sample at 273 K. The CO adsorption isotherms on the sample exhibit a Langmuir-type adsorption.

Results and Discussion

The photocatalytic decomposition of N_2O into N_2 and O_2 at 278 K on degassed Cu/ZSM-5 was reported in a previous paper.[5] The characteristic feature of the N_2O photo-decomposition at 278 K is that the formation of O_2 observed in the gas phase is slower than N_2, but is preferential compared to thermal decomposition at 510 K on the same catalyst. The N_2 formation rate under the irradiation of Cu/ZSM-5 strongly depends on the degassing temperature of the catalyst. In Fig. 1a, the N_2 formation rate under irradiation is plotted as a function of the degassing temperature, showing an increase in the activity by increasing the degassing temperature of the catalyst. These N_2 formation rates were obtained under complete absorption of the irradiated light on the catalyst.

The amount of irreversibly adsorbed CO on the degassed sample is also plotted in Fig. 1b as a function of the degassing temperature. The number of irreversibly adsorbed CO per copper species in the catalyst (CO/Cu ratio) after degassing the sample at 823 K is 0.78. Since it has been well known that CO strongly adsorbs onto Cu^+,[8] the CO/Cu ratio corresponds to the fraction of Cu^+ in total copper ions in the Cu/ZSM-5. The curve shown in Fig. 1b indicates that Cu^+ ions are formed

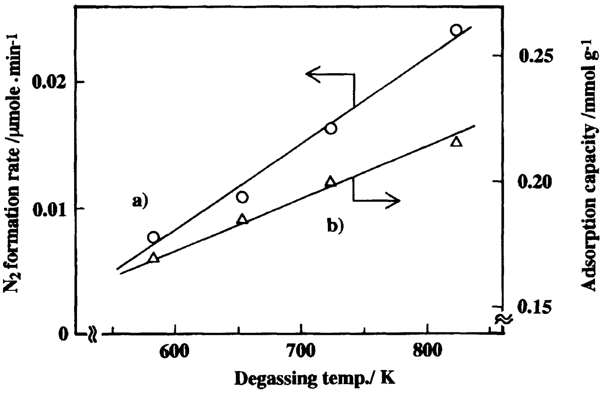

Fig. 1. Variations of (a) the N_2 formation rate under irradiation, and (b) the amount of irreversibly adsorbed CO at 273 K as a function of the degassing temperature of Cu/ZSM-5 (percent exchanges, 145%).

by the reduction of Cu^{2+} ions as the degassing temperature is increased. Centi et al.6) have already found a similar trend of Cu^+ formed on Cu/ZSM-5 by photoluminescence spectroscopy. The reduction of Cu^{2+} is also supported by the disappearance of the light-absorption band at around 700 nm, assigned to the d–d transition of octahedrally coordinated Cu^{2+},9) in diffuse reflectance spectroscopy (DRS), by the degassing of Cu/ZSM-5.5) The desorbed gas from the Cu/ZSM-5 during degassing was found to be H_2O by mass spectroscopy. The desorption of water (or hydroxyl groups and/or lattice oxygen ion, O^{2-}) from the site of Cu^{2+} might cause a reduction of Cu^{2+} into monovalent copper ions, Cu^+.

As clearly shown in Fig. 1, the dependences of the N_2 formation rate under irradiation, and the adsorption capacity of CO, or the CO/Cu ratio, on the degassing temperature are linearly correlated with each other, suggesting the important role of the monovalent copper ions of degassed Cu/ZSM-5 in the photocatalytic decomposition of N_2O. It has been shown that light of wavelength shorter than 300 nm was effective for the photocatalytic N_2O decomposition on the degassed Cu/ZSM-5.5) In addition, the DRS measurement of degassed Cu/ZSM-5 showed strong absorption around 300 nm, attributed to the electronic excitation of Cu^+ ions, $(3d^{10})^1S_0 \rightarrow (3d^9 4s^1)^1D_2$.10) It is, thus, interpreted that the electronic excitation of Cu^+ causes the N_2O decomposition. A similar role of the Cu^+ of Cu/SiO_2 in the NO photodecomposition has been proposed by Anpo et al.11)

It was found that the 83% copper-exchanged Cu/ZSM-5 catalyst degassed at 723 K, containing an amount of Cu^+ (CO/Cu ratio 0.89) smaller than the 145% copper-exchanged catalyst (CO/Cu ratio 0.78), showed N_2O decomposition activity (per Cu^+) of 70%, compared to the activity shown by the latter catalyst. This means that the monovalent copper ion present on excessively Cu ion-containing ZSM-5 shows a higher activity for the N_2O photodecomposition than dose the less Cu ion-containing ZSM-5. The reactivity and/or photochemical property of Cu^+ depends on the exchange degree of copper cations in the zeolite.

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