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Photocatalytic Decomposition of Nitrous Oxide on Cu Ion-Containing ZSM-5 Catalyst

The decomposition of nitrogen oxides (NO_x) is an important reaction in the reduction of global air pollution. Studies on the thermal- (*1, 2*) and photo- (*3, 4*) decomposition of nitric oxide (NO) into nitrogen and oxygen have been reported on Cu ion-containing zeolite catalysts such as Cu/ZSM-5 (*1–3*) and Cu/SiO_2 (*4*). Recently, Giamello *et al.* (*5*) have proposed the interaction of NO molecule with the Cu ion-exchanged ZSM-5 at room temperature, resulting in the reduction/oxidation of Cu ions through the nitrosylic adducts adsorbed on the Cu ions, by means of infrared and electron spin resonance spectroscopies.

In addition to the NO decomposition, the decomposition of nitrous oxide (N_2O) over various metal and oxide catalysts (*6–11*) has received much attention for its unique behavior as an oxidizing agent compared to conventional oxidizing agents, such as molecular oxygen in, for instance, benzene oxidation (*12, 13*), and its contributions to the stratospheric ozone destruction and greenhouse effect. However, the difficulty, in the catalytic removal of nitric oxide from the exhaust gas of engines, of the conversion of NO yielding an appreciable fraction of N_2O in the oxygen-rich condition has been pointed out. The thermal decomposition of N_2O requires high temperatures above 573 K (*14*) since molecular oxygen is not evolved because of its tight binding on the catalyst surface in N_2O decomposition below 573 K (*9*). Photodecomposition of N_2O has been also reported over semiconductors such as ZnO (*15, 16*) and TiO_2 anchored onto porous Vycor glass (PVG) (*17*). Over these photocatalysts, trapping of the photoformed electron by N_2O molecules to form N_2O^- ions is proposed to be a key process in N_2O photodecomposition. The N_2O^- ions have been directly detected by ESR, and its decomposition into N_2 and O^- ions has been reported by Anpo *et al.* (17). However, no evolution of gaseous oxygen molecule during N_2O photodecomposition has been reported except for the decomposition shown in the study by Tanaka and Blyholder over ZnO (*16*).

In the present article, the authors report the photocatalytic decomposition of N_2O into N_2 and O_2 at 278 K over a Cu ion-exchanged ZSM-5 catalyst. The mechanism of the N_2O photodecomposition is discussed on the basis of the N_2O photodecomposition rate dependence on the irradiated light wavelength and on the diffuse reflectance spectrum (DRS) of the Cu/ZSM-5 catalyst. The role of the electronic excitation of monovalent Cu ion (Cu^+) (*3, 4*) in the N_2O photodecomposition is emphasized.

Na–ZSM-5(Si/Al = 41), prepared by the procedure proposed by Yoshimura *et al.* (*18*), was ion-exchanged at 353 K for 12 h in an aqueous $Cu(NO_3)_2$ solution of 0.1 *N*, washed with distilled water for several times, and dried at 383 K for 24 h, followed by calcination at 773 K for 5 h. The content of Cu in the Cu-exchanged ZSM-5 zeolite thus prepared (Cu/ZSM-5) was analyzed to be 1.74 wt% (145% exchanged) by atomic absorption spectrometry. The XRD pattern of the Cu/ZSM-5 was identical to that of the parent Na–ZSM-5, and no peaks due to CuO were detected. These observations imply that the Cu ions are incorporated within the ZSM-5 cavities without formation of a large CuO crystal either in the pore structures or on the external surface of the zeolite, consistent with the report on the Cu ion

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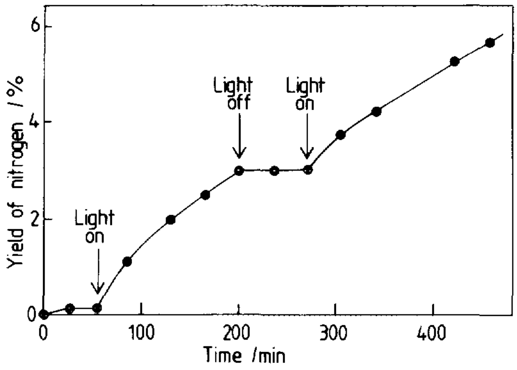

FIG. 1. The change of N_2 yield for the decomposition of N_2O at 278 K on the degassed Cu/ZSM-5 catalyst.

dispersion in a Cu ion-exchanged ZSM-5 zeolite by means of the X-ray absorption (XANES/EXAFS) spectroscopy (*19*).

The Cu/ZSM-5 was degassed ($<1 \times 10^{-4}$ Torr, 1 Torr = 133.3 Pa) at 723 K for 2 h prior to being used in the reaction. The products were analyzed by gas chromatography. The reaction of 20 Torr of N_2O (99.8% purity) diluted by 30 Torr of He was carried out at 278 K in the conventional closed gas-circulating system with a volume of 163 ml to which a quartz-made reactor with a bottom of a flat, transparent quartz plate was installed (*20*). The powdered Cu/ZSM-5 catalyst was spread on the bottom. The light was irradiated to the catalyst with a medium-pressure mercury lamp (H-400P, Toshiba Co., Ltd.) through a water filter. Various UV-cut filters (Toshiba, Co., Ltd.) were used to examine the irradiation wavelength efficient in the reaction.

The diffuse reflectance spectra (800–240 nm) were observed with a Shimadzu spectrophotometer (MPS-2000) at room temperature, using $BaSO_4$ as a reference material. The zeolite was ground carefully as the light scattering became as uniform as possible. For the DSR measurements, the ground sample was placed in a quartz cell with two planer windows (2 mm separation) and degassed at 723 K.

Figure 1 shows the change in the nitrogen yield for the N_2O decomposition at 278 K on the Cu/ZSM-5 powder degassed at 723 K. During the reaction in the dark, little nitrogen was formed. When the Cu/ZSM-5 was irradiated by the light of the Hg lamp through a water filter, the N_2 formation was initiated immediately and increased with irradiation time. As soon as the irradiation ceased, the N_2 formation immediately stopped also. The initial N_2O decomposition activity was reproduced when the catalyst was again irradiated. This response of the N_2O decomposition activity to the irradiation strongly indicates that the photoinduced N_2O decomposition occurs on the Cu/ZSM-5 powder. About two nitrogen molecules per Cu atom of the catalyst formed after 450 min, obviously indicating that the photoinduced N_2O decomposition on the Cu/ZSM-5 occurs catalytically at 278 K.

The N_2/O_2 ratio in the photocatalytic decomposition product was in the range from 4 to 5 at the initial stage of the reaction (<200 min) and gradually decreased to 3 with an increase in reaction time. The N_2/O_2 ratio observed is larger than that in the stoichiometry of 2 ($N_2O \rightarrow N_2 + \frac{1}{2}O_2$, $N_2/O_2 = 2$), but smaller than the ratio found for the N_2O thermal decomposition on the Cu/ZSM-5 catalyst at 473 K (*21*).

When the Cu/ZSM-5 was irradiated through UV-cut filters, UV-34, UV-32, and UV-30 (*22*), no N_2O decomposition was occurring. With the UV-28 filter, however, the N_2O decomposition proceeded with the rate of 15% of that without the UV-cut filter. This implies that the light of wavelength shorter than 300 nm was effective for the N_2O photodecomposition on the Cu/ZSM-5.

The Cu/ZSM-5 degassed at 723 K showed a strong absorption band at around 240–400 nm with the absorption maximum at 270–280 nm on its diffuse reflectance spectrum (Fig. 2b). This absorption band corresponds to the $(3d^{10})^1S_0 \rightarrow (3d^94s^1)^1D_2$ electronic transition of Cu^+ ions in zeolite cavities (*23*) of the absorption band 322–227 nm. Therefore, it is suggested that the excitation of the Cu^+ ions causes the N_2O photodecomposition.

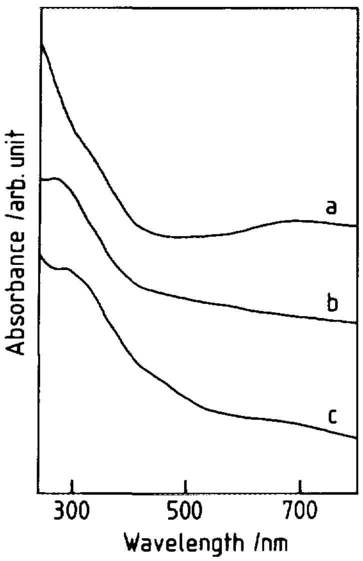

FIG. 2. The diffuse reflectance spectra of Cu/ZSM-5 catalyst (a) after treatment with O_2 (100 Torr) at 673 K and degassed at room temperature, (b) after degassing at 723 K for 2 h, (c) (b) plus irradiation at 278 K for 6 min in the presence of N_2O (20 Torr).

The absorption around 700 nm (Fig. 2a), assigned to the *d–d* transition of octahedrally coordinated Cu^{2+} ions (*24, 25*), disappeared by the degassing at 723 K of the Cu/ZSM-5 (Fig. 2b). This disappearance is attributable to the partial reduction of the Cu^{2+} ions to low valence copper such as Cu^+ and/or Cu^0 as well as to the desorption of water (or OH groups and/or lattice O^{2-}) from the Cu^{2+} sites. The Cu/ZSM-5 treated by hydrogen (50 Torr) at 603 K followed by degassing at the same temperature gave a different diffuse reflectance spectrum from that obtained on the simply degassed Cu/ZSM-5. Therefore, it is plausible that the oxidation state of the copper in ZSM-5 after degassing at 723 K is not metallic Cu^0 but Cu^+. The Cu^{2+} ions in the ZSM-5 should be reduced to the Cu^+ ion during evacuation by releasing the oxygen molecule according to the mechanism suggested by Jacobs *et al.* (*26*).

It is, thus, interpreted that the N_2O photodecomposition on the Cu/ZSM-5 catalyst results from the electronic excitation of Cu^+ ions formed by degassing at 723 K, $(3d^{10})^1 S_0 \rightarrow (3d^9 4s^1)^1 D_2$. An electron transfer from the excited Cu^+ to the anti-bonding molecular orbital of N_2O must trigger the decomposition of the N_2O into a nitrogen and an adsorbed oxygen atom, O(a). A similar role of the excited Cu^+ ions has been proposed for the NO photodecomposition on Cu/ZSM-5 catalyst (*3, 4*). The N_2O photodecomposition on Cu/ZSM-5 seems to proceed faster than the NO photodecomposition on the similar catalyst reported in previous paper (*3*), which might correspond to the quantum yield (for N_2 formation) of N_2O molecule higher than that of NO molecule observed in Hg photosensitized decomposition (*27, 28*).

The formation of the molecular oxygen in the N_2O photocatalytic decomposition on Cu/ZSM-5 suggests that the recombination of the O(a), resulting in the desorption of oxygen molecules, is preferable under photoirradiation condition. The recovery of the octahedrally coordinated Cu^{2+} ion was scarcely detected on the diffuse reflectance spectrum of the Cu/ZSM-5 irradiated in the presence of 20 Torr N_2O (Fig. 2c). Therefore, it is concluded that the Cu^+ ion is reformed after the N_2O decomposition induced by the electronically excited Cu^+ ions and is enrolled in the photocatalysis. Further kinetic investigations are necessary to clarify the details of N_2O photodecomposition on Cu/ZSM-5.

REFERENCES

1. Iwamoto, M., Yahiro, H., Mine, Y., and Kagawa, S., *Chem. Lett.*, 213 (1989).
2. Li, Y., and Hall, W. K., *J. Catal.* **129**, 202 (1991).
3. Anpo, M., Shioya, Y., Nomura, T., Giamello, E., Morterra, C., Centi, G., and Che, M., *in* "Meeting Abstracts of Catalysis Society of Japan," Vol. 34, No. 2, p. 65. 1992; Anpo, M., Nomura, T., Shioya, Y., Che, M., Murphy, D., and Giamello, E., *in* "Proceedings, 10th International Congress on Catalysis, Budapest, 1992" (L. Guczi, Ed.).
4. Anpo, M., Nomura, T., Kitao, T., Giamello, E., Murphy, D., Che, M., and Fox, M. A., *Res. Chem. Intermed.* **15**, 225 (1991).
5. Giamello, E., Murphy, D., Magnacca, G., Mor-

terra, C., Shioya, Y., Nomura, T., and Anpo, M., *J. Catal.* **136,** 510 (1992).
6. Winter, E. S. R., *J. Catal.* **34,** 431 (1974).
7. Korodulis, C., Latsios, H., Lycourghiotis, A., and Pomonis, P., *J. Chem. Soc. Faraday Trans.* **86**(1), 185 (1990).
8. Christopher, J., and Swamy, C. S., *J. Mol. Catal.* **62,** 69 (1990).
9. Panov, G. I., Sobolev, V. I., and Kharitonov, A. S., *J. Mol. Catal.* **61,** 85 (1990).
10. Tan, S. A., Grant, R. B., and Lambert, R. M., *J. Catal.* **104,** 156 (1987).
11. Yong, Y.-S., and Cant, N., *J. Catal.* **122,** 22 (1990).
12. Iwamoto, M., Hirata, J., Matsukami, K., and Kagawa, S., *J. Phys. Chem.* **87,** 903 (1983).
13. Panov, G. I., Sheveleva, G. A., Kharitonov, A. S., Romannikov, V. N., and Vostrikova, V. A., *Appl. Catal. A: General* **82,** 31 (1992).
14. Li, Y., and Armor, J. N., *Appl. Catal. B* **1,** L21 (1992).
15. Conningham, J., Kelly, J. J., and Penny, A. L., *J. Phys. Chem.* **75,** 617 (1971).
16. Tanaka, K., and Blyholder, G., *J. Phys. Chem.* **75,** 1037 (1971).
17. Anpo, M., Aikawa, N., Kubokawa, Y., Che, M., Louis, C., and Giamello, E., *J. Phys. Chem.* **89,** 5017 (1985).
18. Yoshimura, A., Namba, S., and Yashima, T., *Shokubai* **23,** 232 (1981).
19. Hamada, H., Matsubayashi, N., Shimada, H., Kintaichi, Y., Ito, T., and Nishijima, A., *Catal. Lett.* **5,** 189 (1990).
20. Wada, Y., and Morikawa, A., *Bull. Chem. Soc. Jpn.* **60,** 3509 (1987).
21. Thermal decomposition of N_2O was carried out at 473 K on the same amount of the Cu/ZSM-5. The conversion was smaller than that for the photodecompostion and was saturated at 2.3% after 400 min.
22. The notation of the filters is after Toshiba Co. The number of filter denotes one-tenth of the wavelength (nm) at 50% reduction of the light intensity transmitted.
23. Texter, J., Strome, D. H., Herman, R. G., and Klier, K., *J. Phys. Chem.* **81,** 333 (1977).
24. Tominaga, H., Ono, Y., and Kei, T., *J. Catal.* **40,** 197 (1975).
25. Freeman, J. J., and Friedman, R. M., *J. Chem. Soc. Faraday Trans. I* **74,** 758 (1978).
26. Jacobs, P. A., De Wilde, W., Schoonheydt, R. A., Uytterhoeven, J. B., and Beyer, H., *J. Chem. Soc. Faraday Trans. I* **72,** 1221 (1976).
27. Cvetanović, R. J., *J. Chem. Phys.* **23,** 1203 (1955).
28. Strausz, O. P., and Gunning, H. E., *Can. J. Chem.* **39,** 2549 (1961).

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