Photocatalytic Decomposition of N_2O into N_2 and O_2 on the Silver(I) Ion-Exchanged ZSM-5 Catalyst

Masaya Matsuoka, Woo-Sung Ju, and Masakazu Anpo*
Department of Applied Chemistry, College of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531

(Received March 8, 2000; CL-000232)

Ag^+/ZSM-5 catalysts were prepared by an ion-exchange method. UV-irradiation of the Ag^+/ZSM-5 catalysts in the presence of N_2O led to the photocatalytic decomposition of N_2O into N_2 and O_2 at 298 K. Investigations of the effective wavelength of the irradiated UV-light for the reaction as well as the in-situ characterization of the catalysts by means of UV-Vis, photoluminescence and FT-IR spectroscopies revealed that the photoexcitation of the Ag^+-N_2O complexes formed between gaseous N_2O and the isolated Ag^+ ions exchanged within the zeolite cavities play a significant role in the reaction.

Recently, the design and development of efficient catalytic processes for the decomposition of nitrous oxide (N_2O) are urgently desired due to the serious effects of N_2O leading to the greenhouse effect and the destruction of the ozonosphere. So far, transition metal-exchanged pentasil-zeolites such as Co,[1] Fe,[2] Cu,[1,3] and Pr[4] ion-exchanged ZSM-5 have been reported to act as efficient thermal catalysts[1,2] and photocatalysts[3,4] for the decomposition of N_2O. Furthermore, silver(I) ion-exchanged zeolites (Ag/zeolites) exhibit unique and high catalytic reactivities for DeNOx reactions such as the selective catalytic reduction (SCR) of NOx with hydrocarbons[5,6] or dimethyl ether,[7] and the direct photocatalytic decomposition of NO.[8] However, the reactivity of Ag/zeolites with gaseous N_2O, especially the interaction of the Ag species included within zeolites with N_2O under UV-irradiation have not yet been fully investigated. In the present work, highly dispersed Ag(I) (Ag^+) ion catalysts were prepared within the ZSM-5 zeolite by an ion-exchange method and the local structure of the Ag^+ ion as well as its photocatalytic reactivity for the decomposition of N_2O at 298 K have been investigated by in-situ UV-Vis, photoluminescence, and FT-IR techniques, along with an analysis of the reaction products.

The Ag^+/ZSM-5 catalysts (Ag^+/ZSM-5(1.4): 1.4 wt% as Ag metal, 10 % exchanged; Ag^+/ZSM-5(2.9): 2.9 wt%, 20 % exchanged) (SiO_2:Al_2O_3 mole ratio = 23.3) were prepared by an ion-exchange method with an aqueous $AgNO_3$ solution. The Ag^0/ZSM-5(2.9) was prepared by heating Ag^+/ZSM-5(2.9) at 673 K in the presence of a $NH_3/H_2/H_2O$ mixture at a total pressure of 30 Torr. Prior to measurements of the spectra and photocatalytic reactivity, the Ag/ZSM-5 catalysts were heated in air at 673 K, degassed at the same temperature, then heated in 20 Torr of O_2 at 673 K and finally degassed at 473 K. Cu^+/ZSM-5(1.6) (1.6 wt % as Cu metal, 19 % exchanged) was prepared by the evacuation of the Cu^{2+}/ZSM-5 at 973 K.[9] Photocatalytic reactions were carried out at 298 K using a high pressure Hg lamp through a water filter. A UV cut filter ($\lambda > 250$ nm) was used to examine the effect of the irradiation wavelength upon the reaction. The reaction products were analyzed by gas chromatography and mass-spectrometry.

Figure 1 (a), (b) and (c) show the UV-Vis spectra of Ag^+/ZSM-5(1.4), Ag^+/ZSM-5(2.9) and H^+/ZSM-5, respectively. H^+/ZSM-5 exhibits a weak absorption band in wavelength regions shorter than 250 nm. On the other hand, the Ag^+/ZSM-5 catalysts exhibited an intense UV absorption band at around 190 nm which is attributed to the $4d^{10} \rightarrow 4d^9 5s^1$ intraionic electronic transition on the isolated Ag^+ ions,[10,11] and the intensity of the band increases with the increase in the Ag loading. The Ag^+/ZSM-5 catalysts do not exhibit specific absorption bands due to the Ag^0 atoms nor due to the formation of $Ag_n{}^0$ and $Ag_m{}^{n+}$ clusters in wavelength regions longer than 250 nm,[12,13] showing that the isolated Ag^+ ions are the main silver component within the ZSM-5 zeolite. As shown in Figure 1 (d), Ag^0/ZSM-5(2.9) exhibits no intense absorption band at around 190 nm, while the broad absorption band due to the $Ag_n{}^0$ and $Ag_m{}^{n+}$ clusters appear in wavelength regions above 250 nm, indicating that the reduction and aggregation of Ag^+ ions have occurred.

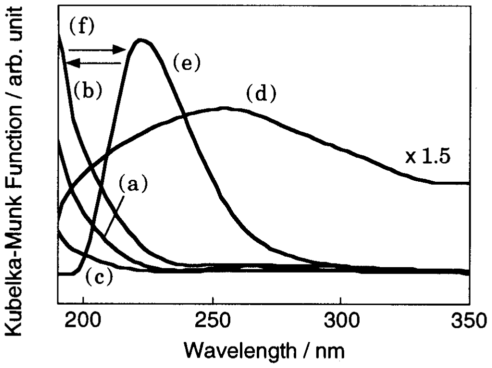

Figure 1. UV-Vis spectra of the Ag^+/ZSM-5(1.4) (a), Ag^+/ZSM-5 (2.9) (b), H^+/ZSM-5 (c), Ag^0/ZSM-5(2.9) (d) and the effect of the addition of N_2O on the UV-Vis spectrum of the Ag^+/ZSM-5(2.9) (e), (f). (e) addition of N_2O : 1 Torr, (f) after the degassing of N_2O at 298 K.

The interaction of N_2O with the Ag^+ ions was investigated by means of in-situ UV-Vis, FT-IR and photoluminescence measurements. As shown in Figure 1 (e), the addition of 1 Torr of N_2O onto the Ag^+ /ZSM-5(2.9) leads to a shift in the UV absorption band of the isolated Ag^+ ion at around 190 nm toward longer wavelength regions of 220 nm, while the evacuation of the system at 298 K leads to the complete restoration of the original absorption band. This indicates that the addition of N_2O results in the formation of an Ag^+–N_2O complex, while the adsorption of N_2O on Ag^+ is weak and reversible. The peak position of the absorption band of the Ag^+–N_2O complex is similar to that observed for the $AgNO_3$ aqueous solution (220 nm), indicating that the absorption band is characterized by the intraionic electronic transition of Ag^+ ($4d^{10} \rightarrow 4d^9 5s^1$),[10] the shift of the absorption band being caused by the change in the coordination sphere of the isolated Ag^+ by the adsorption of N_2O.[10] On the other hand, in the presence of 1 Torr of N_2O, the Ag^+ ZSM-5 catalysts exhibited a specific FT-IR band at 2251 cm^{-1} assigned to the asymmetric stretching mode of adsorbed N_2O,[14] whereas the position of the band (2251 cm^{-1}) is quite different from that of the N_2O species adsorbed onto H^+/ZSM-5 (2227 cm^{-1}) or Ag^0/ZSM-5 (2220 cm^{-1}). The intensity of the band at 2251 cm^{-1} increases with an increase in the Ag loading and the evacuation of N_2O at 298 K led to the complete disappearance of the band, indicating that N_2O adsorbs onto Ag^+ ion reversibly.

As shown in Figure 2 (a), the Ag^+/ZSM-5 catalysts exhibit a photoluminescence at around 336 nm upon excitation at around 200–220 nm. The absorption band and photoluminescence spectrum are attributed to the electronic transition $4d^{10} \rightarrow 4d^9 5s^1$ of the Ag^+ ion and its reverse radiative deactivation process $4d^9 5s^1 \rightarrow 4d^{10}$, respectively.[8,10] As can also be seen in Figure 2, the addition of N_2O onto Ag^+/ZSM-5 led to an efficient decrease in the photoluminescence yields, while the degassing of N_2O after the disappearance of the photoluminescence led to an almost complete recovery of the photoluminescence to its original intensity level. These results indicate that almost all of the isolated Ag^+ moieties within the zeolite cavities can interact with N_2O reversibly to form Ag^+-N_2O complexes.

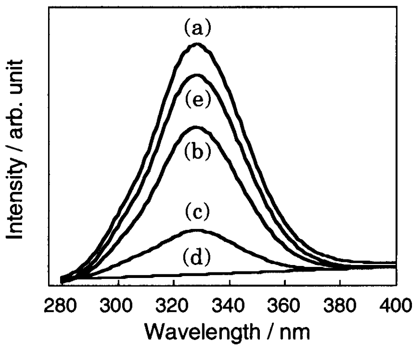

Figure 2. Effect of the addition of N_2O on the photoluminescence spectrum of Ag^+/ZSM-5(2.9) measured at 298 K.
N_2O pressure (in Torr): (a) 0.0, (b) 0.5, (c) 1.0, (d) 5.0, (e) after the degassing of N_2O at 298 K.

Figure 3 shows the reaction profiles of the photocatalytic decomposition of N_2O on Ag^+/ZSM-5(2.9) and Ag^0/ZSM-5(2.9) at 298 K. UV-irradiation of Ag^+/ZSM-5(2.9) in the presence of 1 Torr of N_2O at 298 K leads to the efficient formation of N_2 and O_2 (N_2/O_2=3). The yields of N_2 and O_2 increase with a good linearity against the UV-irradiation time, while under dark conditions these formations could not be detected. The value of the yield of the photo-formed N_2 molecules per total number of Ag^+ ions included in the catalyst exceeded 2.0 after prolonged UV irradiation, and even after this time, the decomposition of N_2O proceeded linearly with the UV- irradiation time, indicating that the reaction proceeds photocatalytically. On the other hand, only a small amount of N_2 was observed on Ag^0/ZSM-5(2.9). These results clearly indicate that Ag^+ ions play a significant role in the photocatalytic decomposition of N_2O. Under UV-irradiation of the catalyst through an UV-25 filter (λ > 250 nm), the photocatalytic decomposition of N_2O proceeded at 4 % of the rate under the full arc of the high pressure mercury lamp. This indicates that the UV-light effective for the reaction lies in wavelength regions of 200–250 nm where the UV absorption band of the Ag^+-N_2O complex exists. These results suggest that the photocatalytic decomposition of N_2O on the Ag^+/ZSM-5 proceeds through the photoexcitation of Ag^+-N_2O complexes. As shown in Figure 3, Ag^+/ZSM-5(2.9) shows higher photocatalytic reactivity as compared with Cu^+/ZSM-5(1.6), and the N_2/O_2 ratios of the reaction products are lower for Ag^+/ZSM-5. These results can be attributed to the fact that the Ag^+ ions more easily desorb the oxygen atoms which is formed during the photocatalytic reaction and in equilibrium with O_2 in the gas phase as compared to the Cu^+ ions.[3]

From these findings, it was concluded that the Ag^+ ions are exchanged within the ZSM-5 zeolite in an isolated state by the ion-exchange method, and the thus formed Ag^+ ions form Ag^+-N_2O complexes in the presence of N_2O, the complexes acting as the reaction precursors for the photocatalytic decomposition of N_2O at 298 K. In-situ UV-Vis, FT-IR and photoluminescence investigations elucidated the significant role the photoexcitation of the absorption band of the Ag^+-N_2O complexes, characterized by the intraionic electronic transition of Ag^+ ion ($4d^{10} \rightarrow 4d^9 5s^1$), plays in the reaction. A detailed study of the mechanisms behind the photocatalytic decomposition of N_2O is being carried out and will be the subject of our future work.

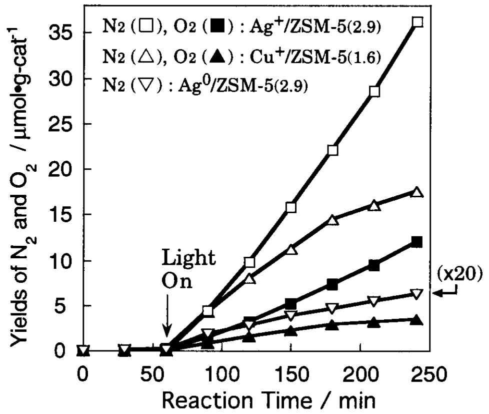

Figure 3. Reaction time profiles of the photocatalytic decomposition of N_2O into N_2 and O_2 on the Ag^+/ZSM-5(2.9), Ag^0/ZSM-5(2.9) and Cu^+/ZSM-5(1.6).

References

1 Y. Li and J. N. Armor, *Appl. Catal. B*, **1**, 21 (1992).
2 K. Yamada, C. Pophal, and K. Segawa, *Micropor. Mesopor. Mater.*, **21**, 549 (1998).
3 K. Ebitani, M. Morokuma, J. H. Kim, and A. Morikawa, *J. Chem. Soc., Faraday Trans.*, **90**, 377 (1994).
4 K. Ebitani, Y. Hirano, and A. Morikawa, *J. Catal.*, **157**, 262 (1995).
5 S. Sato, Y. Yu-u, H. Yahiro, N. Mizuno, and M. Iwamoto, *Appl. Catal.*, **70**, L1 (1991).
6 Z. Li and M. Flytzani-Stephanopoulos, *J. Catal.*, **182**, 313 (1999).
7 K. Masuda, K. Shinoda, T. Kato, and K. Tsujimura, *Appl. Catal. B*, **15**, 29 (1998).
8 M. Matsuoka, E. Matsuda, K. Tsuji, H. Yamashita, and M. Anpo, *J. Mol. Catal.*, **107**, 399 (1996).
9 H. Yamashita, M. Matsuoka, K. Tsuji, Y. Shioya, M. Anpo, and M. Che, *J. Phys. Chem.*, **100**, 397 (1996).
10 J. Texter, T. Gonsiorowski, and R. Kellerman, *Phys. Rev. B*, **23**, 4407 (1981).
11 J. Texter, R. Kellerman, and T. Gonsiorowski, *J. Phys. Chem.*, **90,** 2118 (1986).
12 G. A. Ozin and H. Huber, *Inorg. Chem.*, **17,** 155 (1978).
13 G. A. Ozin, F. Hugues, S. M. Matter, and D. F. McIntosh, *J. Phys.Chem.*, **87**, 3445 (1983).
14 W. Zhang, M. Jia, J. Yu, T. Wu, H. Yahiro, and M. Iwamoto, *Chem. Mater.*, **11**, 920 (1999).