Investigations on the local structure of Ag^+/ZSM-5 catalysts and their photocatalytic reactivities for the decomposition of N_2O at 298 K

Masaya Matsuoka, Woo–Sung Ju,
Hiromi Yamashita and Masakazu Anpo*

Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan.
E-mail: anpo@chem.osakafu-u.ac.jp

Ag^+/ZSM-5 catalysts were prepared by an ion-exchange method and UV-irradiation of the 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 on the effective wavelength of irradiated UV-light for the reaction as well as the in-situ characterization of the catalysts by means of XAFS, 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 play a significant role in this reaction.

Keywords: Photocatalysis, N_2O decomposition, Ag^+, ZSM-5, XAFS, UV-Vis, Photoluminescence, FT-IR

1. Introduction

It has been reported that silver(I) ion-exchanged zeolites (Ag^+/zeolites) exhibit unique and high catalytic reactivities for DeNOx reactions such as the selective catalytic reduction of NOx with hydrocarbons (Sato *et al.*, 1991; Li *et al.*, 1999) or dimethylether (Masuda *et al.*, 1998) and the direct photocatalytic decomposition of NO (Matsuoka *et al.*, 1996). However, the reactivity of Ag^+/zeolites with gaseous N_2O has not yet been fully investigated. In the present work, highly dispersed Ag^+ ion catalysts were prepared within the ZSM-5 zeolite by an ion-exchange method and the local structure of the Ag^+ ions as well as their photocatalytic reactivity for the decomposition of N_2O at 298 K have been investigated by in-situ XAFS, UV-Vis, photoluminescence, and FT-IR techniques, along with an analysis of the reaction products.

2. Experimental

Ag^+/ZSM-5 catalysts (Ag^+/ZSM-5(1.4): 1.4 wt% as Ag metal, Ag^+/ZSM-5(2.9): 2.9 wt%) (SiO_2:Al_2O_3 mole ratio = 23.3 : 1) were prepared by an ion-exchange method with an aqueous $AgNO_3$ solution. 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. The Ag K-edge XAFS spectra were obtained at the BL01B1 facility of SPring-8 in the transmission mode at 298 K under vacuum without exposing in air after pretreatment. The cell made of quartz having furnace section, stopcock and kapton windows was used for the in-situ XAFS measurements. Si(311) monochromator was used to monochromatize the X-rays from the 8 GeV electron storage ring. Photon energy was calibrated by edge position in the K-edge absorption spectrum of Ag foil. The normalized spectra were obtained by procedures described in previous papers (Tanaka *et al.*, 1988), and the Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range of 3-10 $Å^{-1}$. The curve fitting of the EXAFS data was carried out by employing the iterative nonlinear least-squares method of Levernberg (Tanaka *et al.*, 1988) and the empirical backscattering parameter sets extracted from the shell features of silver compounds. Photocatalytic reactions were carried out at 298 K using a high pressure Hg lamp through a water filter. An 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.

3. Results and discussion

Figure 1 (a) and (b) show the UV-Vis spectra of Ag^+/ZSM-5 (1.4) and Ag^+/ZSM-5(2.9), respectively. H^+/ZSM-5 exhibits a rather 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 can be attributed to the $4d^{10}\rightarrow 4d^9 5s^1$ intraionic electronic transition on the isolated Ag^+ ions (Texter *et al.*, 1981), while the intensity of the band increases with an increase in the Ag loading. It was found that these 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 (Ozin *et al.*, 1983), showing that the isolated Ag^+ ions are the main silver component within the ZSM-5 zeolite.

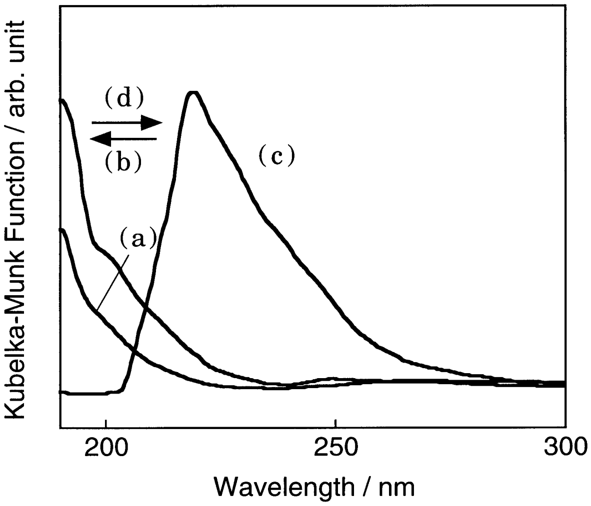

Figure 1
UV-Vis spectra of the Ag^+/ZSM-5(1.4) (a), Ag^+/ZSM-5(2.9) (b), and the effect of the addition of N_2O on the UV-Vis spectrum of the Ag^+/ZSM-5 (2.9) (c), (d).
(c) addition of N_2O : 1 Torr, (d) after the degassing of N_2O at 298 K.

Figure 2 shows the XANES and FT-EXAFS (Fourier transformed EXAFS) spectra of the catalysts together with those of Ag foil and Ag_2O. XANES spectra of the Ag foil and bulk Ag_2O exhibit several well-defined bands (A) due to multiple scattering at around 25530-25540 eV and other bands arising from continuum resonances involving a multiple scattering effect in the region above 25550 eV, while the contribution of these bands are significantly small in the XANES spectra of the Ag^+/ZSM-5 catalysts. This implies that silver ions are anchored within the micropores of the ZSM-5 zeolite in a highly dispersed state without forming a large cluster of Ag metal or Ag_2O.

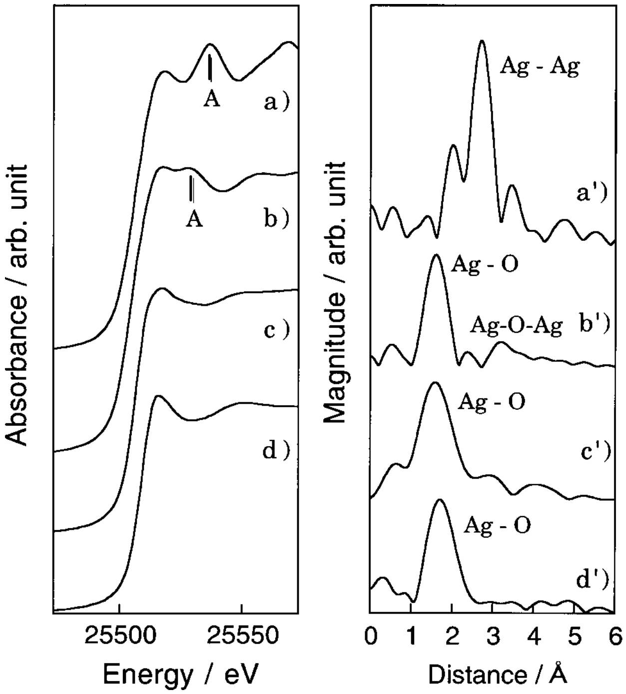

Figure 2
XANES (a-d) and FT-EXAFS (a'-d') spectra of Ag foil (a, a'), Ag_2O (b, b'), Ag^+/ZSM-5(2.9) (c, c') and Ag^+/ZSM-5(1.4) (d, d').

In the FT-EXAFS spectrum of Ag^+/ZSM-5(1.4), only a single peak due to the neighboring oxygen atom (Ag-O) can be observed but no peak due to the neighboring Ag atoms (Ag-Ag, Ag-O-Ag) could be observed, showing that Ag ions exist in an isolated state in ZSM-5. In the FT-EXAFS spectrum of Ag^+/ZSM-5(2.9), a peak due to the Ag-Ag scattering can be observed at around 3 Å (phase shift is not corrected), while the intensity of the peak is quite weak as compared to that of Ag foil. This indicates that highly dispersed Ag ion is the major species in the Ag^+/ZSM-5(2.9) although small amount of aggregated Ag species can be seen in this sample with higher Ag loading. The curve fitting analysis of the Ag-O peak of the EXAFS spectrum of Ag^+/ZSM-5(1.4) indicates that Ag^+ ions exist in a 2-coordinate sphere, i. e., with a coordination number (Ag-O) of 1.9, atomic distance of 2.15Å and Debye-Waller factor of 0.009 $Å^2$.

The interaction of N_2O with the Ag^+ ions was investigated by means of in-situ UV-Vis, FT-IR and photoluminescence measurements. The addition of 1 Torr of N_2O onto the Ag^+/ZSM-5(2.9) led to a shift in the UV absorption band of the isolated Ag^+ ions at around 190 nm toward longer wavelength regions of 220 nm, while the evacuation of the system at 298 K led to the complete recovery of the original absorption band, as shown in Fig. 1 (c). 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. 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 the adsorbed N_2O (Zhang *et al.*, 1999), 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 the Ag^+ ion reversibly.

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 (Texter *et al.*, 1981). 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 the 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.

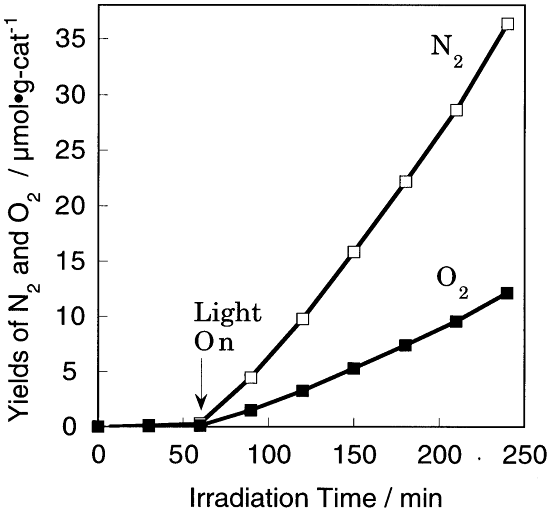

Figure 3
Reaction time profiles of the photocatalytic decomposition of N_2O into N_2 and O_2 at 298K on Ag^+/ZSM-5(2.9).

Figure 3 shows the reaction profiles of the photocatalytic decomposition of N_2O on Ag^+/ZSM-5(2.9). 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, no formation of N_2 could be observed on H^+/ZSM-5. 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 ($\lambda > 250$ 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 the wavelength regions of 200-250 nm where the UV absorption band of the Ag^+-N_2O complex exists. These results show that the photocatalytic decomposition of N_2O on the Ag^+/ZSM-5 proceeds through the photoexcitation of Ag^+-N_2O complexes.

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 plays in the reaction. A detailed study of the mechanisms behind the photocatalytic decomposition of N_2O is presently being carried out and will be the subject of our future work.

References

Li, Z. & Flytzani-Stephanopoulos, M. (1999). *J. Catal.* **182**, 313-327.

Masuda, K., Shinoda, K., Kato, T. & Tsujimura, K.(1998). *Appl. Catal. B* **15**, 29-35.

Matsuoka, M., Matsuda, E., Tsuji, K., Yamashita, H. & Anpo, M. (1996). *J. Mol. Catal*. **107**, 399-403.

Ozin, G. A., Hugues, F. , Matter, S. M. & McIntosh, D. F. (1983). *J. Phys. Chem.* **87**, 3445-3450.

Sato, S., Yu-u, Y., Yahiro, H., Mizuno, N. & Iwamoto, M. (1991). *Appl. Catal*. **70**, L1.

Tanaka, T., Yamashita, H., Tsuchitani, R., Funabiki, T. & Yoshida, S. (1988). *J. Chem. Soc., Faraday Trans. 1* **84**, 2987-2999.

Texter, J., Gonsiorowski, T. & Kellerman, R. (1981). *Phys. Rev. B* **23**, 4407-4418.

Zhang, W., Jia, M., Yu, J., Wu, T., Yahiro, H. & Iwamoto, M. (1999). *Chem. Mater*. **11**, 920-923.

Received 31 July 2000 • Accepted 4 October 2000