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In situ characterization of the Ag^+ ion-exchanged zeolites and their photocatalytic activity for the decomposition of N_2O into N_2 and O_2 at 298 K

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Abstract

Ag^+ ion-exchanged zeolites (Ag^+/ZSM-5, Ag^+/Y) were prepared by an ion-exchange method. XAFS measurements showed that Ag^+ ion exists in a two-coordinate sphere within the pore structure of ZSM-5, while aggregated Ag species ($Ag_n{}^0$ or $Ag_m{}^{n+}$ clusters) are formed within Y-zeolite. It was found that photocatalytic decomposition reaction of N_2O into N_2 and O_2 at 298 K proceeds much efficiently on Ag^+/ZSM-5 as compared to Ag^+/Y. In situ UV-Vis, photoluminescence and FT-IR investigations revealed that N_2O adsorbs onto the isolated Ag^+ ion to form Ag^+–N_2O adduct within ZSM-5, and the photoexcitation of thus formed Ag^+–N_2O adduct is the most important step of the photocatalytic decomposition reaction of N_2O.

Keywords: Photocatalysis; N_2O decomposition; Ag^+; Zeolites

1. Introduction

Among ion-exchanged zeolites, Ag^+ ion-exchanged zeolites (Ag^+/zeolites) are quite unique materials since they exhibit high activities for various photochemical reactions such as photochemical/thermal cleavage of water into H_2 and O_2 [1], photo-oxygen production from water [2], photo-dimerization of alkanes [3], and photocatalytic decomposition of NO [4,5]. Ag^+/zeolites also act as efficient thermal catalysts for the deNO$_x$ reactions such as the selective catalytic reduction (SCR) of NO$_x$ with hydrocarbon [6,7] or dimethylether [8]. However, the reactivity of Ag^+/zeolites with gaseous N_2O, especially their interactions with N_2O in their photoexcited states has not yet been fully investigated. In the present work, highly dispersed Ag^+ ion catalysts were prepared within the cavities of ZSM-5 and Y-zeolite by an ion-exchange method and the local structure of the Ag^+ ions introduced 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.%, Ag^+/ZSM-5(2.9): 2.9 wt.% as Ag metal) (SiO_2:Al_2O_3 mole ratio = 23.3:1) and Ag^+/Y (Ag^+/Y(2.6): 2.6 wt.% as Ag metal) (SiO_2:Al_2O_3 mole ratio = 5.6:1) catalyst were prepared by an ion-exchange method with an aqueous $AgNO_3$ solution. Prior to measurements of the spectra and photocatalytic reactivities, the Ag^+/zeolite 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^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. In situ UV-Vis spectra were measured at 298 K using a double-beam digital spectrophotometer (Shimadzu UV-2200A). FT-IR spectra were recorded at 298 K with an FT-IR spectrometer (JASCO FT-IR 8500) using the self-supported wafers of the catalyst with a spectral resolution of 2 cm^{-1} in transmission mode. In situ photoluminescence spectra were recorded at 298 K with a spectrofluorophotometer (Spex Fluorolog III) using a quartz cell equipped with a stopcock allowing gas adsorption. 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

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kapton windows was used for the in situ XAFS measurements. Si(3 1 1) 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 [9], 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 [9] 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. A UV cut filter (UV-25: $\lambda > 250$ nm) was used to examine the effect of the irradiation wavelength upon the reaction. The reaction products were analyzed by gas chromatography.

3. Results and discussion

Fig. 1 shows the UV-Vis spectra of Ag^+/ZSM-5(1.4), Ag^+/ZSM-5(2.9), Ag^+/Y(2.6) and H^+/ZSM-5. 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 can be attributed to the $4d^{10} \rightarrow 4d^9 5s^1$ intraionic electronic transition on the isolated Ag^+ ions [10,11], 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 [12,13], showing that the isolated Ag^+ ions are the main silver component within the ZSM-5 zeolite. As shown in Fig. 1(d), Ag^+/Y(2.6) exhibits no absorption band at around 190 nm, while the broad absorption band due to $Ag_n{}^0$ and $Ag_m{}^{n+}$ clusters appear in wavelength regions above 250 nm, indicating that the reduction and aggregation of Ag^+ ions have occurred within Y-zeolite.

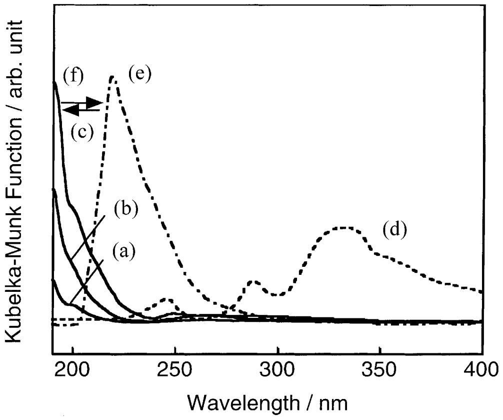

Fig. 1. UV-Vis spectra of the H^+/ZSM-5 (a), Ag^+/ZSM-5(1.4) (b), Ag^+/ZSM-5(2.9) (c), Ag^+/Y(2.6) (d) and the effect of the addition of N_2O on the UV-Vis spectrum of the Ag^+/ZSM-5(2.9) (e, f); (e) addition of N_2O: 133.3 Pa, (f) after the degassing of N_2O at 298 K.

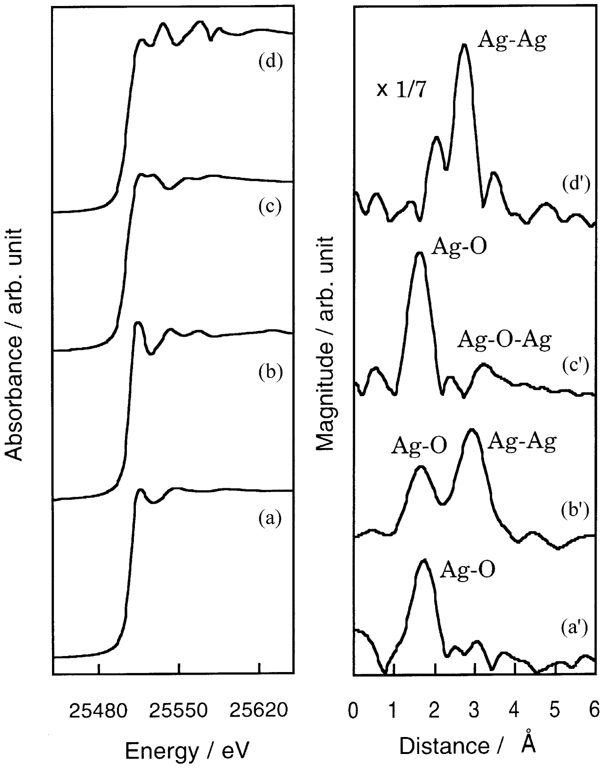

Fig. 2. XANES (a–d) and FT-EXAFS (a′–d′) spectra of Ag^+/ZSM-5(2.9) (a, a′), Ag^+/Y(2.6) (b, b′), Ag_2O (c, c′) and Ag foil (d, d′).

Fig. 2 shows the XANES and FT-EXAFS (Fourier transform of EXAFS) spectra of Ag^+/ZSM-5(2.9) and Ag^+/Y(2.6) catalysts together with those of Ag_2O and Ag foil. All FT-EXAFS data are given without corrections for phase shifts. Shapes and positions of the bands due to multiple scattering in XANES spectra of the Ag^+/ZSM-5(2.9) and Ag^+/Y(2.6) are quite different from those of Ag_2O and Ag foil, indicating that the large cluster of Ag_2O or Ag metal are not formed within zeolite cavities. In the FT-EXAFS of Ag^+/ZSM-5(2.9), only a single peak due to the neighboring oxygen atom (Ag–O) can be observed but no peak due to Ag–Ag bond could be observed, showing that large Ag metal clusters are not formed within ZSM-5. The curve fitting analysis of the Ag–O peak of the EXAFS spectrum of Ag^+/ZSM-5(2.9) indicates that Ag^+ ions exist in a two-coordinate sphere, i.e., with a coordination number (Ag–O) of 1.85, atomic distance of 2.16 Å and Debye–Waller factor of 0.009 $Å^2$ [14]. On the other hand, as shown in Fig. 2(b′), Ag^+/Y(2.6) exhibits an intense peak due to the Ag–Ag bond in addition to a peak due to the Ag–O bond, indicating that the aggregation of Ag^+ ion has occurred. It should be noted that Y-zeolite has a much higher density of the ion-exchangeable sites than ZSM-5 as a result of its lower SiO_2/Al_2O_3 ratio. The high density of the ion-exchangeable sites may allow the silver cations to exist so close to each other that they aggregate quite easily during the pretreatment of the catalyst, as reported in the case of Cu^+/Y-zeolite [15].

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 Fig. 1(e) and (f), the addition of 133.3 Pa 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. In the case of Ag^+/Y(2.6), such a spectral shift of the UV absorption band due to the aggregated Ag species was not observed in the presence of N_2O. This indicates that the added N_2O adsorbed onto the isolated Ag^+ ion to form an Ag^+–N_2O adduct, while the adsorption of N_2O on Ag^+ is weak and reversible.

As shown in Fig. 3, in the presence of 133.3 Pa 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 [16], 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}, peak intensity was around 70% of that observed for H^+/ZSM-5). The intensity of the band at 2251 cm^{-1} observed for Ag^+/ZSM-5 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 isolated Ag^+ ion reversibly. On the other hand, the addition of 133.3 Pa of N_2O on to the Ag^+/Y(2.6) does not lead to the appearance of any new band except for the peak due to N_2O adsorbed onto the H^+/Y (2239 cm^{-1}) with weak intensity, confirming that N_2O does not adsorb onto the aggregated silver species.

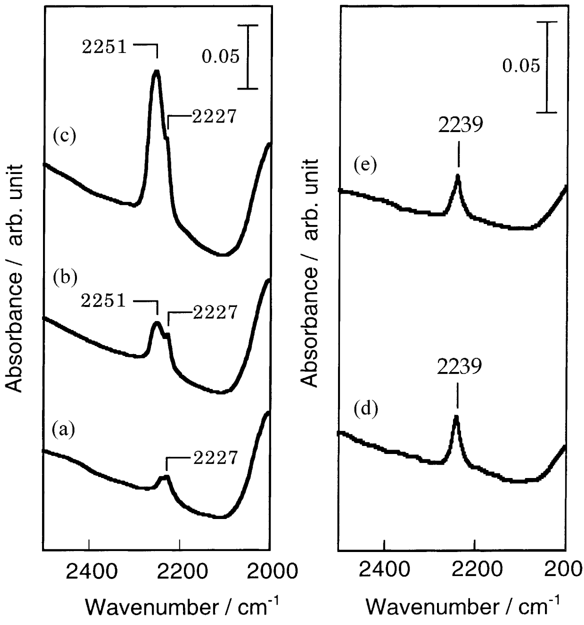

Fig. 3. FT-IR spectra of N_2O adsorbed on H^+/ZSM-5 (a), Ag^+/ZSM-5(1.4) (b), Ag^+/ZSM-5(2.9) (c), H^+/Y (d) and Ag^+/Y(2.6) (e) catalysts at 298 K. Added N_2O: 133.3 Pa.

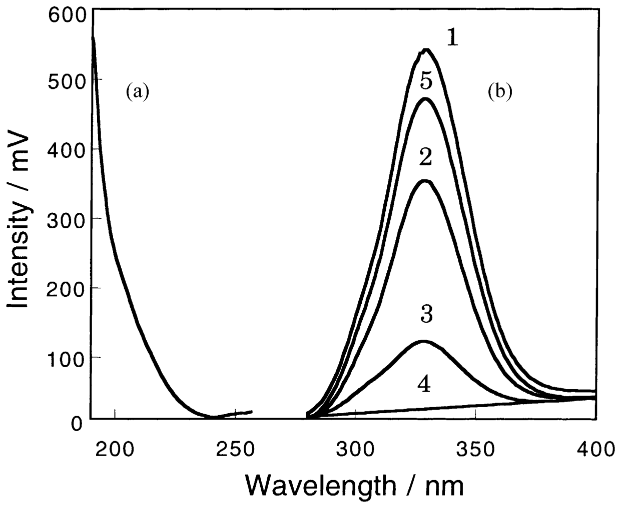

Fig. 4. Observed excitation (a) and photoluminescence (b) spectra of the Ag^+/ZSM-5(2.9) and the effect of the addition of N_2O on the photoluminescence. N_2O pressure (in Pa): (1) 0, (2) 66.7, (3) 133.3, (4) 666.5 (5) after the degassing of N_2O at 298 K.

As shown in Fig. 4, Ag^+/ZSM-5 catalysts exhibit a photoluminescence at around 336 nm upon excitation at around 190–230 nm. The absorption spectrum (excitation spectrum) and photoluminescence spectrum are attributed to the electronic transition $4d^{10} \rightarrow 4d^9 5s^1$ of the Ag^+ ion and its radiative deactivation process $4d^9 5s^1 \rightarrow 4d^{10}$, respectively [17,18]. 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 adducts.

Fig. 5 shows the reaction profiles of the photocatalytic decomposition of N_2O on Ag^+/ZSM-5(2.9) and Ag^+/Y(2.6). UV-irradiation of Ag^+/ZSM-5(2.9) in the presence of 133.3 Pa of N_2O at 298 K leads to the 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, evolution of small amount of N_2 and O_2 could be observed on Ag^+/Y(2.6). Furthermore, it was found that only a negligible formation of N_2 was observed on Ag^0/ZSM-5(2.9). These results clearly indicate that the existence of isolate Ag^+ ions as active species is crucial to proceed the photocatalytic decomposition of N_2O. Under UV-irradiation of the catalyst through

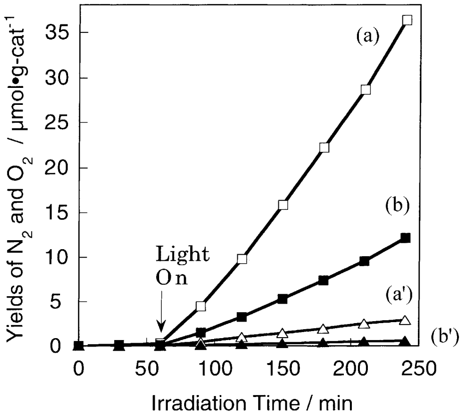

Fig. 5. Reaction time profiles of the photocatalytic decomposition of N_2O into N_2 (a, a′) and O_2 (b, b′) on Ag^+/ZSM-5(2.9) (a, b) and Ag^+/Y(2.6) (a′, b′) catalysts at 298 K.

a 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 adduct exists. These results show that the photocatalytic decomposition of N_2O on the Ag^+/ZSM-5 proceeds through the photoexcitation of Ag^+–N_2O adducts.

From these findings, it was concluded that the two-coordinate Ag^+ ions are exchanged within the ZSM-5 zeolite in an isolated state by the ion-exchange method, while within Y-zeolite, aggregated Ag species were formed. N_2O adsorb onto the isolated Ag^+ ions to form Ag^+–N_2O adducts in the presence of N_2O, the adducts 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 adducts 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.

4. Conclusions

In situ UV-Vis, photoluminescence, FT-IR and XAFS investigations of the Ag^+/zeolite catalysts indicated that two-coordinate isolated Ag^+ ions exist within the ZSM-5 zeolite cavities, which exhibit a photoluminescence spectrum at around 330 nm upon excitation at around 200 nm, while the aggregated Ag species ($Ag_n{}^0$ or $Ag_m{}^{n+}$ clusters) were formed within Y-zeolite. The added N_2O molecules reversibly adsorb on the isolated Ag^+ species, exhibiting a characteristic UV-Vis absorption band at 220 nm, as well as IR absorption peak at 2251 cm^{-1}. The photocatalytic decomposition of N_2O proceeds on the Ag^+/ZSM-5 catalysts to form N_2 and O_2 even at an ambient temperature. The investigations of the effective wavelengths of the irradiated UV light on the reaction indicated that photoexcitation of the absorption band of the Ag^+–N_2O adducts ($\lambda < 250$ nm) is the most important step of the photocatalytic decomposition reaction of N_2O.

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