The Photocatalytic Decomposition of Nitric Oxide on the Silver(I) Ion-exchanged ZSM-5 Catalyst

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UV irradiation of the Ag^+/ZSM-5 catalyst prepared by an ion-exchange method in the presence of NO led to the photocatalytic decomposition of NO into N_2, N_2O and NO_2 at temperatures as low as 298 K. Investigations of in-situ XANES, ESR, and DRS of the Ag^+/ZSM-5 catalyst as well as the effective wavelengths of the irradiated UV light indicated that the excited state of the Ag^+ ion included within the zeolite cavities plays a significant role in the photocatalytic decomposition of NO molecules.

Copper ion-exchanged zeolite catalysts (Cu/zeolite) have attracted a great deal of attention as potential catalysts for the direct decomposition of NO into N_2 and O_2.[1] We have reported that Cu^{2+} ions supported on ZSM-5 zeolite by an ion-exchange method are easily and selectively reduced to Cu^+ ions by an evacuation treatment at temperatures higher than 573 K and that the UV irradiation of the thus formed Cu^+/ZSM-5 catalysts[2] in the presence of NO leads to the photocatalytic decomposition of NO into N_2 and O_2 even at 275 K.

Silver ion-exchanged zeolites (Ag/zeolites) have been reported to show very high activity for the disproportionation of ethylbenzene,[3,4] photochemical / thermal cleavage of water to H_2 and O_2,[5] photo-oxygen production from water,[6] photo-dimerization of alkanes,[7] and the selective reduction of NO by ethylene at around 823K[8] or by ethanol at around 723K.[9] In the present work the remarkably efficient photocatalytic decomposition of NO has been undertaken on the Ag^+/ZSM-5 catalyst at 298 K and the characteristics of the photocatalyst have been investigated by in-situ X-ray absorption near edge structure (XANES), ESR, and diffuse reflectance spectrum (DRS) techniques.

The Ag^+/ZSM-5 zeolite catalyst (SiO_2:Al_2O_3 mole ratio = 23.3) was prepared by an ion-exchange method with an aqueous $Ag(NH_3)_2{}^+$ solution. Silver loading was determined as 6.7 wt% metal by an atomic absorption spectrometer. Prior to the measurements of the spectra and photocatalytic reactivity, the samples were treated with O_2 at 673 K, then degassed at 473 K. The Ag^0/ZSM-5 catalyst was prepared by heating the Ag^+/ZSM-5 in the presence of a mixture of 20 Torr (1 Torr = 133.3 Pa) of H_2 and H_2O at 673 K. Photocatalytic reactions were carried out upon 100 mg of the Ag^+/ZSM-5 and Cu^+/ZSM-5 catalyst 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. XANES spectra were obtained at the BL-10B facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba.

Figure 1 shows the reaction profiles of the formation of N_2 during the photoinduced decomposition of NO molecules on the Ag^+/ZSM-5 catalyst at 298 K. UV irradiation of the Ag^+/ZSM-5 catalyst in the presence of 10 Torr of NO at 298 K led to the formation of N_2, N_2O and NO_2. The formation of O_2 was not observed in the gas phase. As shown in Figure 1, the yield of N_2 increases with a good linearity against the UV irradiation time, while under dark conditions the formation of N_2 and N_2O were not detected. The value of the yield of the photo-formed N_2 molecules per total number of Ag^+ ions included in the catalyst exceeded 1.0 by UV irradiation of 6500 min., and even after this time the decomposition of NO proceeded linearly with the UV irradiation time, indicating that the reaction proceeds photocatalytically. On the Ag^0/ZSM-5 and H^+/ZSM-5 catalysts, only the minor formation of N_2 and N_2O was observed, but it was small and negligible compared with the yield of the reaction on the Ag^+/ZSM-5 catalyst under UV irradiation. These results clearly indicate that the Ag^+ ions play a significant role in the photocatalytic decomposition of NO molecules on the Ag^+/ZSM-5 catalyst. The rate of N_2 formation on the Ag^+/ZSM-5 catalyst is 10 times faster than on the Cu^+/ZSM-5 catalyst (1.9 wt% as Cu),[2] indicating that the photocatalytic decomposition of NO proceeds faster on the Ag^+ ions than on the Cu^+ ions. Under UV-irradiation of the catalyst through the UV-25 filter ($\lambda > 250$ nm), the photocatalytic decomposition of NO proceeded at 15% the rate without the UV-cut filter, i.e., with the full arc of the high pressure Hg lamp. This indicates that the UV-light effective for NO decomposition lies in the wavelength regions of 200 nm to 250 nm.

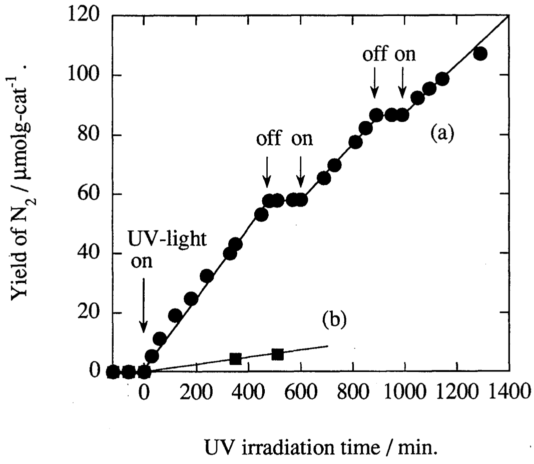

Figure 1. The time profiles of the photocatalytic decomposition reaction of NO into N_2 on the Ag^+/ZSM-5 catalyst (a) and on the Cu^+/ZSM-5 catalyst (b) at 298 K.

Figure 2 shows the diffuse reflectance spectra of the Ag^+/ZSM-5 (a), H^+/ZSM-5 (b), and Ag^0/ZSM-5 (c) catalysts, respectively. The H^+/ZSM-5 exhibits no intense absorption band in the wavelength range of 200 nm to 250 nm. On the other hand, the Ag^+/ZSM-5 catalyst exhibits an intense absorption band at around 220 nm which is attributed to the $4d^{10} \rightarrow 4d^9 5s^1$ electronic transition on the Ag^+ ions.[10] The Ag^0 atoms, and $Ag_n{}^0$ and

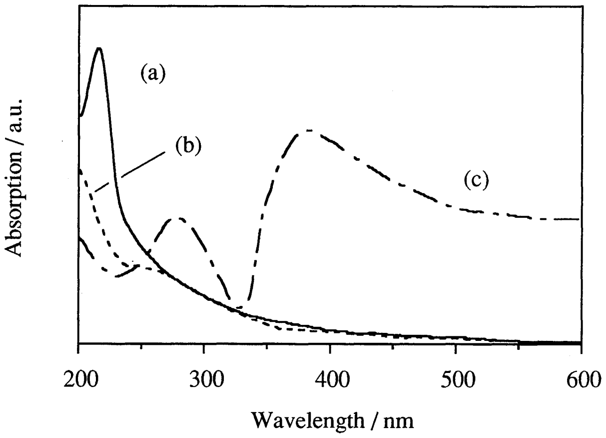

Figure 2. The DRS spectra of the Ag^+/ZSM-5 catalyst (a), H^+/ZSM-5 (b), and Ag^0/ZSM-5 catalyst (c).

$Ag_m{}^{n+}$ clusters are known to exhibit absorption bands in wavelength regions longer than 250 nm.[11,12] However, the Ag^+/ZSM-5 catalyst does not exhibit any absorption bands in this region. Furthermore, no ESR signals assigned to the Ag^0 atoms or Ag^{2+} species were observed with the Ag^+/ZSM-5 catalyst. These results firmly support the conclusion that silver ions are included within the pore structure of the ZSM-5 zeolite as isolated Ag^+ ions.

The dispersion state of Ag^+ species was investigated by XAFS measurements. The XANES spectra of the Ag foil and bulk Ag_2O exhibited several well-defined bands due to multiple-scattering at around 25530 eV and other bands arising from continuum resonances involving a multiple-scattering effect in the region above 25550 eV, while the XANES spectrum of the Ag^+/ZSM-5 catalyst scarcely exhibited any remarkable band due to this effect. This implies that silver ions are anchored onto the inner surfaces of the micro pores of the ZSM-5 zeolite in a high dispersion state without the formation of any large clusters or crystals of the Ag metals or oxides as indicated by the DRS measurements.

The most effective UV lights for the photocatalytic decomposition of NO was found to lie in the same wavelength region as the absorption band of the Ag^+/ZSM-5 catalyst which is attributed to the presence of the isolated Ag^+ ions. These findings suggest that the electronically excited state of the isolated Ag^+ ions plays a vital role in the photocatalytic decomposition of NO on the Ag^+/ZSM-5 catalyst at 298 K.

The ESR measurements indicated that the addition of O_2 or NO at high pressures (> 1 torr) did not lead to the oxidation of Ag^+ to Ag^{2+} on the Ag^+/ZSM-5 catalyst in clear contrast to the easy oxidation of Cu^+ to Cu^{2+} on the Cu^+/ZSM-5 catalyst[13]. Thus, it was elucidated that the Ag^+ ions are chemically stable even under an oxidative atmosphere as well as under the photocatalytic reaction, a major advantage in using the Ag^+/ZSM-5 catalyst as a potential photocatalyst for the direct decomposition of NO at normal temperatures. Another advantage is the lower temperatures of the pretreatment of the original Ag^+/ZSM-5 sample at just 473 K when compared to the preparation of the copper ion catalyst which requires evacuation of the Cu^{2+}/ZSM-5 sample at temperatures higher than 973 K in order to produce Cu^+ ions as active species.[2]

As shown in Figure 2-(c), after H_2 treatment of the Ag^+/ZSM-5 catalyst, the intensity of the absorption band due to the Ag^+ ions at around 220 nm drastically decreases in intensity and the broad absorption band due to the $Ag_n{}^0$ or $Ag_m{}^{n+}$ clusters appears in the wavelength regions above 250 nm, indicating that the reduction and aggregation of the Ag^+ ions has occurred. Considering that the Ag^0/ZSM-5 did not show any photocatalytic reactivity for the decomposition of NO, it became clear that the $Ag_n{}^0$ or $Ag_m{}^{n+}$ clusters were not associated with the NO decomposition reaction.

From these various findings, it was concluded that the photo-exited electronic state of highly dispersed isolated Ag^+ ions ($4d^95s^1$) plays a significant role in the photocatalytic decomposition of NO while an electron transfer from the photo-excited Ag^+ into the π anti-bonding molecular orbital of NO leads to the weakening of the N-O bond and initiates the decomposition of the NO molecule. The remarkably high photocatalytic reactivity of the Ag^+/ZSM-5 catalyst can be attributed to the high chemical stability of the Ag^+ ion and the long lifetime of the excited electronic state as compared with those properties of the Cu^+ ion in the Cu^+/ZSM-5 catalyst. The study of the excited electronic state of the Ag^+ ion on the Ag^+/ZSM-5 catalyst as well as a detailed study of the mechanisms behind the photocatalytic decomposition of NO will be the subject of our future work.

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