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In situ investigations of the photocatalytic decomposition of NO_x on ion-exchanged silver(I) ZSM-5 catalysts

Masakazu Anpo *, Masaya Matsuoka, Hiromi Yamashita

Department of Applied Chemistry, Osaka Prefecture University, Gakuen-cho 1-1, Sakai, Osaka 593, Japan

Abstract

Ag^+/ZSM-5 catalyst was prepared by an ion-exchange method. In situ EXAFS, ESR, photoluminescence, and diffuse reflectance (DR) spectroscopy were applied to characterize the Ag^+/ZSM-5 catalyst. UV irradiation of the Ag^+/ZSM-5 catalyst in the presence of NO led to the photocatalytic conversion of NO into N_2, N_2O and NO_2 at temperatures as low as 298 K. The wavelengths of the effective UV irradiation were determined. The results obtained in this study suggest that electron transfer from excited Ag^+ ion into the π anti-bonding molecular orbital of NO plays a significant role in the photocatalytic decomposition of NO.

Keywords: Photocatalytic decomposition; NO_x; Ag^+/ZSM-5 catalysts

1. Introduction

The application of photocatalysis to reduce global air and water pollution is our dream and hope. Although it is still too early for us to talk about actual applications, it can be said that we are moving in a very positive direction. Presently, we are in the stage of fundamental research, but always our larger goal is to find an effective, efficient, realistic and useful application of our research to improve our environment. With well-defined anchored catalysts, one can expect not only to achieve more active and selective photocatalytic systems, but also to obtain more detailed information on the mechanisms behind the photocatalytic reactions on a molecular scale.

Ion-exchanged copper/zeolite catalysts 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 introduced into zeolites by an ion-exchange or doped in SiO_2 using the sol–gel method are easily and selectively reduced to Cu^+ ions on evacuation at temperatures higher than 573 K. UV irradiation of the thus formed Cu^+/zeolites [2] or Cu^+/SiO_2 catalysts [3,4] in the presence of NO leads to the photocatalytic decomposition of NO into N_2 and O_2 even at 275 K. Results of ESR, IR, and photoluminescence studies suggested that the excited state of the Cu^+ ion produced by UV irradiation ($3d^{10} \rightarrow 3d^9 4s^1$) plays a significant role in the reaction.

In the present work, we have prepared the Ag^+/ZSM-5 catalyst by an ion-exchange method because the Ag^+ ion has the same electronic configuration as the Cu^+ ion (d^{10}) as well as having the advantage of being chemi-

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[*] Corresponding author.

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cally stable in an oxidative atmosphere. Furthermore, ion-exchanged silver/zeolite catalysts have been reported to show very high activity for the disproportionation of ethylbenzene [5,6], photochemical/thermal cleavage of water to H_2 and O_2 [7], photo-oxygen production from water [8], photo-dimerization of alkanes [9], and the selective reduction of NO by ethylene at around 823 K [10] or by ethanol at around 723 K [11]. Along these lines, the present study deals with the in situ characterization of the Ag^+/ZSM-5 catalysts and their photocatalytic reactivities by means of in situ photoluminescence, ESR, FT-EXAFS, and diffuse reflectance (DR) techniques along with an analysis of the reaction products.

2. Experimental

ZSM-5 zeolite (SiO_2:Al_2O_3 mole ratio = 23:1) supplied by the TOSOH corporation was used. The Ag^+/ZSM-5 zeolite catalyst was prepared by ion exchange with an aqueous $Ag(NH_3)_2^+$ solution. After the ion exchange, the sample was washed with distilled water and dried in air at 373 K. Silver loading was determined as 6.9 wt% metal by an atomic absorption spectrometer. Prior to spectroscopic and photocatalytic measurements, samples were degassed at 298 K for 1 h, calcined at 673 K in the presence of 20 Torr of O_2 for 1 h, then degassed at 473 K for 1 h. The Ag^0/ZSM-5 catalyst was prepared by heating the Ag^+/ZSM-5 in the presence of an H_2/H_2O mixture at a total pressure of 20 Torr (H_2/H_2O = 1). Photocatalytic reactions were carried out at 298 K using a high pressure mercury lamp and a water filter. A UV cut-off 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. EXAFS spectra were obtained at the BL-10B facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba. Si(311) channel-cut crystal was used to monochromatize the X-rays from the 2.5 GeV electron storage ring. The Ag K-edge absorption spectra were recorded in the transmission mode at 298 K. The ESR spectra were recorded at 77 K using a JES-RE2X spectrometer operating in the X-band mode. The photoluminescence spectra were recorded with a Shimadzu RF-5000 spectrofluorophotometer at 77 K. DR spectra were recorded with a Shimadzu UV-2200A spectrometer at 298 K.

3. Results and discussion

As shown in Fig. 1, UV irradiation of the Ag^+/ZSM-5 catalyst in the presence of 10 Torr of NO at 298 K was found to lead to the formation of N_2, N_2O and NO_2 (N_2:N_2O:NO_2 = 1.0:0.38:0.10). Formation of N_2 and N_2O is found only under UV irradiation and the yield of these products increases with a good linearity against the irradiation time. 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

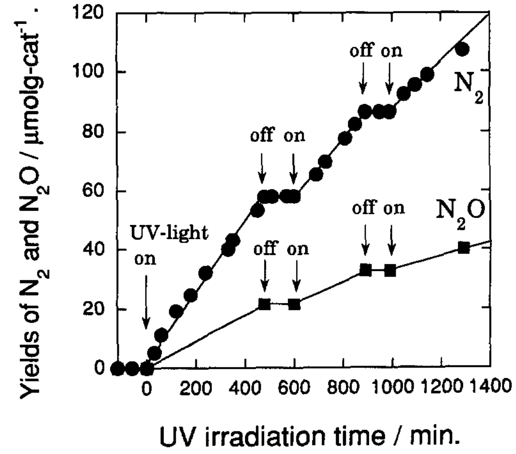

Fig. 1. Time profiles of the photocatalytic decomposition reaction of NO into N_2 and N_2O on the Ag^+/ZSM-5 catalyst at 298 K.

photocatalytically. On the Ag^0/ZSM-5 and H^+/ZSM-5 catalysts, only minor formation of N_2 and N_2O was observed, but it was small and negligible compared to the yield of the reaction above UV irradiated Ag^+/ZSM-5 catalyst. These results clearly indicate that the Ag^+ ions of the catalyst play a significant role in the photocatalytic decomposition of NO. The rate of N_2 formation per one exchanged cation on the Ag^+/ZSM-5 catalyst is 10 times faster than on the Cu^+/ZSM-5 catalyst [2], indicating that the photocatalytic decomposition of NO proceeds faster on the Ag^+ ions than on the Cu^+ ions. As for reaction products, N_2, N_2O, and NO_2 were produced, suggesting that the decomposition of NO on the Ag^+/ZSM-5 catalyst proceeds in a different way from the reaction of NO on the Cu^+/ZSM-5 catalyst to produce N_2 and O_2. (NO_2 was also produced on the Cu^+/ZSM-5 under the higher pressure of NO by the gas phase reaction of NO with O_2). Under UV irradiation of the catalyst through the UV-25 filter ($\lambda > 250$ nm), the photocatalytic decomposition of NO proceeded at 15% of the rate without the UV cut-off filter. This indicates that the UV light effective for NO decomposition lies in the wavelength region of 200 nm to 250 nm.

Fig. 2 shows the FT-EXAFS spectra of the Ag^+/ZSM-5 catalyst (a), bulk Ag_2O (b) and Ag foil (c), respectively. The FT-EXAFS spectrum of Ag_2O (b) exhibits a peak at around 3.5 Å (phase shift is not corrected) which can be attributed to the Ag–O–Ag bonding, and FT-EXAFS of the Ag foil (c) exhibits a peak at around 2.5 Å due to the Ag–Ag bonding. However the FT-EXAFS spectrum of the Ag^+/ZSM-5 catalyst only exhibits a well defined peak due to the neighboring oxygen atoms (Ag–O) at around 1.8 Å. This result suggests that silver is anchored within the micropores of the ZSM-5 zeolite in an isolated state forming neither clusters nor Ag metal or oxide crystals.

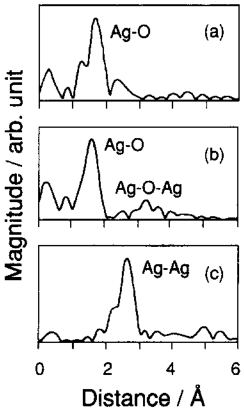

Fig. 2. FT-EXAFS spectra of the Ag^+/ZSM-5 catalyst (a), Ag_2O powder (b), and Ag foil (c).

The diffuse reflectance spectra of the Ag^+/ZSM-5, H^+/ZSM-5, and Ag^0/ZSM-5 catalyst were examined. The H^+/ZSM-5 exhibited no intense absorption band in the 200–250 nm wavelength range. On the other hand, the Ag^+/ZSM-5 catalyst exhibited an intense absorption band at around 220 nm which is attributed to the $4d^{10} \rightarrow 4d^9 5s^1$ electronic transition of the Ag^+ ions [12–14]. The Ag^0 atoms, and Ag_n^0 and Ag_m^{n+} clusters are known to exhibit absorption bands at wavelengths above 250 nm [15,16]. However, no absorption band of the Ag^+/ZSM-5 appears 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 highly dispersed Ag^+ ions. After H_2 treatment of the Ag^+/ZSM-5 catalyst, the intensity of the absorption band of Ag^+ ions at about 220 nm drastically decreased and broad absorption bands of Ag_n^0 or Ag_m^{n+} clusters appeared above 250 nm, indicating that reduction and aggregation of the Ag^+ ions had occurred. Since Ag^0/ZSM-5 did not show any photocatalytic activity for the decomposition of NO, we concluded that the Ag_n^0 or Ag_m^{n+} clusters cannot be associated with the reaction.

Fig. 3 shows the ESR signal obtained after the addition of 7 Torr of NO onto the Ag^+/ZSM-5 catalyst at 77 K. The hyperfine splitting of the signal shows that the electron

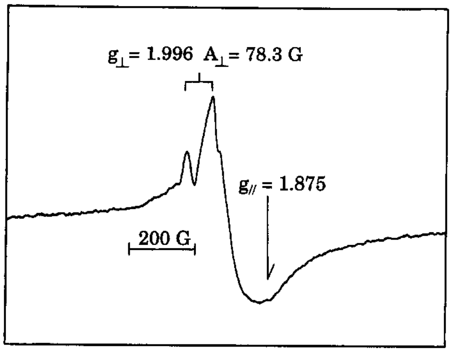

Fig. 3. ESR signal obtained after the addition of NO onto the Ag^+/ZSM-5 catalyst at 77 K.

spin interacts with a nucleus of Ag^+ ($I = 1/2$), suggesting that the NO molecules are adsorbed on the Ag^+ to form a nitrosylic adduct, i.e., $(Ag–NO)^+$ [17]. The evacuation of the system led to the disappearance of the signal, suggesting that the interaction of NO with the Ag^+ ion is weak. On evacuation, no new ESR signal appeared, indicating that the oxidation of Ag^+ to Ag^{2+} by the addition of NO at high pressures ($>$ 1 Torr) did not occur.

UV irradiation of the Ag^+/ZSM-5 catalyst having the $(Ag–NO)^+$ species led to a decrease in the intensity of the ESR signal assigned to the $(Ag–NO)^+$ species with UV irradiation time without the appearance of any new signal. After UV irradiation was stopped, the intensity of the signal returned to its original level. These reversible changes in the ESR signal assigned to the $(Ag–NO)^+$ suggest not only that the $(Ag–NO)^+$ species act as reaction precursors, but also that the photo-induced decomposition reaction of NO proceeds catalytically on the Ag^+/ZSM-5 catalyst.

Fig. 4 shows the photoluminescence spectra of the Ag^+/ZSM-5 catalyst when the absorption band of the Ag^+ ion included in the catalyst is excited by 220 nm beams. This photoluminescence band at around 340 nm can be attributed to the presence of the Ag^+ ion, i.e., to the radiative deactivation $4d^9 5s^1 \rightarrow 4d^{10}$. Fig. 4 also shows the effect of the addition of NO on the photoluminescence of the Ag^+/ZSM-5 catalyst. The addition of NO onto the Ag^+/ZSM-5 catalyst leads to the efficient quenching of the photoluminescence due to the Ag^+ ion. As shown in Fig. 4, after the complete quenching, the evacuation of the system leads to recovery of the photoluminescence to its original intensity. These results clearly suggest that the interaction of the NO molecule with the Ag^+ ion is weak, and that added NO molecules easily interact with Ag^+ species in ground and also in excited states. The photoluminescence of the Ag^+/ZSM-5 catalyst was more easily quenched by the added NO than that of the Cu^+/ZSM-5 catalyst, suggesting that in photo-excited states Ag^+ ions interact with NO molecules more efficiently than Cu^+ ions do.

The most effective wavelengths of UV light for the photocatalytic decomposition of NO (200–250 nm) were found to lie in the same wavelength region as the absorption band and excitation band of the Ag^+/ZSM-5 attributed to the presence of the Ag^+ ions (220 nm). The Ag^+/ZSM-5 catalyst degassed at ambient temperature after UV irradiation for a long period in the presence of 10 Torr of NO did not show any new absorption spectra which could have been attributed to the Ag^0 atoms, Ag_n^0 or Ag_m^{n+} clusters, nor any ESR spectra due to the Ag^{2+} ions. These results clearly indicate that the decomposition of NO molecules proceeds photocatalytically on the Ag^+ ions.

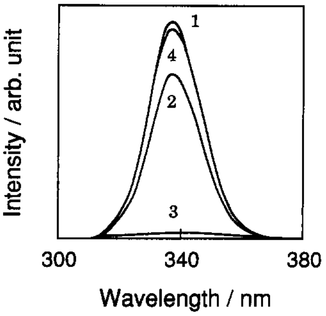

Fig. 4. Photoluminescence spectrum of the Ag^+/ZSM-5 catalyst (1) and the effect of the addition of NO on the photoluminescence (λ_{ex} = 220 nm). NO pressure in Torr: (1) 0.0; (2) 0.2; (3) 4.0; (4) after degassing of NO at 298 K.

Furthermore, 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+} in the Ag^+/ZSM-5 catalyst, in clear contrast to the easy oxidation of Cu^+ to Cu^{2+} in the Cu^+/ZSM-5 catalyst [18]. Since Ag^+ ions are chemically stable even in an oxidative atmosphere, the Ag^+/ZSM-5 catalyst is a potential photocatalyst for the direct decomposition of NO at ambient temperatures. Another advantage is that the Ag^+/ZSM-5 catalyst needs lower-temperature pretreatment (473 K) than the Cu^{2+}/ZSM-5 sample which requires evacuation at temperatures higher than 973 K in order to produce Cu^+ ions as active species [19].

From these various findings we concluded that the photo-excited electronic state of highly dispersed Ag^+ ions ($4d^9 5s^1$) 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 efficient interaction of the excited electronic state of the Ag^+ ion with NO molecules, as compared with those properties of the Cu^+ ion on 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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