

# Incorporation of silver (I) ions within zeolite cavities and their photocatalytic reactivity for the decomposition of N<sub>2</sub>O into N<sub>2</sub> and O<sub>2</sub>

Woo-Sung Ju, Masaya Matsuoka, and Masakazu Anpo<sup>†</sup>

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University,  
1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

**ABSTRACT.** Ag<sup>+</sup>/ZSM-5 catalysts were prepared by an ion-exchange method. UV-irradiation of the Ag<sup>+</sup>/ZSM-5 catalysts in the presence of N<sub>2</sub>O led to the photocatalytic decomposition of N<sub>2</sub>O into N<sub>2</sub> and O<sub>2</sub> 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<sup>+</sup> – N<sub>2</sub>O complexes formed between gaseous N<sub>2</sub>O and the isolated Ag<sup>+</sup> ions exchanged within the zeolite cavities plays a significant role in the reaction.

## 1. INTRODUCTION

It has been reported that silver (I) ion-exchanged zeolites exhibit unique and high catalytic reactivities for De – NO<sub>x</sub> reactions such as the selective catalytic reduction of NO<sub>x</sub> with hydrocarbons or dimethylether and the direct photocatalytic decomposition of NO [1–6]. However, the reactivity of Ag<sup>+</sup>/zeolites with N<sub>2</sub>O, especially under UV-irradiation, has not yet been fully investigated. In the present study, highly dispersed Ag<sup>+</sup> ions as well as their photocatalytic reactivity for the decomposition of N<sub>2</sub>O at ambient temperatures have been investigated by means of in-situ UV-Vis, photoluminescence, FT-IR measurements, along with an analysis of the reaction products.

## 2. EXPERIMENTAL

H<sup>+</sup>/ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=23.8) type of zeolite was used as the parent zeolite. Ag<sup>+</sup>/ZSM-5 catalysts having different Ag content were prepared by a conventional ion-exchange of the corresponding H<sup>+</sup>/ZSM-5 with a dilute AgNO<sub>3</sub> solution at 298 K for 24 h. After the ion-exchange, the samples were washed with distilled water and dried in air at 373 K. The silver loadings of the Ag<sup>+</sup>/ZSM-5 catalysts were determined to be 0.5 ~ 3.9 wt% by an atomic absorption spectrometer.

Prior to spectroscopic and photocatalytic reactivity measurements, samples were degassed at 673 K, calcined at 673 K in the presence of 20 Torr of O<sub>2</sub> for 1 h, and then finally evacuated under a vacuum of < 10<sup>-5</sup> Torr at 473 K for 1 h. Photocatalytic reactions were carried out with the catalysts (50 mg) in a conventional closed system with a flat transparent quartz window using a high pressure mercury lamp through a water filter. UV-cut filter (λ > 250 nm) was

used to examine the effect of the irradiation wavelength upon the reaction. The reaction products, nitrogen and oxygen, were analyzed by gas chromatography.

## 3. RESULTS AND DISCUSSION

The coordination state of the Ag<sup>+</sup> ion species exchanged within the zeolite was investigated by UV-Vis measurements. Figure 1 shows the UV-Vis spectra of Ag<sup>+</sup>/ZSM-5 with various content of Ag ion obtained after pretreatment. Only a sharp absorption band at around 190 nm due to the 4d<sup>10</sup> → 4d<sup>9</sup>5s<sup>1</sup> electronic transition of the isolated Ag<sup>+</sup> ion can be observed for Ag<sup>+</sup>/ZSM-5 [7].

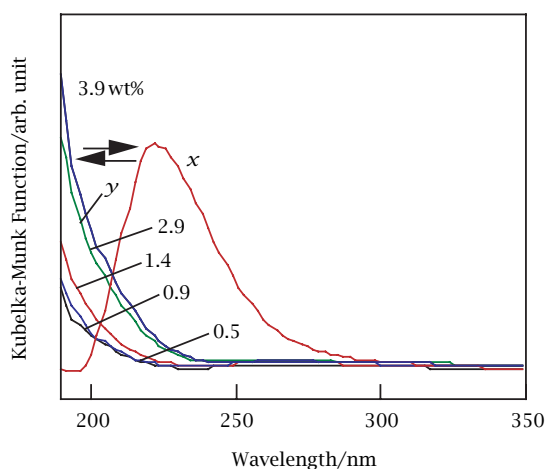


Figure 1. UV-Vis spectra of the Ag<sup>+</sup>/ZSM-5 with different Ag loadings and the effect of the addition of N<sub>2</sub>O on the UV-Vis spectrum of the Ag<sup>+</sup>/ZSM-5 (2.9) at 298 K. (x) after the addition of N<sub>2</sub>O 1 Torr. (y) after the degassing of N<sub>2</sub>O at 298 K.

<sup>†</sup> E-mail: [anpo@ok.chem.osakafu-u.ac.jp](mailto:anpo@ok.chem.osakafu-u.ac.jp)

On the other hand, the addition of nitrous oxide on  $\text{Ag}^+/\text{ZSM-5}$  with a silver loading of 2.9% (denoted as  $\text{Ag}^+/\text{ZSM-5}$  (2.9)) leads to the disappearance of the band at 190 nm and, simultaneously, the appearance of a new band at 220 nm, which can be assigned to the  $\text{Ag}^+ - \text{N}_2\text{O}$  complexes, while the evacuation of the system at 298 K leads to the complete restoration of the original absorption band. These results indicate that the addition of  $\text{N}_2\text{O}$  results in the formation of  $\text{Ag}^+ - \text{N}_2\text{O}$  complexes, which modify the coordination sphere and energy gap of the intraionic electronic transition of  $\text{Ag}^+ (4d^{10} \rightarrow 4d^9 5s^1)$ , however, the adsorption of  $\text{N}_2\text{O}$  on  $\text{Ag}^+$  is weak and reversible.

The interaction of  $\text{N}_2\text{O}$  with  $\text{Ag}^+$  ion was investigated by means of FT-IR spectroscopy. As shown in Figure 2, the  $\text{Ag}^+/\text{ZSM-5}$  (2.9) catalyst exhibits a specific FT-IR band at  $2251 \text{ cm}^{-1}$  in the presence of 1 Torr of  $\text{N}_2\text{O}$ , assigned to the asymmetric stretching mode of the adsorbed  $\text{N}_2\text{O}$  [8], whereas the position of the band ( $2251 \text{ cm}^{-1}$ ) is quite different from that of the  $\text{N}_2\text{O}$  species adsorbed onto  $\text{H}^+/\text{ZSM-5}$  ( $2227 \text{ cm}^{-1}$ ). The evacuation of  $\text{N}_2\text{O}$  at 298 K led to the complete disappearance of the band, indicating that  $\text{N}_2\text{O}$  adsorbs reversibly onto  $\text{Ag}^+$  ion. These results clearly suggest that the adsorption of the  $\text{N}_2\text{O}$  onto the  $\text{Ag}^+$  ion is weak, and the added  $\text{N}_2\text{O}$  molecules easily interact with the  $\text{Ag}^+$  species on the ZSM-5 catalyst.

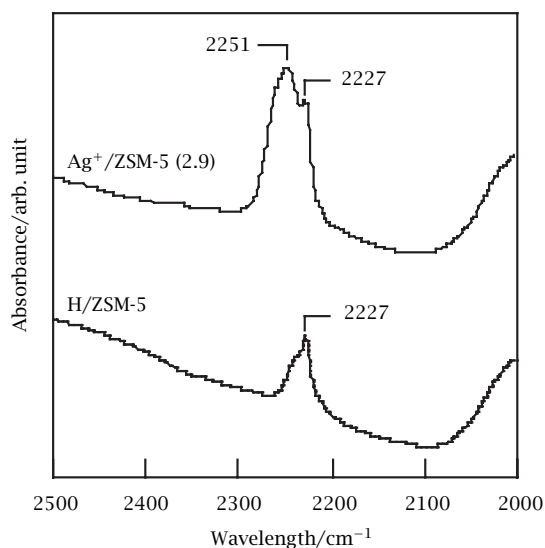


Figure 2. The FT-IR spectra of the  $\text{N}_2\text{O}$  adsorbed on the  $\text{Ag}^+/\text{ZSM-5}$  (2.9) and  $\text{H}^+/\text{ZSM-5}$  catalysts at 298 K. Added  $\text{N}_2\text{O}$  : 1 Torr.

As shown in Figure 3, the  $\text{Ag}^+/\text{ZSM-5}$  catalysts exhibit a photoluminescence at around 330 nm upon excitation at around 220 nm. The absorption band and photoluminescence spectrum can be attributed to the electronic transition ( $4d^{10} \rightarrow 4d^9 5s^1$ ) of the isolated

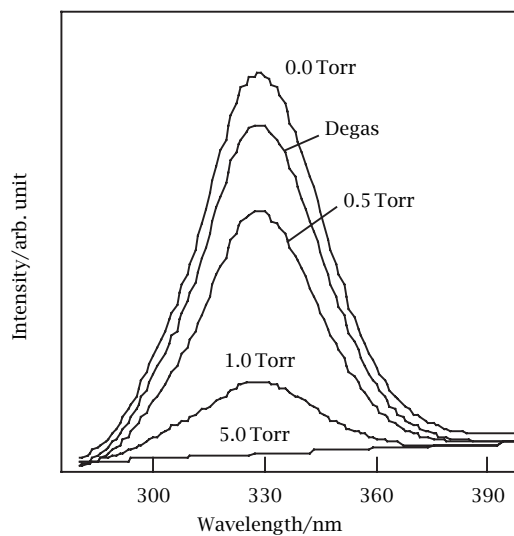


Figure 3. Photoluminescence spectrum of  $\text{Ag}^+/\text{ZSM-5}$  (2.9) and the effect of the addition of  $\text{N}_2\text{O}$  on the  $\text{Ag}^+/\text{ZSM-5}$  (2.9) at 298 K. Degas: after the degassing of  $\text{N}_2\text{O}$  at 298 K.

$\text{Ag}^+$  ion and its reverse radiative deactivation process ( $4d^9 5s^1 \rightarrow 4d^{10}$ ). As can also be seen in Figure 3, the addition of  $\text{N}_2\text{O}$  onto  $\text{Ag}^+/\text{ZSM-5}$  leads to an efficient quenching of the photoluminescence, while the degassing of  $\text{N}_2\text{O}$  after the complete quenching (degas) leads to the recovery of the photoluminescence to its original intensity level. These results clearly suggest that almost all of the isolated  $\text{Ag}^+$  ions can interact reversibly with  $\text{N}_2\text{O}$  to form  $\text{Ag}^+ - \text{N}_2\text{O}$  complexes.

Figure 4 shows the reaction profiles of the photocatalytic decomposition of  $\text{N}_2\text{O}$  on  $\text{Ag}^+/\text{ZSM-5}$  with

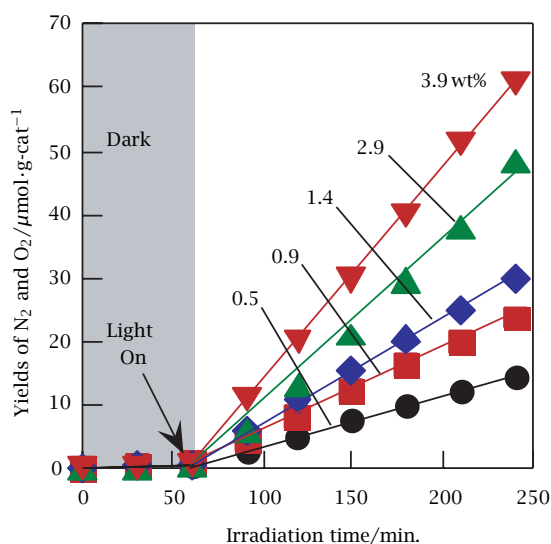


Figure 4. Reaction time profiles of the photocatalytic decomposition of  $\text{N}_2\text{O}$  into  $\text{N}_2$  and  $\text{O}_2$  at 298 K on  $\text{Ag}^+/\text{ZSM-5}$  with different Ag loadings.

different silver loadings at room temperature. UV-irradiation of the  $\text{Ag}^+/\text{ZSM-5}$  catalysts in the presence of  $\text{N}_2\text{O}$  leads to the formation of  $\text{N}_2$  and  $\text{O}_2$ . The yields of  $\text{N}_2$  and  $\text{O}_2$  increase with a good linearity against the UV-irradiation time, while under dark conditions these formations could not be detected, indicating that the reaction proceeds photocatalytically. The reaction rate for  $\text{N}_2\text{O}$  decomposition also increases linearly against the amount of silver loading, suggesting that the isolated  $\text{Ag}^+$  ions are an active species for this reaction. Furthermore, under UV-irradiation of the catalyst through an UV-25 filter ( $\lambda > 250\text{ nm}$ ), the photocatalytic decomposition of  $\text{N}_2\text{O}$  proceeded at 4% of the rate of the reaction under the full arc of a high pressure mercury lamp. This indicates that the efficient UV-light for the reaction lies in wavelength regions of  $200 \sim 250\text{ nm}$  where the absorption band of the  $\text{Ag}^+ - \text{N}_2\text{O}$  complex exists. These results suggest that the photocatalytic decomposition of  $\text{N}_2\text{O}$  on the isolated  $\text{Ag}^+/\text{ZSM-5}$  proceeds through the photo-excitation of  $\text{Ag}^+ - \text{N}_2\text{O}$  complexes.

From these findings, it was found that the isolated  $\text{Ag}^+$  ion is the active species for the photocatalytic decomposition of  $\text{N}_2\text{O}$ , and the reaction proceeds through the photo-irradiation of the absorption band of the  $\text{Ag}^+ - \text{N}_2\text{O}$  complex at around  $220\text{ nm}$ . A detailed study of the mechanisms behind the photocatalytic decomposition of  $\text{N}_2\text{O}$  is presently underway and will be the subject of our future work.

#### 4. CONCLUSIONS

$\text{Ag}^+/\text{ZSM-5}$  catalysts were prepared by an ion-exchange method. UV-irradiation of the  $\text{Ag}^+/\text{ZSM-5}$  catalysts in the presence of  $\text{N}_2\text{O}$  led to the photocatalytic decomposition of  $\text{N}_2\text{O}$  into  $\text{N}_2$  and  $\text{O}_2$  at  $298\text{ K}$ . Investigations of the effective wavelength of the irradiated UV-light for the reaction as well as in-situ characterizations of the catalysts by means of UV-Vis, FT-IR and photoluminescence spectroscopies revealed that the photo-excitation of the  $\text{Ag}^+ - \text{N}_2\text{O}$  complexes formed between  $\text{N}_2\text{O}$  and the isolated  $\text{Ag}^+$  ions exchanged within the zeolite cavities play a significant role in the reaction.

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