Incorporation of silver (I) ions within zeolite cavities and their photocatalytic reactivity for the decomposition of N_2O into N_2 and O_2

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ABSTRACT. $\text{Ag}^+/\text{ZSM-5}$ catalysts were prepared by an ion-exchange method. UV-irradiation of the $\text{Ag}^+/\text{ZSM-5}$ catalysts in the presence of N_2O led to the photocatalytic decomposition of N_2O into N_2 and O_2 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 $\text{Ag}^+ - \text{N}_2\text{O}$ complexes formed between gaseous N_2O and the isolated Ag^+ 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 $\text{De} - \text{NO}_x$ reactions such as the selective catalytic reduction of NO_x with hydrocarbons or dimethylether and the direct photocatalytic decomposition of NO [1-6]. However, the reactivity of $\text{Ag}^+/\text{zeolites}$ with N_2O , especially under UV-irradiation, has not yet been fully investigated. In the present study, highly dispersed Ag^+ ions as well as their photocatalytic reactivity for the decomposition of N_2O 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

$\text{H}^+/\text{ZSM-5}$ ($\text{SiO}_2/\text{Al}_2\text{O}_3=23.8$) type of zeolite was used as the parent zeolite. $\text{Ag}^+/\text{ZSM-5}$ catalysts having different Ag content were prepared by a conventional ion-exchange of the corresponding $\text{H}^+/\text{ZSM-5}$ with a dilute AgNO_3 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 $\text{Ag}^+/\text{ZSM-5}$ 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_2 for 1 h, and then finally evacuated under a vacuum of $< 10^{-5}$ Torr at 473 K for 1 h. Photocatalytic reactions were carried out with the catalysts (50 mg) in a conventional closed system at 298 K with a flat transparent quartz window using a high pressure mercury lamp through a water filter. UV-cut filter ($\lambda > 250$ 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^+ ion species exchanged within the zeolite was investigated by UV-Vis measurements. Figure 1 shows the UV-Vis spectra of $\text{Ag}^+/\text{ZSM-5}$ with various content of Ag ion obtained after pretreatment. Only a sharp absorption band at around 190 nm due to the $4d^{10} \rightarrow 4d^9 5s^1$ electronic transition of the isolated Ag^+ ion can be observed for $\text{Ag}^+/\text{ZSM-5}$ [7].

Figure 1. UV-Vis spectra of the $\text{Ag}^+/\text{ZSM-5}$ with different Ag loadings and the effect of the addition of N_2O on the UV-Vis spectrum of the $\text{Ag}^+/\text{ZSM-5}$ (2.9) at 298 K. (x) after the addition of N_2O 1 Torr. (y) after the degassing of N_2O at 298 K.

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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 N_2O 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 N_2O on Ag^+ is weak and reversible.

The interaction of N_2O with 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 cm^{-1} in the presence of 1 Torr of N_2O , assigned to the asymmetric stretching mode of the adsorbed N_2O [8], whereas the position of the band (2251 cm^{-1}) is quite different from that of the N_2O species adsorbed onto $\text{H}^+/\text{ZSM-5}$ (2227 cm^{-1}). The evacuation of N_2O at 298 K led to the complete disappearance of the band, indicating that N_2O adsorbs reversibly onto Ag^+ ion. These results clearly suggest that the adsorption of the N_2O onto the Ag^+ ion is weak, and the added N_2O molecules easily interact with the Ag^+ species on the ZSM-5 catalyst.

Figure 2. The FT-IR spectra of the N_2O adsorbed on the $\text{Ag}^+/\text{ZSM-5}$ (2.9) and $\text{H}^+/\text{ZSM-5}$ catalysts at 298 K. Added N_2O : 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 N_2O on the $\text{Ag}^+/\text{ZSM-5}$ (2.9) at 298 K. Degas: after the degassing of N_2O at 298 K.

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 N_2O onto $\text{Ag}^+/\text{ZSM-5}$ leads to an efficient quenching of the photoluminescence, while the degassing of N_2O 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 Ag^+ ions can interact reversibly with N_2O to form $\text{Ag}^+ - \text{N}_2\text{O}$ complexes.

Figure 4 shows the reaction profiles of the photocatalytic decomposition of N_2O on $\text{Ag}^+/\text{ZSM-5}$ with

Figure 4. Reaction time profiles of the photocatalytic decomposition of N_2O into N_2 and 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 N_2O leads to the formation of N_2 and O_2 . 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, indicating that the reaction proceeds photocatalytically. The reaction rate for N_2O decomposition also increases linearly against the amount of silver loading, suggesting that the isolated 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 N_2O 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 N_2O 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 Ag^+ ion is the active species for the photocatalytic decomposition of N_2O , 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 nm . A detailed study of the mechanisms behind the photocatalytic decomposition of N_2O 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 N_2O led to the photocatalytic decomposition of N_2O into N_2 and O_2 at 298 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 N_2O and the isolated Ag^+ ions exchanged within the zeolite cavities play a significant role in the reaction.

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