Incorporation of silver (I) ions within zeolite cavities and their photocatalytic reactivity for the decomposition of N\textsubscript{2}O into N\textsubscript{2} and O\textsubscript{2}

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ABSTRACT. Ag\textsuperscript{+}/ZSM-5 catalysts were prepared by an ion-exchange method. UV-irradiation of the Ag\textsuperscript{+}/ZSM-5 catalysts in the presence of N\textsubscript{2}O led to the photocatalytic decomposition of N\textsubscript{2}O into N\textsubscript{2} and O\textsubscript{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 Ag\textsuperscript{+}–N\textsubscript{2}O complexes formed between gaseous N\textsubscript{2}O and the isolated Ag\textsuperscript{+} 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\textsubscript{x} reactions such as the selective catalytic reduction of NO\textsubscript{x} with hydrocarbons or dimethylether and the direct photocatalytic decomposition of NO [1–6]. However, the reactivity of Ag\textsuperscript{+}/zeolites with N\textsubscript{2}O, especially under UV-irradiation, has not yet been fully investigated. In the present study, highly dispersed Ag\textsuperscript{+} ions as well as their photocatalytic reactivity for the decomposition of N\textsubscript{2}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\textsuperscript{+}/ZSM-5 (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}=23.8) type of zeolite was used as the parent zeolite. Ag\textsuperscript{+}/ZSM-5 catalysts having different Ag content were prepared by a conventional ion-exchange of the corresponding H\textsuperscript{+}/ZSM-5 with a dilute AgNO\textsubscript{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 Ag\textsuperscript{+}/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\textsubscript{2} for 1 h, and then finally evacuated under a vacuum of < 10\textsuperscript{-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 (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\textsuperscript{+} ion species exchanged within the zeolite was investigated by UV-Vis measurements. Figure 1 shows the UV-Vis spectra of Ag\textsuperscript{+}/ZSM-5 with various content of Ag ion obtained after pretreatment. Only a sharp absorption band at around 190 nm due to the $4d_10 \rightarrow 4d_9s_1$ electronic transition of the isolated Ag\textsuperscript{+} ion can be observed for Ag\textsuperscript{+}/ZSM-5 [7].

![Figure 1. UV-Vis spectra of the Ag\textsuperscript{+}/ZSM-5 with different Ag loadings and the effect of the addition of N\textsubscript{2}O on the UV-Vis spectrum of the Ag\textsuperscript{+}/ZSM-5 (2.9) at 298 K. (x) after the addition of N\textsubscript{2}O 1 Torr. (y) after the degassing of N\textsubscript{2}O at 298 K.](image-url)
On the other hand, the addition of nitrous oxide on Ag$^+$/ZSM-5 with a silver loading of 2.9% (denoted as Ag$^+$/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 Ag$^+$ – N$_2$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$_2$O results in the formation of Ag$^+$ – N$_2$O complexes, which modify the coordination sphere and energy gap of the intraionic electronic transition of Ag$^+$ ($4d^{10} \rightarrow 4d^95s^1$), however, the adsorption of N$_2$O on Ag$^+$ is weak and reversible.

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

As shown in Figure 3, the Ag$^+$/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 ($4d^{10} \rightarrow 4d^95s^1$) of the isolated Ag$^+$ ion and its reverse radiative deactivation process ($4d^95s^1 \rightarrow 4d^{10}$). As can also be seen in Figure 3, the addition of N$_2$O onto Ag$^+$/ZSM-5 leads to an efficient quenching of the photoluminescence, while the degassing of N$_2$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 Ag$^+$ ions can interact reversibly with N$_2$O to form Ag$^+$ – N$_2$O complexes.

Figure 4 shows the reaction profiles of the photocatalytic decomposition of N$_2$O on Ag$^+$/ZSM-5 with different Ag loadings.
different silver loadings at room temperature. UV-irradiation of the Ag\(^+\)/ZSM-5 catalysts in the presence of N\(_2\)O 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\(_2\)O 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 (\(\lambda > 250\) nm), the photocatalytic decomposition of N\(_2\)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 nm where the absorption band of the Ag\(^+\) – N\(_2\)O complex exists. These results suggest that the photocatalytic decomposition of N\(_2\)O on the isolated Ag\(^+\)/ZSM-5 proceeds through the photo-excitation of Ag\(^+\) – N\(_2\)O complexes.

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

4. CONCLUSIONS

Ag\(^+\)/ZSM-5 catalysts were prepared by an ion-exchange method. UV-irradiation of the Ag\(^+\)/ZSM-5 catalysts in the presence of N\(_2\)O led to the photocatalytic decomposition of N\(_2\)O 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 Ag\(^+\) – N\(_2\)O complexes formed between N\(_2\)O and the isolated Ag\(^+\) ions exchanged within the zeolite cavities play a significant role in the reaction.

REFERENCES
