The photocatalytic reduction of nitrous oxide with propane on lead(II) ion-exchanged ZSM-5 catalysts

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UV irradiation of the Pb^{2+}/ZSM-5 catalyst prepared by an ion-exchange method in the presence of N_2O leads to the decomposition of N_2O into N_2. This reaction is found to be dramatically enhanced by the addition of propane to produce N_2 and oxygen-containing compounds such as ethanol or acetone. UV light effective for the reaction lies in wavelength regions shorter than 250 nm where the absorption band of the Pb^{2+} ion ([Xe] $4f^{14}5d^{10}6s^2 \rightarrow$ [Xe] $4f^{14}5d^{10}6s^1 6p^1$) exists, indicating that the excited state of the isolated Pb^{2+} ions plays a significant role in this decomposition of N_2O both in the absence and the presence of propane, and the role of propane is found to be a capture of oxygen atoms formed by the decomposition of N_2O.

KEY WORDS: photocatalyst; Pb^{2+}; zeolites; N_2O decomposition

1. Introduction

The design of highly efficient and selective photocatalytic systems for applications in the reduction of global air pollution is of vital interest. Especially, the reduction of N_2O, which causes the greenhouse effect and the destruction of the ozonosphere, is urgently required [1–3]. To address such concerns, transition-metal-exchanged zeolites such as Co [4], Pr [5], Fe [6,7], Cu [8–10] and Ag [11–16] ion-exchanged ZSM-5 have generated great interest due to their potential as catalysts or photocatalysts in the decomposition reaction of N_2O. In fact, a typical metal ion-exchanged zeolite, the lead(II) (Pb^{2+}) ion-exchanged zeolite, exhibits unique and high catalytic reactivities for DeNOx reactions such as the selective catalytic reduction (SCR) of NO_x with hydrocarbons [17,18]. However, the photocatalytic reactivities of Pb^{2+}/zeolites with gaseous N_2O have yet to be investigated.

In this study, we have investigated the photocatalytic reactivity of the Pb^{2+}/ZSM-5 catalyst toward the decomposition of N_2O both in the absence and the presence of hydrocarbons such as propane at temperatures as low as 298 K. The local structure of the Pb^{2+} ion species, which play a significant role in the photocatalytic reaction, has been also investigated by means of *in situ* UV-Vis spectra along with an analysis of the reaction.

2. Experimental

The H^+/ZSM-5 ($SiO_2/Al_2O_3 = 23.8$) zeolite (supplied by TOSOH Corp.) was used as the parent zeolite. The Pb^{2+}/ZSM-5 catalysts were prepared by a conventional ion-exchange method using the corresponding H^+/ZSM-5 with a dilute $Pb(NO_3)_2$ 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 loadings of the Pb^{2+}/ZSM-5 catalysts were determined to be 0.9 and 2.7 wt% by an atomic absorption spectrometer.

Prior to spectroscopic and photocatalytic reactivity measurements, the 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 at 473 K for 1 h. The reactions were carried out at 298 K using a high-pressure Hg mercury lamp through a water filter. UV-cut filters ($\lambda > 250$ nm) were used to examine the effect of the irradiation wavelength on the reaction. The reaction products were analyzed by gas chromatography.

3. Results and discussion

UV irradiation of the Pb^{2+}/ZSM-5 catalyst in the presence of N_2O was found to lead to the decomposition of N_2O at 298 K with a good linearity against the irradiation time. Figure 1 shows the reaction time profiles of N_2 yields in the photocatalytic decomposition of N_2O on the 0.9 and 2.7 wt% Pb^{2+}/ZSM-5 catalysts. UV irradiation of the catalyst in the presence of N_2O alone at 298 K leads to the decomposition of N_2O to form N_2 in the gas phase. The yields of N_2 increase with a good linearity against the UV-irradiation time, while under dark conditions these formations could not be detected. The yields of N_2 also increase when the amounts of the Pb^{2+} loadings become higher.

As shown in figure 1, it is found that the photocatalytic decomposition of N_2O proceeds much more efficiently in the coexistence of propane than without propane. This reaction also led to the formation of oxygen-containing compounds such as ethanol and acetone in addition to the evolution of N_2. The turnover frequency of the reaction exceeded

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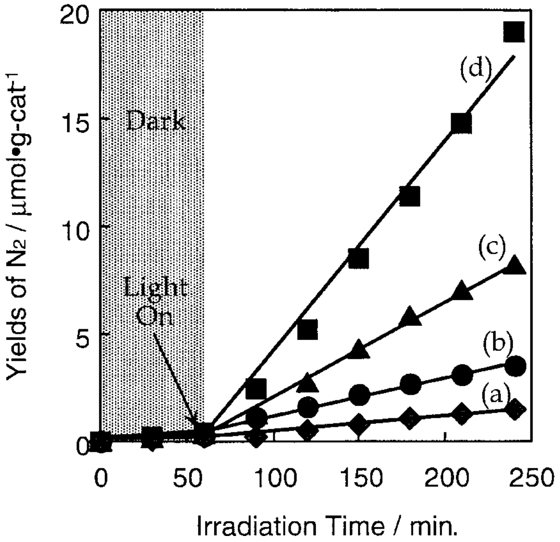

Figure 1. The time profile of the N_2 yields of the photocatalytic reaction of N_2O (a, b) and the effect of the addition of propane on the reaction (c, d) at 298 K. (a, c) 0.9 wt% Pb^{2+}/ZSM-5, (b, d) 2.7 wt% Pb^{2+}/ZSM-5. N_2O 10 Torr, added propane 5 Torr.

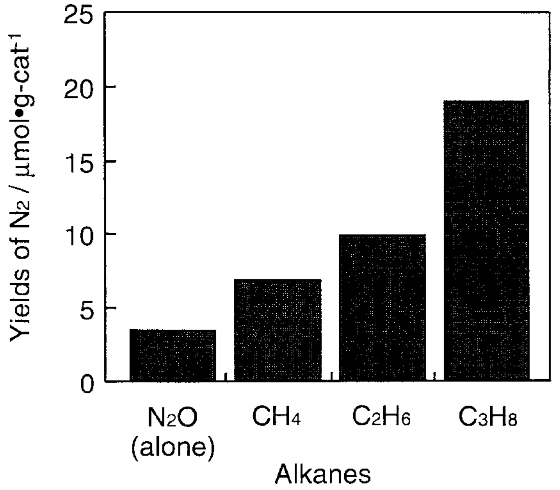

Figure 2. The effect of the addition of alkanes on the photocatalytic decomposition of N_2O on the 2.7 wt% Pb^{2+}/ZSM-5 at 298 K.

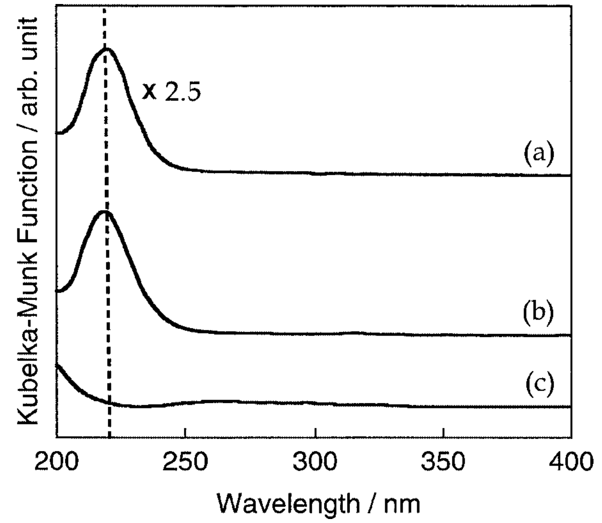

Figure 3. The UV-Vis spectra of the 0.9 wt% Pb^{2+}/ZSM-5 (a), 2.7 wt% Pb^{2+}/ZSM-5 (b) and H^+/ZSM-5 zeolites (c).

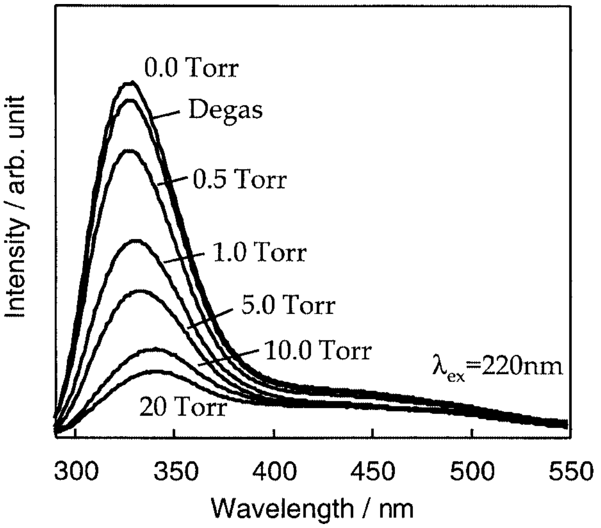

Figure 4. The effect of the addition of N_2O on the photoluminescence spectrum of the 2.7 wt% Pb^{2+}/ZSM-5 at 77 K ($\lambda_{ex} = 220$ nm).

unity after prolonged UV irradiation. These results clearly indicate that the decomposition reaction of N_2O proceeds photocatalytically and efficiently in the presence of propane on the Pb^{2+}/ZSM-5 catalyst. As shown in figure 2, the efficiency of the photocatalytic reduction of N_2O is found to strongly depend on the kind of hydrocarbons used, such as methane or ethane, and among these propane shows the highest enhancement in the reaction rate. These results can be attributed to the fact that the oxygen atoms formed by the photodecomposition of N_2O detach more easily from the isolated Pb^{2+} ions in the presence of propane during the reaction.

Figure 3 shows the UV-Vis spectra of 0.9 (a) and 2.7 wt% Pb^{2+}/ZSM-5 (b), and H^+/ZSM-5 (c), respectively. H^+/ZSM-5 scarcely exhibits an absorption band in wavelength regions shorter than 250 nm. On the other hand, the 2.7 wt% Pb^{2+}/ZSM-5 catalysts exhibit an intense UV absorption band at around 220 nm which is attributed to the intraionic electronic transition on the isolated Pb^{2+} ions. The peak position of the absorption band of the isolated Pb^{2+} ions is similar to that observed for the $Pb(NO_3)_2$ aqueous solution (at around 210 nm), indicating that the absorption band is characterized by the intraionic electronic transition of Pb^{2+} ([Xe] $4f^{14}5d^{10}6s^2 \rightarrow$ [Xe] $4f^{14}5d^{10}6s^16p^1$) [19]. The intensity of the band increased proportionally with the increase in the loading of Pb. Furthermore, the Pb^{2+}/ZSM-5 catalysts do not exhibit any absorption bands in wavelength regions longer than 250 nm, where the absorption band of the PbO powder exhibits (200–470 nm), suggesting that the isolated Pb^{2+} ions are anchored onto the ZSM-5 zeolite.

Figure 4 shows the photoluminescence spectrum of the isolated Pb^{2+} ions attributed to the radiative decay process from the excited state of the intraionic electronic transition of Pb^{2+} ([Xe] $4f^{14}5d^{10}6s^{1}6p^{1} \rightarrow$ [Xe] $4f^{14}5d^{10}6s^{2}$) and the effect of the addition of N_2O on the photoluminescence. As can be seen in figure 4, the addition of N_2O on the catalysts leads to an efficient quenching of the excited state of isolated Pb^{2+} ions, indicating that the N_2O molecules easily interact with the Pb^{2+} in its excited state.

Furthermore, under UV irradiation of the catalyst through an UV-25 filter ($\lambda > 250$ nm), the photocatalytic reduction of N_2O with propane proceeded at 5% of the rate under the full arc of the high-pressure mercury lamp. This indicates that the optimum UV light effective for the reaction lies in wavelength regions of 200–250 nm where the absorption band of the Pb^{2+} ion ($6s^2 \rightarrow 6s^1p^1$) exists. Therefore, it is clear that the reaction rate increases when the amount of Pb^{2+} is increased. All these results clearly suggest that the photocatalytic decomposition of N_2O on Pb^{2+}/ZSM-5 proceeds through the photo-excitation of the isolated Pb^{2+} ions, i.e., the photoexcited isolated Pb^{2+} ions play a significant role in the reaction.

ZSM-5 zeolites exchanged with transition metal ions having a d^{10} electronic configuration, such as Cu^+ or Ag^+, show high photocatalytic reactivities for the direct decomposition of N_2O, however, the reaction rate is usually greatly suppressed by the addition of propane on these catalysts. In the present study, the unique photocatalytic decomposition of N_2O by the addition of propane can be ascribed to the very different reactivity of the excited state of the p-block element, the Pb^{2+} ions with an (s^1p^{1*}) electronic configuration toward N_2O and propane, as compared with the (d^9s^{1*}) electronic configuration of the Cu^+ or Ag^+ ions. A detailed study of the mechanism behind this photocatalytic decomposition of N_2O in the presence of propane is now underway.

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