

Local structure of Pb (II) ion catalysts anchored within zeolite cavities and their photocatalytic reactivity for the elimination of N₂O

Woo-Sung Ju, Masaya Matsuoka, Hiromi Yamashita and Masakazu Anpo*

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

E-mail: anpo@ok.chem.osaksafu-u.ac.jp

The Pb²⁺/ZSM-5 catalyst was prepared by an ion-exchange method and its photocatalytic activity for the decomposition of N₂O under UV irradiation was investigated. In-situ UV-Vis absorption spectroscopy and XAFS (XANES and FT-EXAFS) investigations revealed that the Pb²⁺ ions exist in a highly dispersed state within the pores of the zeolites. UV irradiation of the catalysts in the presence of N₂O led to the photocatalytic decomposition of N₂O into N₂ at temperatures as low as 298K. The effective wavelength of the irradiated UV light indicated that the excited state of the Pb²⁺ ions included within the zeolite cavities plays a significant role in the photocatalytic decomposition of N₂O molecules.

Keywords: photocatalyst, Pb²⁺, zeolites, N₂O decomposition

1. Introduction

The development of efficient catalytic systems for the photocatalytic decomposition of nitrous oxide (N₂O) (Anpo et al., 1998; Y. Li & Armor, 1992) which causes greenhouse effect and the destruction of the ozoneosphere, is of utmost importance. Transition metal exchanged zeolites such as Pr (Ebitani et al., 1995), Fe (Yamada et al., 1998) and Ag (Miyadera, 1997; Matsuoka et al., 1996) ZSM-5 catalysts are of interest due to their potential application as thermal- or photo-induced catalysts in the decomposition reaction of N₂O. On the other hand, recently, Pb²⁺ ion-exchanged zeolites were shown to be effective for the selective catalytic reduction (SCR) of NO_x in the presence of hydrocarbons (Pang et al., 1996). The nature and role, however, as well as the reactivities of Pb²⁺/zeolites with gaseous N₂O have not yet been fully investigated. In the present study, in-situ techniques such as in-situ UV-Vis, photoluminescence and XAFS along with an analysis of the reaction products, have been employed to understand the nature of the active species on the ion-exchanged Pb²⁺/ZSM-5 photocatalyst.

2. Experimental

Pb²⁺/ZSM-5 catalysts were prepared by a conventional ion-exchange method using the corresponding H⁺/ZSM-5 (Si/Al=23.8; TOSOH, Japan) as starting material with a dilute Pb(NO₃)₂ solution. After the ion-exchange, the samples were washed with distilled water and dried in air at 373 K. Atomic

absorption spectroscopy studies revealed the amount of ion-exchanged Pb²⁺ to be 2.7wt% as metal. Prior to spectroscopic and photocatalytic reactivity investigations, the samples were degassed in vacuum at 673 K, calcined in the presence 20 Torr of O₂ at 673 K, and finally evacuated at 473K. The XAFS spectra (XANES and EXAFS) were obtained at the BL01B1 of SPring-8. Si(311) channel-cut crystal was used to monochromatize the X-ray from the 8 GeV electron storage ring. The Pb L III-edge absorption spectra were recorded in the transmission mode at 298 K. Photocatalytic reactions were carried out at 298 K using a high pressure Hg mercury lamp through a water filter. A UV-cut filters ($\lambda > 250$ nm) was employed to examine the effect of wavelength on the photochemical reaction. The reaction products were analyzed by gas chromatography.

3. Results and discussion

The results of UV-Vis measurement studies of Pb²⁺/ZSM-5 (2.7wt%) and H⁺/ZSM-5 are presented in Fig. 1. It can clearly be seen that the Pb²⁺/ZSM-5 sample shows an intense absorption band at around 220nm, while only negligible absorption can be observed for the parent zeolite. Similar peak positions have been observed for the Pb(NO₃)₂ aqueous solution (220 nm), indicating that the absorption band is attributed to the intraionic electronic transition ([Xe] 6s² → 6s¹6p¹) of the isolated Pb²⁺ ions (Pascual et al., 1976).

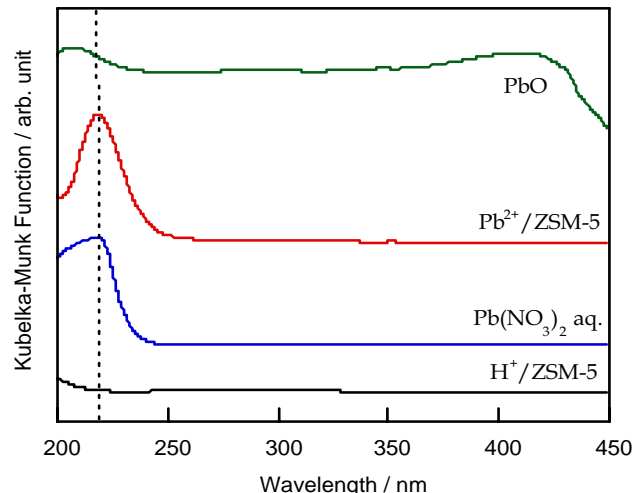


Figure 1

The UV-Vis spectra of PbO, Pb²⁺/ZSM-5, Pb(NO₃)_{2(aq)} and H⁺/ZSM-5.

The XANES and Fourier transformed EXAFS (FT-EXAFS) spectra of Pb²⁺/ZSM-5 are presented in Fig. 2 along with those of the standard PbO sample. The FT-EXAFS spectra data of PbO show two strong peaks at 1.8 and 3.4 Å (phase shift is not corrected), which can be attributed to the Pb-O and Pb-O-Pb bonding, respectively. The absence of a peak at 3.4 Å in the FT-EXAFS of Pb²⁺/ZSM-5 clearly suggests the presence of highly dispersed Pb²⁺ ions within the zeolite cavities, in agreement with UV-Vis spectroscopic investigations. From the results obtained by the curve-fitting analysis of the FT-EXAFS spectra, it was

found the Pb zeolites consist of 3-coordinate lead ions with an atomic distance of 2.3 Å (Pb-O).

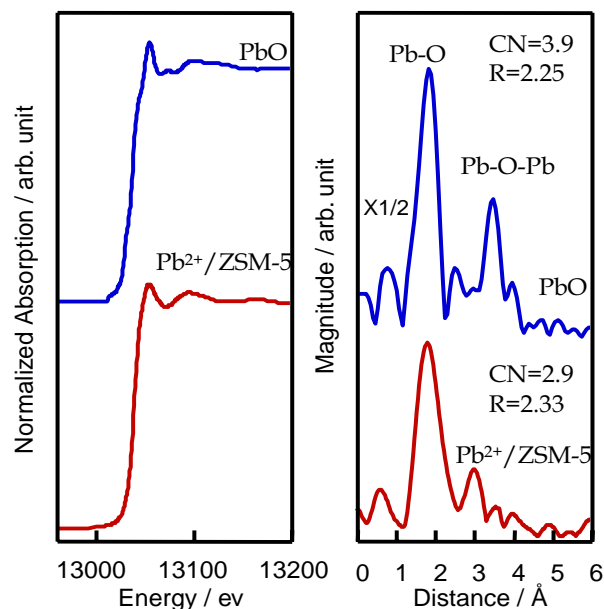


Figure 2

The XANES spectra and FT-EXAFS spectra of 2.7wt% for the Pb/ZSM-5 catalyst and PbO.

Pb²⁺/ZSM-5 exhibits photoluminescence at around 330nm upon excitation at around 220nm. The position of the excitation band at 220nm is in good agreement with that observed for the Pb(NO₃)₂ solution, which is attributed to the electronic transition 6s²→6s¹6p¹ of the Pb²⁺ ions. Therefore, the excitation band at around 220 nm and the photoluminescence band at around 330 nm can be attributed to the presence of the isolated Pb²⁺ ions, i.e., to the 6s²→6s¹6p¹ excitation and its radiative deactivation process of 6s¹6p¹→6s², respectively. Furthermore, the addition of N₂O onto Pb²⁺/ZSM-5 led to an efficient quenching of the photoluminescence, while the degassing of N₂O after the complete quenching led to the recovery of the photoluminescence to its original intensity level. These results clearly suggest that the interaction of the N₂O molecules with the Pb²⁺ ions is weak, and that the added N₂O molecules easily interact with the Pb²⁺ species in their excited states (6s¹6p¹ state).

The results of the photocatalytic decomposition of N₂O at 298 K are presented in Fig. 3. It is clear that the yields of N₂ show a good linear relation with the UV-irradiation time, with no detectable N₂ formation under dark conditions, indicating that the reaction proceeds photocatalytically. Photo-decomposition under a UV-25 filter (λ>250 nm) proceeded 5% of the yield of the N₂ rate compared to full UV-illumination. This suggests that the Pb²⁺/ZSM-5 catalyst is active under UV light irradiation in the 200~250 nm wavelength regions where the absorption band of the isolated Pb²⁺ ions exist and the photocatalytic decomposition of N₂O proceeds on the excited isolated Pb²⁺ ions. Furthermore, it is also found that the photocatalytic

decomposition of N₂O proceeded much more efficiently in the coexistence of propane than the direct photocatalytic decomposition of N₂O without propane. Detailed investigations to clarify the mechanism behind the reaction are now underway.

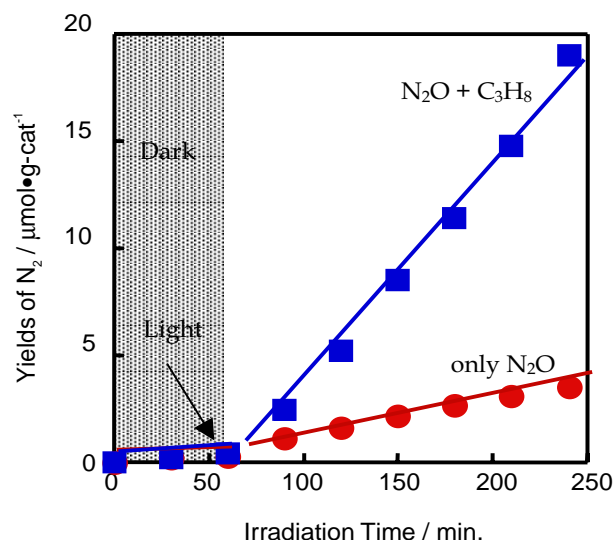


Figure 3

The effect of the addition of Alkane species on the N₂O photocatalytic decomposition of 2.7wt% Pb/ZSM-5.

4. Conclusion

From these various findings, the highly dispersed Pb²⁺ containing ZSM-5 photocatalysts have been synthesized employing an ion-exchange method. In-situ UV-Vis spectroscopy and EXAFS studies clearly indicate the existence of isolated Pb²⁺ ions within the zeolite channels. The study about photocatalytic reaction indicate that the catalyst is more active under irradiation of UV light in the wavelength regions of 200~250 nm, suggesting that the excited state Pb²⁺([Xe]6s²→[Xe]6s¹6p¹) ions play a significant role as the active species in the photocatalytic decomposition of N₂O.

References

- Anpo, M., Matsuoka, M., Hanou, K., Mishima, H., Yamashita, H. & Patterson, H. H. (1998). *Coordination Chemistry Reviews*, **171**, 175-184.
- Ebitani, K., Hirano, Y. & Morikawa, A. (1995). *J. Catal.*, **157**, 262-265.
- Li Y. & Armor, John N. (1992). *Appl. Catal. B*, **1**, 21-29.
- Matsuoka, M., Matsuda, E., Tsuji, K., Yamashita, H. & Anpo, M. (1997). *J. Molecular Catalysis A*, **107**, 399-403.
- Miyadera, Tatsuo (1997). *Appl. Catal. B*, **13**, 157-165.
- Morterra, C., Giamello, E., Cerrato, G., Centi, G. & Perathoner, S. (1998). *J. Catal.*, **179**, 111-128.
- Pang, X. Y., Zeng, H. C., Wu, J. C. & Li, K. (1996). *Appl. Catal. B*, **9**, 149-165.
- Pascual, J. L., Cabrera J. M. & Agullo-Lopez, F. (1976). *Sol. Sta. Comm.*, **19**, 917-920.
- Yamada, K., Pophal, C. & Segawa, K. *Micropor. Mesopor. Mater.*, (1998). **21**, 549-555.