

XAFS study on active Pr sites in zeolite as a photocatalyst for decomposition of nitrous oxide

Kohki Ebitani,^a Akio Nishi,^b Yoshiaki Hirano,^{b1} Hisao Yoshida,^c Tsunehiro Tanaka,^d Tomoo Mizugaki,^a Kiyotomi Kaneda^a and Akira Morikawa^e

^aGraduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan. E-mail: kaneda@cheng.es.osaka-u.ac.jp

^bGraduate School of Science and Engineering, Tokyo Institute of Technology, Meguro, Tokyo 152-8552, Japan.

^cGraduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan.

^dGraduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan.

^eDepartment of Kansei Engineering, Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567, Japan.

¹Present Address: Nippon Shokubai Co., Ltd., Suita, Osaka 564-8512, Japan.

The praseodymium-exchanged mordenite degassed at 873 K acted as a highly active heterogeneous photocatalyst for the stoichiometric decomposition of N₂O. Analysis of Pr L₃-edge EXAFS revealed that the Pr species were isolated each other in the large channel of zeolite, and that the active Pr species were coordinated by *ca.* four oxygen atoms and one Al atom. On the other hands, the inactive Pr species are surrounded by *ca.* 10 oxygens of adsorbed waters. The former low-coordinated Pr species allowed a strong adsorption of N₂O, which could be the first step of the decomposition reaction.

Keywords: praseodymium, L₃-edge, decomposition of nitrous oxide, photocatalyst.

1. Introduction

The investigations on the optical and spectroscopic properties of rare earth ions have been extensively reported in relation to the transition of the electrons situated in the inner 4f levels to the 5d orbitals (4f-5d transition) or to other 4f levels (f-f transition) (Suib *et al.*, 1984; Arakawa *et al.*, 1984). The ions in their excited state, generated by the absorption of light, have possibility of transfer their excited energy to other molecules around them (Calvert & Pitts, 1966). Such energy transfer could lead to the photocatalysis by the rare earth ions. However, the heterogeneous photo-catalysis by rare earth cations, originated from the photo-excitation of the electron situated in the inner 4f orbital, has not been reported.

In the previous paper, we found that the rare earth ions acted as heterogeneous photocatalysts for the decomposition of dinitrogen monoxide (N₂O) at 285 K, and reported that praseodymium ions in a cavity of a zeolite, *i. e.*, mordenite, showed the highest activity (Ebitani *et al.*, 1995). In addition, the praseodymium ion-exchanged mordenite catalyst, denoted by Pr-M hereafter, had an unique advantage that the N₂:O₂ molar ratio in the photodecomposition products was 2. Such a stoichiometric decomposition of N₂O has not been attained by other photocatalysts such as ZnO (Tanaka & Blyholder, 1971) and Cu⁺/zeolites (Ebitani *et al.*, 1994) due to a strong affinity of oxygen species on the active metal sites.

The novel and prominent photocatalysis of the rare earth elements should be associated to their specific structure. Here, we report an

active structure of Pr cations by means of Pr L₃-edge XAFS study combined with kinetic and adsorption measurements.

2. Experimental

The Pr-M was prepared by an ion-exchange of the sodium type mordenite (Na-M), whose Si:Al atomic ratio is 7.5:1.0, in an aqueous solution of PrCl₃ (60 mM), followed by the calcination at 723 K. The Pr content determined by ICP measurement was 2.96 wt%, corresponding to ion-exchanged degree of 43 %.

The praseodymium L₃-edge X-ray absorption spectra were recorded in a fluorescence mode at the EXAFS facilities installed on the BL-7C line of the Photon Factory at the National Laboratory for High Energy Physics (KEK-PF), Tsukuba, Japan. To extract the empirical parameters of Pr-O and Pr-Al shells, the experiments were performed on Eu₂O₃ and LaAlO₃ of known structures as reference materials of the respective shells. The procedure of the data reduction was described in the literature (Tanaka *et al.*, 1988). Data treatments were carried out with the FACOM M-780 computer system of the Data Processing Center of Kyoto University.

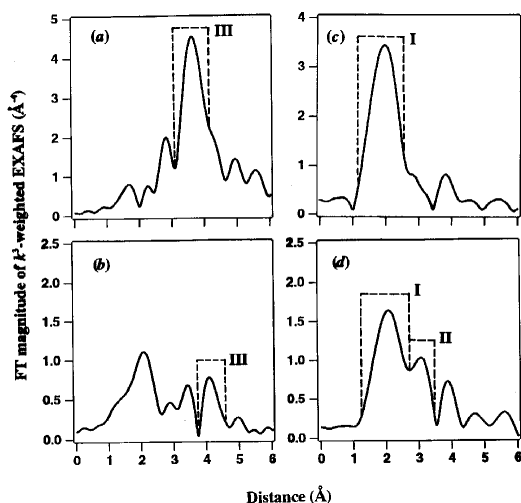
The detailed procedure for the photodecomposition of N₂O was reported in the previous paper (Ebitani *et al.*, 1994). Notably, the photocatalytic activity of the Pr-M was observed when the Pr-M was degassed in a vacuum at higher temperatures above 600 K. Furthermore, the decomposition of N₂O scarcely occurred on the degassed Pr₆O₁₁, Pr/SiO₂ (3 wt%), and Na-M even under the irradiation.

The amount of N₂O adsorption on the Pr-M was volumetrically determined at 273 K using Varatron MKS sensor (type 627A). The amount of chemisorbed or strongly adsorbed N₂O was estimated from the difference of the 1st and 2nd isotherms. The latter was successively obtained after degassing the N₂O-covered sample at 273 K.

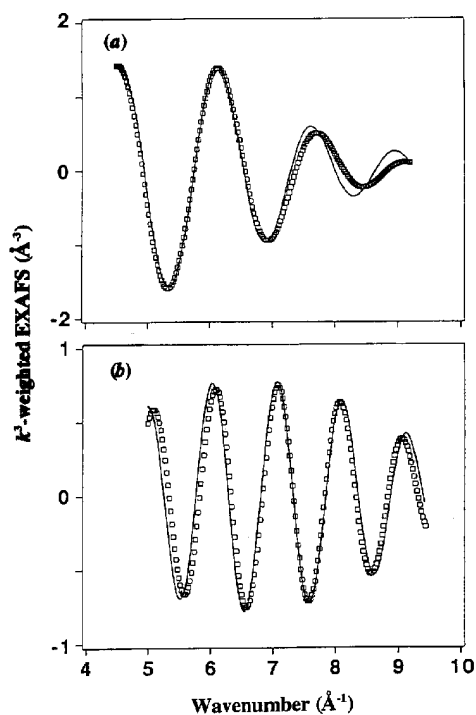
3. Results and discussion

The catalytic decomposition of N₂O into N₂ and O₂ (N₂/O₂ = 2) proceeded only when the degassed Pr-M was irradiated by the light of wavelength shorter than 270 nm, and the rate of N₂ formation, or photodecomposition of N₂O, was proportional to the intensity of the irradiated light from the Hg lamp. The measurement of a diffuse-reflectance UV-VIS spectrum revealed a strong absorption at the wavelength of light around 230 nm, ascribed to the transition of electrons situated in the inner 4f orbitals of Pr³⁺ ion (4f²5s²5p⁶, ³H₄) either to 4f (³H₄ → ¹S₀) and 5d states (Cornall *et al.*, 1969; Piper *et al.*, 1974). The above results clearly indicate that the decomposition of N₂O on the Pr-M is a photochemical process in which the excitation of the Pr³⁺ ion participates.

Figure 1 shows the Fourier transforms (FTs) of *k*³-weighted EXAFS oscillation of Pr L₃-edge for the Pr₆O₁₁, Pr/SiO₂, and Pr-M samples (Phase shift was not corrected). It should be noted that no considerable Pr-Pr shell, which is detected in the FTs for Pr/SiO₂ and Pr₆O₁₁ bulk at around 4 Å (peak III), was observed for the Pr-M. In the spectrum of the Pr-M degassed at 873 K (Fig. 1-*d*), the peaks appeared at around 2 Å (peak I) and 3 Å (peak II). The peak I and II are inversely Fourier transformed in order to estimate the scattering shell as shown in Figure 2 in real lines. These EXAFS curves are fitted by using Eu-O and La-Al shells, respectively, in place of Pr-O and Pr-Al shells. These parameters were extracted from FTs of Eu₂O₃ and LaAlO₃.


Figure 1

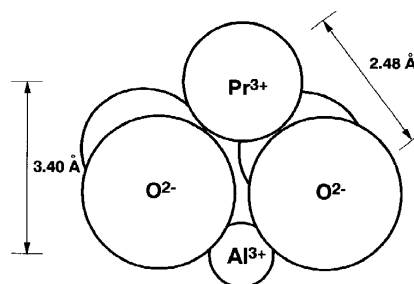
Fourier transforms of k^3 -weighted EXAFS of (a) Pr_6O_{11} , (b) Pr/SiO_2 , (c) Pr-mordenite, and (d) Pr-mordenite degassed at 873 K.


Figure 2

Inverse Fourier transforms (real line) of (a) peak I (1.2-2.7 \AA) and (b) peak II (2.6-3.5 \AA). Dotted lines represent calculated EXAFS by using Eu-O (a) and La-Al (b) shells, respectively.

The best fitting results are shown in Figure 2 as dotted lines. The bond distance (R) and coordination number (CN) were evaluated to be 2.48 \AA , 4.5 for the peak I, and 3.40 \AA , 0.7 for the peak II, respectively. The analyses on other peaks confirmed that there are no Pr-Pr shell. The above results showed that the Pr^{3+} cations in mordenite cavity are isolated each other and are surrounded by 4 or 5 oxygen anions and 1 aluminum cation. Combined with the crystal

structure of mordenite (Mortier *et al.*, 1975), we proposed an one-sided coordination sphere around the Pr^{3+} cation as an active state for the photodecomposition of N_2O in Figure 3. It was supposed that the monomeric Pr^{3+} cation in the mordenite is bound to 4 oxygen atoms (O7 and O3) at the wall site in the large channel (Iton & Turkevich, 1977), presumably corresponding to the T1 site.


Figure 3

Proposed schematic structure around Pr^{3+} cation within the mordenite cavity. The distance between O^{2-} ions was assumed to be 3.04 \AA .

The curve-fitting analysis of the peak I observed for inactive Pr-M (Fig.1-c) using Eu-O shell parameters showed the R and CN of 2.48 \AA and 10. The desorption of water was detected during the degassing the Pr-M at elevated temperatures. Therefore, the inactive Pr cations were surrounded by oxygens of *ca.* 10 water molecules. This number is reasonable since a maximum coordination number of water to Pr^{3+} cation is 9 (Ryan & Jørgensen, 1966).

The activity of the isolated Pr cations should be related to the highly coordinative unsaturation of Pr ions situated in the mordenite cavity. To ensure this, the amount of chemisorbed N_2O was measured. It was shown that one Pr^{3+} cation was capable to capture two N_2O molecules in an average (*ca.* 0.35 mmol g^{-1}). Since no chemisorption of N_2O was observed on the Na-M and on the Pr_6O_{11} , the strong adsorption must occur on the isolated Pr^{3+} cations. Figure 4 (b) depicts FTs of Pr L_3 -edge EXAFS of the active Pr-M sample after the chemisorption of N_2O molecules. The intensity of the peak I was larger than that of simply degassed Pr-M sample (a). These results clearly support the chemisorption of N_2O in the vicinity of the isolated Pr cations. Adsorption of water on the degassed Pr-M resulted in the complete loss of chemisorption ability of the Pr ions and a drastic increase of the intensity of the peak I as shown in Figure 4 (c).

The rate of the photodecomposition was independent on the pressure of N_2O between 0.1 and 0.7 kPa. However, it was proportional to the amount of chemisorbed N_2O on the Pr-M. In Figure 5, the dependence of the initial photodecomposition rate of N_2O (10 min) as well as of the $\text{N}_2:\text{O}_2$ ratio in the product on the amount of the chemisorbed N_2O on the Pr-M are displayed. The amount of chemisorbed N_2O was controlled by changing the amount of the introduced N_2O on the Pr-M. Under these experiments, the introduced N_2O was completely adsorbed on the Pr-M. It was well demonstrated that the rate of N_2 formation was proportional to the amount of the chemisorbed N_2O . At large chemisorbed amounts, the rate became close to that in the presence of sufficient amounts of N_2O in the gas phase, expressed by a dotted line (c). From the results mentioned above, it is proposed that an N_2 molecule was formed during the photodecomposition of chemisorbed N_2O molecules on the isolated Pr^{3+} cation site. The decomposition of chemisorbed N_2O on the Pr ions is initiated by the photoexcitation of the Pr^{3+} cations,

followed by the sensitization to form its excited states such as N_2O^* or N_2O^- .

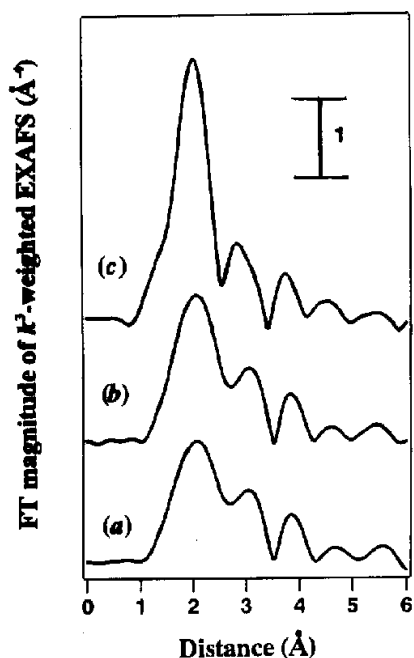


Figure 4

Fourier transforms of k^3 -weighted EXAFS of (a) Pr-M degassed at 873 K, followed by adsorption of (b) N_2O , or (c) H_2O at 273 K.

As shown in Figure 5, in the absence of N_2O in the gas phase, the $N_2:O_2$ ratio in the product is so high, compared to the stoichiometric decomposition, especially when the ratio of the amount of chemisorbed N_2O to a Pr^{3+} cation is less than 1. This evidence stresses that the rate of O_2 desorption from the Pr^{3+} cation site is essentially very slow compared to that of N_2 . On the other hand, the $N_2:O_2$ ratio decreases and keeps almost a constant value close to the stoichiometric decomposition when the $N_2O:Pr^{3+}$ ratio is maintained at the values higher than 1. This result implies an easiness of O_2 evolution from such atomic oxygen species that was generated by the photodecomposition of N_2O molecules on the isolated Pr^{3+} cation site with plural or presumably two chemisorbed N_2O molecules.

4. Conclusions

From the Pr L_3 -edge XAFS study for the Pr ion-exchanged mordenite, it is concluded that the low-coordinated active Pr species were isolated each other and bound to oxygen and Al atoms at the wall site in the large channel of mordenite. The Pr species could strongly capture two N_2O molecules. The decomposition of N_2O was initiated by the photoexcitation of 4f electrons of the Pr cations in the $[Pr^{3+}(N_2O)_2]$ species, followed by the energy transfer to adsorbed N_2O molecules. When the $N_2O:Pr^{3+}$ ratio is higher than 1, an O_2 molecule was smoothly evolved *via* the recombination of the oxygen atom species on the same Pr^{3+} cation site.

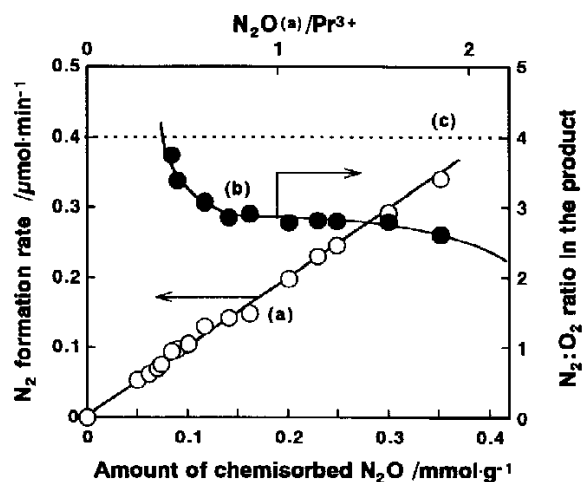


Figure 5

Dependences of (a) N_2 formation rate and (b) $N_2:O_2$ ratio in the product during the photodecomposition of N_2O as a function of the amount of chemisorbed N_2O on the Pr-M. The dotted line (c) denotes the N_2 formation rate in the presence of sufficient amounts of the gaseous N_2O . $N_2O_{(a)}$ expresses N_2O molecules in the chemically adsorbed state.

This work is partly defrayed by the Grant-in-Aid from the Ministry of Education, Science, Sports and Culture of Japan (No.07228220). The X-ray absorption experiments have been performed under the approval of the Photon Factory Program Advisory Committee (Proposal No.95G206).

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