2001A0563-UX-np BL01B1

XAFS Analysis on Fine Structure of Infinitesimal Palladium Species Immobilized on Hydroxyapatite Surface

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1. Introduction Hydroxyapatite (HAP) is a highly-functionalized inorganic material in many areas such as artificial bones, adsorbents, ion-exchangers, and catalysts[1] because of their large cation exchange ability. Recently, we found that the HAP-bound Pd (PdHAP) acts as a highly effective and reusable heterogeneous catalyst for aerobic alcohol oxidation and the Heck coupling reactions. Interestingly, the catalytic activity of the PdHAP strongly depends on the Ca/P ratio in the HAP. In this report, the structure of infinitesimal Pd species on the PdHAP surface was analyzed by Pd K-edge XAFS spectroscopy.

2. Experimental Two types of calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ (HAP-0) and $Ca_9(HPO_4)(PO_4)_5(OH)$ (HAP-1), were synthesized according to the literature[2]. HAP-bound Pd (PdHAP) was prepared by soaking the HAP in acetone solution of $PdCl_2(PhCN)_2$. The Pd content of the PdHAP was 0.015 mmol·g^{-1}.

Pd K-edge X-ray absorption spectra were recorded at room temperature using a fluorescence-yield collection technique at the beam line 01B1 station attached with Si(311) monochromator. The yield was collected using the 19-element solid-state detector. The procedures for data reduction are described in elsewhere[3].

3. Results and Discussions The Fourier transforms (FTs) of the fresh PdHAP-0 and PdHAP-1 are depicted in Fig. (A) and (B), respectively. The lack of the peak due to a Pd-Pd shell in the second coordination sphere supports a formation of isolated Pd^{2+} species on these catalysts. The curve-fitting analysis for the peak at around 1.5 Å for the PdHAP-0 using Pd-O and Pd-Cl shell parameters shows that the isolated Pd cation was surrounded by 2 chlorines and 2 oxygens. On the other hand, the Pd^{2+} of the PdHAP-1 was surrounded by 4 oxygens, suggesting that the Pd ions are situated in Ca defect sites of the HAP-1. Such a Pd^{2+} location in the PdHAP-1 do not allow a structural change during the alcohol oxidation (D), whereas large particles of Pd^0 are formed on the PdHAP-0 under the same conditions (C). Large particles of Pd^0 on the Pd-HAP-0 are responsible for the aerobic alcohol oxidation. The prominent catalysis of the PdHAP-1 in the Heck reaction can be ascribed to a high stability of the isolated active Pd^{2+} species against the reduction at the surface of the Ca deficient HAP.

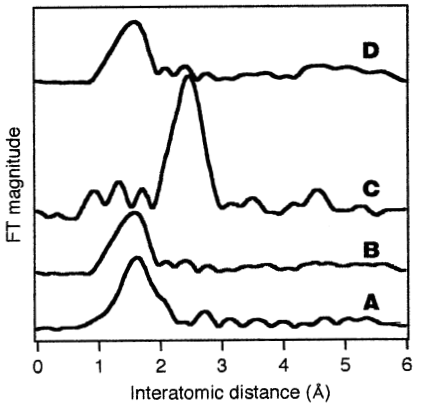

Figure. Fourier-transformed k^3-weighted EXAFS of (A) PdHAP-0, (B) PdHAP-1, (C) used PdHAP-0, and (D) used PdHAP-1 for the oxidation of 1-phenyl-ethanol. Phase shift was not corrected.

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[2] Sugiyama, S. *et. al. J. Chem. Soc., Farad. Trans.* **1996**, *92*, 293.
[3] Tanaka, T. *et. al. J. Chem. Soc., Farad. Trans.* **1988**, *84*, 2987.

2001A0570-UX-np BL01B1

High-Resolution Study of Controlled Deexcitation of Nuclear Isomers

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Nuclear spin-isomers can have high energies of internal excitation, high angular momenta, J, and long lifetimes against spontaneous decay. The 31 year isomer of $^{178}Hf^{m2}$ is a particularly interesting example. It stores 2.445 MeV per atom with J = 16. Theory had predicted that absorption of X-rays could excite such nuclei to higher energy states from which decay to the ground state would be accelerated. The first experimental proof made with synchrotron radiation, SR was conducted at SPring-8 in March, 2001. X-rays were tuned from 9000 to 13,000 eV in 5 eV steps. Spontaneous decays of the $^{178}Hf^{m2}$ isomeric nuclei were accelerated for some X-ray energies.

In the current experiment, detail obtained by tuning more restricted energy ranges with steps of 0.5 eV proved that the energies most effective in accelerating the decay of the isomers were those corresponding to the ionization edges of the L-shell electrons surrounding them. In comparison, impurity radionuclides in ground states showed no such effect. The fractional increases in decay rate shown in Fig.2 correspond to a branch for the acceleration of the order of 2 x 10^{-3} of the L-shell photoionization cross section.

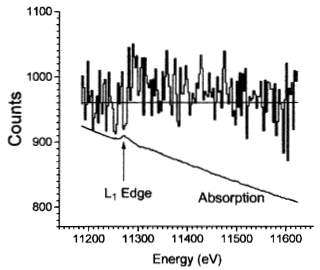

Fig.1 γ-ray intensities emitted by ^{178}Hf isomers irradiated by SR energies shown.

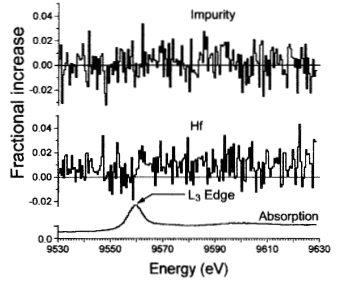

Fig.2 γ-rays emitted by isomeric nuclei and impurities when irradiated with x-rays.