XAFS ANALYSIS OF FINE STRUCTURE OF PALLADIUM SPECIES IMMOBILIZED ON HYDROXYAPATITE SURFACE

The evolution of environmentally acceptable organic synthesis routes is an ultimate goal of the present-day chemistry. One of the promising approaches to "Green & Sustainable Chemistry" is the replacement of conventional methods employing toxic and/or hazardous stoichiometric reagents by atom-efficient catalytic alternatives. Heterogeneous catalysts have the advantages of being operationally simple, as well as enabling unprecedented reactions based on specific surface ensemble sites within a regular arrangement. Achieving precise architectures of active metal species on solid surfaces is one of the most important challenges in creating highly functionalized heterogeneous catalysts. Currently, we are developing high-performance metal catalysts using unique properties of clay minerals as macroligands for catalytic active centers [1].

Hydroxyapatites (HAPs) possess Ca^{2+} sites surrounded by PO_4^{3-} tetrahedra parallel to the hexagonal axis, as shown in Fig. 1, and are of considerable interest in many areas because of their ion-exchange ability, adsorption capacity, and acid-base properties. The chemical composition of HAPs can be varied from the stoichiometric form to the Ca-deficient one. Here, we present two new classes of HAP-bound Pd complexes designed with strict compositional and structural control [2]. Both stoichiometric and Ca-deficient HAPs are employed, and the catalysts exhibit specific novel functions as heterogeneous Pd catalysts. The precise construction of Pd species described here also represents a great contribution to modern palladium chemistry.

HAPs were synthesized from $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$ by a precipitation method. Selecting appropriate Ca/P molar ratios yielded the stoichiometric $Ca_{10}(PO_4)_6(OH)_2$ (Ca/P=1.67, HAP-0) and Ca-deficient $Ca_9(HPO_4)(PO_4)_5(OH)$ (Ca/P= 1.50, HAP-1). The treatment of the HAP-0 and HAP-1 with an acetone solution of $PdCl_2(PhCN)_2$ yielded HAP-bound Pd complexes, PdHAP-0 and PdHAP-1, respectively (Pd content: 0.02 mmol·g^{-1}).

The characterization of the PdHAPs using physicochemical methods such as X-ray diffraction, X-ray photoelectron spectroscopy, and inductively coupled plasma spectrometry revealed that the palladium species are immobilized by adsorption on the HAP surface. Furthermore, the results of Pd *K*-edge X-ray absorption near-edge structure spectra of both PdHAPs confirmed the divalent state of all Pd species. A monomeric Pd species was evidenced by the absence of peaks at around 2.5 Å in the Fourier transform (FT) of k^3-weighted extended X-ray absorption fine structure (EXAFS) data for the PdHAPs (Figs. 2(a) and 2(b)) (**BL01B1**).

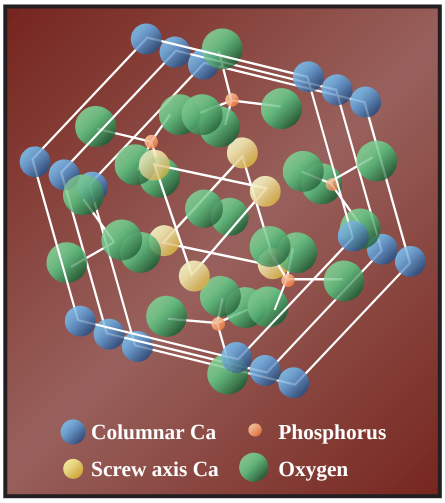

Fig. 1. Structure of hydroxyapatite.

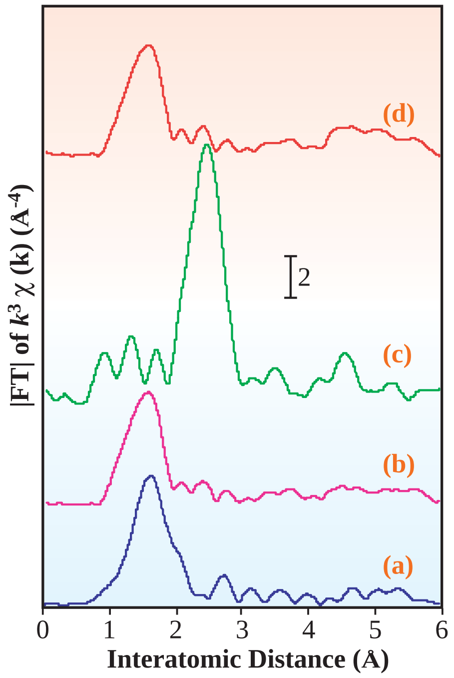

Fig. 2. FTs of k^3-weighted Pd *K*-edge EXAFS experimental data for **(a)** PdHAP-0, **(b)** PdHAP-1, **(c)** recovered PdHAP-0 and **(d)** recovered PdHAP-1 for the oxidation of 1-phenylethanol. The phase shift was not corrected.

The inverse FT of the peaks at around 1-2 Å for the PdHAP-0 was well fitted using Pd-Cl and Pd-O shells, whereas the best fit for the PdHAP-1 was achieved using only a Pd-O shell. It was conclusively established that a monomeric $PdCl_2$ species was grafted by chemisorption on the HAP-0 surface (Fig. 3(a)), and a monomeric Pd^{II} phosphate complex surrounded by four oxygens was formed at a Ca-deficient site of the HAP-1 (Fig. 3(b)). Two unique monomeric Pd species with intrinsically different surroundings can be created on the solid surfaces through the precise control of the Ca/P ratios of the parent hydroxyapatites.

The oxidation of alcohols into carbonyl compounds is one of the most pivotal functional group transformations in organic synthesis. The PdHAP-0 was an effective heterogeneous catalyst for the aerobic oxidation of a wide variety of alcohols, giving the corresponding ketones and aldehydes in high yields. In a 250 mmol scale reaction of 1-phenylethanol without organic solvents, the oxidation proceeded smoothly and the turnover number (TON) of acetophenones based on Pd approached 236,000. This TON is three orders of magnitude larger than those previously reported for any catalyst systems under an atmospheric O_2 pressure.

The FT EXAFS for the recovered PdHAP-0 exhibited a single peak at approximately 2.5 Å due to the formation of Pd metal, as shown in Fig. 2(c). TEM also revealed the presence of Pd nanoparticles with a diameter of *ca*. 40 Å and a narrow size distribution (σ = 5.7 Å) (Fig. 4). The ICP analysis of the filtrate confirmed that no leaching of Pd species occurred during the above oxidations. Notably, the above oxidations hardly occurred in the presence of the PdHAP-1, and that there were no structural changes at around the PdII center (Fig. 2(d)).

Recently, we have also found that the PdHAP-0 can be an efficient heterogeneous catalyst for the dehalogenation of aryl halides, deprotection of the *N*-benzyloxycarbonyl group from amino acids using 1 atm of H_2, and the dehydrogenation of indolines into indoles that serve as versatile intermediates for the synthesis of pharmaceuticals and agrochemicals [3].

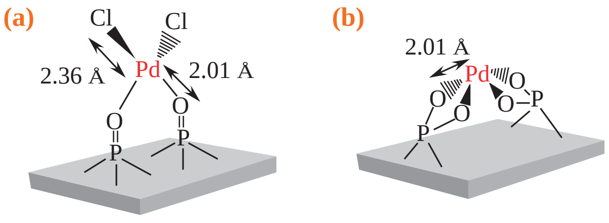

Fig. 3. Proposed surface structures around Pd^{II} of PdHAP-0 **(a)** and PdHAP-1 **(b)**. The nearest oxygen and chlorine atoms around the Pd^{II} are shown.

The Heck coupling reaction has received considerable attention due to its enormous synthetic potential to form new carbon–carbon bonds. Commercial applications have, however, been limited by low TONs. We found that the PdHAP-1 is an outstanding catalyst for the Heck reaction. For example, the TON based on Pd reached 47,000 for 24 h in the reaction of bromobenzene with styrene. The recovered PdHAP-1 kept an original monomeric Pd^{II} structure and was recyclable with retention of its catalytic activity. It can be concluded that the high catalytic activity of the PdHAP-1 is ascribed to the exceptional robust structure of monomeric Pd^{II} species.

We expect that our immobilizing protocol using hydroxyapatites will offer an attractive route for the design of high-performance nanostructured catalysts at the atomic level with the aim of realizing environmentally friendly chemical processes. XAFS measurement gives us precise and reliable information about the local structure of infinitesimal metal species immobilized on the solid surface.

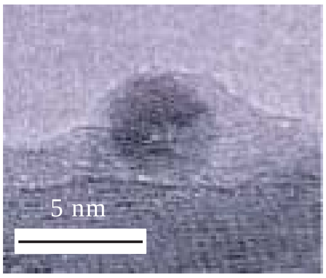

Fig. 4. Transmission electron micrograph of the Pd nanoparticle for the recovered PdHAP-0 catalyst after the oxidation of 1-phenylethanol.

Kiyotomi Kaneda

Graduate School of Engineering Science,
Osaka University

E-mail: kaneda@cheng.es.osaka-u.ac.jp

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