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Finding Hydrogen-Storage Capability in Iridium Induced by the Nanosize Effect

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Supporting Information

ABSTRACT: We report nanosize-induced hydrogen storage in Ir, which does not absorb hydrogen in its bulk form. The mean diameter of the obtained Ir nanoparticles was estimated as 1.5 ± 0.5 nm by transmission electron microscopy. Hydrogen storage was confirmed by solid-state ^{2}H NMR and hydrogen pressure−composition isotherm measurements.

Recently, metal nanoparticles have attracted attention not only for new electronic, magnetic, optical, and catalytic properties but also for new types of hydrogen-storage alloys.[1,2] Much attention regarding hydrogen storage has been focused on nanoparticles of hydride-forming metals that can absorb hydrogen in the bulk state,[3] but there have been few reports on nanosize effects on the non-hydride-forming elements.

Iridium is an important transition-metal catalyst for promoting alkene, aldehyde, and ketone hydrogenation,[4] although it does not form a hydride (Ir−H).[5] In particular, for acetone hydrogenation to 2-propanol, which is a useful chemical in various applications such as chemical heat pumps and fuel cells, Ir nanoparticles provide exceptional activity, with the highest selectivity (95% 2-propanol) at the highest conversion (100%) for any catalyst reported to date. As its bulk metal is almost inactive for the hydrogenation reaction, the decrease in the size is of considerable significance in providing the great catalytic activity. From these high catalytic activities mentioned above, Ir is expected to show nanosize-induced hydride formation. This paper discusses the hydrogen-storage capability of Ir nanoparticles even though bulk Ir does not absorb hydrogen.[5]

It is well-known that metal nanoparticles show chemical and physical properties that differ from those of the bulk metals. Their unique properties are based on their high surface-to-volume ratio and quantum size effects.[6] In particular, nanosized metals show characteristic phase behaviors, such as a lowering of their melting point[7] and spontaneous alloying.[8] As the hydrogen-storage properties of a metal are strongly related to its electronic state,[5] metal nanoparticles are expected to show specific hydrogen-storage properties according to their structure or size.[3,9] We have shown that compared with bulk Pd, hydrogen atoms are strongly trapped inside Pd nanoparticles because of the formation of stable Pd−H bonds.[3a] The nanosize effect is expected to allow us to develop nanosize-induced hydrogen-storage materials in non-hydride-forming metals, such as Fe, Ru, Pt, and Ir, as these metals have a strong affinity toward hydrogen molecules. Here we report on the hydrogen-storage capability in Ir induced by the nanosize effect.

Poly(*N*-vinyl-2-pyrrolidone) (PVP)-protected Ir nanoparticles were prepared by the alcoholic reduction of iridium(III) chloride in the presence of PVP. An aqueous solution of $IrCl_3$ was added to an ethanol solution of PVP, and the mixture was refluxed for 3 h with vigorous stirring. During reflux, the color of the solution turned to dark-brown, indicating the generation of a colloidal dispersion of Ir nanoparticles. The UV−vis spectrum of the Ir precursor solution showed absorption peaks at 440 and 490 nm, which correspond to a ligand-to-metal charge-transfer transition.[10] After thermolytic reduction by ethanol, these absorption peaks completely disappeared, indicating that the Ir^{3+} ions had been reduced to Ir(0) during reflux (Figure S1 in the Supporting Information). X-ray photoelectron spectroscopy (XPS) revealed that the Ir nanoparticles exhibited two energy bands at 64.2 and 61.3 eV, which are typical values for the $4f_{5/2}$ and $4f_{7/2}$ electrons of metallic Ir(0) (Figure 1a). As shown in Figure 1b, Ir nanoparticles showed a powder X-ray diffraction (PXRD) pattern originating from a single face-centered-cubic (fcc) lattice. Compared with the diffraction peaks of a bulk Ir sample, those of the Ir nanoparticles are extremely broadened, indicating that the size of the nanoparticles is small (estimated as 1.0 nm using the Scherrer equation). These results demonstrate the formation of Ir nanoparticles by the alcoholic reduction method.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of the obtained Ir nanoparticles are shown in Figure 2. It was found that the synthesized nanoparticles were monodisperse, and the mean diameter was estimated to be 1.5 ± 0.5 nm, which is consistent

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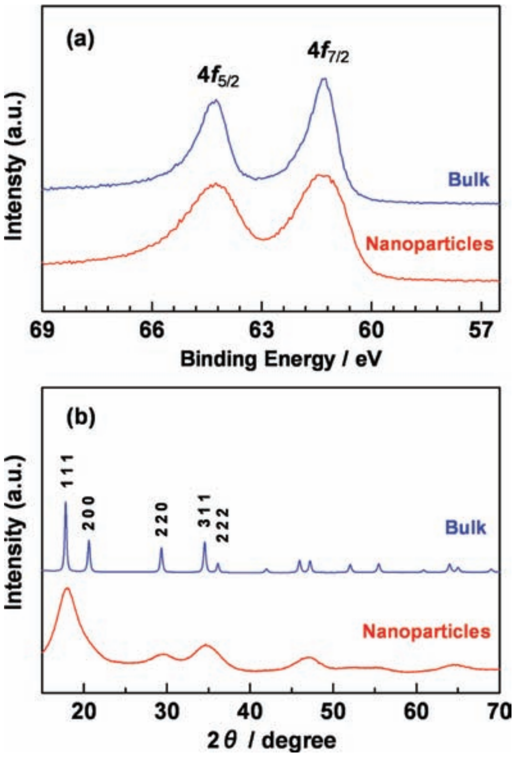

Figure 1. (a) XPS spectra and (b) PXRD patterns of Ir nanoparticles and bulk Ir.

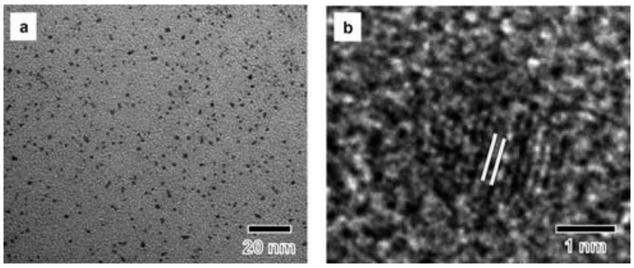

Figure 2. (a) TEM and (b) HRTEM images of Ir nanoparticles.

with the crystal size of 1.0 nm estimated from the Le Bail fitting of the PXRD pattern. In the HRTEM image, the nanoparticles exhibited well-defined crystalline lattice fringes, and the diameter was estimated to be 0.22 nm, in agreement with the Ir(111) lattice plane.

It is known that hydrogen molecules are dissociated into hydrogen atoms on metal surfaces and that the individual atoms permeate inside the metal lattice to form metal−hydrogen bonds. To elucidate the interstitial ^{2}H atoms following hydrogen absorption in Ir nanoparticles, we performed solid-state ^{2}H NMR measurements. As shown in Figure 3a, a broad absorption line with a full width at half-maximum (fwhm) of ca. 100 ppm and a sharp line around 0 ppm were observed. In the spectra for $^2H_2$ gas and bulk Ir, only an absorption line at 3.4 ppm was observed (Figure 3b,c). It is reasonable to attribute the sharp component in the spectrum of the Ir particles to free deuterium gas ($^2H_2$) and the broad component to deuterium atoms (^{2}H) absorbed in the particles. This broad component for Ir nanoparticles is attributed to deuterium atoms (^{2}H) whose motions are restricted to within the Ir lattice. Our NMR experimental results clearly demonstrate the existence of a hydrogen-storage capacity in Ir induced by the nanosize of the particles, while bulk Ir does not absorb hydrogen.

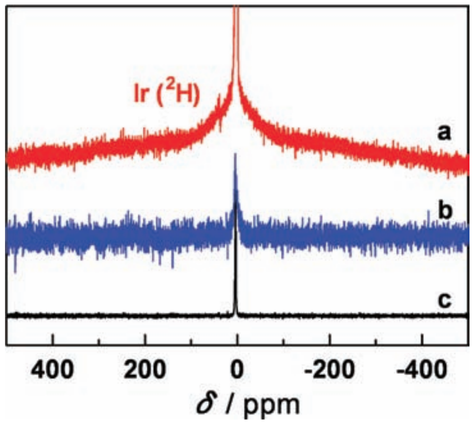

Figure 3. (a) Solid-state ^{2}H NMR spectrum of (a) Ir nanoparticles. The spectra of (b) a bulk Ir sample and (c) $^2H_2$ gas were also measured for reference. All of the samples were measured at a $^2H_2$ gas pressure of 86.7 kPa at 303 K.

The pressure−composition (PC) isotherms of the Ir samples were measured to quantify how much hydrogen was absorbed by the Ir nanoparticles. As shown in Figure 4, the hydrogen concentration (H/Ir ratio) of Ir nanoparticles increased with increasing hydrogen pressure at 303 K, while the bulk Ir sample did not absorb hydrogen at all. This result indicates nanosize-induced hydrogen storage in a metal that does not absorb hydrogen in the bulk form. Hysteresis in the hydrogen absorption/desorption curve was observed, implying hydride formation (Ir−H) in the Ir lattice. Interestingly, a dependence of the hydrogen concentration on the measurement temperature was clearly observed. The concentrations of hydrogen absorbed at a hydrogen pressure of 101.3 kPa were 0.18, 0.16, and 0.15 H/Ir at 303, 333, and 373 K, respectively. The concentration increased with decreasing measurement temperature, indicating that hydrogen-storage processes involve an exothermic reaction between Ir nanoparticles and hydrogen atoms. The nanosize provides a favorable environment for hydrogen absorption in Ir.

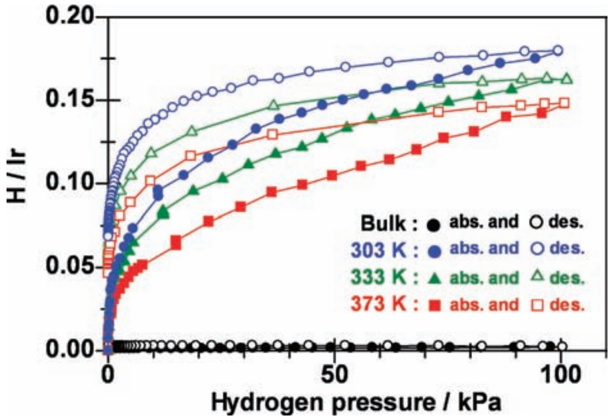

Figure 4. PC isotherms of bulk Ir at 303 K (black) and Ir nanoparticles at 303 K (blue), 333 K (green), and 373 K (red). The H/Ir ratio shows the number of hydrogen atoms divided by the total number of Ir atoms.

It is well-known that hydrogen atoms absorbed in metal or a metal electrode have much stronger reducing power.[11] The high catalytic activity for the hydrogenation reaction observed in Ir nanoparticles may originate not only from the high surface-to-volume ratio but also from the absorbed hydrogen atoms. The discovery of nanosize-induced hydrogen storage in Ir suggests that the catalysis mechanism associated with hydrogen is related to highly concentrated hydrogen atoms on the subsurface of the metal.

In summary, we have for the first time demonstrated the existence of a hydrogen-storage capacity in Ir induced by the nanosize of the particles, while bulk Ir does not absorb hydrogen. The specific size that induces a hydrogen-storage capability in Ir is currently under investigation. We believe that the results reported here will contribute not only to the development of novel hydrogen absorption nanostructured materials but also to clarification of the catalysis mechanism associated with hydrogen.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and electronic spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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