Nanosize-Induced Hydrogen Storage and Capacity Control in a Non-Hydride-Forming Element: Rhodium

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S Supporting Information

ABSTRACT: We report the first example of nanosize-induced hydrogen storage in a metal that does not absorb hydrogen in its bulk form. Rhodium particles with diameters of <10 nm were found to exhibit hydrogen-storage capability, while bulk Rh does not absorb hydrogen. Hydrogen storage was confirmed by in situ powder X-ray diffraction, solid-state ^{2}H NMR, and hydrogen pressure−composition isotherm measurements. The hydrogen absorption capacity could be tuned by controlling the particle size.

Research into the reaction of metals with hydrogen is very important for the development of potential applications, such as effective catalysts for hydrogenation or advanced materials for hydrogen storage and purification. Many investigations into hydrogen storage using bulk metals or alloys have been carried out over the past half-century.[1] On the other hand, metal nanoparticles as hydrogen-storage materials have received scant attention.[2] Previous studies of the hydrogen-storage properties of metal nanoparticles have been confined to hydride-forming elements, and there have been no reports concerning nanosize effects on non-hydride-forming elements.

It is well-known that metal nanoparticles show chemical and physical properties that differ from those of bulk metals because of their unique properties based on their high surface-to-volume ratio and quantum size effects.[3] In particular, nanosized metals show characteristic phase behaviors, such as lowering of the melting point[4] and spontaneous alloying.[5] As the hydrogen-storage properties of a metal are strongly related to its electronic state,[1] metal nanoparticles are expected to show specific hydrogen-storage properties according to their structure or size. We have shown that in comparison with bulk Pd, hydrogen atoms are strongly trapped inside Pd nanoparticles because of the formation of stable Pd−H bonds.[2a] Even non-hydride-forming elements in the bulk are expected to exhibit a hydrogen-storage capability as a result of nanosize effects. In particular, there is the possibility that nanosize-induced hydrogen storage can be exhibited by non-hydride-forming metals such as Fe, Ru, Pt, Ir, and Rh, as these metals have a strong affinity toward hydrogen molecules.[1,6a,7] Here we report the first example of nanosize-induced hydrogen storage by a metal that does not absorb hydrogen in its bulk form.

Rhodium is a major catalyst in many types of reactions because of its unique properties as a catalyst in hydrogenation, hydroformylation, and carbonylation reactions and in emission gas purification.[6] Although it is well-known that Rh reacts strongly with hydrogen molecules and can dissociate hydrogen atoms on its surface, bulk Rh does not form a stable hydride. Therefore, Rh has been considered not to have hydride-forming or hydrogen-storage capability. This paper discusses the hydrogen-storage capability of Rh particles with diameters of <10 nm, even though bulk Rh does not absorb hydrogen. Moreover, the concentration of absorbed hydrogen in the Rh nanoparticles can be tuned by controlling the particle size.

The Rh nanoparticles were synthesized from the polyol reduction of rhodium chloride ($RhCl_3$) in the presence of poly(N-vinyl-2-pyrrolidone) (PVP).[8] Transmission electron microscopy (TEM) images of the Rh nanoparticles showed that the mean diameters of the nanoparticles used were 2.4 ± 0.5, 4.0 ± 0.7, and 7.1 ± 1.2 nm (Figure 1). Control of the nanoparticle size was performed by changing the concentration of Rh precursor and/or PVP.[9] All of the Rh nanoparticles showed powder X-ray diffraction (PXRD) patterns originating from a single face-centered-cubic (fcc) lattice.[9] The diffraction peak broadened for the smaller Rh nanoparticles, consistent with the Scherrer equation.[9]

It is known that hydrogen permeates the interior of a metal or alloy lattice as individual atoms and that these interstitial hydrogen atoms induce an expansion in the metal lattice.[1,2a] To elucidate the lattice expansion following hydrogen absorption in Rh nanoparticles, we performed in situ PXRD measurements on the BL02B2 beamline at SPring-8.[10] The position of the diffraction peaks of the Rh nanoparticles shifted continuously to
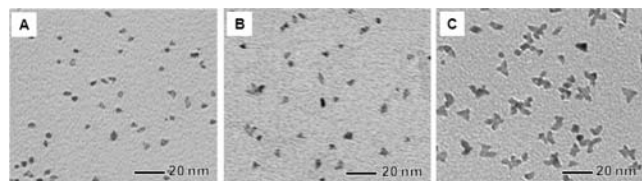
Figure 1. TEM images of Rh nanoparticles with mean diameters of (A) 2.4 ± 0.5, (B) 4.0 ± 0.7, and (C) 7.1 ± 1.2 nm.
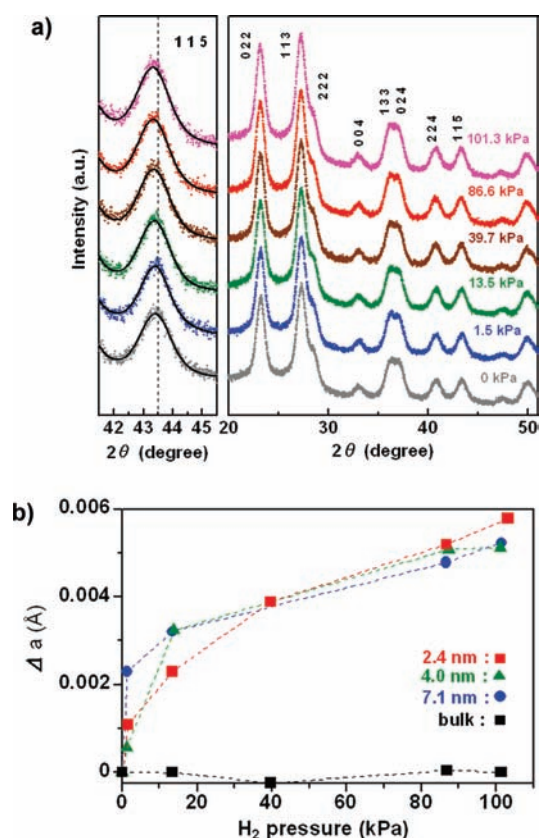
Figure 2. (a) In-situ PXRD patterns of 2.4 nm diameter Rh nanoparticles during the process of hydrogen absorption. Black lines show curves obtained from Le Bail fitting. (b) Increase in the lattice constant (Δa) of the Rh samples estimated from the Le Bail fits of the diffraction patterns during hydrogen absorption.

lower angles in response to increasing hydrogen pressure (see Figure 2a for 2.4 nm Rh nanoparticles and the Supporting Information for 4.0 nm, 7.1 nm, and bulk samples). The hydrogen-pressure dependence of the lattice constants was determined from Le Bail fitting of the diffraction patterns and the change in lattice constant (Δa) with the absorption of hydrogen. As shown in Figure 2b, the lattice constants increased with increasing hydrogen pressure for all of the Rh nanoparticles, indicating that the Rh atoms within the lattice were forced apart. This behavior can be the consequence of hydrogen atoms penetrating the inside of the Rh lattice and expanding it. On the other hand, the lattice constant of bulk Rh exposed to H_2 does not change at all.[9] These results strongly suggest that the nanosized Rh particles absorb hydrogen gas.

Solid-state ^2H NMR measurements were carried out to investigate the state of the ^2H atoms in the Rh nanoparticles
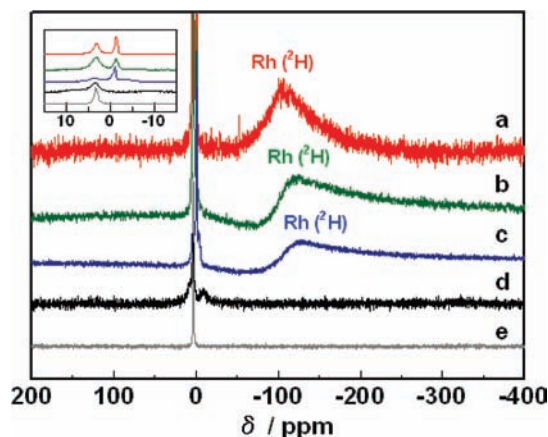

Figure 3. Solid-state ^2H NMR spectra of Rh nanoparticles with diameters of (a) 2.4, (b) 4.0, and (c) 7.1 nm. Spectra for (d) a bulk Rh sample (d) and (e) $^2H_2$ gas were also measured for reference. The inset shows expansions of the spectra near 0 ppm. All of the spectra were measured at a pressure of 86.7 kPa of $^2H_2$ gas at 303 K.

(Figure 3). Sharp lines at ca. 0 ppm and broad absorption lines at ca. -100 ppm were observed for all of the Rh nanoparticles. The NMR spectra expanded around 0 ppm are shown in the Figure 3 inset. In the spectra for $^2H_2$ gas and bulk Rh, only a peak at 3.4 ppm was observed. In addition to this peak, a sharp component appeared at -1.2 ppm in the spectra of the three nanoparticle samples. On the basis of a comparison of these spectra, it is reasonable to attribute the spectral component observed at 3.4 ppm to free deuterium gas. Because the component observed at -1.2 ppm was very sharp and located near the signal from $^2H_2$ gas, it can be assigned to deuterium atoms (^2H) diffusing and/or exchanging with free deuterium on the nanoparticles' surfaces.[2a] The broad component in the spectra was observed only for the nanoparticles. This component is attributed to deuterium atoms (^2H) whose motions are restricted to within the Rh lattice and experience an insufficiently averaged electric field gradient on the nucleus. The peak position of the broad component for the Rh nanoparticles was located at high field (ca. -100 ppm). This implies that the nuclear spins of the ^2H atoms located inside the Rh nanoparticles are polarized from the interaction with the polarized electron spins of the s and d conduction electrons of the Rh nanoparticles arising from the formation of hydride (Rh$-$H). This observation contrasts with the low-field shift of the ^2H atoms absorbed in Pd hydride.[11] The d band in Pd hydride is almost filled, so the spin correlation is weakened and the Knight shift is the dominant factor in the NMR shift of ^2H in Pd hydride.[12] On the other hand, as a large number of holes exist in the d band of Rh, the spin correlation between the conduction electrons of the Rh hydride is large enough to cause spin polarization in the ^2H atoms in the Rh hydride. This high-field shift of ^2H in Rh hydride is the first such observation to be reported. Our NMR experimental results clearly indicate the formation of Rh hydride.

Pressure$-$composition (PC) isotherms of the Rh samples were measured at 303 K to quantify how much hydrogen was absorbed by the Rh nanoparticles. As shown in Figure 4, the concentration of hydrogen in the Rh nanoparticles with diameters of <10 nm increased with increasing hydrogen pressure, while the bulk Rh sample did not absorb hydrogen at all. This result provides the first example of nanosize-induced hydrogen
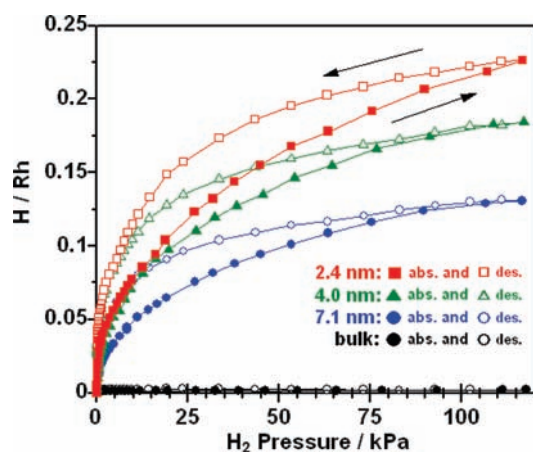
Figure 4. PC isotherms of the Rh samples at 303 K. The isotherms were measured along the direction of the arrows. The H/Rh ratio shows the number of hydrogen atoms divided by the total number of Rh atoms.

storage in a metal that does not absorb hydrogen in the bulk form. A hysteresis in the hydrogen absorption/desorption curve was observed, providing evidence of hydride formation (Rh−H) in the Rh lattice. Interestingly, a size dependence of the concentration of hydrogen (H/Rh ratio) was clearly observed. The concentrations of hydrogen absorbed at a hydrogen pressure of 101.3 kPa were 0.13, 0.17, and 0.23 H/Rh for the 7.1, 4.0, and 2.4 nm diameter nanoparticles, respectively. The concentration increased with decreasing Rh particle size, indicating that the concentration of hydrogen in Rh could be systematically controlled by tuning the size of the nanoparticles. Surprisingly, the value of the H/M ratio of the Rh nanoparticles with a diameter of 2.4 nm was equal to that of Pd nanoparticles (H/Pd = 0.22).[2a] The nanosize provides a favorable environment for hydrogen absorption in Rh.

It has been reported that in the PC isotherm of Pd nanoparticles, an incomplete recovery occurs, that is, the PC curve of Pd does not completely return to the starting point when the process is reversed.[2a] The PC isotherms of the Rh nanoparticles in this work showed reversible adsorption/desorption behavior, as shown in Figure 4. The complete recovery of the PC isotherms of the Rh nanoparticles may allow for facile and effective hydrogen adsorption/desorption performance.

In summary, we have demonstrated for the first time the existence of a nanosize-induced hydrogen-storage capacity in Rh nanoparticles, in contrast to bulk Rh, which does not absorb hydrogen. Moreover, the hydrogen concentration in the Rh nanoparticles was controllable by tuning the particle size. The specific size that induces a hydrogen-storage capability in Rh is currently under investigation. We believe that the results reported here will contribute to the development of novel nanostructured hydrogen-absorption materials.

■ ASSOCIATED CONTENT

⑤ Supporting Information. Experimental details and XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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