In situ electron microscopy analysis on thermal stability of PdRu-Rh nanoparticles

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Solid solution nanoparticles of Pd and Ru which are both side neighbors to Rh in the periodic table show high NO_x reducibility comparable to or better than Rh [1]. Thus, PdRu alloy nanoparticles are strongly expected as alternate material for Rh as the three-way catalyst. However, Pd and Ru are immiscible to each other at equilibrium and the solid solution is readily decomposed. To stabilize the solution, ternary alloy nanoparticles have been produced by adding Rh to PdRu. In this study, we have aimed to confirm the thermal stability of PdRu-Rh alloy nanoparticles, and have performed in situ heating scanning transmission electron microscopy observation.

PdRu-Rh solid solution nanoparticles (atomic composition 1:1:1) were synthesized by solvent extraction method [2]. We operated an atomic resolution analytical electron microscope (JEM-ARM200CF) at 80 kV of accelerating voltage in the ultramicroscopy research center in Kyushu University. In situ heating observations were performed with an Aduro™ specimen heating holder (Protochips Inc.). We used the high angle annular dark-field (HAADF) method for observation and energy dispersive X-ray spectroscopy (XEDS) method for local atom composition analysis.

Figure (a) shows a STEM-HAADF image and composition profiles from XEDS line analysis of a couple of PdRu-Rh alloy nanoparticles at room temperature. Two nanoparticles are closely located. As shown in the composition profiles, the particles are of the alloyed solid solution. Figure (b) shows a STEM-HAADF image of the couple and composition profiles after annealing at 500 °C for 2.0 hours. The particle shape gets rounded and Pd covers the particle surface after annealing. The adjacent two particles have been connected by surface diffusion. Pd is noticeably enriched at the contact. This means that the surface diffusion of Pd dominates the particle sintering. On the other hand, Pd has decreased at the particle interior. The Pd enrichment at surface is explained in terms of the surface energy of the three elements, namely 2379 mJ/m^2 for Pd is considerably smaller than 4192 and 3764 mJ/m^2 for Ru and Rh respectively [3].

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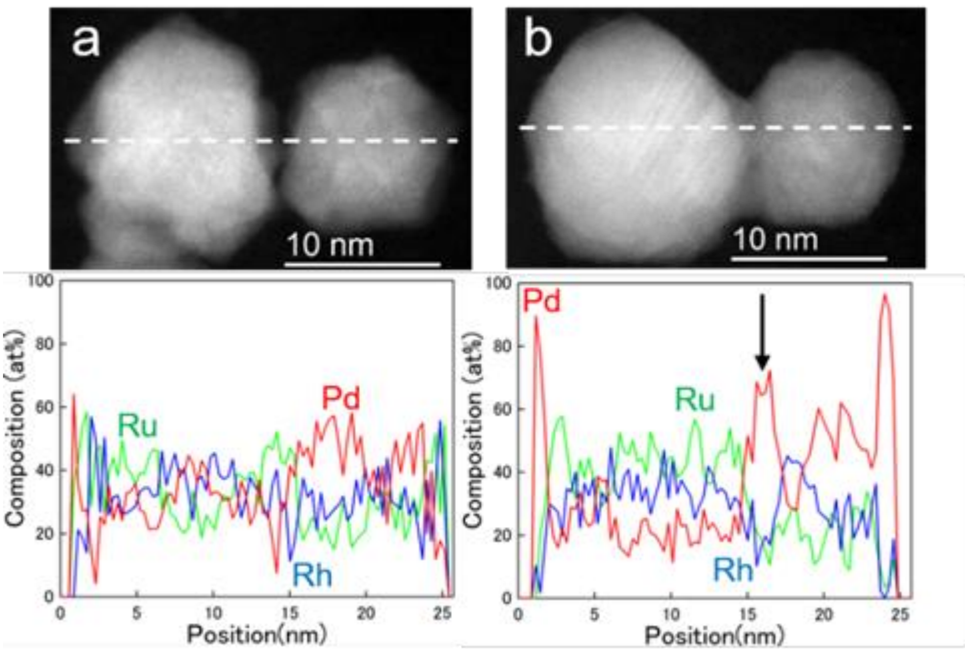

Figure. STEM-HAADF images and XEDS composition profiles for PdRu-Rh alloy nanoparticles (a) before heating, (b) heated at 500 °C for 2.0 hours.