

## Effect of O<sub>2</sub>, CO, and NO on the Surface Segregation in a Rh<sub>50</sub>Pd<sub>50</sub> Bulk Crystal and a comparison to Rh<sub>50</sub>Pd<sub>50</sub> Nanoparticles

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We present an in-situ study of the interaction of a bimetallic Rh<sub>50</sub>Pd<sub>50</sub> bulk crystal with O<sub>2</sub>, CO, and NO using ambient pressure x-ray photoelectron spectroscopy and compare it to results for 10 nm nanoparticles with the same overall composition. The surface of the bulk crystal has less Rh present under both oxidizing and reducing conditions than the nanoparticles under identical conditions. Segregation and oxidation/reduction proceeds quicker and at lower temperature for nanoparticles than for the bulk crystal. The near surface of the Rh<sub>50</sub>Pd<sub>50</sub> bulk crystal after high temperature vacuum annealing is ca. 9% Rh measured by XPS. Heating in 0.1 Torr O<sub>2</sub> to 350 °C increases the Rh surface composition to ca. 40%. The surface can then be reduced by heating in H<sub>2</sub> at 150 °C, leading to a reduced surface of 30% Rh. Titration of CO from this Rh-rich surface proceeds at a much lower pressure than on the Rh-deficient starting surface.