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Microstructural Investigations of High Productivity Au-Pd Catalysts for the Synthesis of Hydrogen Peroxide via Direct Combination of H_2 and O_2

A. A. Herzing,* M. Watanabe,* C.J. Kiely,* B. E. Solsona,** J. Edwards,** P. Landon,**
A. F. Carley,** and G. J. Hutchings**

* Department of Materials Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015-3195, USA

** Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff, CF10 3TB UK

There is considerable interest in using hydrogen peroxide (H_2O_2) as an oxygen source in the fine chemicals industry due to the environmentally benign by-product of such reactions: water. However, current production methods of H_2O_2 render it more costly than other common oxygen donors. The direct combination of H_2 and O_2 to form H_2O_2 is a highly desirable but difficult reaction to bring about because the reaction conditions that are required to create H_2O_2 also drive the decomposition of H_2O_2 to water. Recent work on H_2O_2 production has focused on Pd based catalysts operating under highly dangerous explosive conditions (elevated temperature and pressure) for hydrogen [1]. In an effort to efficiently produce H_2O_2 by direct combination of H_2 and O_2 in a safer manner, nanocrystals of Au, Pd, and Au-Pd alloy were impregnated via an incipient wetness method onto α-Fe_2O_3 particles. The catalysts were subsequently calcined in air at 400 ^oC and then reduced in H_2 at 500 ^oC. When catalytically tested under non-explosive conditions (low pressure, low temperature), it was found that significant H_2O_2 production was achieved when a 1:1 ratio of Au to Pd was used.

Using a VG Systems HB 603 STEM operating at 300 kV and equipped with an XEDS detector for chemical analysis, these catalysts were investigated in order to characterize the chemical and physical nature of the metal and oxide particles. As shown in Figure 1, the metal particles exhibit a bi-modal size distribution with the larger particles typically around 30 nm while the smaller were less than 10 nm in size. STEM-XEDS mapping revealed the presence of alloy particles, since the Au M_2 and Pd L_1 signals always originated from spatially coincident areas. In order to extract more information from these maps, they were subjected to Multi-Variate Statistical Analysis (MSA), a statistical method ideally suited to analysis of spectral images of small particles [2]. Clearly, the Pd L_1 (Fig. 1(b)) map suggests that the Pd is concentrated at the perimeter of the particles leaving a Au-rich region (Fig. 1(c)) in the particle center.

Further evidence for this segregation effect can be seen in the HREM image shown in Figure 2 of a solitary Au-Pd particle. A slight change in contrast is observed at a radius of approximately 15 nm from the particle center. This most likely arises from a sudden change in composition from Au-rich in the interior to Pd-rich at the perimeter. Pd (Z=46) and Au (Z=79) differ sufficiently in atomic mass that a region containing more Au would appear slightly darker than a region that was rich in Pd. The lack of Moire fringes which should arise due to lattice parameter or crystal structure mismatch, suggests that the Pd-rich shell remains metallic rather than being oxidized to PdO.

Finally, the presence of a core-shell structure with Pd segregating preferentially to the surface is also evidenced by the XPS data shown in Figure 3. While the uncalcined sample clearly shows the presence of both Au and Pd, both spectra from the calcined sample and the subsequently reduced sample show only Pd. Since XPS is a highly surface sensitive technique, this suggests that the calcination process brings about surface segregation of Pd.

This type of Pd segregation is unexpected since the Au-Pd system exhibits complete solid solubility, and any composition should yield a random distribution of both alloying constituents. However, previous evidence of this type of segregation has been observed in the Au-Pd bulk alloys when they have been calcined at elevated temperature in oxygen [3]. This phenomenon presumably occurs because of the lower bond energy of Pd-O relative to Au-O. Furthermore, a subsequent reduction of the bulk alloy in H_2 resulted in removal of the oxide layer without re-equilibration of the surface composition. The significance of having Pd enriched Au-Pd nanoparticles for the efficient production of H_2O_2 from H_2 and O_2 is currently being considered.

References
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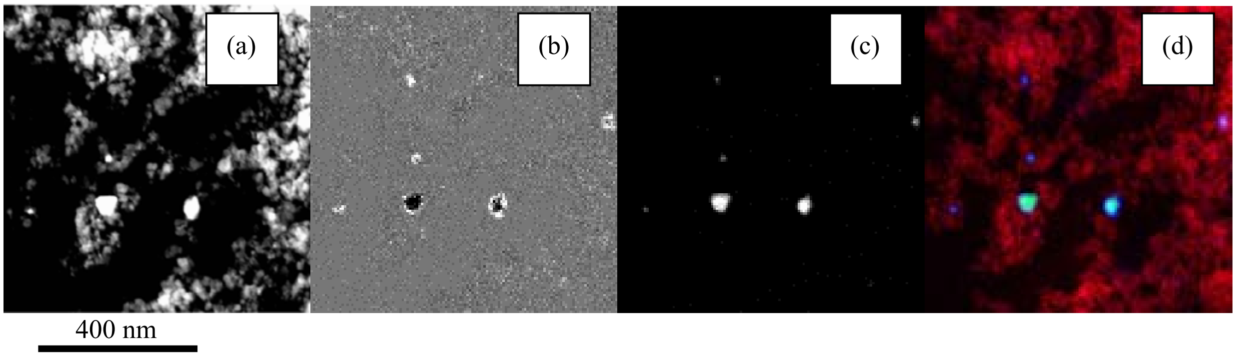

FIG. 1. (a) HAADF image of 2.5%Au-2.5%Pd/Fe_2O_3 (b) Pd L_1 STEM-XEDS map (c) Au M_2 STEM-XEDS map (d) RGB image of three XEDS maps (red = O, blue = Pd, green = Au)

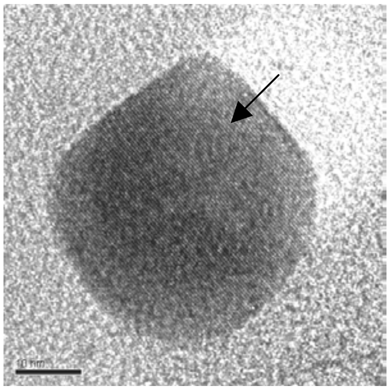

FIG. 2. HRTEM image of a single Au-Pd particle showing probable core-shell structure. The arrow indicates an abrupt contrast change.

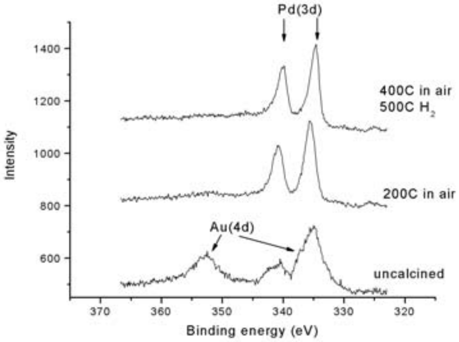

FIG. 3. XPS spectra from the 2.5%Au-2.5%Pd/Fe_2O_3 catalysts showing the emergence of Pd surface segregation during calcination and subsequent reduction.