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Elemental Mapping of Nanoscale Structures in the Aberration-Corrected Analytical Electron Microscope

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Modern analytical electron microscopes (AEM's) are powerful instruments for the structural and chemical characterization of materials at the nanoscale, and recent developments promise to further enhance their capabilities. Spherical aberration-correctors have made possible the formation of ultrafine electron probes with a total current that is comparable to that in the uncorrected instrument **[1]**, making the aberration-corrected AEM ideally suited for microanalysis at the nanoscale.

In addition, the acquisition of spectrum images in the AEM, whereby an individual spectrum (XEDS or EELS) is acquired at each image pixel of an operator defined image area, can now be routinely performed on many instruments. The highly redundant datasets produced in this fashion lend themselves to post-acquisition data mining and statistical processing, such as principal component analysis (PCA), which can further enhance the quality of AEM microanalytical data **[2,3]**.

These techniques have been employed to characterize several interesting nanoscale structures. For example, the morphological development of bimetallic nanoparticles in a heterogeneous catalyst system as a function of synthesis conditions was monitored via XEDS in an aberration-corrected VG HB603 STEM. The elemental maps presented in Fig. 1 were acquired from a series of Au-Pd/Al_2O_3 catalysts which were subjected to various heat treatment temperatures and atmospheres **[4]**. STEM-XEDS analysis revealed that the metal particles in this catalyst were altered from homogeneous Au-Pd alloys in the as-synthesized state to Au-rich core/Pd-rich shell particles during calcination due to the preferential migration and oxidation of Pd at the particle surfaces. Subsequent reduction of the catalyst did not result in re-homogenization of the bimetallic particles, since the majority retained their Pd-rich surfaces. However, a minority of particles exhibited an unexpected morphological inversion, resulting in a Au-rich surface with a Pd-rich core (not shown), which is the favored structure in terms of surface energetics.

Similar techniques were employed to analyze nanoscale zero-valent iron (nZVI) particles. These materials were synthesized via reduction of $FeCl_3$ **[5]** by $NaBH_4$, and are highly effective for the absorption and detoxification of many environmental contaminants. It was found that the particle surfaces consisted of a disordered FeO_x species surrounding a polycrystalline core of Fe nanoparticles (Fig. 2(a,c)). To enhance their effectiveness, the nZVI particles were also impregnated with Pd, and, contrary to expectations, the dopant metal was not found on the particle surface. Instead the Pd traversed the outer oxide layer in order to interact with the interior Fe nanoparticles, forming a Pd-rich interfacial layer between the Fe core and FeO_x shell.

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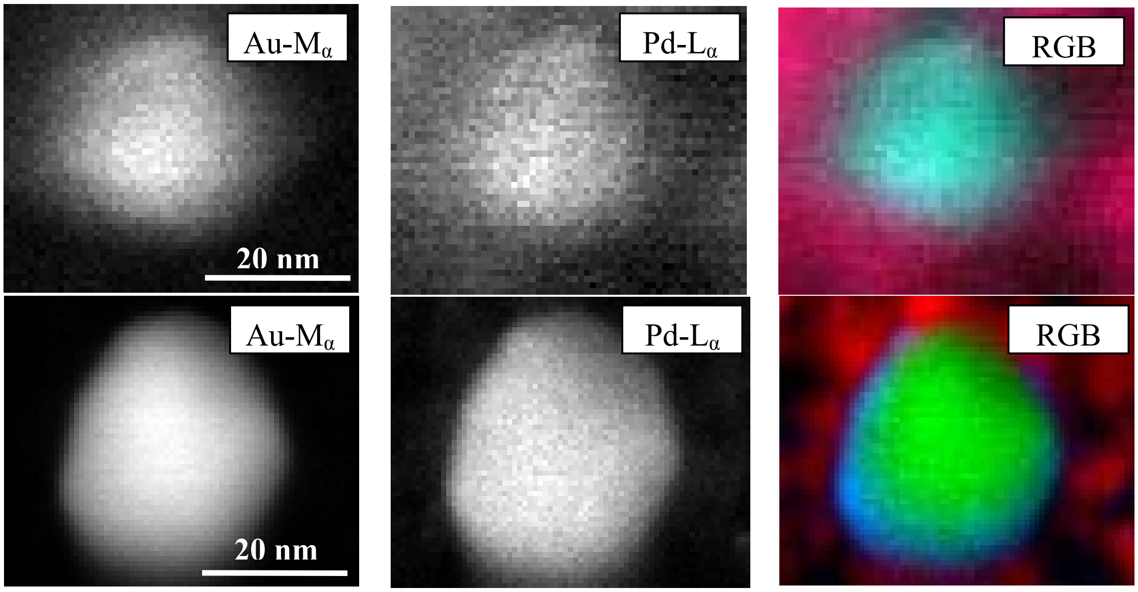

Figure 1 – Comparison of Au (green) and Pd (blue) elemental distributions in bi-metallic catalyst particles supported on Al_2O_3. The as-synthesized catalyst contains homogeneous Au-Pd particles (top) while the particle surfaces become enriched with Pd after calcination at 400 ^{o}C (bottom).

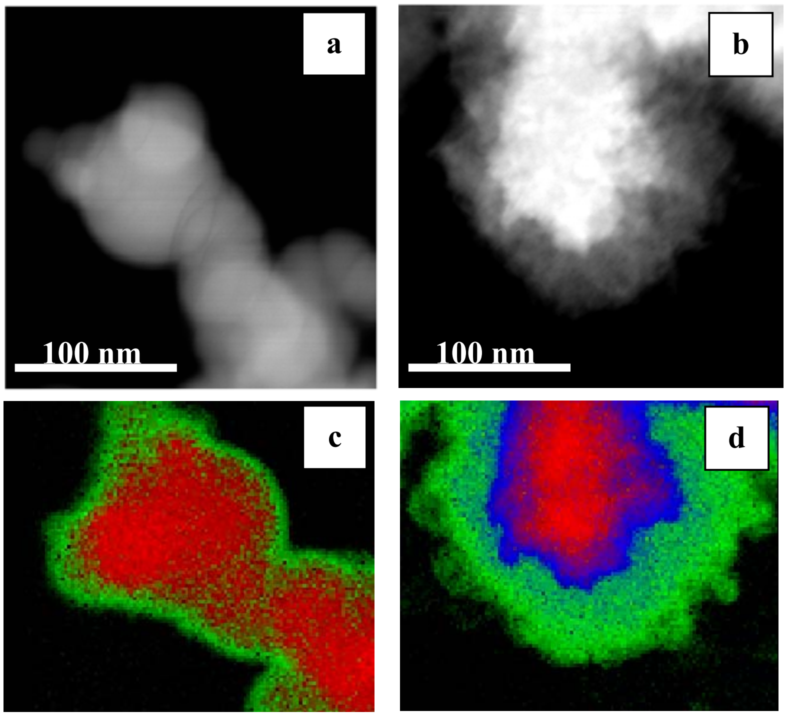

Figure 2 – ADF images of nZVI particles (a) as synthesized and (b) after impregnation with 1.5wt.% Pd. RGB reconstructions of STEM-XEDS spectrum image data after PCA processing shows an FeO_x surface layer (green) surrounding an Fe core (red) in the as-synthesized particles (c). Upon impregnation (d), the Pd traverses the oxide layer to react preferentially with the internal Fe, forming a highly Pd-rich layer at the Fe/FeO_x interface (blue).