

## Direct Observation of Single Atoms in Sinter-Resistant and Bimetallic Catalyst Systems Synthesized by Atomic Layer Deposition

K. B. Low<sup>1</sup>, Y. Lei<sup>2</sup>, J. L. Lu<sup>2</sup>, J. W. Elam<sup>2</sup>

<sup>1</sup> Research Resources Center, University of Illinois at Chicago, Chicago, IL 60607

<sup>2</sup> Energy Systems Division, Argonne National Laboratory, Lemont, IL 60439

Noble metal nanoparticles with dimensions smaller than 10nm on metal oxides supports have received great attention due to their outstanding catalytic performance [1]. In particular, palladium (Pd)-based catalytic systems prepared by atomic layer deposition (ALD) have been demonstrated to be highly active for the oxidative dehydrogenation of alkane [2] and methanol decomposition reactions [3]. The rationale behind employing ALD as a promising choice for noble metal catalyst synthesis is its ability to form highly conformal thin films or highly dispersed nanoparticles on high aspect-ratio surfaces using sequential, self-limiting surface reactions [4]. Nanoparticle size and compositional configuration can be controlled by precisely adjusting the number and sequence of ALD reaction cycles, respectively. Therefore, successful synthesis of highly-controlled heterogeneous catalytic systems is contingent upon a thorough understanding of the relevant ALD reaction mechanisms on specific supports, and the ability to atomically visualize early particle growth dynamics and resultant nanostructures.

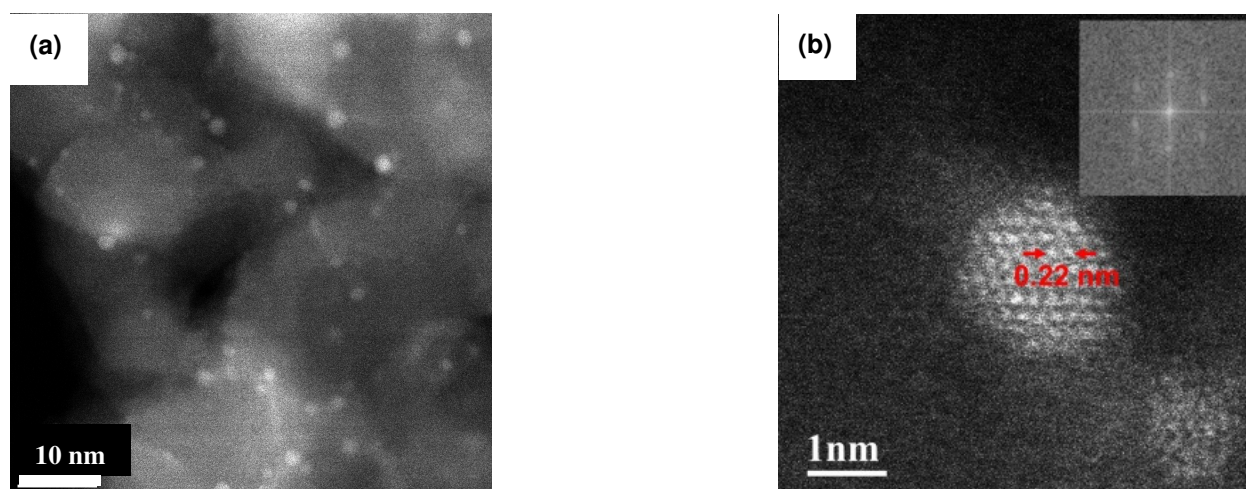
In this paper, we reveal the two half-reactions involved in ALD of Pd using palladium hexafluoroacetylacetonate ( $\text{Pd}(\text{hfac})_2$ ) precursor on  $\text{TiO}_2$  surface and apply our understanding of the mechanisms towards the synthesis of Pd nanoparticles on  $\text{TiO}_2$ -coated  $\text{SiO}_2$  supports. Upon final reduction of Pd at  $200^\circ\text{C}$ , which removes the hfac ligands, metallic Pd particles that are less than 2 nm in size can be reproducibly achieved and were visualized under high-angle annular dark-field (HAADF) imaging mode using a probe-corrected scanning transmission electron microscopy (STEM) (Figure 1a and b).

This Pd ALD process was then employed as the basis for synthesis of more advanced heterogeneous catalytic systems. Through subsequent deposition of a  $\text{TiO}_2$  protective layer over the  $\text{Pd}(\text{hfac})_2$  precursor followed by hfac ligand removal, discrete single Pd atoms, dimers and trimers can be dispersed extensively over  $\text{TiO}_2$ -coated  $\text{Al}_2\text{O}_3$  supports, which are clearly resolved in the STEM-HAADF image in Figure 2a. These highly-dispersed and protected Pd atomic-sized catalysts exhibit reactivities that are superior to the non-protected, nanometer-sized counterparts, and are demonstrated to be sinter-resistant up to  $300^\circ\text{C}$  in oxygen. The 50%-conversion temperature of protected Pd catalysts is also distinctively lower than non-protected systems.

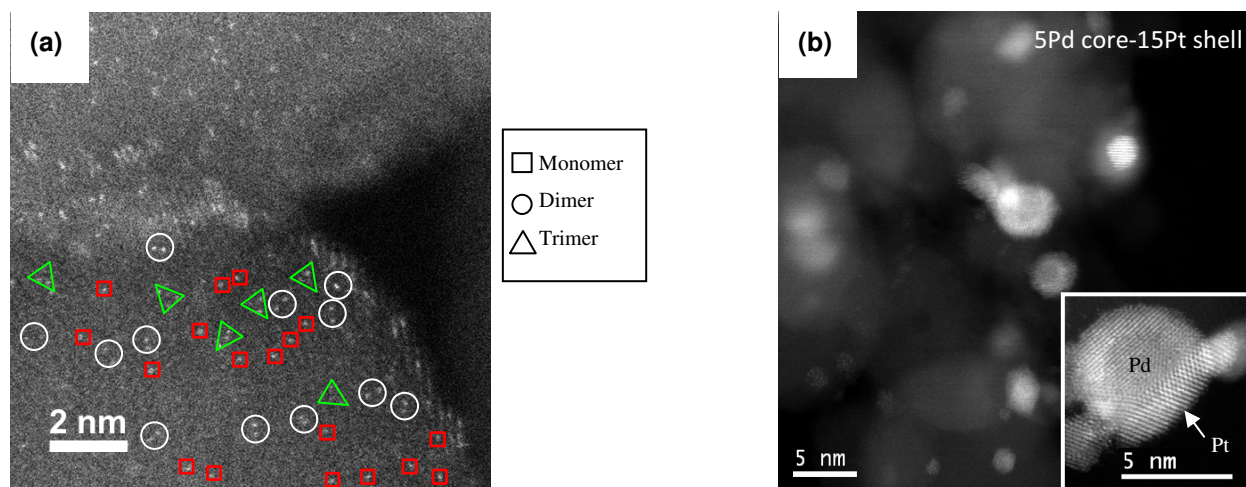
Finally, we demonstrate the application of ALD towards synthesis of advanced Pt/Pd bimetallic heterogeneous catalytic system, which has been claimed to exhibit enhanced activity and selectivity [5]. Five ALD cycles of Palladium nanoparticles were dispersed onto  $\text{TiO}_2$ -coated  $\text{Al}_2\text{O}_3$  supports via ALD, followed by 15 ALD cycles of Pt coating. The resultant morphology is of an ideal core-shell structure, which was visualized through STEM-HAADF imaging (Figure 2b) [6].

## References:

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 [6] This material is based upon work supported as part of the Institute for Atom-efficient Chemical Transformations (IACT), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. The JEOL JEM-ARM200CF STEM instrument at UIC RRC was partially funded by NSF MRI-R2 award number DMR-0959470ARRA.



**Figure 1.** STEM-HAADF images showing (a) the dispersion of Pd nanoparticles on TiO<sub>2</sub>-coated SiO<sub>2</sub> supports; and (b) atomic-resolution of a single catalyst particle revealing its Pd (111) lattice fringes.



**Figure 2.** STEM-HAADF images of (a) sinter-resistant Pd monomers, dimers and trimers; and (b) bimetallic Pd/Pt core-shell nanostructures dispersed onto TiO<sub>2</sub>-coated Al<sub>2</sub>O<sub>3</sub> supports.