

## ***Ex-situ* and *in-situ* Microscopy Study of ZrO<sub>2</sub>-stabilized Pd/Al<sub>2</sub>O<sub>3</sub> Catalysts**

Shuyi Zhang<sup>1,2</sup>, Tzia Ming Onn<sup>3</sup>, Raymond J. Gorte<sup>3</sup>, George W. Graham<sup>1</sup>, Xiaoqing Pan<sup>2,4</sup>

<sup>1</sup> Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States

<sup>2</sup> Department of Chemical Engineering and Materials Science, University of California–Irvine, Irvine, California, United States

<sup>3</sup> Department of Chemical and Biomolecular Engineering, University of Pennsylvania, 34th Street, Philadelphia, Pennsylvania, United States

<sup>4</sup> Department of Physics and Astronomy, University of California–Irvine, Irvine, California, United States

Stability issues are of great importance in emissions-control catalysis, in which high temperatures and redox cycling can lead to severe deactivation due to coarsening of metal catalyst particles. Supported Pd is the one of the most widely used catalysts for methane oxidation, and contact between Pd and some oxides, such as CeO<sub>2</sub>, is known to promote the reaction. Further, encapsulation of Pd particles by thin shells of these oxides (e.g., Pd@CeO<sub>2</sub>) has been found to provide good thermal stability [1]. Alternatively, the deposition of thin overlayers of the oxide onto a supported metal catalyst by atomic layer deposition (ALD) has proven to be an equally effective, though simpler way to both stabilize Pd at high temperature and enhance catalytic activity [2]. In this work, we use atomic scale Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive Spectroscopy (EDS) to study the spatial distribution of a very thin ZrO<sub>2</sub> overlayer deposited by ALD onto high-surface-area alumina-supported Pd. The stability of the ZrO<sub>2</sub> overlayer was also examined by dynamic *in-situ* microscopy, conducted at 150 Torr O<sub>2</sub> at elevated temperatures.

The Pd/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by incipient wetness, using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> that had been stabilized by calcining in air at 1173 K for 24 h. The catalyst was calcined at 673 K in air for 6 h to remove any organics and nitrates. The final loading of the sample was 1wt % Pd. ALD of ZrO<sub>2</sub> was conducted in a home-built deposition system described before [3]. Both ZrO<sub>2</sub> coated and uncoated samples were made for comparison, followed by calcination at 773 K and 1073 K in air. *In-situ* microscopy was conducted with a Protochips Atmosphere<sup>TM</sup> system on a double Cs corrected microscope JEOL 3100R05 operated at 300 kV.

After 50 ZrO<sub>2</sub> deposition cycles, ZrO<sub>2</sub> appeared to be a thin layer, ~1 nm thick, covering part of the Al<sub>2</sub>O<sub>3</sub> surface. High angle annular dark field (HAADF) imaging, in which ZrO<sub>2</sub> appears brighter than Al<sub>2</sub>O<sub>3</sub> because of the atomic number difference between Zr and Al, allows the ZrO<sub>2</sub> surface layer to be distinguished from Al<sub>2</sub>O<sub>3</sub>, as shown in Figure 1a. EDS elemental maps, including Pd, Zr, and Al, on the region enclosed by yellow rectangular in Figure 1b, confirm that the brightness variation on Al<sub>2</sub>O<sub>3</sub> is due to the presence of Zr, and they further confirm that the PdO particles are fully covered by the ZrO<sub>2</sub> layer as a result of the coincidence of Zr and Pd in the spectra. The initial particle size in both the ALD coated and uncoated sample is comparable, ~5 nm in diameter after 773 K calcination. However, the sizes of PdO particles with the ZrO<sub>2</sub> covering remained unchanged after heating to 1073 K in air. In contrast, the size of the particles almost doubled in the uncoated PdO/Al<sub>2</sub>O<sub>3</sub> sample after the same treatment. The ZrO<sub>2</sub> coated sample shows significantly enhanced methane oxidation activity after increasing calcination temperature, however, the uncoated sample shows decreased activity.

*In-situ* TEM observations provided a dynamic picture of the structural evolution of the ZrO<sub>2</sub> layer upon air calcination, as shown in Figure 2 a-f. The initial continuous Zr layer, shown in Figure 2a, starts to break up, migrate and form small particles, ~1 nm, at temperatures as low as 773 K, which then become stable at 973 K, as shown in Figure 2 b-f. These observations provide information about one of the effects of calcination temperature on catalytic activity. [4]

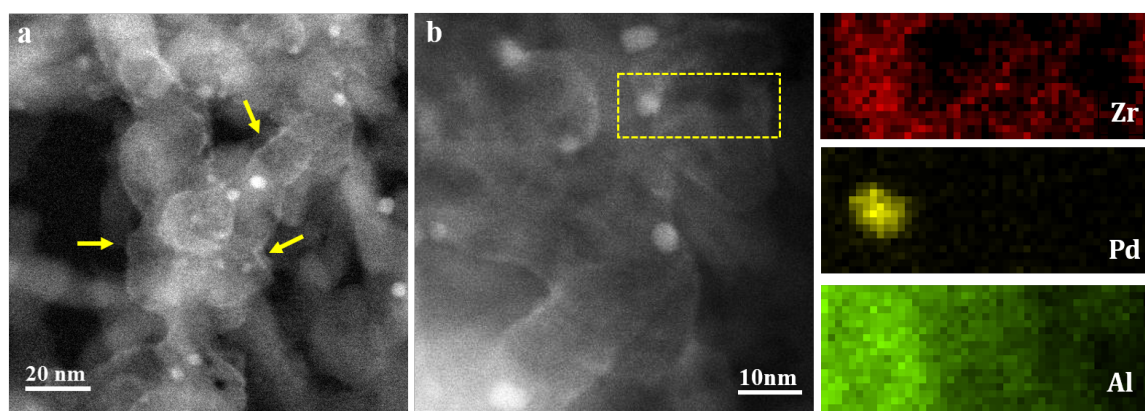
References:

[1] Chen, C. *et al*, ACS Catal. **4**, (2014), 3902.

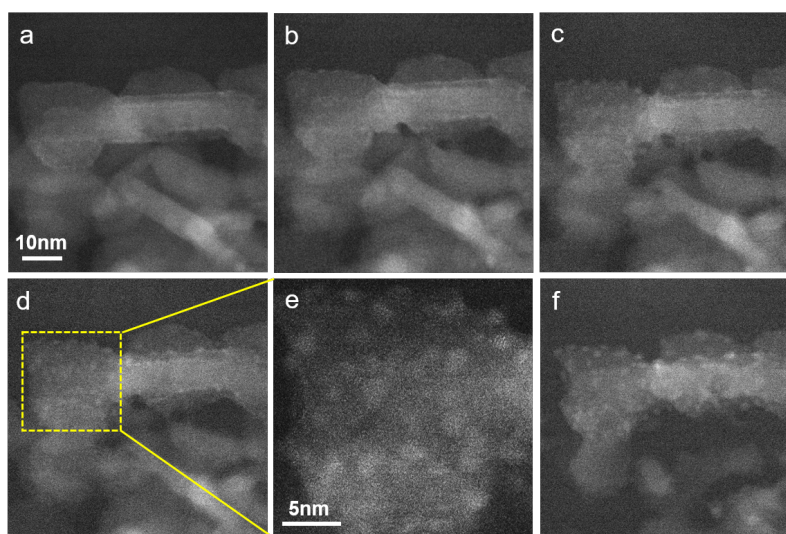
[2] Lu, Junling, *et al.*, Science **335** (2012), 1205.

[3] Yu, A. S *et al*, J. Electrochem. Soc. **160** (2013), 1225.

[4] The authors gratefully acknowledge funding from the National Science Foundation under grants DMR-0723032 and CBET-115940.



**Figure 1.** HAADF images showing the presence of the ZrO<sub>2</sub> overlayer after 50 ALD cycles. The Zr coating appears to be brighter on the edges, shown both in a (marked by yellow arrows) and b, and confirmed by EDS mapping of Zr, Pd and Al conducted on the region enclosed by the yellow rectangular in b.



**Figure 2.** Sequential STEM images of uncalcined (fresh) ZrO<sub>2</sub> coated PdO/Al<sub>2</sub>O<sub>3</sub> catalysts obtained *in-situ* under 150 Torr O<sub>2</sub> in the TEM gas cell at a temperatures of (a) 573 K; (b, c) 773 K for 0 and 3 min, respectively; (d, e) 873 K; and (f) 973 K.