

## AC-TEM Investigation of Metal-Support Interfacial Structure and its Impact on Activity in CeO<sub>2</sub>-Supported Pt Catalysts

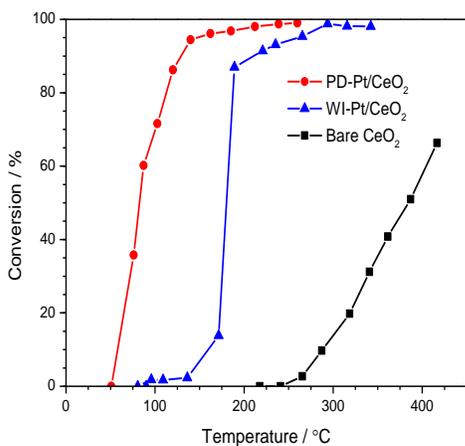
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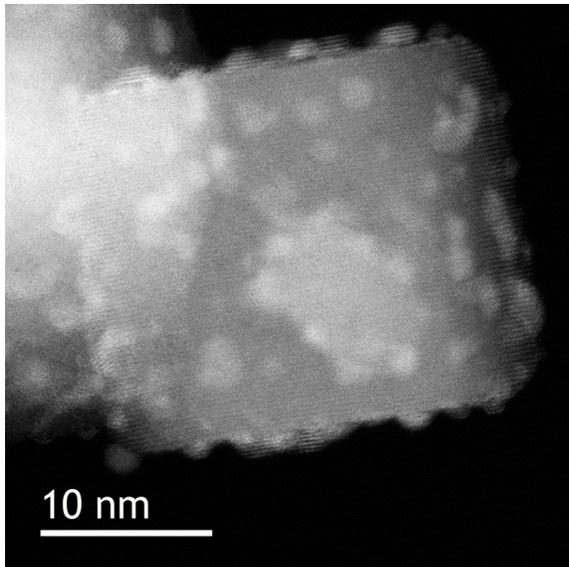
In heterogeneous catalysis, metal-support interactions may improve performance. In Pt/CeO<sub>2</sub>, the enhancement arises from CeO<sub>2</sub>'s ability to donate oxygen locally at the metal-support interface. The ease with which oxygen is removed from CeO<sub>2</sub> has been shown theoretically to depend on the interfacial atomic structure [1]. At present, though, there is little experimental data on the atomic structures that comprise the Pt-CeO<sub>2</sub> interface. Additionally, the effects of different deposition methods on interfacial structure and catalytic activity have gone largely uninvestigated. Two deposition methods are of interest to this work: impregnation and photodeposition. Using aberration-corrected TEM and STEM, the present study investigates the effect of the metal deposition method on the interfacial structure and catalytic activity of Pt/CeO<sub>2</sub> catalysts.

Nanostructured CeO<sub>2</sub> cubes were impregnated with an aqueous solution of PtCl<sub>4</sub> to obtain a sample with 2.0 wt% Pt loading (WI - Pt/CeO<sub>2</sub>). To prepare photodeposited Pt/CeO<sub>2</sub> (PD - Pt/CeO<sub>2</sub>), 100 mg of CeO<sub>2</sub> cubes were dispersed in 100 mL of water. An identical volume of PtCl<sub>4</sub> solution was added to this solution, along with 10 vol% methanol. The dispersion was subjected to 1 hour of illumination (~1-6 eV energy range). After deposition, both samples were calcined in air at 450 °C for 16 hours. Images of the fresh PD powders were obtained with a FEI Titan AC-TEM operating at 300 kV and an ARM 200F AC-STEM operating at 200 kV. The CO oxidation performance of each catalyst was also tested.

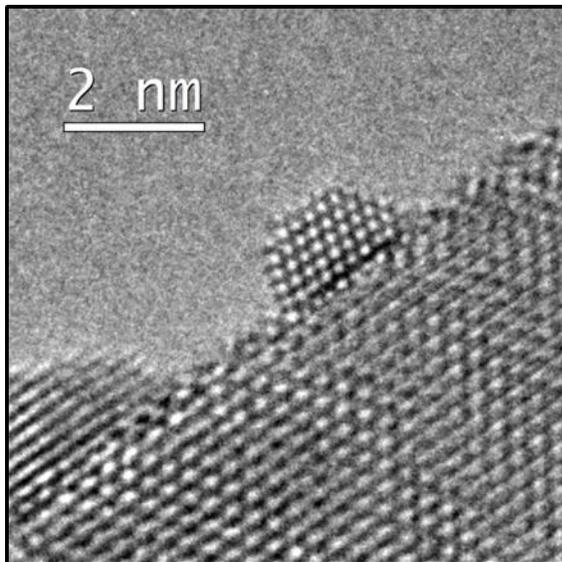
The light-off curves for the two Pt/CeO<sub>2</sub> catalysts are shown in Figure 1, along with the performance of the bare CeO<sub>2</sub> powder. The PD-Pt/CeO<sub>2</sub> catalyst appears much more active than the WI-Pt/CeO<sub>2</sub> catalyst and bare CeO<sub>2</sub>. In Figure 2, a typical Z-contrast STEM image of PD-Pt/CeO<sub>2</sub> shows ~3 nm Pt nanoparticles dispersed on a CeO<sub>2</sub> cube. Figure 3 displays a typical Pt particle situated on a CeO<sub>2</sub> cube. Interestingly, all Pt nanoparticles deposited through the photodeposition method present (200) planes at the metal-support interface (e.g., Figures 2 and 3). At present, it is unclear whether the difference in activity between PD-Pt/CeO<sub>2</sub> and WI-Pt/CeO<sub>2</sub> is due to a difference in interfacial structure. Pt nanoparticle size distributions and interfacial atomic structures will be determined with AC-S/TEM. Results will attempt to establish atomic-level relationships between the interface and activity [2].



**Figure 1.** Light-off curves demonstrate that PD-Pt/CeO<sub>2</sub> is the most active for CO oxidation.



**Figure 2.** HAADF-AC/STEM image shows a  $\sim 3$  nm Pt nanoparticles decorating a CeO<sub>2</sub> cube.



**Figure 3.** AC-TEM image shows Pt and CeO<sub>2</sub> meet with (200) planes at the interface.

**References:**

[1] Vayssilov, G., *et al.*; Nature Materials **10** (2011), p. 310 - 315.

[2] We gratefully acknowledge the support of NSF grant CBET-1604971 and ASU's John M. Cowley Center for High Resolution Electron Microscopy.