

Controlled Synthesis of Metal-Support Interface for High Activity CeO₂-Supported Pt Nanoparticles

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In heterogeneous catalysis, metal-support interactions may improve performance. Pt nanoparticles on CeO₂, for example, are more active for CO oxidation than those dispersed on non-reducible metal oxides. The enhancement arises from CeO₂'s ability to donate oxygen locally at the metal-support interface. The ease with which oxygen is removed from CeO₂ 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-CeO₂ interface. Additionally, even though the metal deposition method creates the metal-support interface, 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. Impregnation is a conventional method and serves as a benchmark. Photodeposition, which involves the reduction of Pt ions by electrons photoexcited within the CeO₂, has not been explored in this catalyst system. 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/CeO₂ catalysts.

Nanostructured CeO₂ cubes were impregnated with an aqueous solution of PtCl₄ to obtain a sample with 2.0 wt% Pt loading (WI-Pt/CeO₂). To prepare photodeposited Pt/CeO₂ (PD-Pt/CeO₂), 100 mg of CeO₂ cubes were dispersed in 100 mL of water. An identical volume of PtCl₄ solution was added to this solution, along with 10 vol% methanol. The dispersion was stirred and subjected to 1 hour of illumination from a 450 W Newport Xe arc lamp (~1-6 eV energy range). The resultant gray particles were dried in air overnight. After deposition, both samples were calcined in air at 450 °C for 16 hours. Images of the fresh PD-Pt/CeO₂ powders were obtained with a FEI Titan AC-TEM operating at 300 kV and an ARM 200F AC-STEM operating at 200 kV; energy dispersive X-ray spectra (XEDS) were acquired with a JEOL X-ray detector. The CO oxidation ($\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2$) performance of each catalyst was tested by loading 83 mg of powder into an ISRI RIG-150 quartz microreactor. The samples were first reduced at 400 °C for 4 hours in a stream of 5% H₂/Ar flowing at 40 standard cubic centimeters per minute (SCCM). Following cool-down, the gas stream was switched to 2 SCCM O₂ and 40 SCCM 10% CO/He, while the reactor bed was heated from 50 – 450 °C. Product gasses were analyzed with a Varian 3900 gas chromatograph.

The resultant light-off curves for the two Pt/CeO₂ catalysts are shown in Figure 1, along with the performance of the bare CeO₂ powder. The PD-Pt/CeO₂ catalyst appears much more active than the WI-Pt/CeO₂ catalyst, converting 50% of the reactants at ~80 °C, compared to ~180 °C for the WI-Pt/CeO₂ catalyst and ~380 °C for the bare CeO₂. In Figure 2, a typical Z-contrast STEM image of PD-Pt/CeO₂ shows ~3 nm Pt nanoparticles dispersed on a CeO₂ cube. The presence of Pt is confirmed by the Pt M_α peak seen at 2.05 keV in the XEDS spectra shown in Figure 3. Figure 4 displays a typical Pt particle situated on a CeO₂ cube. The Pt particle exhibits (111) and (200) surfaces, and it presents a (200) plane to the (200) plane of CeO₂. Interestingly, all Pt nanoparticles deposited through the photodeposition method appear to show the same behavior (see Figures 2 and 4, for example), which suggests that the technique offers control over the nanostructure of the metal-support interface. At present, it is unclear whether the large difference in activity between PD-Pt/CeO₂ and WI-Pt/CeO₂ is due to a difference in interfacial

structure. Another possibility is that the photodeposition method produces smaller Pt particles than the impregnation method. To this end, Pt nanoparticle size distributions and interfacial atomic structures will be determined with AC-S/TEM. The results will be analyzed with the aim of establishing atomic-level structure-function relationships between the metal-support interface and catalytic activity [2].

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.

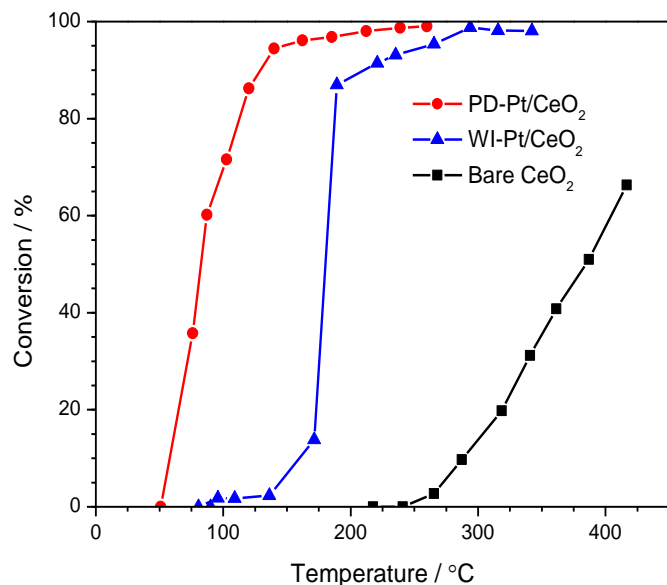


Figure 1. Light-off curves demonstrate that PD-Pt/CeO₂ is the most active for CO oxidation.

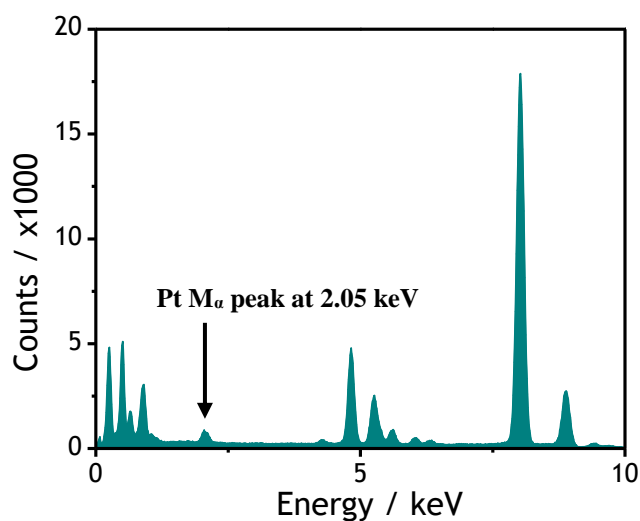


Figure 3. XEDS spectrum shows Pt M α peak at 2.05 keV, confirming its presence in Figure 2.

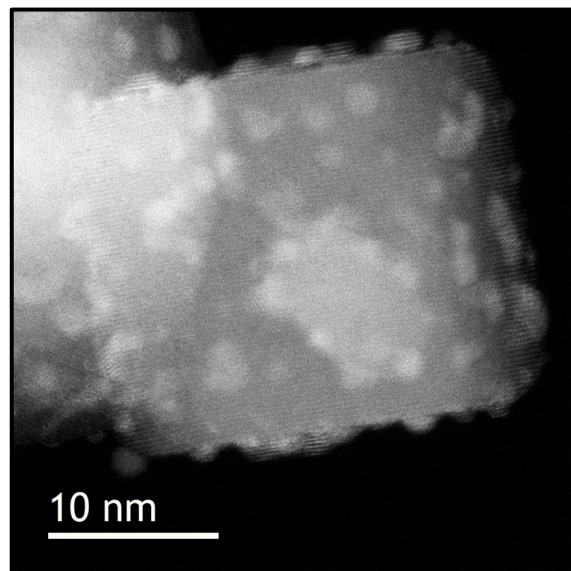


Figure 2. HAADF-AC/STEM image shows ~3 nm Pt nanoparticles decorating a CeO₂ cube.

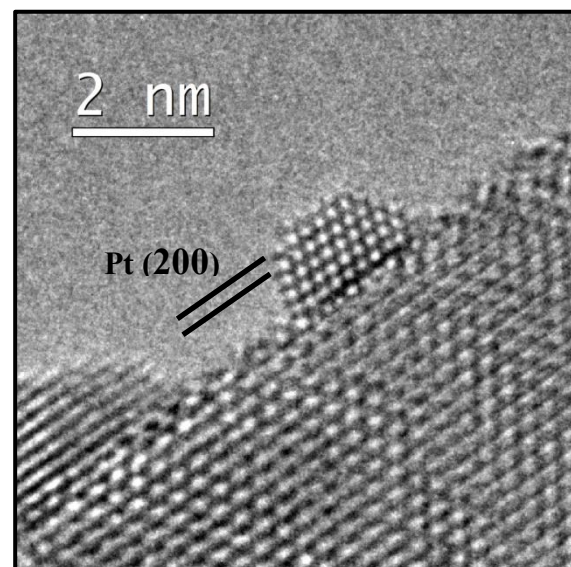


Figure 4. AC-TEM image shows Pt and CeO₂ meet with (200) planes at the interface.