

Operando TEM Investigation of CeO₂-Supported Pt Catalysts During CO Oxidation

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Heterogeneous catalysts accelerate reactions by reducing the activation energy for the rate limiting step. Even with environmental transmission electron microscopy (ETEM), atomic-level structure-activity relationships are difficult to determine due to the number of structures that form dynamically during catalysis. Discerning relevant structures may be facilitated by studying supported metal systems with active sites localized at the metal-support interface. Here, we use *operando* techniques in an image-corrected ETEM (AC-ETEM) to visualize the atomic structures forming at and near the Pt/CeO₂ interface during CO oxidation.

Nanostructured CeO₂ cubes were loaded with 2 wt. % Pt by a photodeposition technique. Approximately 1 mg of the catalyst powder was impregnated onto a glass microfiber pellet and a Ta grid [1]. The Ta grid and pellet were loaded into an Inconel Gatan furnace-style heating holder. The Inconel holder was determined to be unreactive at the temperatures of interest in this study. An FEI Titan AC-ETEM tuned to a negative C_s condition was used for *operando* imaging. Approximately 1 Torr of CO and 0.5 Torr of O₂ was admitted into the cell. The pressure stabilized over an hour and then the sample was heated to 350 °C. Images were acquired at 300 kV with an incident electron flux of $\sim 1,000 \text{ e}^-/\text{\AA}^2/\text{s}$. A residual gas analyzer (RGA) measured the gas composition within the cell, allowing for changes in activity to be tracked.

Figure 1 shows the RGA reporting the unambiguous *in situ* conversion of CO and O₂ to CO₂. Interestingly, our work with this catalyst demonstrated it achieves conversions approaching 100% at 200 °C, so interfacial atomic behavior observed at this temperature can be inferred to correspond to the processes of catalysis. Figure 2 shows a series of AC-ETEM images acquired 1 second apart at 200 °C in 1.5 Torr of stoichiometric CO and O₂. A Pt nanoparticle is seen to restructure dynamically, suggesting that the bonding with the underlying CeO₂ is constantly changing. The inset diffractograms in (b) and (c) reveal that the Pt nanoparticle rotates into (on the left side) and away from (on the right side) the CeO₂ support, through an angle of 6.8°. The interfacial instability driving the restructuring may be due to the creation and annihilation of oxygen vacancies during the Mars van Krevelen oxidation process [2].

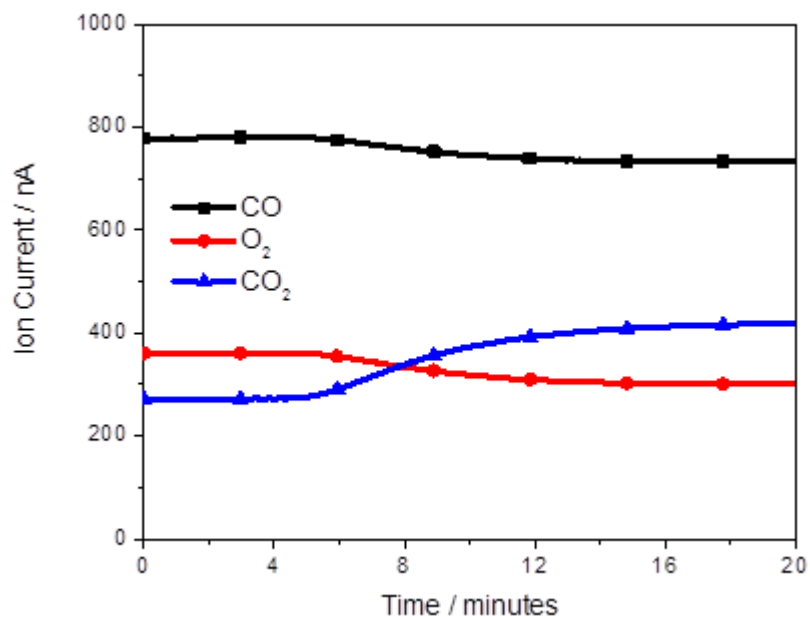


Figure 1. *In situ* mass spectrometry unambiguously detects conversion of CO and O₂ to CO₂ when the sample is heated to 350 °C, at $t = 4$ minutes.

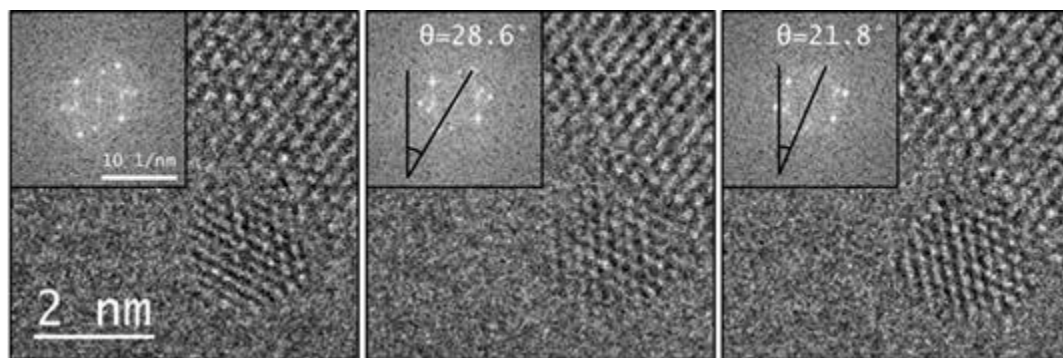


Figure 2. AC-ETEM images of a Pt nanoparticle on the edge of a CeO₂ cube, taken in 1.5 Torr of CO and O₂ at 200 °C (a). The inset FFTs show that the particle rotates through an angle of 6.8°, with the rotation directed as a rocking along the plane of the metal-support interface.

References:

- [1] Miller, B. K., *et al.*; Ultramicroscopy 156 (2015)
- [2] We gratefully acknowledge the support of NSF grant CBET-1604971 and ASU's John M. Cowley Center for High Resolution Electron Microscopy.