

Atomic-Resolution *Operando* Observations of Nanostructured Pt/CeO₂ Catalysts Performing CO Oxidation

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Heterogeneous catalysts accelerate reactions by reducing the activation energy for the rate limiting step. The specific locations on the catalyst at which the activation energy is lowest – the so-called *active sites* – are poorly understood, as catalytically relevant atomic structures only emerge under reaction conditions. Even with *in situ* TEM, atomic-level structure-activity relationships are difficult to determine due to the large number of surface structures that form dynamically during catalysis. Discerning catalytically relevant structures may be facilitated by studying supported metal systems in which the active sites are localized to the metal-support interface. The rate of CO oxidation ($\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2$) over Pt/CeO₂ has been shown to depend strongly on the perimeter length of the metal-support interface [1]. However, at present there is no experimental data on the atomic structures that comprise the Pt/CeO₂ interface *during catalysis*. Here, we use *operando* techniques in an image-corrected environmental TEM (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, and their activity for CO oxidation was confirmed [2]. An aqueous dispersion of the catalyst powder was wet-impregnated onto an inert borosilicate glass microfiber pellet, leading to a loading of ~1 mg Pt/CeO₂ [3]. A drop of the dispersion was placed onto a 200 mesh Ta grid pre-reduced in H₂ at 400 °C for 2 hours. The Ta mesh 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 ~1,000 e⁻/Å²/s. A residual gas analyzer (RGA) measured the gas composition within the cell, allowing for changes in activity to be tracked. Estimates of the *in situ* conversion, X_{CO} , can be made with the below equation, where i_j is the RGA current reported for species j , $i_{j[0]}$ is the current reported at zero conversion, and σ_j is the standard ionization cross section [3].

$$X_{\text{CO}} = \frac{\text{CO}_{\text{reacted}}}{\text{CO}_{\text{in}}} = \frac{\text{CO}_2_{\text{produced}}}{\text{CO}_{\text{in}}} \sim \left(\frac{i_{\text{CO}_2} - i_{\text{CO}_2[0]}}{\sigma_{\text{CO}_2}} \right) / \frac{i_{\text{CO}[0]}}{\sigma_{\text{CO}}}$$

Figure 1a) shows the RGA current reported for CO, O₂, and CO₂. When the sample temperature increases to 350 °C (at approximately 4 minutes), the CO₂ signal is seen to increase while the CO and O₂ signals simultaneously decrease – demonstrating the *in situ* conversion of CO and O₂ to CO₂. Figure 1b) plots the *in situ* conversion obtained at this temperature as a function of time. After 20 minutes, the conversion approaches a value of ~16%. Interestingly, our work with this catalyst showed that it achieves conversions approaching 100% at 200 °C [2]. The lack of *in situ* conversion below 350 °C suggests that too little catalyst was loaded onto the *operando* pellet. However, since the catalyst is known to be active at 200 °C, 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 Torr of CO and 0.5 Torr of O₂. A Pt nanoparticle is seen to restructure dynamically, suggesting that the bonding with the underlying CeO₂ is constantly changing. The inset FFTs 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°. In the FFTs, spots corresponding to CeO₂ do not move, indicating that the change in angle is due to Pt restricting and not image drift. The interfacial instability driving the nanoparticle's restructuring may be caused by the rapid creation and annihilation of oxygen vacancies during the Mars van Krevelen oxidation process, which is the hypothesized mechanism for CO oxidation over Pt/CeO₂ catalysts [1, 4].

References:

- [1] M. Cargnello *et al*, *Science* **341** (2013), p. 771.
 [2] J.L. Vincent, V. O'Keefe and P.A. Crozier, *Science* **341** (2013).
 [3] B.K. Miller, T.M. Barker and P.A. Crozier, *Ultramicroscopy* **156** (2015), p. 18.
 [4] We gratefully acknowledge the support of NSF grant CBET-1604971 and ASU's John M. Cowley Center for High Resolution Electron Microscopy.

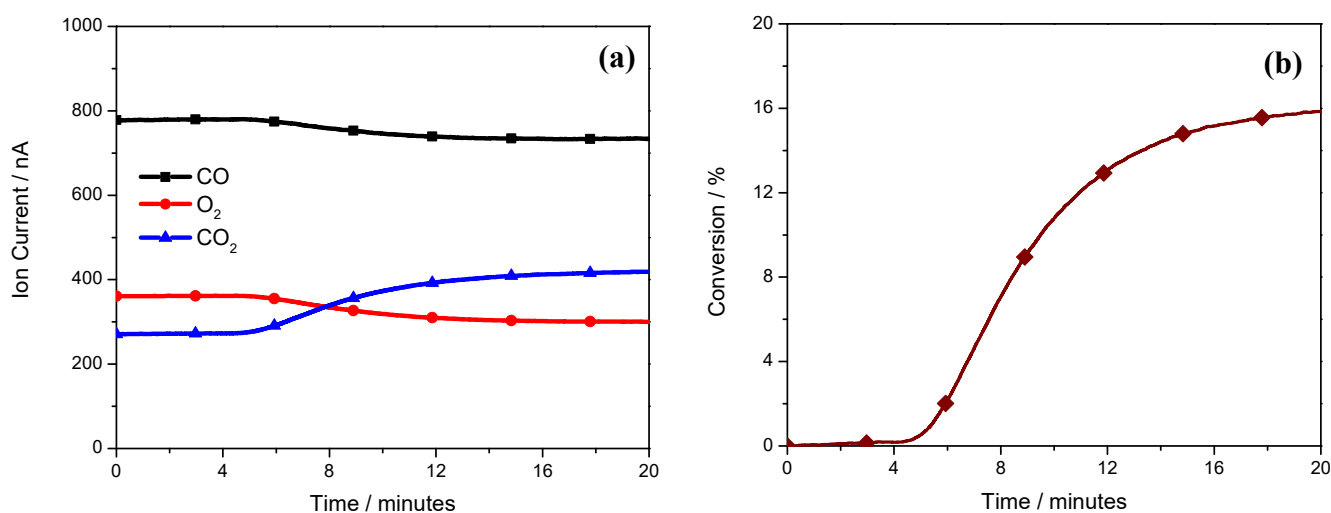


Figure 1. *In situ* mass spectrometry detects conversion of CO and O₂ to CO₂ when the sample is heated to 300 °C, at $t = 4$ minutes (a). The conversion can be estimated from the RGA current, and approaches ~16% (b). Signals were measured every 10 seconds; symbols shown every 35 data points.

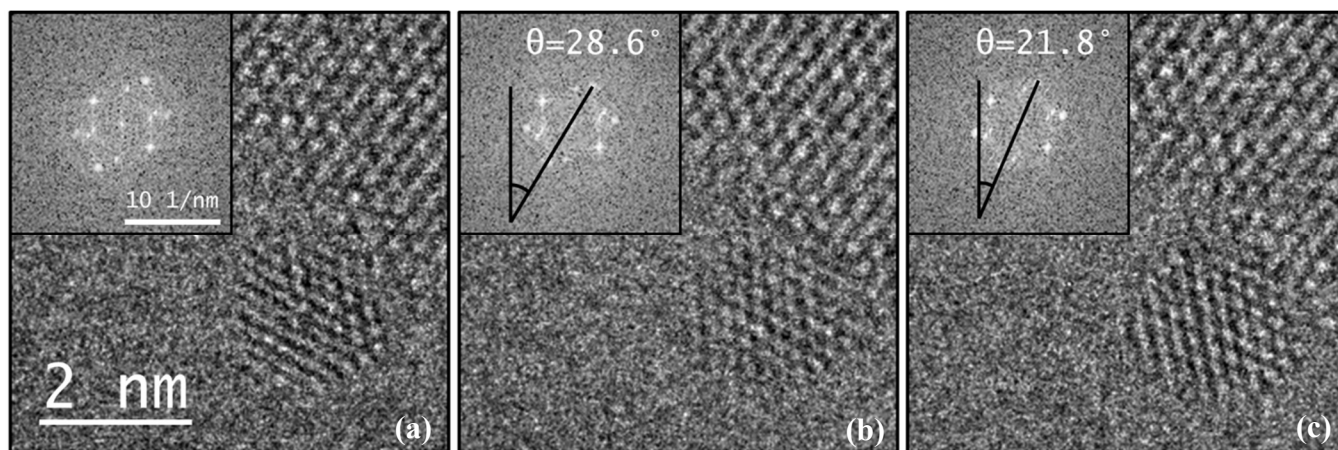


Figure 2. AC-ETEM images of a Pt nanoparticle anchored to the edge of a CeO₂ cube, taken in 1.5 Torr of stoichiometric CO and O₂ at 200 °C (a). The inset FFTs show that the particle rotates through an angle of 6.8°, with the rotation directed as a rocking along the plane of the metal-support interface.