

***Operando* Insight into Oxygen Transfer at Pt/CeO₂ Interfaces during CO Oxidation**

Joshua L. Vincent^{1*} and Peter A. Crozier¹

¹ School for the Engineering of Matter, Transport, and Energy, Arizona State University, Tempe, Arizona 85287-6106

*Corresponding author: Joshua.Vincent@asu.edu

Oxygen transfer is a critical functionality in many technologies ranging from solid oxide fuel cells to environmental catalysis. In these applications, catalytically active metal nanoparticles (e.g., Pt) are typically dispersed on reducible oxides (e.g., CeO₂), since reducible oxides can transfer lattice oxygen to reactive adsorbates at the metal-support interface. Photoelectron spectroscopy and density functional theory studies suggest that oxygen transfer is mediated by complicated interfacial vacancy pathways that depend strongly on the local atomic structure of the interface and proximal surfaces [1]. A fundamental understanding of the interfacial and surface structures that facilitate oxygen transfer is needed and lacking. The responsible structures are expected to emerge and be dynamic under reaction conditions. At present, there is little experimental data on the atomic structures that comprise the Pt/CeO₂ interface and nearby surface *in reactive gases* or *during catalysis*. Here, we use *in situ* and *operando* techniques in an image-corrected environmental transmission electron microscope (ETEM) to visualize the atomic structures forming at and near the Pt/CeO₂ interface, both in reactant gases or during CO oxidation.

Nanostructured CeO₂ cubes were synthesized, loaded with 17 wt.% Pt nanoparticles, and used as a model catalyst system. A FEI Titan ETM tuned to a negative C_s condition at 300 kV was used for *in situ* and *operando* imaging, with a typical e⁻ flux of 1–2*10³ e⁻/Å²/s. Special sample preparation techniques involving an *operando* pellet reactor allowed for a large mass of catalyst to be loaded into the ETM (in this case, ~240 μg) [2]. A roughly equimolar mixture of 0.57 Torr of CO and O₂ was admitted into the ETM cell while the catalyst was heated to 300 °C. *In situ* electron energy-loss spectroscopy (EELS) was implemented to track the gas composition, allowing catalytic conversions to be detected and quantified.

Figure 1 shows a CeO₂-supported Pt nanoparticle in 0.57 Torr of CO and O₂ at 144 °C, which corresponds to a CO conversion (X_{CO}) of 0%. Under these conditions, the Pt particle and the Pt/CeO₂ interface appear stable enough to yield clearly resolved Pt and Ce columns. Next, we wanted to study the evolution of the metal-support interface at higher temperatures – and higher CO conversions. Figure 2 shows the *in situ* CO conversion determined with EELS from 250 °C to 297 °C. The inset (a) displays an energy-loss spectrum recorded at 297 °C, which shows two labeled peaks that correspond to CO and CO₂. Figure 3 shows a series of 25-frame composite *operando* images of CeO₂-supported Pt nanoparticles in 0.57 Torr of roughly equimolar CO and O₂. In composite image Figure 1a, ($X_{CO} = 0\%$), clearly resolved Ce columns are visible at the surface of the CeO₂ and near the Pt/CeO₂ interface. The Pt nanoparticles here also show clear lattice fringes and a well-defined interfacial orientation relationship. At higher CO conversions, the Pt nanoparticles were seen to reconfigure, and the interfacial and proximal surfaces were seen to restructure dynamically. In composite image Figure 1b, ($X_{CO} = 14\%$), the fringes in the Pt nanoparticles have blurred along the (100) direction, indicating their translational motion across the CeO₂. At 24% conversion, the Pt has become so dynamic that it appears with uniform gray contrast during the time scale of the image acquisition (0.5 sec). The fact that Pt reconfiguration is correlated with CO conversion suggests that the bonding environment around the interface has destabilized from lattice oxygen transfer. The conversion of CO is also correlated with Ce columns near the interface smearing or losing visibility

altogether. Recent work on CeO₂ links Ce cation displacement with oxygen exchange, so we speculate that the highly dynamic sites may represent the active sites for interfacial lattice oxygen transfer [3, 4].

References:

- [1] Vayssilov, G., *et al.*; Nature Materials **10** (2011), p. 310–315.
 [2] Miller, B. K., Barker, T. M., and Crozier, P. A.; Ultramicroscopy **156** (2015), p. 18-22.
 [3] Lawrence, E. L., *et al.*; Microscopy and Microanalysis **24 S1** (2018), p. 54-55
 [4] We gratefully acknowledge the support of NSF grant CBET-1604971 and ASU's John M. Cowley Center for High Resolution Electron Microscopy.

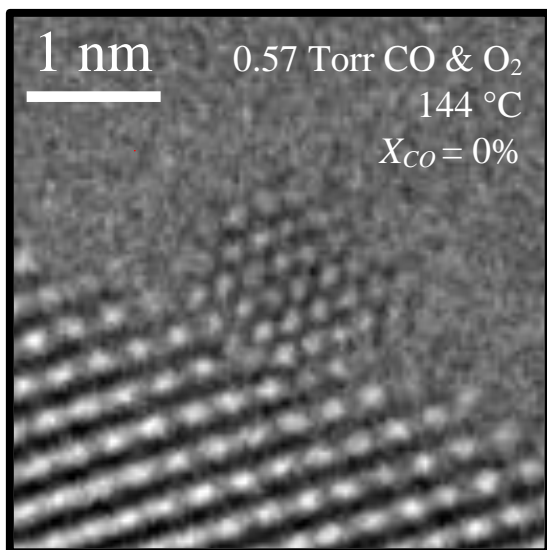


Figure 1. CeO₂-supported Pt nanoparticle imaged in 0.57 Torr of CO and O₂ at 144 °C. Under these conditions, the particle and interface appear stable enough to yield clearly resolved Pt and Ce columns.

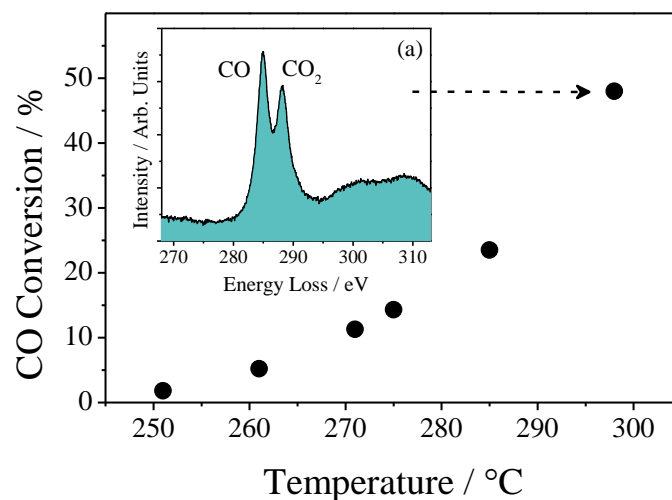


Figure 2. CO conversions in the TEM determined from *in situ* EELS. Inset (a) is an energy-loss spectrum from 297 °C which shows the conversion of CO to CO₂.

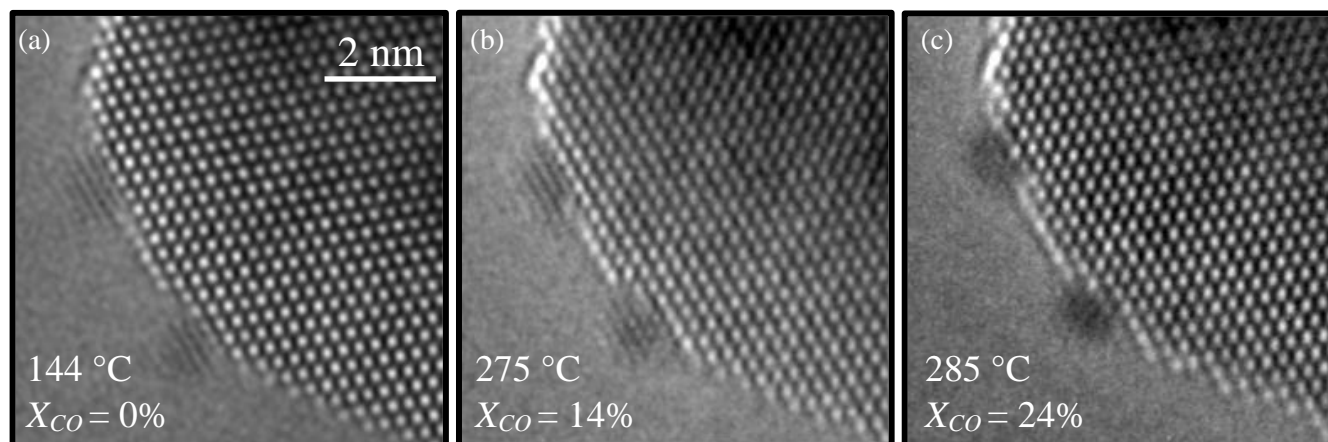


Figure 3. 25-frame composite images of Pt/ CeO₂ nanoparticles *during catalysis* in 0.57 Torr of roughly equimolar CO and O₂, at conditions of (a) 0% CO conversion at 144 °C, (b) 14% conversion at 275 °C, and (c) 24% conversion at 285 °C. As the conversion increases, the Pt becomes more dynamic, and loses fringe visibility. At the same time, the neighboring Ce columns become more blurred.