Chemical Engineering Doctoral Defense

Atomic-resolution In Situ and Operando Visualization of Oxygen Transfer Reactions over CeO2-supported Pt Catalysts

School for Engineering of Matter, Transport and Energy

Joshua Vincent
Advisor: Peter A. Crozier

Abstract

Oxygen transfer reactions are central to the functionality of many catalytic processes, including those underlying automotive exhaust emissions control and clean energy conversion. The catalysts used in these applications typically consist of metal nanoparticles dispersed on reducible oxides (e.g., Pt/CeO2), since reducible oxides can transfer their lattice oxygen to reactive adsorbates at the metal-support interface. There are many outstanding questions regarding the atomic and nanoscale spatial variation of the Pt/CeO2 interface, Pt metal particle, and adjacent CeO2 oxide surface during catalysis. To this end, in this thesis a range of computational and experimental techniques centered around aberration-corrected environmental transmission electron microscopy (AC-ETEM) were developed and employed to visualize and characterize the atomic-scale structural behavior of CeO2-supported Pt catalysts under reaction conditions (in situ) and/or during catalysis (operando).

A finite element model of the operando ETEM reactor was developed to simulate the gas and temperature profiles during conditions of catalysis. The model provides a tool for relating the reactant conversion measured with spectroscopy to the reaction rate of the catalyst that is imaged on the TEM grid. This aberration-corrected operando TEM approach was leveraged to investigate structure-activity relationships for CO oxidation over Pt/CeO2 catalysts. Correlating atomic-level imaging with catalytic turnover frequency reveals a direct relationship between activity and dynamic structural behavior that (a) destabilizes the supported Pt particle, (b) marks an enhanced rate of oxygen vacancy creation and annihilation, and (c) leads to increased strain and reduction in the surface of the CeO2 support.

To further investigate the structural meta-stability (i.e., fluxionality) of 1 – 2 nm CeO2-supported Pt nanoparticles, time-resolved in situ AC-ETEM was employed to visualize the catalyst's dynamical behavior with high spatiotemporal resolution. The results of this work provide insight into the atomic-level dynamic structural reconfigurations that can occur in reducible oxide-supported metal nanoparticle catalysts. Finally, new advances in data science and deep learning-based convolutional neural networks were leveraged to investigate and critically evaluate novel denoising techniques for ultra-low signal-to-noise images of catalytic nanoparticles. The approaches described here may be applicable to a wide range of atomic resolution imaging applications that are characterized by ultra-low signal-to-noise.

June 24, 2021; 11 AM; ERC 490;
Zoom Link: https://asu.zoom.us/j/81709697054