Correlative Structure-Bonding and Stability Studies of Pt/γ-Al₂O₃ Catalysts

Henry O. Ayoola¹, Qing Zhu¹, Cecile S. Bonifacio¹, Matthew P. McCann¹, Matthew T. Curnan¹,⁴, Stephen D. House¹, Joshua Kas², John J. Rehr², Eric A. Stach³, Wissam A. Saidi⁴, and Judith C. Yang¹

¹ Dept. of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA (USA)
² Dept. of Physics, University of Washington, Seattle, WA (USA)
³ Center for Functional Materials, Brookhaven National Laboratory, Upton, NY (USA)
⁴ Dept. of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, PA (USA)

Pt supported on gamma-alumina (γ-Al₂O₃) is one of the most important heterogeneous catalysts, with technologically important applications including oil refining and catalytic converters [1]. An important property of this catalyst is its stability. Understanding the bonding interactions between Pt and γ-Al₂O₃ is key as they will influence the shape, dispersion, and ultimately stability of Pt nanoparticles (NPs) [2]. Probing these atomic-scale interactions requires direct correlation between theoretical simulations and experimental measurements, which in turn necessitates a model catalyst. We have synthesized a model system of Pt NPs dispersed on single-crystal γ-Al₂O₃ which enables us to study properties of the catalyst system with enough simplicity to allow direct correlation between experimental results and simulations. Single-crystal γ-Al₂O₃ was synthesized by oxidation of NiAl (110) [3]. 2-3 nm Pt NPs were deposited on the γ-Al₂O₃ surface using electron beam evaporation. Cross-sectional TEM samples of the Pt/γ-Al₂O₃ were prepared using the focused ion beam (FIB) lift-out technique on an FEI Helios dual beam FIB-SEM. Using this model system, we are studying Pt/γ-Al₂O₃ bonding and Pt NP stability, both ex situ and in situ, using cutting-edge microscopy and spectroscopy techniques in combination with theoretical simulations.

A critical first step in the comparison of theoretical simulations to experimental results for Pt/γ-Al₂O₃ is the accurate description of γ-Al₂O₃. Many crystal structures for γ-Al₂O₃ can be found in the literature. Two of the most commonly cited are the spinel model and the monoclinic model proposed Digne et al. [4]. We have determined that the monoclinic model [4] can be used to accurately simulate the O-K near-edge EELS spectrum, despite the model spinel being more accurate to the true structure of γ-Al₂O₃ [5].

Once we determined that the monoclinic model can be used for γ-Al₂O₃ EELS simulations with reasonable accuracy, we investigated the bonding at the Pt/γ-Al₂O₃ interface. Aberration-corrected EELS spectra were collected along the Pt/γ-Al₂O₃ interface at cryo-temperature using a Hitachi HD2700C STEM operated at 200 kV with a Gatan Enfina spectrometer, which revealed a unique pre-peak in the O-K EELS at the interface (Figure 1a). Cryo-temperature (using a Gatan Ultra Low Temperature Double-Tilt (ULTDT) cryo-holder) was used to minimize the effect of beam damage on the EELS spectra. Multiple structures based on the monoclinic γ-Al₂O model were constructed to simulate the Pt/γ-Al₂O (111) interface using density functional theory (DFT). O-K near-edge EELS were then simulated using FEFF9 for each of these structures and compared with the experimentally obtained EELS spectra. The simulated EELS from the model with Pt bonded to a surface Al atom and an O adatom on a vacancy-free site best agreed with the energy and intensity of the O-K edge pre-peak observed in experiment (Figure 1b).

We are now studying the stability of Pt NPs on γ-Al₂O₃ in situ using environmental TEM. Preliminary results suggest support-influenced Pt nanoparticle behavior in H₂ and O₂ environments at room temperature; with 1.5 nm Pt NPs rapidly agglomerating under H₂ exposure (Figure 2) and 1.5 nm Pt NPs
dispersing under O\textsubscript{2} exposure. We will study the size and shape dynamics of Pt NPs on $\gamma$-Al\textsubscript{2}O\textsubscript{3}, as well as the role of the interface, during H\textsubscript{2}/O\textsubscript{2} exposure using our model system [6].

References:

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Figure 1. (a) High-angle annular dark-field (HAADF)-STEM image of the Pt/$\gamma$-Al\textsubscript{2}O\textsubscript{3} interface. The area of the interface where the spectrum image was acquired is highlighted in blue. Extracted O-K edge EELS spectra from the pixels labeled 1 and 2 are plotted showing the pre-peak in 1 but not in 2. (b) Structural model of the Pt/$\gamma$-Al\textsubscript{2}O\textsubscript{3}(111) interface developed in DFT and corresponding O-K edge EELS signal from interface O atoms simulated with FEFF9 showing match to pre-peak energy.

Figure 2. ETEM images of Pt/$\gamma$-Al\textsubscript{2}O\textsubscript{3} acquired \textit{in situ} during exposure to 1.2x10\textsuperscript{-2} Pa H\textsubscript{2} at room temperature.