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Correlative Structure-Bonding and Stability Studies of Pt/γ-Al_2O_3 Catalysts

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Pt supported on gamma-alumina (γ-Al_2O_3) 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-Al_2O_3 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-Al_2O_3 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-Al_2O_3 was synthesized by oxidation of NiAl (110) [3]. 2-3 nm Pt NPs were deposited on the γ-Al_2O_3 surface using electron beam evaporation. Cross-sectional TEM samples of the Pt/γ-Al_2O_3 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-Al_2O_3 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-Al_2O_3 is the accurate description of γ-Al_2O_3. Many crystal structures for γ-Al_2O_3 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 spinel model being more accurate to the true structure of γ-Al_2O_3 [5].

Once we determined that the monoclinic model can be used for γ-Al_2O_3 EELS simulations with reasonable accuracy, we investigated the bonding at the Pt/γ-Al_2O_3 interface. Aberration-corrected EELS spectra were collected along the Pt/γ-Al_2O_3 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-Al_2O model were constructed to simulate the Pt/γ-Al_2O_3 (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 interface 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-Al_2O_3 *in situ* using environmental TEM. Preliminary results suggest support-influenced Pt nanoparticle behavior in H_2 and O_2 environments at room temperature; with 1.5 nm Pt NPs rapidly agglomerating under H_2 exposure (Figure 2) and 1.5 nm Pt NPs dispersing under O_2 exposure. We will study the size and shape dynamics of Pt NPs on γ-Al_2O_3, as well as the role of the interface, during H_2/O_2 exposure using our model system [6].

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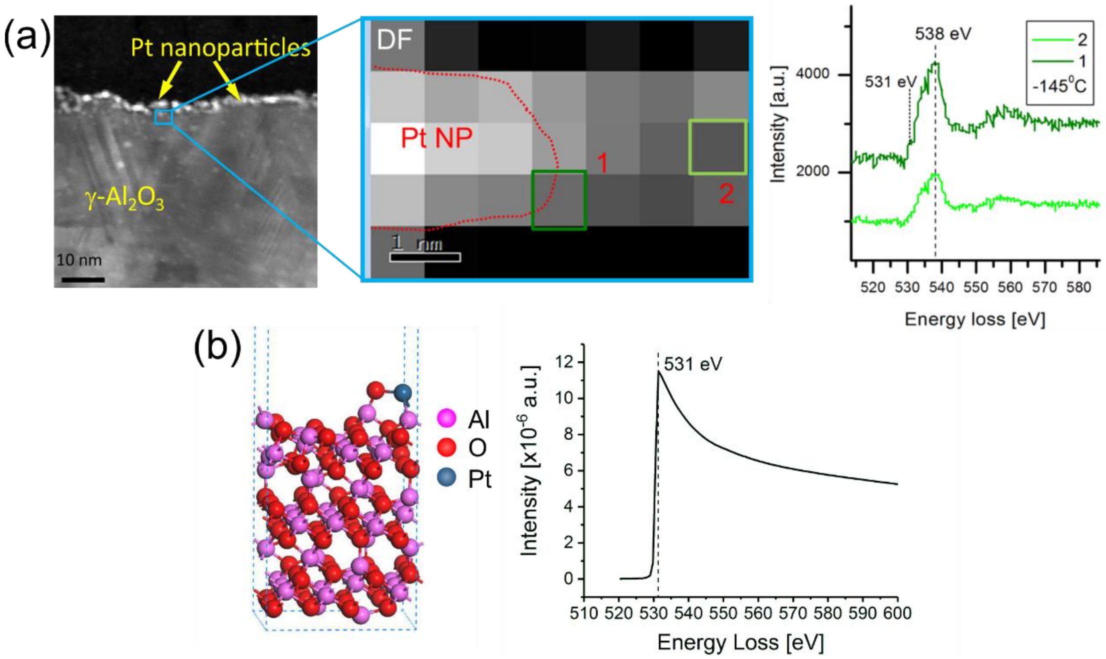

Figure 1. (a) High-angle annular dark-field (HAADF)-STEM image of the Pt/γ-Al_2O_3 interface. The area of the interface where the spectrum image was acquired is highlighted in blue. Extracted O-K edge EELS spectra from the pixels labeled 1 and 2 are plotted showing the pre-peak in 1 but not in 2. (b) Structural model of the Pt/γ-Al_2O_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.

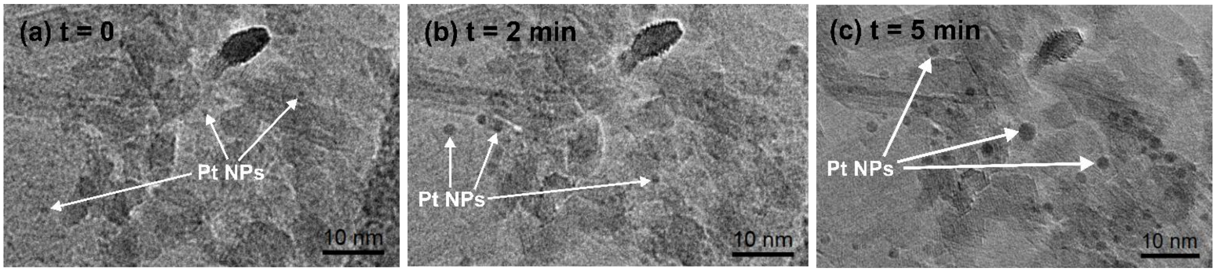

Figure 2. ETEM images of Pt/γ-Al_2O_3 acquired *in situ* during exposure to 1.2×10^{-2} Pa H_2 at room temperature.