

Investigation of the Structural and Electronic Properties of Pt/ γ -Al₂O₃, a Model Catalyst System

Cecile S. Bonifacio¹, Qing Zhu¹, Dong Su², Fernando Vila³, Henry O. Ayoola¹, Stephen D. House¹, Josh Kas³, John J. Rehr³, Eric A. Stach², Wissam A. Saidi⁴, and Judith C. Yang¹

¹. Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15260

². Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973

³. Department of Physics, University of Washington, Seattle, WA 98195

⁴. Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, PA 15260

Pt/ γ -Al₂O₃ is possibly the most important heterogeneous catalyst system based on its application in numerous technologically important processes, including oil refining, catalytic converters, and fuel cells [1,2], making it the subject of numerous experimental and theoretical studies. The bulk structure and surfaces of γ -Al₂O₃ under catalytic conditions are complex, thus the system remains poorly understood. For example, Digne et al. [3] argued that the defective spinel structure of γ -Al₂O₃ is not correct based on DFT calculations combined with thermodynamic models. To bridge the gap between experiment and theory, the nature of the binding sites (and the modification of these sites) of Pt nanoparticles (NPs) to the well-defined crystalline γ -Al₂O₃ surface will be investigated using electron energy loss spectroscopy (EELS) and theoretical simulations to understand the effect of the support on the catalytic properties of the system.

The model γ -Al₂O₃ catalyst system was prepared by first growing the single crystalline γ -Al₂O₃ thin films through the controlled oxidation of NiAl (110) and then depositing Pt NPs using a UHV dual e-beam evaporator. Cross-section TEM samples of the Pt/ γ -Al₂O₃ were prepared using the focused ion beam (FIB) lift-out technique. EELS data were acquired across the Pt NP and γ -Al₂O₃ (110) substrate interface and on the bulk γ -Al₂O₃ substrate at room (RT) and cryo temperatures. Simulated EELS O K edge signals on the two areas on the sample were computed based on plane wave DFT optimized for Digne's γ -Al₂O₃ structure using FEFF9 code.

Scanning transmission electron microscopy (STEM) observations show that the cryo temperature conditions prevented issues related to electron-beam damage such that no holes and no growth of the EELS O K pre-peak were observed after EELS acquisition. The O K pre-peak (* in Figure 1) was consistently present in spectra taken at the Pt/ γ -Al₂O₃ interface at cryo temperature but not in those acquired at room temperature (c.f., Figure 1d and 1b, respectively). The calculated EELS O K signals for the Pt on (110) γ -Al₂O₃ exhibited a similar pre-peak at 532 eV correlating to the experimental EELS O K data. The observed O K pre-peak can be attributed to surface defects, such as vacancies, that may pin the Pt NPs. This is similar to the O K pre-peak EELS results in the La_{0.5}Sr_{0.5}CoO_{3- δ} structure, where the pre-peak was shown to be due to the ordering of high concentration of O vacancies [4,5].

Additional EELS experiments are underway to identify the regions and conditions (e.g., areas with twins on the γ -Al₂O₃, pristine γ -Al₂O₃ at cryo conditions) that produce the pre-peak to ultimately explain its origin. Likewise, EELS O K signal calculations using FEFF9 are concurrently in progress for comparison with the experimental data [6].

References:

- [1] G. Ertl, "The Handbook of Heterogeneous Catalysis", (Wiley-VCH, Weinheim), p. 2012
 [2] P. Euzen, "Handbook of Porous Materials", ed. J. Weitkamp, (Wiley -VCH, Weinheim), p. 1591.
 [3] M. Digne *et al.*, Journal of Catalysis **226** (2004), p.54.
 [4] R.F. Klie *et al.*, Physics Review Letters **99** (2007),p. 047203.
 [5] J. Gazquez *et al.*, Nano Letters **11**(2011), p. 973-976.
 [6] CSB, QZ, HOA, SDH and JCY acknowledge financial support by DOE Basic Energy Sciences (DE FG02-03ER15476) and the Center for Functional Nanomaterials (CFN) at Brookhaven National Lab supported by the Office of Basic Energy Sciences of the US Department of Energy Contract No. DE-SC0012704.

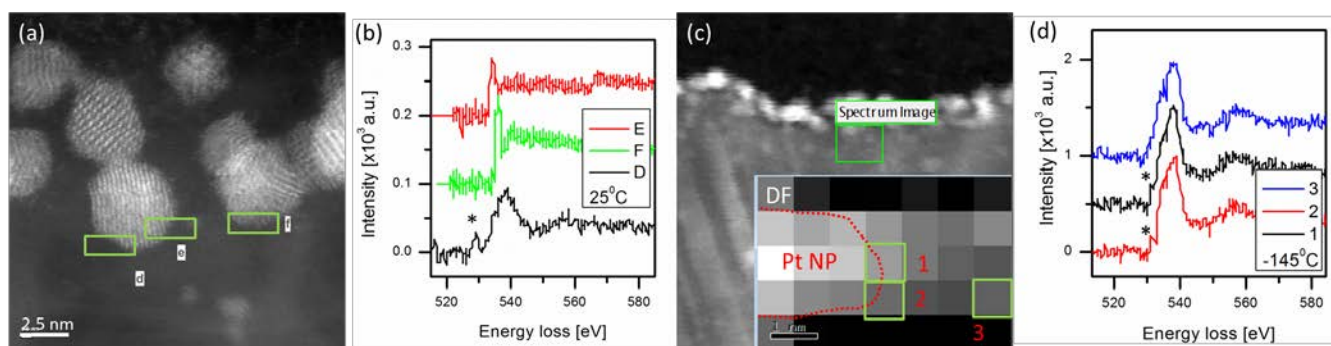


Figure 1. High-angle annular dark-field (HAADF) images and the corresponding EELS O K signals from the Pt/ γ -Al₂O₃ interface acquired at room temperature (**a,b**) and at cryo temperature (**c,d**). A pre-peak (marked as *) in the O K signal was intermittently observed in the spectra from the Pt/ γ -Al₂O₃ interface. No pre-peak was detected from Spectrum 3 in (**d**), which was acquired from the γ -Al₂O₃ substrate.

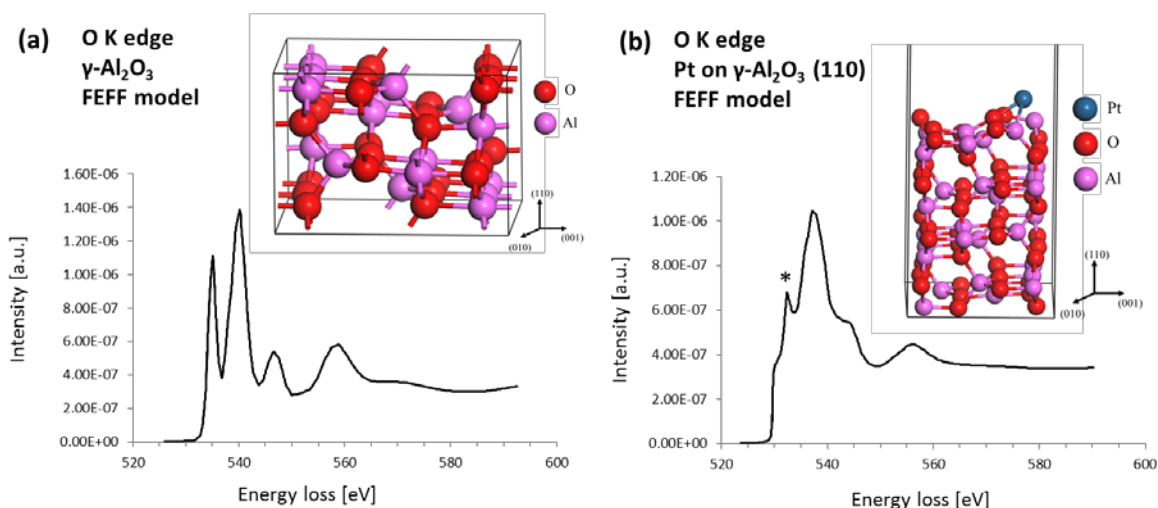


Figure 2. Atomistic model and calculated EELS O K edge using the FEFF9 code of the of the bulk γ -Al₂O₃ (**a**) and for Pt on γ -Al₂O₃ (110) (**b**). A similar O K pre-peak (marked as *) from experiment was observed in (**b**).