Investigation of the Structural and Electronic Properties of Pt/$\gamma$-Al$_2$O$_3$, a Model Catalyst System

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Pt/$\gamma$-Al$_2$O$_3$ 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 $\gamma$-Al$_2$O$_3$ under catalytic conditions are complex, thus the system remains poorly understood. For example, Digne et al. [3] argued that the defective spinel structure of $\gamma$-Al$_2$O$_3$ 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 $\gamma$-Al$_2$O$_3$ 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 $\gamma$-Al$_2$O$_3$ catalyst system was prepared by first growing the single crystalline $\gamma$-Al$_2$O$_3$ 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/$\gamma$-Al$_2$O$_3$ were prepared using the focused ion beam (FIB) lift-out technique. EELS data were acquired across the Pt NP and $\gamma$-Al$_2$O$_3$ (110) substrate interface and on the bulk $\gamma$-Al$_2$O$_3$ 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 $\gamma$-Al$_2$O$_3$ 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/$\gamma$-Al$_2$O$_3$ 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) $\gamma$-Al$_2$O$_3$ 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$_{3-\delta}$ 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 $\gamma$-Al$_2$O$_3$, pristine $\gamma$-Al$_2$O$_3$ 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:

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**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).