

Spatial Decorrelation of Ceria Surface Reduction and Platinum Surface Loading Site

Peter Tieu¹, Jaeha Lee², Chaitanya Gadre³, Xingxu Yan⁴, Wenjie Zang⁴, Phillip Christopher², Xiaoqing Pan^{3,4,5*}

¹. Department of Chemistry, University of California, Irvine, CA, USA.

². Department of Chemical Engineering, University of California, Santa Barbara, USA.

³. Department of Physics and Astronomy, University of California, Irvine, CA, USA.

⁴. Department of Materials Science and Engineering, University of California, Irvine, CA, USA.

⁵Irvine Materials Research Institute, University of California, Irvine, CA, USA.

* Corresponding author: xiaoqinp@uci.edu

Ceria (CeO_2) is a widely studied material which has applications as automotive emission control catalysis, oxygen storage, the water-gas shift reaction, and hydrocarbon-oxidation due to its property as a reducible metal oxide [1]. The high propensity to lose oxygen atoms in low oxygen partial pressure and/or high temperature environments enable ceria to serve in many redox processes. It has been reported that the pretreatment history and the presence of dopant metals such as platinum, palladium, and rhodium can enhance desirable properties of ceria. The details about how such pretreatment changes the ceria is a constant field of new information. Of particular interest is how the presence of platinum enables the reduction of the cerium at the surface from the 4+ to 3+ oxidation state in a hydrogen environment. Spectroscopic measurements have suggested hydrogen spillover enables the reduction of the ceria surface but an atomistic view can aid in furthering the understanding of ceria surface reduction which previous studies lacked [2]. Herein, we use *in situ* STEM imaging to observe the structure directly combined with coreloss EELS to spatially map the location of cerium reduction.

Platinum in various weight loadings was loaded onto commercial ceria nanoparticles (10-15 nm in size), resulting in samples with platinum single atoms and with nanoparticles. Samples were drop cast onto a silicon nitride membrane window for use in a gas cell (Protochips, USA) for *in situ* studies in a double aberration-corrected JEOL ARM300CF at 300 kV. EELS data was acquired with a K2 direct electron detector (Gatan, USA) and processed with principal component analysis.

Various weight loadings of Pt/ CeO_2 and commercial ceria, as a control, were imaged before, during, and after *in situ* reduction in 5% H_2/Ar for one hour (**Figure 1a, d, e**). *In situ* EELS measurements were acquired and used to generate maps showing the spatial distribution of the Ce oxidation states based on the ratio of the Ce M5 and M4 peak heights (**Figure 1b, c, f, g**) [3]. A comparison of the Ce oxidation state maps and the corresponding HAADF images of the Pt/ CeO_2 samples showed no spatial correlation between the platinum species and the location of Ce^{3+} formation. Instead, the Ce^{3+} appeared primarily at boundaries between ceria nanoparticles, especially in the case of platinum nanoparticle loading. Such a result shows that the spillover hydrogen does not immediately form Ce^{3+} at the junction between the platinum species and the ceria but instead mobilizes along the ceria surface to these boundaries where the reduction process is facilitated. In contrast, commercial ceria showed no strong prevalence of ceria surface reduction nor aggregation of the Ce^{3+} . Thereafter, high magnification observations of these boundaries were performed.

In situ observations of the boundaries between ceria nanoparticles indicated that there is a rearrangement leading to alignment at these boundaries which is not reversible. An EELS time series of Pt/CeO₂ at the same boundary following sequential reduction, oxidation, and reduction shows that Ce³⁺ formation occurs much more rapidly in the second reduction after boundary alignment has already occurred, indicating that the initial alignment plays a role in ceria surface reduction (**Figure 2a**). *Ex situ* samples of commercial ceria and Pt/CeO₂ before and after reduction showed the initial random orientation changed drastically for the Pt/CeO₂ but not for commercial ceria, indicating that the alignment occurs broadly when platinum is present (**Figure 2b, c**). The images provide details of an important step in the ceria surface reduction.

By combining *in situ* EELS and imaging to study ceria surface reduction, we can see that an atomistic view gives further details about the mechanism of the surface reduction which was not previously known through bulk spectroscopy. The spatial mapping of the cerium oxidation state combined with HAADF imaging clearly show the spatial decorrelation between the surface reduction site and the platinum loading site, leading to further investigation of the structure changes *in situ*. This work demonstrates that previous models may not fully encompass material transformation and TEM can provide more details to help improve material design [4].

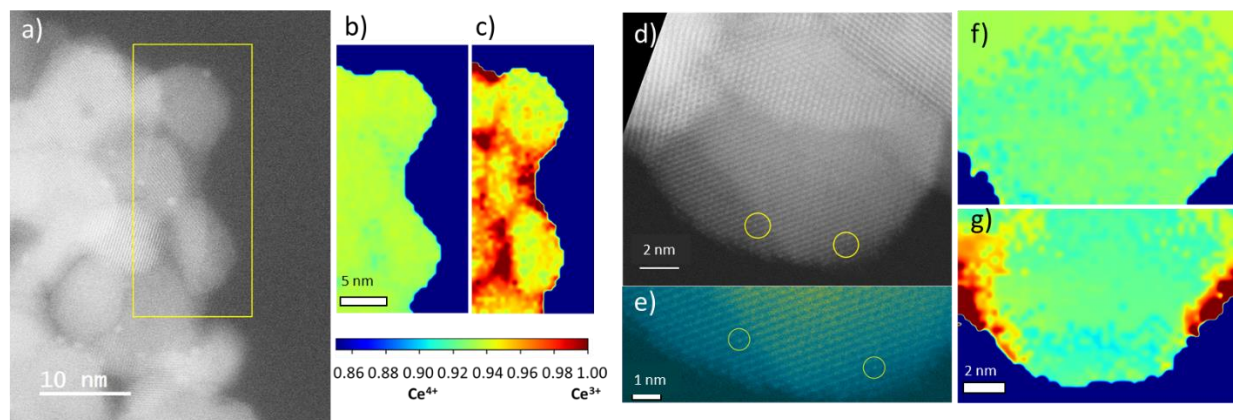


Figure 1. a) HAADF image and Ce M5/M4 ratio map of the yellow box b) before and c) after reduction of 2% Pt/CeO₂. Color scale below. d) HAADF image and e) magnified false color image of 0.1% Pt/CeO₂ with yellow circles indicating Pt single atoms. Ce M5/M4 ratio maps f) before and g) after reduction showing the location of ceria surface reduction occurring away from the Pt single atoms.

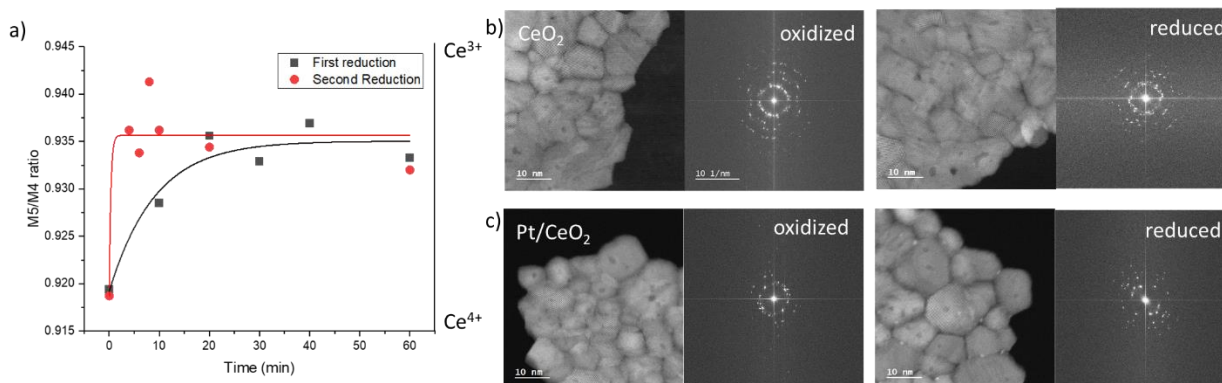


Figure 2. a) EELS time series of one boundary in Pt/CeO₂ following sequential reduction, oxidation, and reduction indicating that Ce³⁺ formation occurs much more rapidly after the first reduction. HAADF

images and the corresponding FFTs of *ex situ* oxidized and reduced b) CeO₂ and c) Pt/CeO₂ samples showing the random orientation of the ceria nanoparticles remain after reduction for CeO₂ but not for Pt/CeO₂. Scalebar is the same for all FFTs.

References:

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