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Detection of Adsorbates Induced Changes on Pt/CeO_2 Catalyst using *In situ* Electron Holography

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Heterogeneous catalysis is an important approach to control chemical transformations in which a set of reactants are converted to products on a catalyst surface. Detection of surface species upon exposure to reactants is important to understand catalytic functionalities of the nanoparticles e.g., active site determination. Exposure to various gases changes the surface chemistry and electronic properties of the nanoparticle [1]. Off-axis electron holography could be used as a technique in which these adsorbate-induced changes would be detected by measuring the phase change of the fast electron as it interacts with the modified nanoparticle surface [2] Recent work has shown the possibility of doing electron holography in the presence of gas inside the microscope without a significant drop in fringe visibility [3]. In this work, we aim to detect the presence of surface species on Pt nanoparticles supported on CeO_2 upon interaction with CO. This reaction was chosen for this investigation because CO binds strongly with Pt even at room temperature giving a significant surface coverage.

Pt was impregnated on CeO_2 using a wet impregnation method followed by calcination at 300C for 2 hours and reduction at 400℃ for 2 hours in 5% H_2/Ar gas [4]. XRD showed peaks from pure ceria. *In situ* catalytic conditions were set up using the environmental transmission electron microscope (ETEM) by heating the sample to 250℃ and under 0.1 torr of CO pressure. This microscope is equipped with an aberration correction thus enabling us to do imaging with sub angstrom spatial resolution. Off-axis electron holograms were collected at this experimental condition with a positive biprism voltage.

Figure 1 shows a phase contrast TEM image at room temperature under the vacuum (a) and under 10^{-4} Torr of CO pressure (b). Under the CO gas environment, there is a visible "ring" formation around the Pt nanoparticles. The ring was visible and quite stable under a long exposure of electron beam. Given that this ring wasn't detected in vacuum environment, it is associated with the interaction of CO with the Pt nanoparticle surface. **Figure 2a** shows electron holograms from the similar region collected at a biprism voltage of ~160 V at 250 ℃. 10 holograms of the same particle were captured to improve the signal-to-noise. Using custom holographic phase reconstruction scripts in Digital Micrograph, a phase image was generated and is shown in **figure 2b**. It is clearly seen that the ring is detected around the Pt nanoparticle (marked by faint green false color) and corresponds to a phase shift of 0.1 rad (**figure 2c**). The sharp ascent of the phase shift from Pt nanoparticle is also visible in **figure 2c**. More surface adsorbate detection experiments are being performed and will be presented [5].

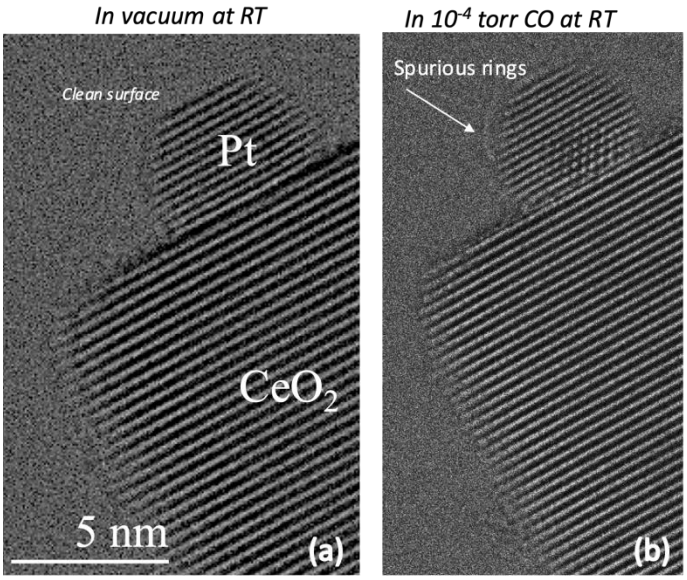

Figure 1. TEM images of Pt/CeO2 under (a) vacuum and room temperature and (b) 10^{-4} Torr of CO at room temperature (RT). The appearance of ring in CO is visible.

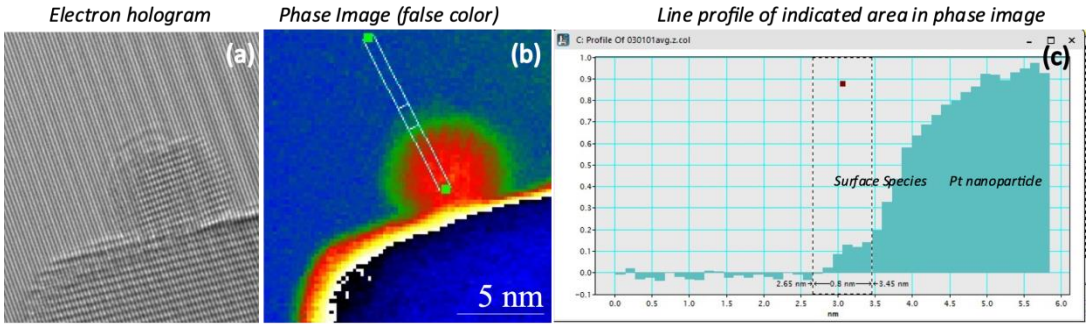

Figure 2. (a) Electron hologram of the same nanoparticle under in situ conditions, (b) retrieved phase image and (c) line profile from phase image showing the adsorbate and Pt nanoparticle induced phase shift of the fast electron.

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