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Stability of Supported Pd Nanoparticles During Exposure to Oxidizing and Reducing Environment

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Phase stability of transition metal nanoparticles during exposure to elevated temperature and gaseous environment is a highly relevant topic in catalytic research with broad implications for rationalization of catalytic properties and design of new catalytic materials. For Pd based catalysts, the phase stability under oxidizing environment represents an important topic as many Pd based catalysts are used in various oxidation reaction. While the general features of Pd oxidation are rather well understood [1,2], the mechanism that controls the stability of Pd when prepared in the form of supported nanoparticles are still actively studied. For instance, the interaction of Pd with an oxide substrate can result in some intriguing properties, such as hysteresis of PdO dissociation/formation during heating/cooling cycles [3,4]. In Pd/Al_2O_3 system, the hysteresis is approximately 210°C, which is significantly higher than for other Pd-based catalysts supported on CeO_2 and TiO_2 with hysteresis as low as 45°C and 80°C, respectively.

In order to address the issue of stability of Pd, we have performed a series of atomic-level *in-situ* TEM observations of Pd nanoparticles supported on various substrates, including CeO_2, γ/δ-Al_2O_3, ZrO_2 and SiO_2. The *in-situ* Transmission Electron Microscopy observations were performed with environmental FEI Titan 80-300 equipped with a CEOS C_s -image corrector, and operated at 80kV and 300kV under a set of well defined environmental conditions in the pressure range of ~10^{-3}- 10^{1}mbars. The composition and switching of gasses was controlled with a custom-built gas unit, and the samples were heated with MEMS based Aduro^{TM} Protochips holder in the temperature of up to 500°C.

In the present work, we will present high-resolution TEM observations that depict the atomic level process associated with a phase transformation of Pd to PdO on CeO_2. An example of such an observation is shown in Fig.1. In this particular case, the observation shows a transformation of Pd nanoparticle to PdO during an exposure of ~1 mbar of O_2 at 400°C. The initial step of transformation include a formation of surface oxide (Fig.1(b)), and subsequent nucleation and growth of PdO as shown in Fig1(c). Based on the current observations, we will discuss the mechanistic aspect of Oxygen interaction with Pd, and present a model for formation of PdO. In addition to oxidation studies, we will also present a complementary observation depicting the reverse transformation of PdO to Pd. In the second part of the presentation, we will present atomic level observations depicting oxidation properties of Pd nanoparticles supported on various oxide substrates. We will address the differences in the oxidation behavior that arise from the particle support interaction, and provide a plausible explanation for the intriguing hysteresis effect associated with PdO stability during heating/cooling cycles. Lastly, we will discuss the effect of electron beam during environmental TEM observations, and present examples where electron beam causes a strong interaction with the substrate leading to electron beam

induced artifacts. This work was supported by the Chemical Imaging Initiative at Pacific Northwest National Laboratory [5].

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[5]. The work was conducted in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at PNNL.

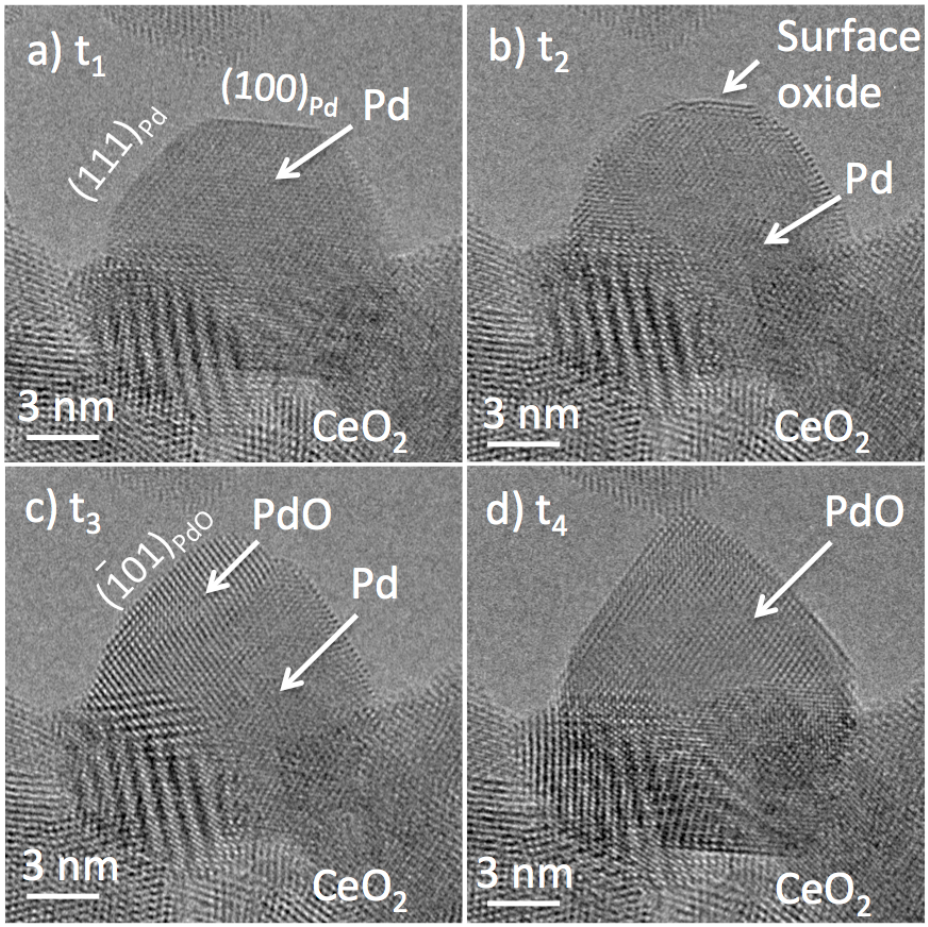

Fig.1. High resolution ETEM observation of Pd to PdO transformation at oxygen partial pressure of ~1 mbar and temperature of 400°C (a) Initial Pd nanoparticle supported on CeO_2. (b) Transition period corresponding to the formation of surface oxide (c) Transition period corresponding to growth PdO (d) Final stage of transformation corresponding to the formation of PdO.

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