

Supplemental Information for Anomalous Metal Vaporization from Pt/Pd/Al<sub>2</sub>O<sub>3</sub> under Redox Conditions

Andrew C. Meng,<sup>1</sup> Ke-Bin Low,<sup>2</sup> Alexandre C. Foucher,<sup>1</sup> Yuejin Li,<sup>2</sup> Ivan Petrovic,<sup>2</sup> Eric A. Stach<sup>1,3</sup>

<sup>1</sup> Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA, 19104

<sup>2</sup> BASF Corporation, Iselin, NJ 08830

<sup>3</sup> Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA, 19104

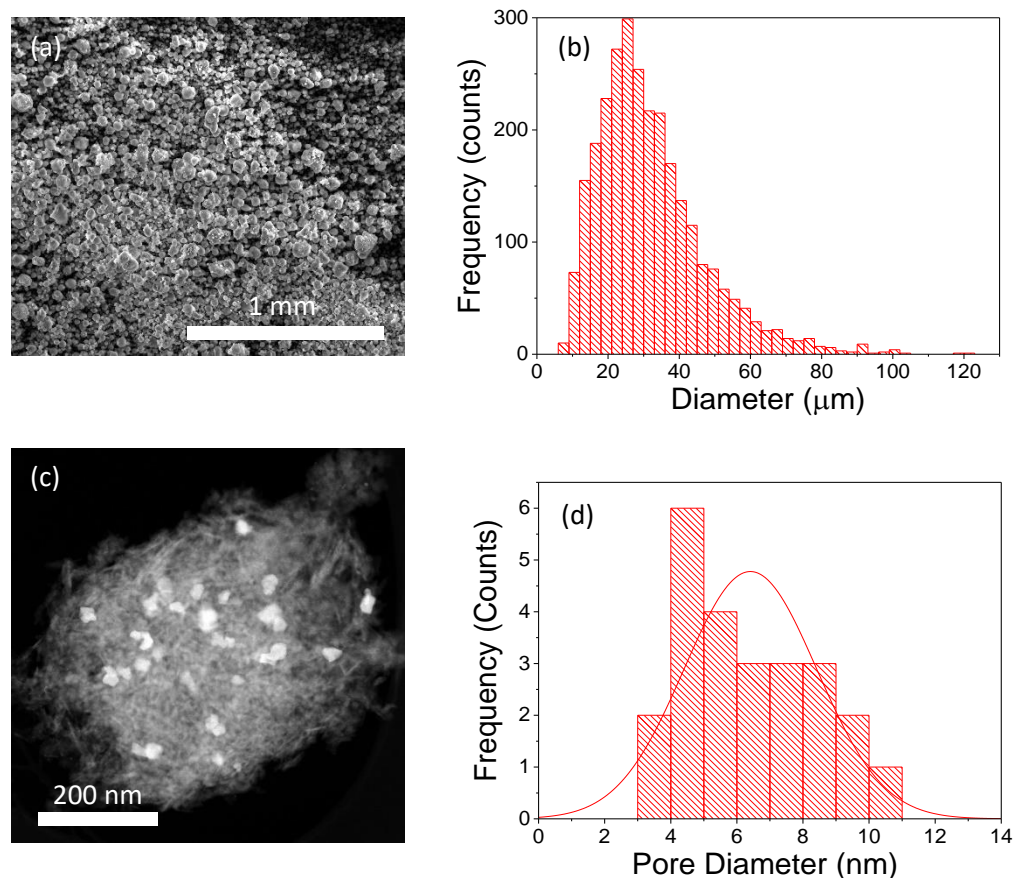


Figure S1 a) SEM image of fresh Pt/Pd/Al<sub>2</sub>O<sub>3</sub> catalyst and b) Particle Size Distribution (PSD); c) aberration corrected HAADF-STEM image of fresh Pt/Pd/Al<sub>2</sub>O<sub>3</sub> catalyst and d) pore size distribution

Based on the PSD, the volume specific surface area (not including pores) is approximately  $0.2 \mu\text{m}^2/\mu\text{m}^3$ , assuming spherical particles. If  $\gamma\text{-Al}_2\text{O}_3$  ( $3.65 \text{ g/cm}^3$ ) comprises most of the oxide support, this yields  $0.05 \text{ m}^2/\text{g}$ . To estimate the pore surface area, we threshold the STEM image to find the area fraction occupied by pores, which is approximately 30%. After measuring  $> 20$  pores, we have an average pore radius of 3 nm. Assuming pores don't intersect, and that their length is equal to the integrated average of the particle thickness (reasonable to assume given that contrast in the STEM image is consistent with a pore that extends for the entire thickness of the particle), this means that the combined pore surface area in a single particle is given by  $A = \pi^2 r_{\text{particle}}^3 / r_{\text{pore}}$ . This is a conservative estimate because this assumes straight cylindrical pores with minimal tortuosity. Combining this relation with the information in the PSD, we estimate the specific surface area of the oxide support to be  $\sim 200 \text{ m}^2/\text{g}$  or on the order of  $100 \text{ m}^2/\text{g}$ , a very rough estimate.

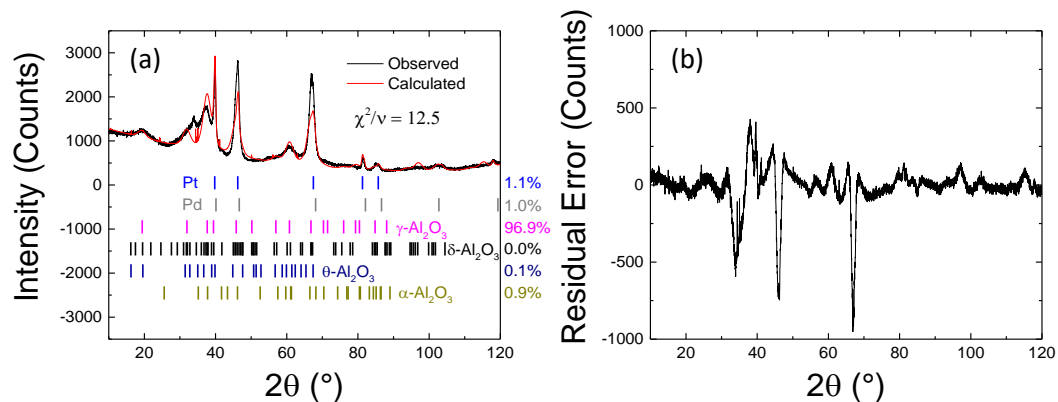


Figure S2 Rietveld Refinement of Fresh Pt/Pd/Al<sub>2</sub>O<sub>3</sub> showing a) observed and calculated XRD pattern and b) residual error

The fresh catalyst XRD data are fit to reference patterns for Pt (01-070-2057), Pd (00-046-1043),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (01-079-1557),  $\delta$ -Al<sub>2</sub>O<sub>3</sub> (00-046-1131),  $\theta$ -Al<sub>2</sub>O<sub>3</sub> (00-035-0121),  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (01-089-3072). Rietveld refinement (Panalytical Highscore) yields 1.1 wt% Pt, 1.0 wt% Pd, 96.9 wt%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 0.0 wt%  $\delta$ -Al<sub>2</sub>O<sub>3</sub>, 0.1 wt%  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, and 0.9%  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The reduced chi squared value of the fit is 12.5. The metal to oxide support ratio and the Pt to Pd ratio are close to what is expected as measured by EDS.

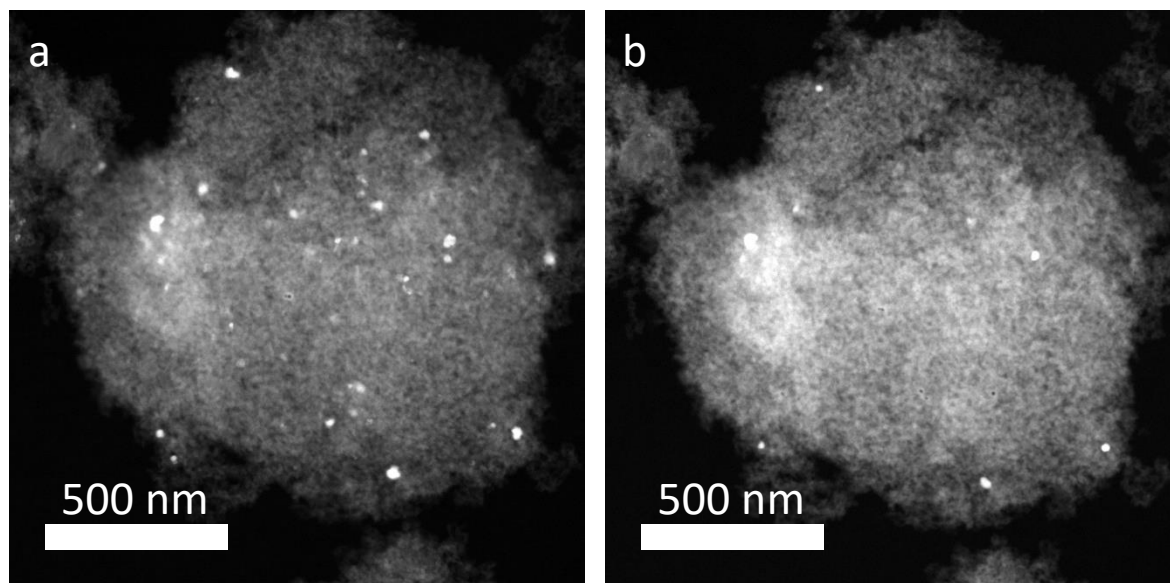


Figure S3 STEM Image of Pt/Pd/Al<sub>2</sub>O<sub>3</sub> a) Before and b) After 1000s Oxidation at 700°C in 1 atm O<sub>2</sub> (1 sccm) with Electron Beam Blanked

The effect of the electron beam was analyzed by repeating the *in-situ* oxidation experiment with the electron beam blanked during heating under O<sub>2</sub> flow. The STEM image acquired at room temperature in 1 atm air prior to connecting the gas lines shows many Pt/Pd nanoparticles (Figure S3a). The beam is then blanked before the gas lines are connected and O<sub>2</sub> flow (1 sccm) is initiated. The temperature is ramped to 700°C at ~20°C/s, and the sample is oxidized at 700°C for 1000s, after which the electron beam is unblanked and another STEM image is taken (Figure S3b). The same disappearance of Pt/Pd particles is observed even in the absence of the electron beam.

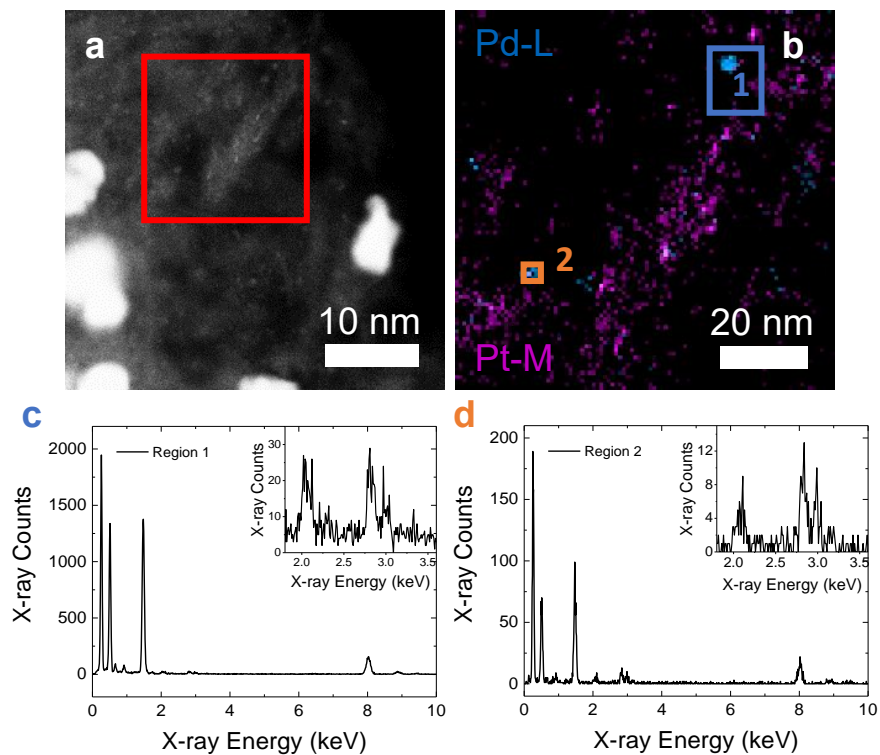


Figure S4 EDS Spectrum of small nanoparticles on support region, pre-oxidation a) Fig. 4c b) Fig 4d c) spectrum from blue and orange rectangular regions of interest in b)

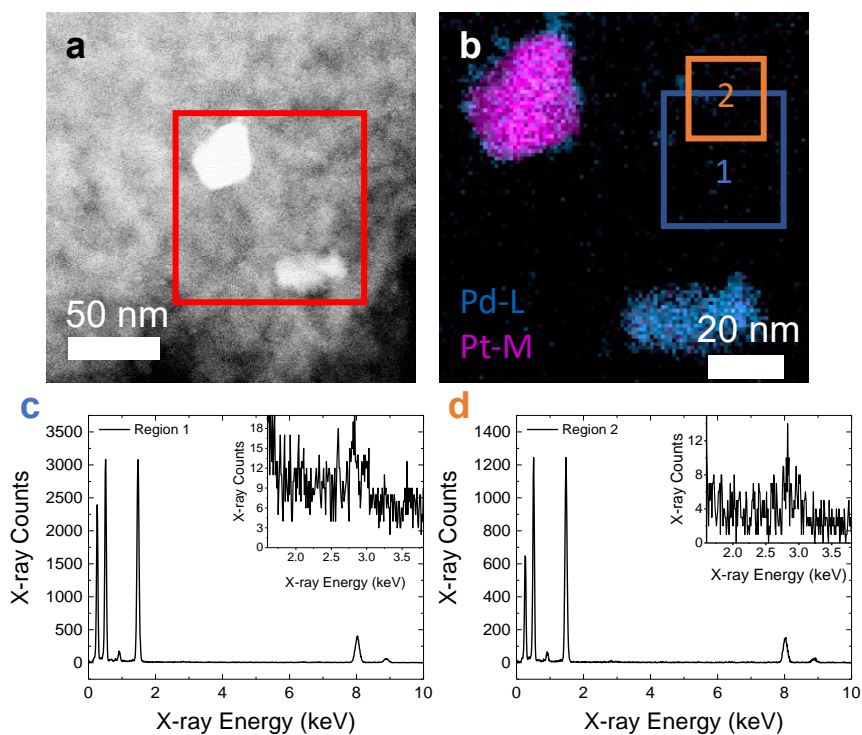


Figure S5 EDS Spectra of support region, post-oxidation a) Fig. 4e b) Fig. 4f c) spectrum from blue and orange rectangular regions of interest

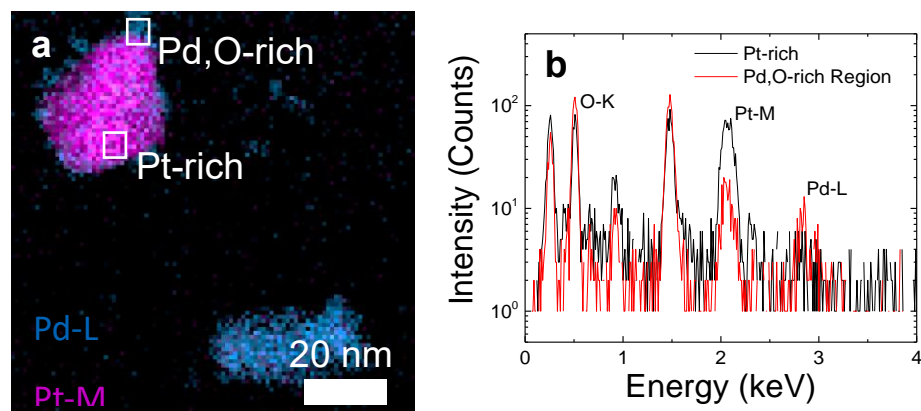


Figure S6 EDS a) map and b) spectra of Pt- and Pd-rich regions in *ex-situ* oxidized Pt/Pd/Al<sub>2</sub>O<sub>3</sub>

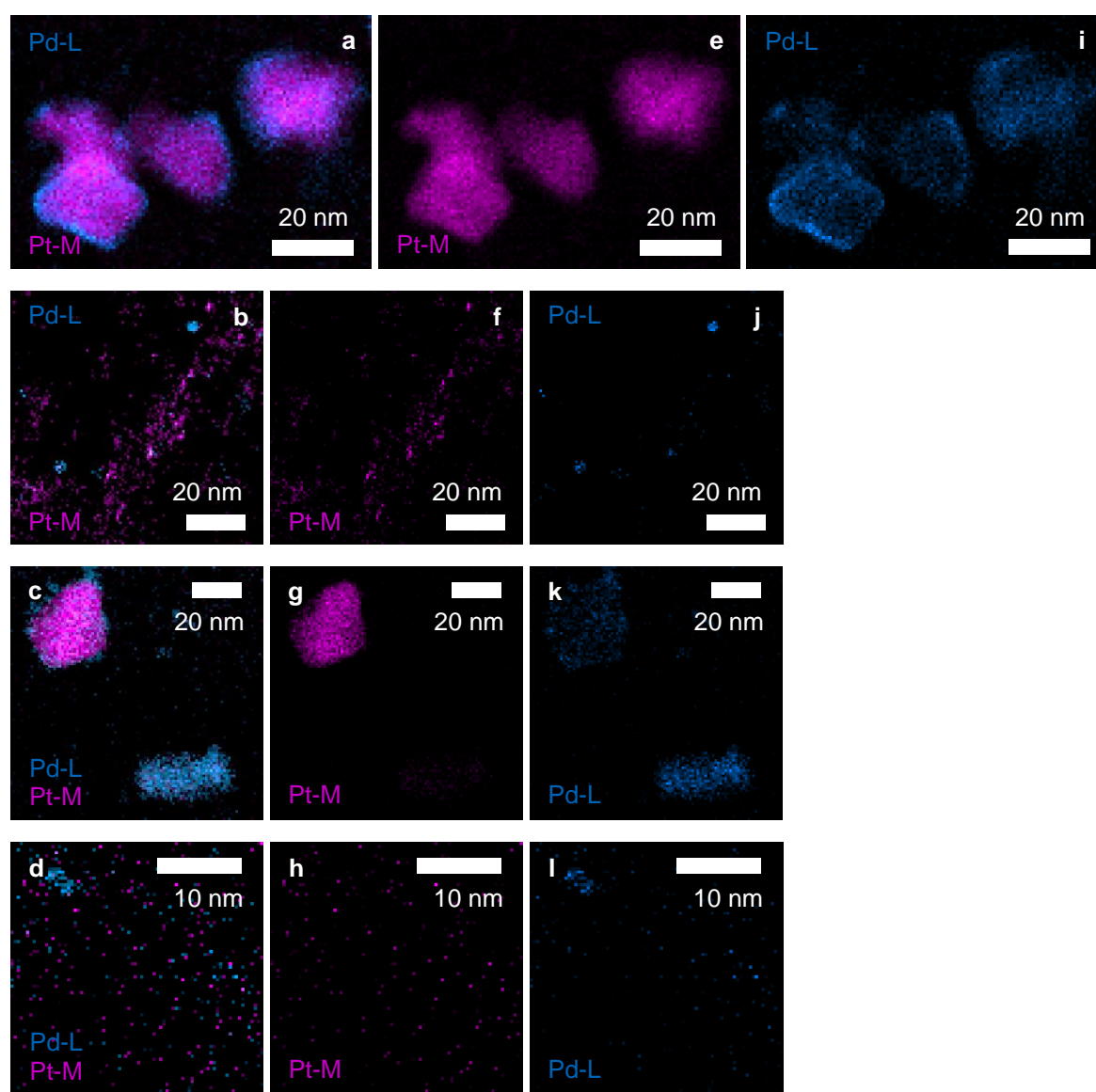


Figure S7 (a-d) Composite-, (e-h) Pt-, and (i-l) Pd-STEM-EDS Maps Showing Pt/Pd Mixing



Figure S4 shows that the Pt-M (2.048 keV) and Pd-L (2.838 keV) x-ray signals are both present in the support regions of the catalyst prior to oxidation due to the presence of many small nanoparticles (< 5 nm diameter). The signal to noise ratio for both peaks is > 4. This is consistent with expectations for this bimetallic catalyst. The Pt and Pd signals are low due to the low mass loading of Pt/Pd (1.33 wt%/0.67 wt% loading) on Al<sub>2</sub>O<sub>3</sub>. The small nanoparticles dispersed on the oxide support in this fresh sample also have a very high surface area to volume ratio.

Figure S5 shows that there is almost no Pt-M (2.048 keV) x-ray signal remaining in regions of the support after oxidation (signal to noise ratio of Pt-M peak << 4). However, the Pd-L peak is still discernable, although the signal to noise ratio is decreased (~2.5) compared to that of the fresh sample (> 4). This data is consistent with Pt vaporization and Pd diffusion on the surface of or into the bulk of the oxide support during oxidation. The Pd signal is likely decreasing because the Pd is becoming more uniformly distributed over the entire oxide support at a lower concentration during the oxidation process. Figure S6 shows EDS spectra from the Pt- and Pd-rich regions. The O-K signal is slightly higher in the Pd-rich region, which could be consistent with segregation of a PdO phase.

Although the composite maps appear to show that Pt and Pd do not mix, this is not the case. The individual elemental maps for Pt and Pd show that the two metals mix significantly. Figure S7e and Figure S7i, for example, show that Pd composition in the core of the particles in Figure S7a is lower than in the shell but still nonzero; these figures also show that the Pt composition in the shell of the particles is lower than in the core but still nonzero.

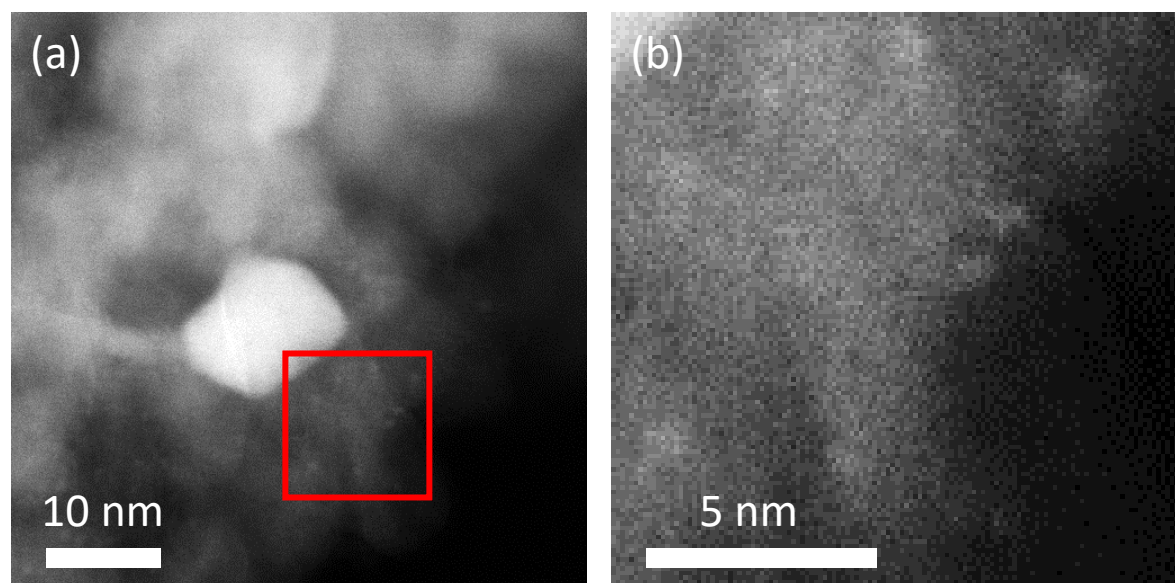


Figure S8 Aberration Corrected HAADF-STEM image and magnified inset of *ex-situ* aged Pt/Pd/Al<sub>2</sub>O<sub>3</sub> exhibiting small metallic clusters (700°C aging conditions under 1 atm O<sub>2</sub> (500 sccm flow rate)).

Figure S8 depicts some small sub-nanometer metallic clusters on *ex-situ* oxidized catalyst.