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Size-dependent crystallinity and relative orientations of nano-Pt/γ-Al_2O_3

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Platinum nanoparticles (NPs) on γ-Al_2O_3 support is known as an active catalytic system [1]. Recently, *in situ* X-ray Absorption Spectroscopy (XAS) measurements of this system showed negative thermal expansion, where the nearest neighbor Pt-Pt bond distances decreased with increasing temperature. This unusual phenomena must involve the charge transfer interactions between the Pt particle and the γ-Al_2O_3 support [2]. Preliminary theoretical simulations revealed that the energetically favorable Pt nanoparticle structures, including their bond-lengths, depend quite sensitively on orientation, surface structure and defects on the γ-Al_2O_3 surface. For example, O vacancies tend to pin the Pt nanoparticle and significantly change their structure, including a decrease of their bond-lengths with increasing temperatures. Therefore detailed knowledge of the atomic structure of both Pt particles and γ-Al_2O_3, as well as their structural correlations, is necessary. Although high-angle annular dark-field (HAADF) technique is widely used in imaging heterogeneous catalytic materials because of the high contrast of the heavy metal relative to the low-Z support, the information from the support is limited, see Fig. 1 (Fig. 1 is a HAADF image which shows Pt particles with an average size of 2.9 nm). Phase contrast given by high-resolution transmission electron microscopy (HRTEM) provides sub-nano information of both the Pt and γ-Al_2O_3 simultaneously. The samples were prepared by impregnating the Pt^{2+} precursor, $Pt(NH_3)_4(OH)_2{\cdot}H_2O$, on γ-Al_2O_3, reducing in H_2 gas at 573 K in order to remove the ligands to form metallic nanoparticles [2]. The sizes of Pt particle were controlled by the loading amount, where 1 wt% produced an average Pt sizes of ~1nm and heavy loading of 5 wt% produced sizes of ~2.9 nm [2]. The TEM samples were prepared by spreading a drop of Pt/γ-Al_2O_3 suspension in ethanol onto an ultra-thin C-grid, naturally dried. The HRTEM observations were carried out with JEM 2100FEG S/TEM, operated at 200 kV.

Fig. 2 is an HRTEM image taken from the 1 nm Pt sample. We noted that the crystallinity of the Pt particles is size-dependent. The 1 nm Pt particles or smaller did not show clear evidence for crystallinity. The lack of uniform bond-lengths and order is supported by XAS and theoretical simulations. The 2.9 nm Pt sample showed F.C.C. structure, and a = 0.39 nm, where a few particles contained twin boundaries. The HREM image in Fig. 3 is selected to show orientation correlation of a Pt particle with its support. The Pt particle with [110] zone axis located on the γ-Al_2O_3 with [100] axis, rotated with an angle of ~25.5° between Pt (002) and γ-Al_2O_3 (004) planes. Fig. 4 is a profile-view of an edge-on Pt particle on γ-Al_2O_3, and the Pt particle shows in spherical shape with faceted surfaces (not indexed due to the its off-alignment to the incident beam). It is clearly seen that the Pt particle was well contacted to its support, with atomic level clean interface. The miss-orientation of Pt particles on γ-Al_2O_3 (well contacted with rotated angles) indicates weak interfacial interaction of Pt/γ-Al_2O_3 system, and it is different from the contact-epitaxial growth of metal particles deposition to the substrates.

References

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[2] J. H. Kang, L. D. Menard, R. G. Nuzzo, A. I. Frenkel, *J. Am. Chem. Soc.* 128 (37), (2006)12068.
[3] This research is funded by Department of Energy – Basic Energy Sciences (DE-FG02-03ER15476).The TEM characterizations were carried out at Nanoscale Fabrication and Characterization Facility (NFCF) at the University of Pittsburgh.

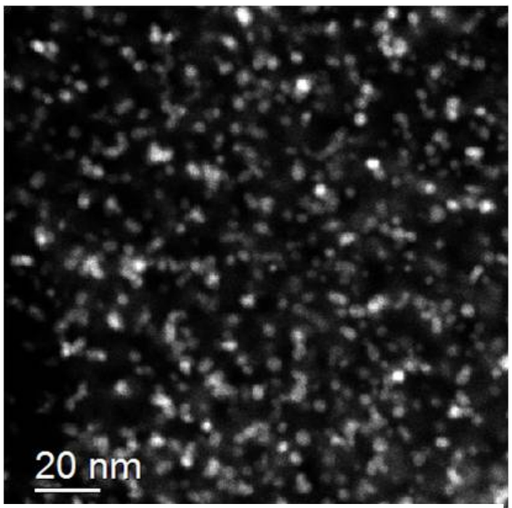


FIG. 1. HAADF image of Pt particles with an average size of ~2.9 nm.

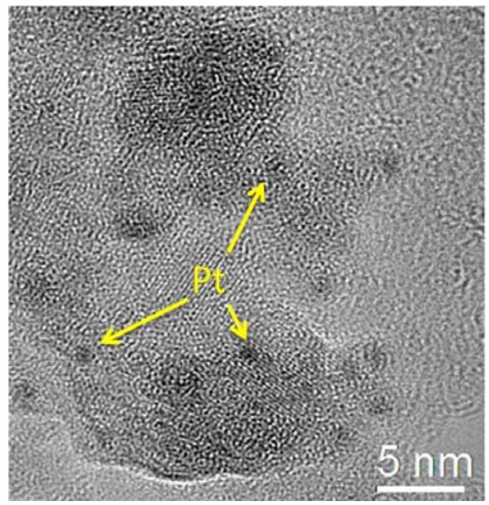
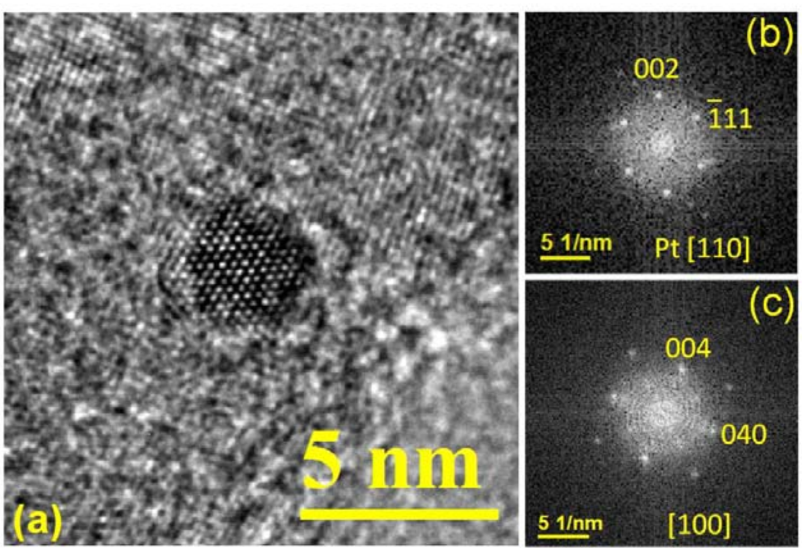


FIG. 2. HREM image of Pt particles and γ-Al_2O_3. The average size of Pt particles is ~0.9 nm.



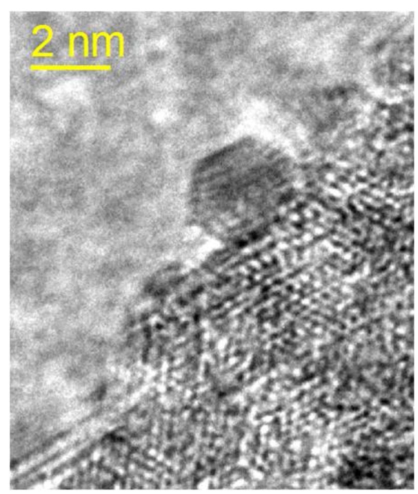


FIG. 3. HREM image of a Pt [110] particles on γ-Al_2O_3 [100]. (b) and (c) are FFT from the Pt particle and γ-Al_2O_3, respectively.

FIG. 4. (on the right) HREM profile-view of a Pt particle on the edge of its γ-Al_2O_3 support.