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HREM, EXAFS and MD Studies on Size-Dependent Crystallinity of Pt Nanoparticles Supported on γ-Al_2O_3

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The catalytic system of nanoscale Pt particles on γ-Al_2O_3 support is widely applied for oxidation of hydrocarbon and CO, in fuel cells, and as a catalyst microsensor. A novel phenomenon of negative thermal expansion (NTE) was found in this system as Pt particle sizes reduced to ~1 nm[1]. The novel size effects may result from the change of atomic structure. We employed high-resolution transmission electron microscopy (HREM) to observe thousands of individual Pt particles with a size range from sub- up to 5 nm, to gain the statistics of the crystallinity versus Pt particle sizes; with extended X-ray absorption fine-structure spectroscopy (EXAFS) we measured the general order-disorder trends of Pt-Pt bond length distributions from samples with different average sizes. The first-principle molecular dynamics (MD) simulation was applied to Pt_{37}/γ-Al_2O_3 system to find its stable structures. 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 to remove the ligands[1]. The Pt particle sizes were controlled by the loading amount, where 1 wt% produced an average Pt size of ~1nm, 3 wt% produced an average size of 2.1 nm and heavy loading of 5 wt% produced a average size of ~2.7 nm. The TEM samples were prepared by spreading a drop of Pt/γ-Al_2O_3 suspension in ethanol onto an ultra-thin C-grid, and dried in vacuum. The HREM observations were carried out with JEM 2100FEG S/TEM, operated at 200 kV. In order to enhance the contrast of ~1 nm Pt particles to the γ-Al_2O_3 support and C-film, focal series reconstruction technique, a software package (HREM Research Inc.) was employed and the TEM images were filtered at zero loss energy with Gatan GIF Tridiem.

Fig. 1 shows representative HREM images, Pt nanoparticles adopting disordered structure in (a) and a particle forming an FCC structure in (b). Fig. 1(c) is the enlarged image of the particle in (b) and its FFT in (d) indicated [110] orientation of the crystalline Pt particle was parallel to the beam. Through observations of many different-size Pt particles, we found that all Pt particles smaller than 1 nm adopted disordered structure; Pt particles larger than 2.5 nm possess crystalline structure. There was a transition regime of sizes from 1.1 to 2.4 nm, in which more than 80% Pt particles tend to form disordered structure and less than 20% particles tend to form crystalline structure. The static disorder parameters of Pt-Pt bond lengths were measured in temperature-resolved EXAFS experiments using samples same as those observed by TEM. All the measurements were conducted in inert atmosphere (He) or in H_2 for protection from the oxidation of metals. The results of static disorder parameters (variance) from both He and H_2 atmospheres in Fig. 2 shows the trend of increasingly disordered distribution of Pt-Pt bond lengths with decreasing sizes of Pt NPs. This general trend from the ensemble of Pt NPs is well consistent with the statistics of HREM observations from many individual Pt particles. In order

to understand the order/disorder transition in the regime from 1.1 to 2.4 nm, we used MD simulation to study Pt_{37} on γ-Al_2O_3 (001) surface. Fig. 3 shows the structures of (a) the relaxed truncated cuboctahedron structure of Pt_{37} and (b) the non-bulk-like, with average first nearest neighbor bond length and coordination number is 2.67 Å and 6.4 for (a), and 2.65 Å and 6.3 for (b), respectively. The disordered structure is 1.53 eV in total energy or 0.04 eV per Pt atom lower than the ordered one. This result agrees well with our experimental observation that, around 1 nm, most of the supported Pt nanoparticles prefer a disorder structure, except for very few that is locked in a deep local minimum.

References

[1] J. H. Kang, L. D. Menard, R. G. Nuzzo, A. I. Frenkel, *J. Am. Chem. Soc.* 128 (37), (2006)12068.

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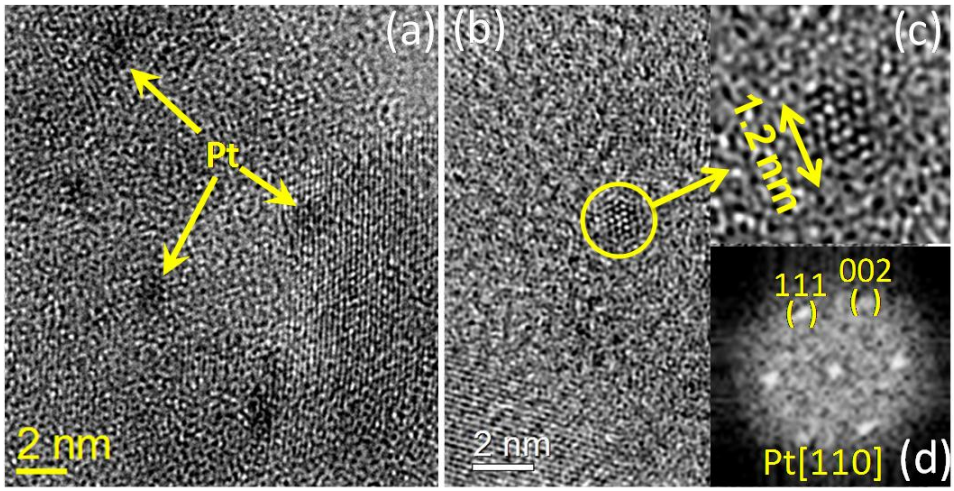

FIG. 3. Representative HREM images of Pt on γ-Al_2O_3, (a) Pt nanoparticles with disordered structure and (b) a Pt particle with FCC structure along [110] orientation.

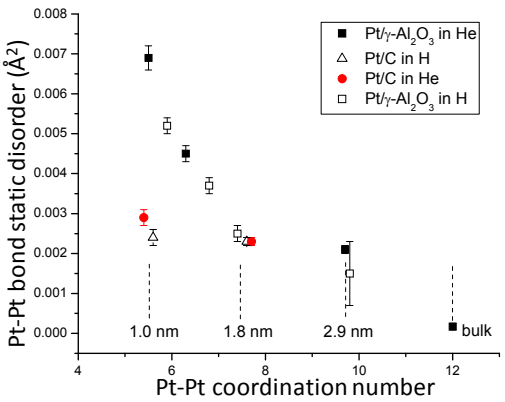

FIG. 2. EXAFS measurements illustrating strong sensitivity of the bond-length disorder on Pt sizes. The static disorder increased gradually as the particles sizes or coordination number decreases.

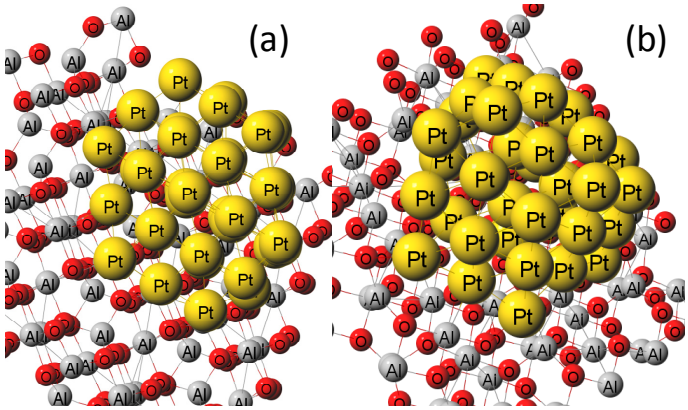

FIG. 3. MD simulation of Pt_{37}/γ-Al_2O_3 (001), (a) ordered truncated cuboctahedron with FCC-stacking and (b) disordered structure (color codes, Pt: yellow, Al: gray, O: red). The particle diameter in both configurations is about 1.1 nm.

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