

## Aberration-corrected STEM Study of Atomically Dispersed Pt<sub>1</sub>/FeO<sub>x</sub> Catalyst with High Loading of Pt

Botao Qiao<sup>1,2</sup>, Aiqin Wang<sup>2</sup>, Tao Zhang<sup>2</sup> and Jingyue Liu<sup>1</sup>

<sup>1</sup>. Department of Physics, Arizona State University, Tempe 85281, USA.

<sup>2</sup>. State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy Sciences, Dalian 116023, China

Single-atom catalysis is emerging as a new frontier in the field of catalysis [1]. It not only maximizes the atom efficiency of the metal (especially the expensive and scarce noble metal) in supported catalysts but also possesses the potential to bridge heterogeneous and homogeneous catalysis. Furthermore, with single atoms as active centers, theoretical predictions and correlations to experimental data become possible. Single-atom catalyst (SAC) systems have been successfully developed and proved to be effective for various reactions [1-3]. However, most of these SACs were loaded with very small amount of metal since high-loading levels usually result in the formation of metal nanoclusters/particles. Fabrication of SACs with high metal loading remains a challenge. The fundamental study of the synthesis processes of SACs and the effects of the post-treatment on the properties of SACs are both of fundamental interest and practical significance. We report here the synthesis of high metal loading Pt<sub>1</sub>/FeO<sub>x</sub> catalyst and how the post-treatment affected the Pt dispersion.

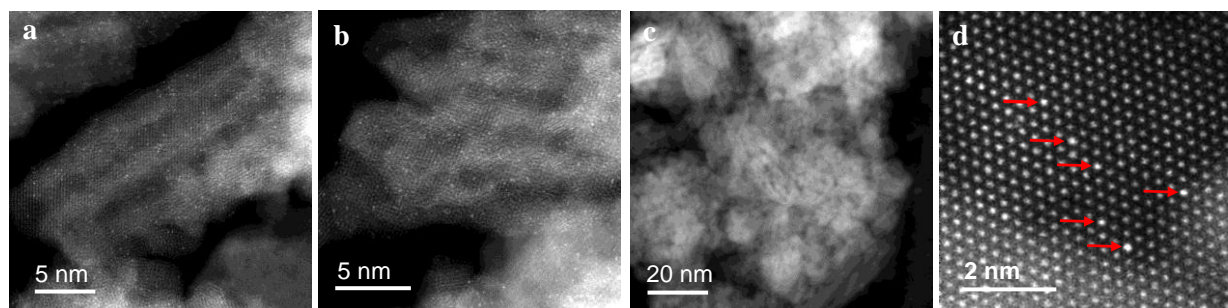
In our previous work [4-5], we found that for the Pt/FeO<sub>x</sub> catalyst with same preparation method (co-precipitation (CP) method) and post-treatment procedure (calcination at 400 °C for 5 hours and reduction at 200 °C for 0.5 hours), the 0.17 wt% of Pt loading resulted in SAC while a ~2.0 wt% loading of Pt resulted in the formation of nanoparticles with diameters of 1-2 nm and subnano clusters with sizes < 1 nm. Clearly, the high Pt loading facilitates the formation of larger particles or clusters. However, it is not clear how these cluster/particle species are formed: They could form during the co-precipitation process or during the calcination process since it is generally accepted that calcination could result in sintering of highly dispersed nano species [6]. The metal particles could also form during the activation processes of the catalysts since it has been reported that Pt could sinter under reduction while re-disperse under calcination [7]. In this work, we performed a systematic study, by aberration-corrected STEM, of a 2.0 wt% Pt/FeO<sub>x</sub> catalyst and examined how the different post-treatments affect the individually isolated Pt atoms supported on high-surface-area FeO<sub>x</sub>. The preliminary results showed that Pt existed as isolated single atoms under calcination at elevated temperatures as high as 600 °C. The reduction treatment, however, resulted in the movement of isolated single Pt atoms to form subnano clusters and nanoparticles.

The 2.0 wt% Pt/FeO<sub>x</sub> was synthesized by the CP method as previously reported [4, 5]. Typically, a suitable amount of H<sub>2</sub>PtCl<sub>4</sub>·6H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O mixture solution was dropwise added into Na<sub>2</sub>CO<sub>3</sub> solution at 50 °C. After being stirred and aged for 2 hours, respectively, the sample was filtered and washed with deionized water for several times to remove the residual Cl<sup>-</sup>. The resultant precipitate was dried at 60 °C for 5 hours and the catalyst was denoted as 2Pt/FeO<sub>x</sub>. The 2Pt/FeO<sub>x</sub> catalyst was further calcined at 600 °C for 5 hours (denoted as 2Pt/Fe<sub>2</sub>O<sub>3</sub>-C600) or directly reduced at 200 °C for 1 hour under 5 vol% H<sub>2</sub>/He (denoted as 2Pt/FeO<sub>x</sub>-R200). Figure 1 displays representative STEM high-angle annual dark-field (HAADF) images of the 2Pt/FeO<sub>x</sub> catalyst, clearly revealing isolated Pt atoms dispersed on/in the FeO<sub>x</sub> support with high number density (Figure 1a and 1b). The low magnification

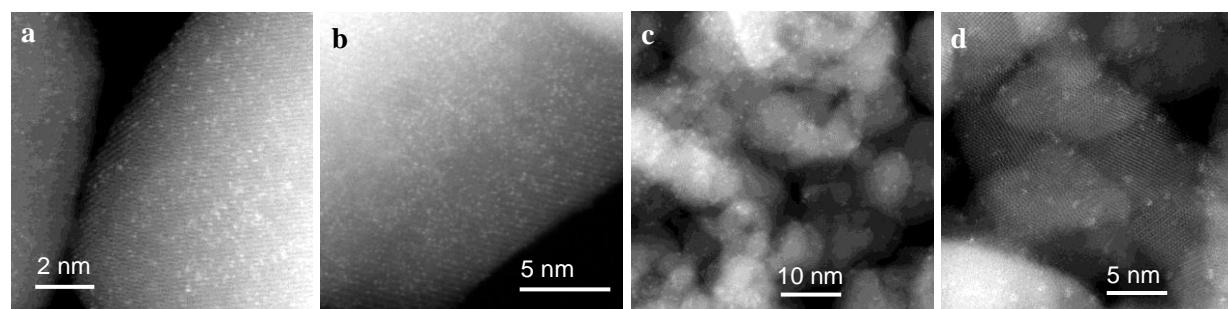
image (Figure 1c) does not show any Pt nanoparticles/clusters, suggesting that even with 2.0 wt% Pt loading it is possible to form atomically dispersed SAC. The high magnification image (Figure 1d) shows that Pt atoms occupy the locations of the Fe sites. After being calcined at 600 °C, the Pt still existed as isolated single atoms (Figure 2a and b), suggesting that the SAC is extremely stable under oxidation conditions. However, when the as-synthesized 2Pt/FeO<sub>x</sub> was reduced at 200 °C for 30 minutes most isolated Pt single atoms disappeared and small Pt clusters were formed (Figure 2c and d), suggesting that under reduction environment the atomically dispersed Pt single atoms sintered, presumably due to the change of the surface chemistry and/or structure of the FeO<sub>x</sub> support.

#### Reference:

- [1] X.-F. Yang et al., *Acc. Chem. Res.* **46** (2013), p. 1740.
- [2] M. Flytzani-Stephanopoulos and B.C. Gates, *Annu. Rev. Chem. Biomol. Eng.* **3** (2012), p. 545.
- [3] M. Flytzani-Stephanopoulos, *Acc. Chem. Res.* **47** (2013), p. 783.
- [4] B. Qiao et al., *ACS Catal.* **4** (2014), p. 2113.
- [5] B. Qiao et al., *Nat. Chem.* **3** (2011), p. 634.
- [6] W.Z. Li et al., *Nat. Commun.* **4** (2013), p. 2481.
- [7] Y. Nagai et al., *Angew. Chem. Int. Ed.* **47** (2008), p. 9303.
- [8] This research was funded by Arizona State University. We gratefully acknowledge the use of facilities in the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University.



**Figure 1.** STEM-HAADF images of the as-synthesized 2Pt/FeO<sub>x</sub> catalyst show uniform distribution of isolated Pt atoms (a, b), no presence of Pt nanoparticles (c) and Pt occupancy of the Fe sites (d).



**Figure 2.** STEM-HAADF images of 2Pt/Fe<sub>2</sub>O<sub>3</sub>-C600 (a, b) and 2Pt/FeO<sub>x</sub>-R200 (c, d) show isolated Pt atoms at elevated temperatures under calcination condition (a, b) and formation of Pt clusters/particles after reduction treatment (c, d).