doi:10.1017/S1431927614010010
Microsc. Microanal. 20 (Suppl 3), 2014

Characterization of Sub-Nanometer Pt Cluster Formation on γ-$A1_2O_3$ via *Ex Situ* Reductions using MEMS-Based Heating Technology

Sergio I. Sanchez[1], Lawrence F. Allard[2], Wharton Sinkler[1] and Steven A. Bradley[1]

[1.] UOP LLC, a Honeywell Company, Des Plaines IL, USA
[2.] Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge TN, USA

Pt/γ-Al_2O_3 is one of the most widely studied petrochemical catalyst systems in research, as it is the basis for the generation of high-octane fuels and the production of chemical precursors used for specialty products [1]. Despite the significant effort used to analyze this system, many questions remain regarding the final state of the catalyst. Recent studies show that Pt clusters reside amidst several atomic dispersions (individual atoms, dimers, and trimers) [2,3]. Recently, work by others [4] has shown that individual atoms can be functional, promoting CO oxidation and thereby introducing a new chemical pathway into the product stream. Thus, understanding the process and conditions under which the atomic dispersions form may enable the ability to manage their fraction relative to the number of Pt clusters. The present work is an *ex situ* study that attempts to understand how the distributions of sub-nanometer Pt clusters and atomic dispersions change as a function of reduction time, and demonstrates how this technique can be used to study the reduction kinetics for other heterogeneous catalysts.

A catalyst was prepared by loading 0.35 wt % Pt onto γ-Al_2O_3 with a surface area of ~200 m^2/g. The catalyst was reduced in an *ex situ* reactor, while being heated using Protochips Aduro™ thermal E-chip technology [5]. The MEMS-based E-chip allows rapid heating and quenching of the catalyst, which was deposited on a holey carbon film on the E-chip heater membrane. Reductions were conducted at 500°C in 4 % H_2/Ar gas at 300 Torr, for 5-, 15-, 30-, 60- and 90-min intervals. The specimen was protected appropriately from the atmosphere during transfer between the reaction chamber and column. Highangle annular dark-field (HAADF) images were recorded systematically between reduction periods on a JEM 2200FS STEM/TEM fitted with a CEOS GmbH probe corrector, with a nominal STEM resolution of 0.7nm. The untreated sample was examined as prepared (oxidized).

Atomic resolution images enable evaluation of the number of clusters relative to the dispersed atoms, dimers and trimers (e.g., large circles, small circles, squares and triangles, respectively, in Fig. 1). The same regions were examined after each successive reduction treatment, allowing us to relate changes in the proportion of clusters to the atomic dispersions as a function of reduction time. Figure 2 illustrates how the number of individual atoms changes with time in a reducing atmosphere of 500°C for a normalized imaging area of 535 nm^2. While the number of dimers and trimers is unchanged throughout the duration of reduction, the number individual atoms does fluctuate. Approximately 45–50 Pt atoms were counted during the initial 5 minutes of reduction, unchanged from the oxidized sample. A dramatic change was noted however after 15 minutes, where the number of individual atoms observed was reduced to half. Extended reduction periods made no significant change to this number.

Cluster size was shown to plateau at ~ 0.6 nm after 15 min of reduction, coincident with the steadying of individual atom density observed after 15 min (Fig. 2). The cluster density was relatively invariant after 15 min of reduction time. Figure 3 shows three images collected at the same location, for reduction times of 0-, 15- and 30-min, indicating significant differences from 0 →15 min of reduction, whereas from 15 → 30 min (and up to 90 min) of reduction no major differences are apparent. Thermodynamics

appear to play a role in the ratio of clusters to atomic dispersions. The data also point to unexpected kinetics in cluster formation. The latter two subjects will be discussed in the context of the data [6].

References

[1] H. F. Rase, *Handbook of Comm'l Catalysts: Hetergeneous Catalysts;* CRC Press: Boca Raton, 2000.
[2] J. Liu, ChemCatChem. **3** (2011) p. 934.
[3] A. K. Datye, J. Catal. **216** (2003) p. 144.
[4] B. Qiao *et al.* Nat. Chem. **3** (2011) p. 634.
[5] L. F. Allard *et al.*, *Micros. Res. & Tech.,* **72**(3) 208-215 (2008).
[6] Research supported in part by Oak Ridge National Laboratory's Center for Nanophase Materials Sciences, which is sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy.

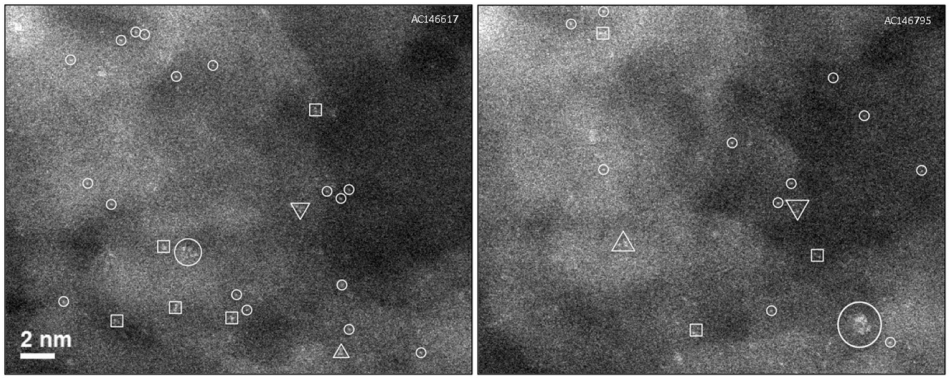
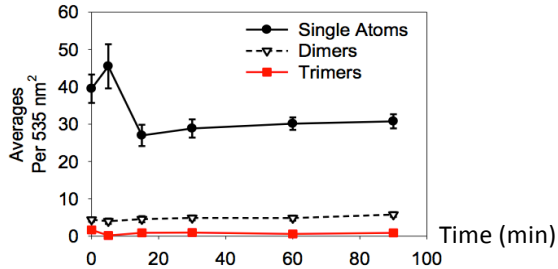


Figure 1. Example of HAADF images of atoms, dimers, trimmers and clusters of Pt on γ-Al_2O_3 a) as oxidized, and b) after 15 min reduction at 300 Torr and 500°C. The same general area of support is shown; the number of single atoms diminishes with reduction. See text for details.

Figure 2. Plot showing the effects of reductions at 500°C on cluster growth and distribution of atomic species. See text for details.



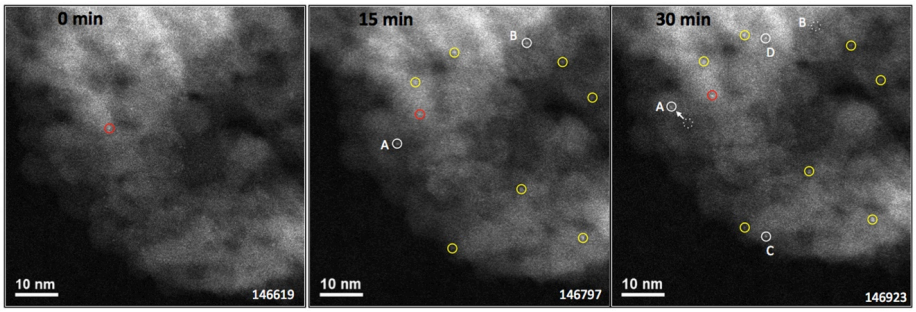


Figure 3. HAADF images showing cluster growth at 300 Torr H_2/Ar for: (a) 0, (b) 15 and (c) 30 min. Essentially the same area of support is seen in each figure. Fine clusters are observed to appear after 15 min at 500°C, and most remained stable at 30 min, and even up to 60 min reduction time. Those circled in yellow did not move between 15 and 30 min, but cluster A appeared to shift, cluster B disappeared, and new clusters C and D appeared. Details of the counting methodology will be discussed.

https://doi.org/10.1017/S1431927614010010 Published online by Cambridge University Press