

## Nano-Structural Changes in Supported Pt Catalysts during CO Oxidation

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### Introduction

Emission treatment catalysts including three-way, lean NO<sub>x</sub>, SCR-, and oxidation catalysts contain supported metal clusters as active components [1, 2]. Extensive studies have not established a correlation of the activity of these catalysts with nanostructure and substrate effects. Even the nanostructure of supported catalysts is not well understood. For example, while previous Z-contrast imaging reports the presence of 3-atom clusters and allocate anomalous long Pt-Pt bond to OH terminated Pt clusters [3], recent EXAFS studies suggest thermal metal-metal bond contraction after hydrogen reduction of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [4] whose TEM shows particles in 0.5-1.5 nm range centered at ~0.9 nm consisting of 15±9 atoms on average.

We have embarked upon a systematic theoretical and experimental study of “experimentally simple but theoretically complex” catalyst systems to understand the nanostructure and reactivity correlation and translate this knowledge into the design of superior emission catalysts [5]. Recent theoretical studies show that the formation of oxides of small Pt clusters (1-10 atoms) is significantly more exothermic than the formation of oxides from bulk metals and that nanoclusters are also structurally distinct from bulk oxides [5, 6]. In this report, we describe the nanostructure of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and changes therein under CO oxidation conditions. We have employed the ORNL ex-situ reactor system [7] to monitor the nanostructural change in Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> that occurs during CO-oxidation, and the results will also be presented.

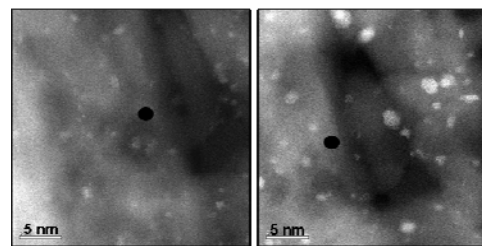
### Materials and Methods

We synthesized 1 nm 2%Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 25 nm 2%Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with H<sub>2</sub>PtCl<sub>6</sub>•6H<sub>2</sub>O followed by calcination in air at 450°C and 650°C, respectively. CO oxidation studies were carried out on a standard bench-top reactor. Stainless steel TEM grids, coated with a conductive film of holey LaCrO<sub>3</sub>, were dry-dipped into catalyst powders to prepare samples for treatment in an *ex-situ* reactor, and then for examination by electron microscopy. [5]. The Pt nanostructural changes in catalyst were monitored by imaging the fresh and aged samples on a Hitachi HD-2000 scanning transmission electron microscope (STEM) in the high-angle annular dark-field (HA-ADF) mode and a JEOL 2200FS STEM/TEM fitted with a CEOS Co. aberration corrector for the probe, to obtain HA-ADF images at 0.1 nm resolution.

### Results and Discussion

The dark-field STEM imaging of 1 nm Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> shows features identical to those reported by Kang et al. in terms of particle size distribution [4]. The ACEM HA-ADF STEM images of this catalyst, on the other hand, show that there are single atoms, 2-3 atom clusters, and several 10-20 atom clusters of Pt (Fig. 1). The directly measured Pt-Pt bond distances are 2.35, 2.54, 2.7, and 3.2Å for 2-atom clusters, and 2.3, 2.8 Å for 3-atom clusters. These do not match with theoretical models [3, 6], perhaps due to projection effects and/or substrate interactions [3]. There are no unusual features in 25 nm Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> but the reactivity differences between 1 nm

Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 25 nm Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are noticeable in CO oxidation. The CO oxidation studies were carried out by placing a fresh sample of 1 nm Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the reactor and the temperature was increased until CO conversion became quantitative. The reaction was stopped and the reactor was cooled to room temperature. The CO oxidation reaction was repeated 2 more times. In the first cycle, CO oxidation began at 210°C while the third cycle required only 180°C for the CO oxidation initiation. The 80% conversion occurred at ~280°C and quantitative conversion required almost 450°C. The initiation of CO oxidation for 25 nm Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> occurred at ~250°C but became quantitative also at this temperature. We noticed Pt particle size growth in samples of 1 nm Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> collected after CO oxidation studies. This led us to expose catalyst samples on TEM grids to CO oxidation conditions in our *ex-situ* reactor and monitor nanostructural changes in several locations (e.g. Fig. 1). To our surprise, we found that even the initiation of CO oxidation causes particle size growth.



**Figure 1:** ACEM HA-ADF STEM images of fresh 2%Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showing mostly small Pt clusters of uniform size (left). The exact same spot (for reference, the filled circles indicate same area) after exposure to CO oxidation initiation conditions (right).

### Significance

The ACEM HAADF-STEM images reveal single atoms, 2-3 atoms clusters, and several 10-20 atom clusters of Pt in 1 nm 2%Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The *ex-situ* reactor in conjunction with ACEM HA-ADF STEM allows monitoring of nanostructural changes in supported catalyst under various operating conditions as illustrated by the example in this presentation.

### References

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