

Bridging the Gap between Theory and Experiments – Nano-structural Changes in Supported Catalysts under Operating Conditions

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ABSTRACT

Computational approaches have been limited to examining catalytic processes using models that have been greatly simplified in comparison to real catalysts. Experimental studies, especially on emission treatment catalysts, have primarily focused on fully formulated systems. Thus, there remains a knowledge gap between theory and experiments. We combine the power of theory and experiment for atomistic design of catalytically active sites that can translate the fundamental insights gained directly to a catalyst system suitable for technical deployment. In this article, we describe our results on a model platinum-alumina catalyst that is a common constituent of emission treatment catalysts such as three-way, NO_x trap, oxidation, and HC-SCR catalysts.

We present theoretical and experimental studies of the oxidation and reactivity of Pt catalyst clusters towards O, CO, and NO_x. Our theoretical studies indicate that the reaction energetics are strongly dependent on the size of the clusters as well as the extent of oxidation of the clusters, and the energetics of CO and NO oxidation may be more favorable on the oxidized clusters than metallic clusters because of the weakened adsorption of O, CO and NO. Experimentally, we have observed that the aberration-corrected HA-ADF STEM images of Pt/γ-alumina support show that there are single atoms, 2-3 atom clusters, and several 10-20 atom clusters of Pt.

We also found that the Pt particles size has an impact on CO oxidation initiation and completion temperatures. Substrate effects were studied for equivalent Pt particle size distributions on both θ-alumina and γ-alumina supports. Particle size effects were investigated on Pt/γ-alumina catalysts with Pt particle size distribution centered at 1 nm and 12 nm, respectively. We will describe our results on substrate and Pt particle size effects. In addition, we will also present our study of nano-structural changes in model catalysts on exposure to various reaction conditions.

INTRODUCTION

The emission reduction catalysts including three-way catalyst, oxidation catalyst, and lean NO_x traps are heterogeneous catalysts.¹ Starting with the development of oxidation catalyst in the 1970s, the emission treatment catalysts have been developed by trial and error methods.¹ While this method has been quite successful, this approach is very time consuming and inefficient. Despite the availability of modern instrumentation for catalyst characterization, the lean NO_x trap development took more than a decade before it was implemented in limited release vehicles.^{2,3}

The catalyst development has not benefited from computational approaches primarily because the focus of theoretical models has been limited to gas-phase cluster studies. In part, this was due to the limitation of computing power. The availability of advance computing has enabled recent studies on supported catalysts, employing density functional theory. This research provides insights into the roles of under-coordination sites, the particle-support interface, altered oxidation state, and quantum size effects⁴⁻⁷. Growth pathways for supported platinum clusters have been experimentally studied⁸ in the 1970s and have only been recently examined by first-principle density functional theory⁹. Results show that charge transfer from Pt atoms to O atoms of the substrate provides driving force for the anchoring of Pt clusters on alumina and Pt clustering is strongly preferred.

In recent years, we have focused on “catalysis by design” approach. In this approach, a large number of candidate materials can be examined by theoretical modeling and only most promising candidates are synthesized and evaluated experimentally. In a previous paper, we described preliminary results on this approach and summarized our experimental and theoretical studies of Pt clusters.¹⁰ In this paper we provide a validation of theoretical studies by experimental observations and briefly mention theoretical studies

published elsewhere.^{11,12} If these results can be generalized, i.e. “catalyst by design” approach can be validated, it will speed up the pace of invention in catalyst research. Theoretical studies will be able to rapidly examine a variety of catalyst materials for emission treatment and only a few promising candidate materials will need to be studied experimentally. The incentive for the selection of Pt clusters for model studies, presented in this paper, stems from the fact that supported platinum is an integral part of these catalyst systems.

EXPERIMENTAL DETAILS

The supported Pt catalyst was prepared by suspending commercial γ -Al₂O₃ in an aqueous chloroplatinic acid (Aldrich) solution and the suspension was gradually dried to obtain a free-flowing powder. The pyrolysis of the powder at a rate of 1°/min to 450°C for 4h furnished 0.6-1.5 nm Pt clusters on γ -Al₂O₃. Further sintering for 5h at 650°C resulted in Pt agglomeration to furnish particles of ~12 nm supported on γ -Al₂O₃.

The catalyst samples were characterized by several methods. The X-ray powder diffraction patterns were collected on a Scintag X-ray diffractometer employing CuK radiation. A Hitachi HD-2000 scanning transmission electron microscope (STEM) and a JEOL 2200FS FEG STEM/TEM with a hexapole aberration-corrector (ACEM) were used to obtain high-angle annular dark-field (HA-ADF) images of Pt catalyst samples.

CO-oxidation studies were carried out on one of two reactors and found to be reproducible. First reactor is a BTRS-Jr reactor (Autoclave Engineers) connected to an Agilent 6890 gas chromatograph. The second reactor is a gas flow reactor set-up, comprised of a furnace and mass flow controllers, which was connected in-line to Rosemount Analytical MLT analyzers.

The ORNL *ex-situ* reactor has been described previously in detail.¹¹ This reactor was employed to monitor nano-structural changes in a catalyst under simulated operating conditions.

RESULTS AND DISCUSSION

Supported Pt nanoclusters can be easily synthesized by depositing platinum salts on commercially available support materials and subsequent pyrolysis. Freshly prepared samples do not exhibit diffraction peaks assignable to platinum due to small particle size. Sintering at 650°C results in samples containing 12 nm Pt particles. Our studies on these samples are described in the following sections.

Pt/ γ -Al₂O₃ NANOCLOUDS

The nanostructure of supported Pt catalysts is not well understood. The Z-contrast imaging reports in literature describe the presence of 3-atom clusters and allocate anomalous long Pt-Pt bond to OH terminated Pt

clusters.¹² Recent EXAFS studies, on the other hand, suggest thermal metal-metal bond contraction after hydrogen reduction of Pt/ γ -Al₂O₃ whose TEM shows particles in 0.5-1.5 nm range centered at ~0.9 nm consisting of 15±9 atoms on average.¹³

Theoretical modeling^{14,15} suggests that pure Pt clusters are easily oxidized, thus supported Pt nanoparticles should primarily be in oxidized forms in an oxidizing environment. A +4 oxidation state (i.e., Pt:O=1:2) is favored thermodynamically by Pt atoms. Pt clusters have very different oxidation energetics and oxidized structures compared to the bulk phase.

Our dark-field STEM imaging of 1 nm Pt/ γ -Al₂O₃ shows features similar to those reported previously¹³ in terms of particle size distribution. The ACEM HA-ADF STEM images of this catalyst, on the other hand, show that there are several single atoms, 2-3 atom clusters, and 10-20 atom clusters of Pt [Figure 1].

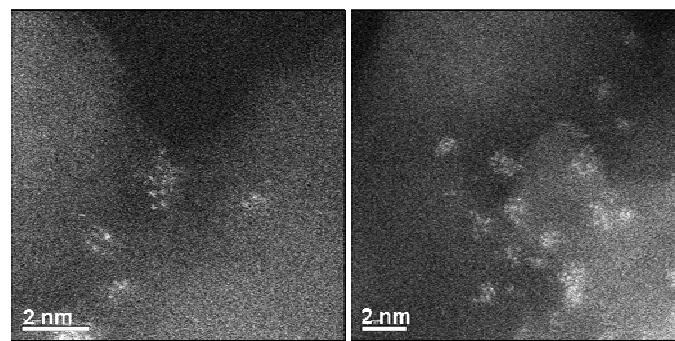


Figure 1: Representative ACEM HA-ADF STEM images of 1 nm Pt/ γ -Al₂O₃

The directly measured Pt-Pt bond distances give varying distances of 2.35, 2.54, 2.7, and 3.2 Å for 2-atom clusters, and 2.3, 2.8 Å for 3-atom clusters. Theoretical studies^{14,15} show that Pt-Pt bond distances for 2-atom and 3-atom clusters are 2.33 and 2.5 Å for metallic clusters. The Pt-Pt bond distances of 2.57 and 2.63 Å are calculated for Pt₂O₂ and Pt₃O₃ clusters and 2.78 and 2.75 Å for Pt₂O₄ and Pt₃O₆ clusters. These Pt-Pt bond distances are less than the Pt-Pt bond distances in bulk PtO (3.14 Å) and Pt₂O (3.62 Å). While the directly measured Pt-Pt bond distances appear to match with the theoretically calculated Pt metal and oxide clusters, the projection effects and/or substrate interactions could lead to shorter bond distances than the actual bond distances in such clusters. It is also important to note that theoretical studies suggest that platinum oxide clusters prefer 2-dimensional structure while the original metallic nanoclusters are three dimensional. We observed only three-dimensional structures.

NANO-STRUCTURAL CHANGES IN SUPPORTED Pt CATALYSTS DURING CO OXIDATION

For CO oxidation study, a sample of our 1 nm Pt catalyst was placed in the reactor and exposed to CO, O₂, and N₂ in a 5%/5%/90% mixture. The CO oxidation initiates at

180°C then quickly completes at 210°C. After twice cooling and re-testing a third time, no change in the quantitative conversion temperature is observed [Figure 2].

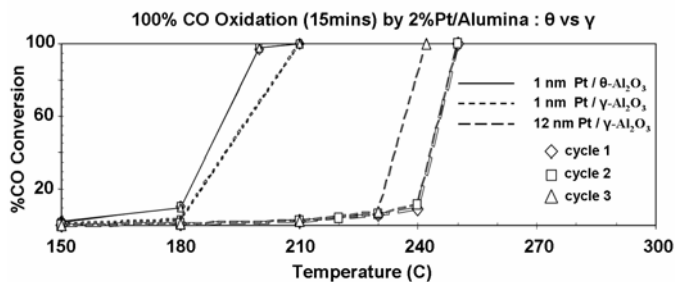


Figure 2. Quantitative CO oxidation cycled 3 times presented as a function of temperature comparing the different temperature ramps required for 1 nm Pt on θ - Al_2O_3 , 1 nm Pt on γ - Al_2O_3 and 12 nm Pt on γ - Al_2O_3 .

In order to correlate nano-structural changes with CO oxidation event, we stopped reaction once it reached quantitative conversion at 210°C and the catalyst sample was collected. It was loaded on a TEM sample grid by dry-dipping. STEM imaging indicates an average Pt size of 1.9 nm with the clusters/particles ranging in size from 0.7-3.8 nm, see figure 3. Figure 4 compares the particle size distribution of the catalyst exposed to quantitative CO oxidation conditions with that seen for the fresh catalyst.

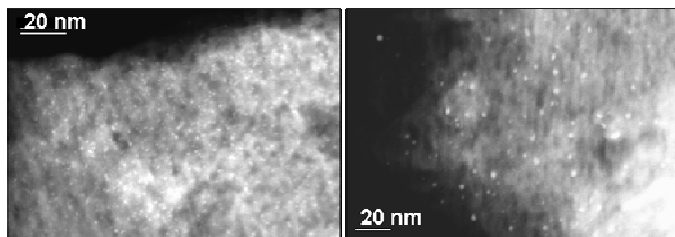


Figure 3. STEM images of fresh 1nm 2%Pt/ γ -alumina (left) and after quantitative CO oxidation testing (1 cycle 210°C, right).

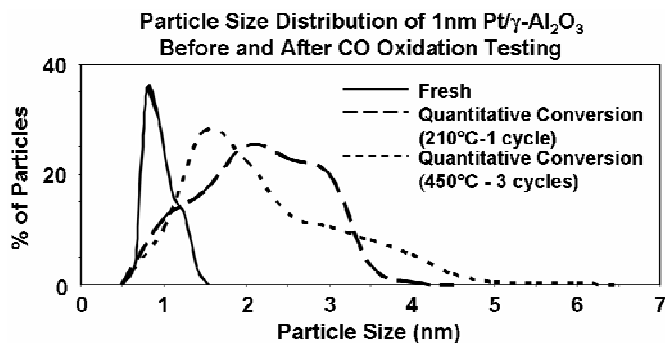


Figure 4. Particle size distribution of supported Pt-nano-clusters from STEM imaging of multiple areas, for fresh and quantitative CO oxidations tested samples.

Another sample of the catalyst was exposed to CO oxidation reaction conditions and the temperature was increased to 450°C after attaining quantitative conversion at 210°C and the reaction was stopped. After the reactor was allowed to cool, the reaction was restarted and again temperature was increased to 450°C after attaining quantitative CO oxidation. After a third cycle, the catalyst sample was also collected.

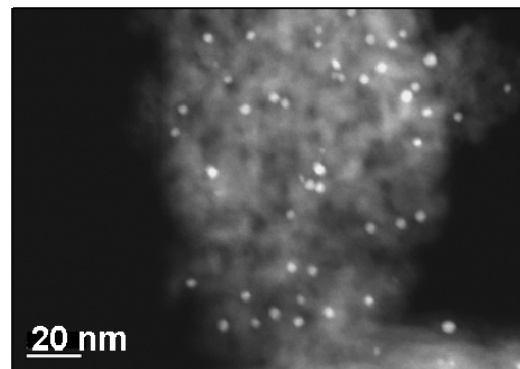


Figure 5. STEM images of 1nm 2%Pt/ γ -alumina after three cycles of CO oxidation at 450°C.

STEM imaging of multiple areas indicates an average Pt size of 2.0nm but range from 0.7-5.6 nm [Figure 5]. Figure 4 shows the particle size distribution that appears to be bimodal. The distribution of smaller particles is centered at 1.5 nm while that of the larger ones at 3.5 nm.

The nano-structural changes seen under the above described conditions led us to investigate this catalytic reaction employing ORNL's *ex-situ* reactor. As described previously, the *ex-situ* reactor allows us to expose catalyst samples on a TEM grid to various catalyst operating conditions and the structural changes then can be repeatedly monitored in selected areas by electron microscopy. The fresh sample was exposed to the following operating conditions (1) Quantitative CO oxidation conditions, (2) Quantitative CO oxidation but temperature raised to 450°C for 2 cycles, and (3) Quantitative CO oxidation conditions but temperature raised to 450°C – 3rd cycle. The fresh sample showed small Pt clusters and single Pt atoms (Figure 6). The same spots in multiple areas were monitored by ACEM after exposure to the above mentioned conditions. Atomic resolution electron imaging of the sample after 2 cycles of quantitative CO oxidation at 450°C shows that the Pt cluster/particles have sintered significantly and only a very few clusters around the 1 nm size can now be seen (Figure 6C). The larger particle surprisingly did not exhibit any atomic order; however, in other sample areas after 2 cycles of quantitative CO oxidation at 450°C atomic ordering was seen. After 3 cycles of quantitative CO conversion at 450°C, the number of larger Pt clusters/particles increased further. These Pt particles typically exhibited well ordered structures as can be seen in Figure 6.