Epitaxy of the Metal and Oxide Phases in Pt-Pd ‘Janus’ Particles in 800 °C Air-aged Diesel Oxidation Catalysts

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There is a critical need for exhaust gas treatment catalysts that provide high reactivity at low temperatures, which are encountered in modern, efficient internal combustion engines. However, these emission control catalysts must also survive harsh environments encountered in operations at high loads, such as towing a trailer up a mountain pass. Modern diesel oxidation catalysts contain platinum (Pt) and palladium (Pd) to catalyze oxidation reactions of CO, NO and hydrocarbons. Pd is known to improve the performance and durability of the Pt-based catalysts. The nature of Pd-Pt bimetallic particles in catalysts aged at high temperatures is not well understood. When heated in air, Pt forms large metallic particles due to vapor phase transport of volatile PtO₂ [1]. On the other hand, Pd transforms into the tetragonal PdO phase which has very low vapor pressure and hence can stay dispersed [5]. Previous work has suggested that core-shell structures may form where an oxide covers the metallic core [4], however such a structure is not consistent with the catalytic performance, since these catalysts perform better than Pt-only or Pd-only catalysts. Understanding the origins of the synergy between Pt and Pd was the goal of this work.

Our approach involves a novel catalyst support where ZrO₂ is deposited as a shell layer on nonporous silica spheres. This catalyst support provides exceptional thermal stability as shown by its high BET surface area after calcination at 900°C for 2 hours, and the resulting catalysts are considerably more active than those prepared on alumina supports used in industry [3]. Several samples were prepared that contain similar metal loading, but varying Pd:Pt ratios. A detailed study of the reactivity and additional characterization of these catalysts will be presented elsewhere [2], here we focus on just one catalyst having a 1:1 Pd:Pt ratio. We used TEM and XEDS to investigate the nature of the catalyst particles and surfaces after 800°C aging in air for 10h. Low magnification BF TEM images shows the 1:1 Pd:Pt sample containing biphase particles where both phases are exposed to the reaction (no core-shell structure was observed). It is evident that the oxide phase is conjoined with the metal phase, and the resulting particles can be thought of as ‘Janus’ particles (Figure 1). Additionally, both the oxide and metal phases contain both Pt and Pd, as verified through STEM-XEDS analysis. We believe this is the thermodynamically stable state of the catalyst, since it is observed after undergoing aging at a high temperature for an extended period of time. Higher magnification views (Figure 2) show that the oxide phase (which can be indexed to the tetragonal PdO structure) has an epitaxial relationship with the metallic portion of the nanoparticle. Specifically, the metallic Pd-Pt (220) planes are orthogonal to the PdO (110) lattice planes.

The significance of this work is that it presents the first evidence of a particle structure that can explain the unusual stability of Pt-Pd catalysts when aged in realistic conditions for an extended period. This
particle structure explains how these particles can provide the benefit of the catalytic performance of metal and oxide surfaces in exhaust control catalysts, where the bimetallic catalyst outperforms the metal-only or oxide-only diesel oxidation catalysts. Further study of the thermodynamics of these particles via DFT computations and investigation of the chemical potential of the Pt and Pd components is currently in progress [6].

Figure 1. A HRTEM image showing a typical ‘Janus’ particle where the metallic PdPt phase is attached to an oxide phase indexed as PdO. The ZrO$_2$ support is also shown. This particle comes from the aged 1:1 Pd:Pt sample.
Figure 2. An ABF STEM image taken at high magnification to show the epitaxial growth of the (Pd,Pt)O phase to the metallic PdPt. The metallic phase can be identified as the dark portion on the left side of the image and the oxide portion as the lighter section on the right side of the image. The (Pd,Pt)O (110) lattice fringes are labeled to help illustrate the direction of the epitaxial growth from the Pd-Pt metallic phase.

References:

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