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Formation of Pt-Pd 'Janus' Biphasic Particles During High Temperature Aging of Diesel Oxidation Catalysts

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Platinum (Pt) and palladium (Pd) constitute the active component of emission control systems for diesel emission control. The benchmark target performance of these systems, recommended by the US Department of Energy (DOE), is to convert 90% of criteria pollutants by 150°C. To achieve this, the materials must survive being exposed to oxygen while also being heated to high temperatures. Under these conditions, Pt is known to sinter and form extremely large particles due to vapor phase transport of volatile PtO_2, losing surface area, and becoming much less catalytically active [1]. Pd is commonly added to slow down the rate of sintering, thereby improving the thermal stability of the catalyst [2]. A recent study showed that a bimetallic PtPd catalyst outperforms its monometallic counterparts for relevant catalytic reactions [3]. The authors attributed this to the microstructure of catalyst, which showed biphasic Janus structures after reaction. These Janus structures contain an oxide and metallic portion that are conjoined at an interface, allowing both phases to be exposed to the reaction stream, resulting in catalytic performance attributed to the metal and oxide components. While these unique structures have been shown to be beneficial in achieving conversion at lower temperatures, the mechanism of their formation is not well understood.

Our recent work hypothesized that the vapor-phase transport of PtO_2 is mitigated in the presence of PdO because the PdO acts as a trap to capture the volatile PtO_2 [4]. This was concluded based on STEM-EDS data that showed high concentrations of Pt in the oxide phase, which is consistent with the role Pd plays in slowing the rate of sintering of Pt particles. Additionally, the Pt assisted the Pd in allowing it to remain metallic when it would typically form a stable bulk oxide. We referred to these catalysts as self-healing because the mobile species, which are primary contributors to catalyst sintering, are effectively returned back to the active site [4]. This is a unique phenomenon in heterogenous catalysis because these catalysts effectively recycle the atoms that escape from the surface, which otherwise would result in anomalously large Pt particles [1]. In industrial practice, the regeneration of deactivated catalysts requires an external input, such as a change in the working environment from reducing to oxidizing. The unusual self-healing nature of the Pt-Pd catalysts needs further study to unravel the operating mechanisms.

In this work we are conducting an ex-situ and in-situ study of the formation of biphasic metal-oxide particles. A monometallic Pt catalyst supported on spinel ($MgAl_2O_4$) was physically mixed with a monometallic PdO catalyst supported on a lanthanum oxide-doped alumina (La-Al_2O_3) and subjected to 800°C aging in air for 10 hours to study the vapor phase transport of Pt and subsequent capture by PdO under these conditions. We observed, via TEM, that the Pt formed was transported through the vapor phase and captured on the alumina support, forming bimetallic PtPd particles with a Janus structure (Figure 1a and 1b), but a portion of the PdO remained as small particles and appeared to not interact with the PtO_2 vapor (Figure 1c and 1d). EDS maps illustrated this well by showing the Pt concentrated to areas where the Janus structures were seen, while the Pd was observed in the Janus structures as well as dispersed in the form of nanoparticles located everywhere on the alumina support (Figure3a-c). These results confirm that PtO_2 is captured by the PdO, the first step in the formation of the Janus structure.

Current work is focused on employing in-situ TEM to watch the changes in morphology and microstructure in these self-healing catalysts as they undergo redox cycling. For these studies, we prepared a bimetallic PtPd catalyst on a (SiO_2@ZrO_2) support where ZrO_2 was deposited as a shell on nonporous silica spheres. The spherical geometry of this support helps to provide edge-on views of the metal particles [3]. Further, the use of this support was to establish the generality of our TEM observations of biphasic particles on a range of catalyst supports, confirming that they are thermodynamically stable under these treatment conditions. The catalysts were first heated at 800°C in air for 50 hours to achieve the thermodynamically stable state. In the ETEM, the catalyst was subjected to a reduction treatment in H_2 at various temperatures up to 800°C. A distinct change in morphology was observed, with the oxide portion completely disappearing as the particle transformed into a Pt-Pd alloy. Oxidation of these bimetallic particles reveals how the biphasic particles form. The in-situ heating study yields insights into the mechanisms underlying the remarkable thermal stability of Pt-Pd diesel oxidation catalysts and their self-healing character. The findings will have a broad impact on developing high temperature stable and durable catalysts for energy conversion.

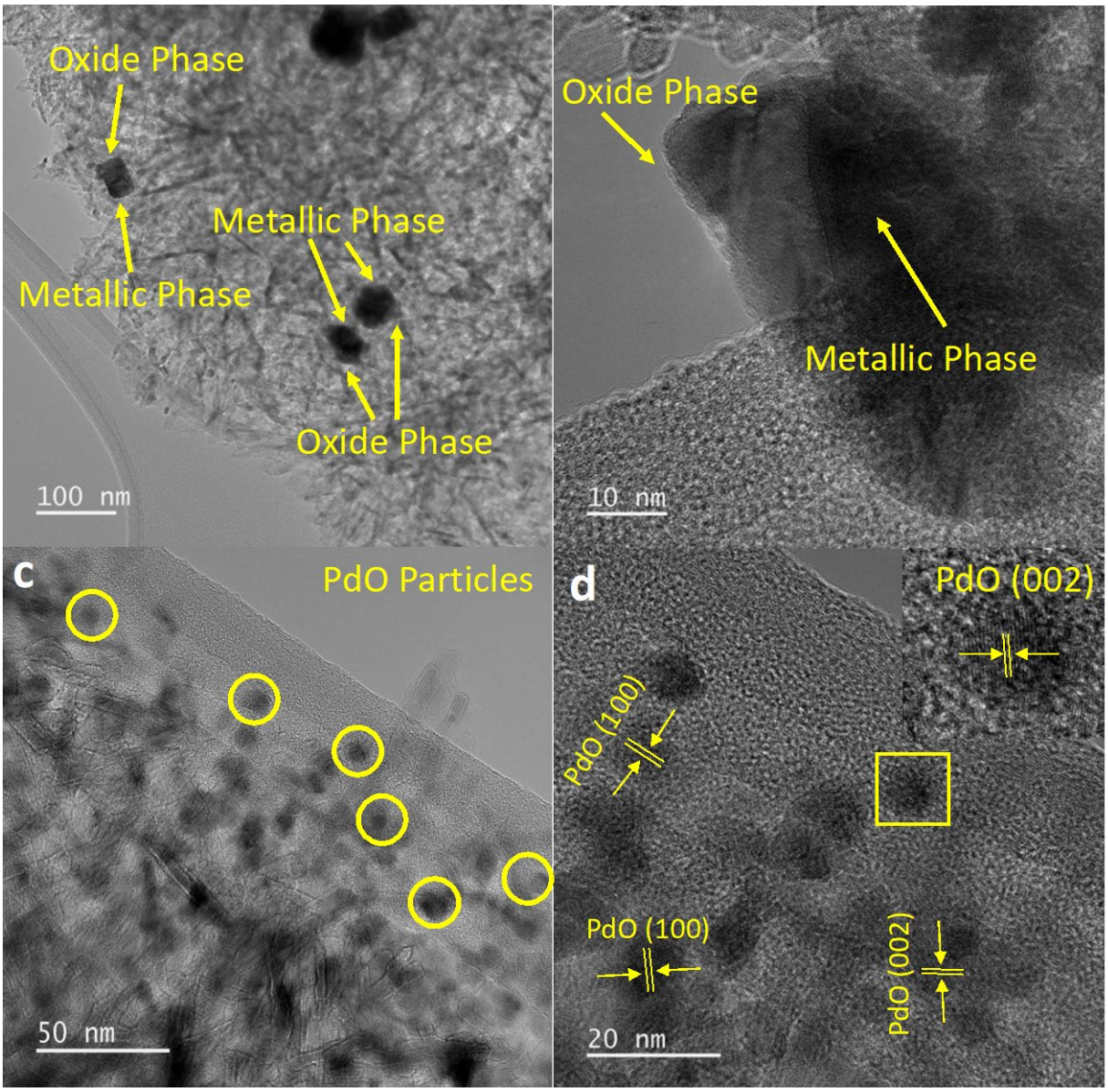

Figure 1: Images from the monometallic Pt catalyst supported on spinel structure ($MgAl_2O_3$) physically mixed with a monometallic PdO catalyst supported on lanthanum-doped alumina (La-Al_2O_3) and subjected to 800°C aging in air for 10 hours. (a) Low magnification TEM image of the sample, showing biphasic particles scattered throughout the support. (b) High magnification view of one of the biphasic particles, showing the Janus structure. The light oxide portion is conjoined to the dark metallic portion at an interface. (c) Low magnification view of the dispersed PdO phase, seen as dark, spherical objects distributed throughout the support. (d) High magnification view of a few of the PdO particles, revealing their internal microstructure and is labeled for some of the particles. Since the lattice fringes are difficult to see at this magnification, a digitally magnified particle originating from the yellow-boxed region is shown as an insert in the upper right corner. Here, the lattice fringes are easily seen and have been labeled as well, for convenience.

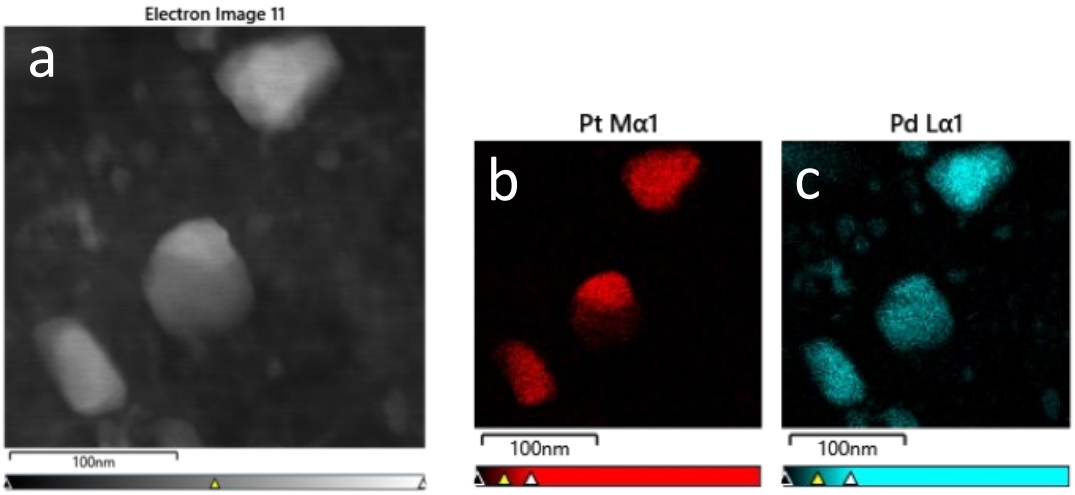

Figure 2: EDS elemental mapping data from the physically mixed Pt/$MgAl_2O_4$ and PdO/La-Al_2O_3 and subjected to 800°C aging in air for 10 hours. (a) The STEM ADF image of the region analyzed. The image contrast reveals the biphasic Janus particles wherein the oxide portion (lighter contrast) is conjoined to the brighter metallic portion. (b) The Pt $M_{\alpha 1}$ elemental map showing Pt to be present in the Janus particles. (c) The Pd $L_{\alpha 1}$ elemental map showing the smaller, bright objects seen in the STEM image in (a) to be Pd-only nanoparticles that did not transform into the Janus particles.

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