

Designing Catalysts for Meeting the DOE 150 °C Challenge for Exhaust Emissions

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As more efficient combustion engines are developed for transportation, it is expected that less heat will be wasted in the exhaust, leading to lower exhaust temperatures. Hence DOE has set a goal of achieving 90% conversion of target pollutants by 150 °C [1]. To meet exhaust emission standards, it is necessary to develop catalysts that provide light off at lower temperatures than the current generation of catalysts (which become active at ~200 °C). The new targets cannot be achieved simply by increasing the loading of noble metals. One way to achieve higher reactivity at low temperatures is by control of the crystallite size of the platinum group metal (PGM) nanoparticles [2]. Smaller particles and sub-nanometer clusters show higher reactivity, and in the limit, we can envision single atom catalysts, which provide the highest atom efficiency to reduce noble metal usage, since every atom is involved in the catalytic cycle. The challenge is to make these single atom and sub-nm structures durable so they can survive high temperature aging protocols and demonstrate performance under realistic conditions. This presentation will highlight approaches to enhance the reactivity and thermal durability of emissions control catalysts.

The primary process for the degradation of PGM-based heterogeneous catalysts is Ostwald ripening, where mobile species emitted from the nanoclusters migrate over the support surface (or through the vapor phase), to form large particles [3]. After aging, only a fraction of the precious metal is available for catalysis. For example, when Pt/alumina diesel oxidation catalysts are aged in air at 800 °C for one week (the DOE aging protocol), the initially dispersed Pt (Fig. 1a) forms aggregates exceeding 100 nm in diameter, where less than 1% of the Pt is on the surface (Fig. 1b). This results in the loss of catalytic activity. Building on our study of the fundamentals of catalyst sintering [3,4] we reasoned that one way to slow the processes of Ostwald ripening would be to trap the mobile species emitted from the PGM nanoparticles. We found that PdO is able to trap mobile Pt species very effectively, forming Pt-Pd nanoparticles [5]. We have concluded that trapping of PtO₂ by PdO constitutes an important mechanism for the improved durability of diesel oxidation catalysts. Continuing our search for metal oxides that are effective at trapping Pt, we discovered that cerium oxide powders were very effective at trapping Pt. As described by us recently [6], a physical mixture of Pt/alumina with ceria helped preserve the catalytic activity of the Pt catalyst for CO oxidation, even after aging at 800 °C for one week (Fig. 1c) since all of the Pt after aging was present in atomically dispersed form (Fig. 1d). Atom trapping constitutes a facile approach for preparing single atom catalysts that are thermally durable and can withstand high temperatures (Fig. 1e). Besides ceria and PdO, we have seen other examples of atom trapping which help in achieving greater durability and improved regeneration of heterogeneous catalysts. For example, when Pd/La-alumina is calcined at 700 °C in air, we form atomically dispersed Pd species which lead to

excellent low temperature reactivity for CO oxidation [7]. Likewise, when Pt-Sn/Al₂O₃ is calcined under oxidizing conditions, we found that the Pt was redispersed, since the Sn atoms on the support served as traps for the mobile PtO₂ species [8]. In this presentation we will describe how the generation of atom trapping sites on catalyst supports provides a novel approach for the design of catalysts for energy conversion and exhaust treatment that provide high durability and reactivity [9].

References:

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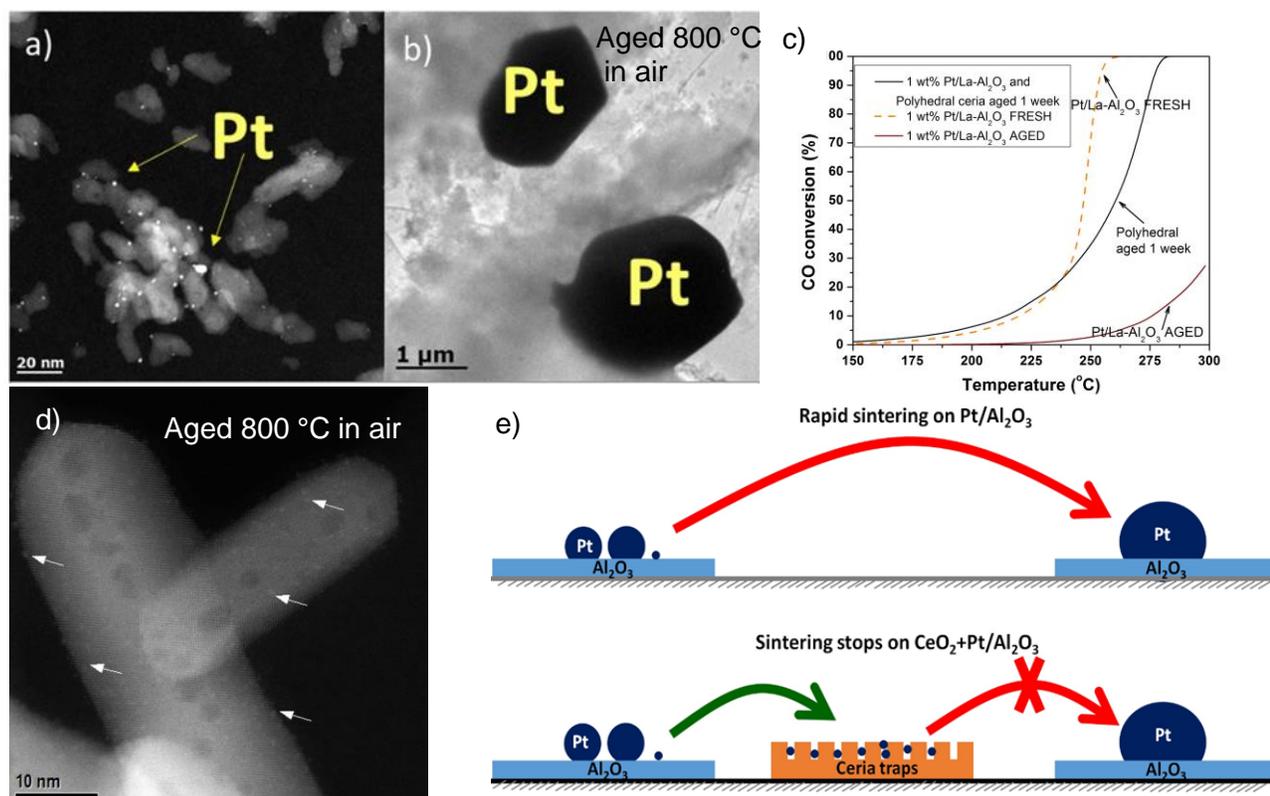


Figure 1. a) 1wt% Pt/La-Al₂O₃ fresh and (b) after aging in flowing air at 800 °C for 10h; (c) CO oxidation activity of the fresh and aged 1 wt% Pt/La-alumina and when polyhedral ceria was physically mixed before aging; (d) AC-STEM image showing atomically dispersed Pt in the physically mixed ceria; (e) illustration of the process of atom trapping that helps preserve the atomic dispersion of Pt.