

Adatom Emission from Nanoparticles: Implications for Ostwald Ripening

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Currently, precious metals such as Pt, Pd, and Rh are used in catalytic converters for treatment of exhaust gases from gasoline and diesel engines. These catalysts help remove pollutants, such as nitrogen oxides as well as CO and hydrocarbons, all of which result in smog and respiratory problems in urban environments. The supplies of precious metals are limited worldwide, but there is increasing demand for clean energy. Hence, there is a need to develop more active catalysts that provide long-term stable performance at elevated temperatures with minimal use of precious metals such as Pt. A serious problem facing catalysts is the loss of activity during use. The primary mechanism by which automotive catalysts lose activity is through growth of nanoparticles, via a process known as Ostwald ripening [1]. Several research groups have shown that Pt sinters readily under oxidizing conditions, leading to poor durability [1-3]. The restructuring of Pt under oxidizing conditions can be dramatic, as reported by Wu and Phillips, but Graham et al. demonstrated that addition of Pd to Pt led to improved stability [3-4].

In this work, we have used model catalysts to study the emission of atoms from nanoparticles, one of the key steps in Ostwald ripening. Electron beam evaporation was used to synthesize Pt, Pd, and 50% Pt-50% Pd samples on silica TEM grids. Each sample was first reduced in flowing 5% H₂/N₂ at 750°C for 2 hours. Then each sample was aged in flowing air at 800°C for 1.5 hours. Figure 1 shows HAADF-STEM (High-Angle Annular Dark Field Scanning Transmission Electron Microscopy) images of the Pt and the bimetallic sample before and after aging. The Pt-Pd bimetallic sample showed significant growth in particle size after aging and a dramatic drop in the number of particles per square micron, whereas the Pt-only sample showed fewer particles but no significant particle growth. We determined the mass of metal on each sample assuming spherical particles and found that the effective thickness of the Pt layer decreased from 2.4 Å to 1.3 Å, which amounts to a 47% decrease in the mass of Pt. In contrast, the Pt-Pd sample lost only 9% of its mass. Since the loss of the metal is caused by emission of atoms, which is related to the vapor pressure of the metal (or metal oxide complex), the results show a significant decrease in atom emission due to the presence of Pd in the Pt. The vapor pressure of Pt-Pd alloys has been studied in the literature and it was reported that the system shows only a modest degree of non-ideality, implying that the drop in vapor pressure should at most be 50%, while we see over 80% decrease in metal emission rates.

The composition of the bimetallic sample determined from EDS (Energy Dispersive X-Ray Spectroscopy) before aging was determined to be 39.4% Pt and 60.6% Pd. After aging, the composition was 32.7% Pt and 67.3% Pd. The images show that the nanoparticles remained in the metallic state, with only a few instances where a palladium oxide phase segregated from the Pt-Pd alloy. The similarity of compositions of the individual nanoparticles after aging to those before

aging is very surprising since Pt is known to form a volatile metal oxide, but Pd is not. These results are intriguing because they imply that both Pt and Pd can be transported under oxidizing conditions. We have planned in-situ TEM experiments to study Pt and Pd mobility under oxidizing conditions, and further work is underway to study the role of the oxide support. These model catalyst studies shed light on the atomic scale phenomena involved in Ostwald ripening of automotive catalysts.

References

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- [6] This research was supported by NSF PIRE grant OISE-0730277 and made use of some of the facilities at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

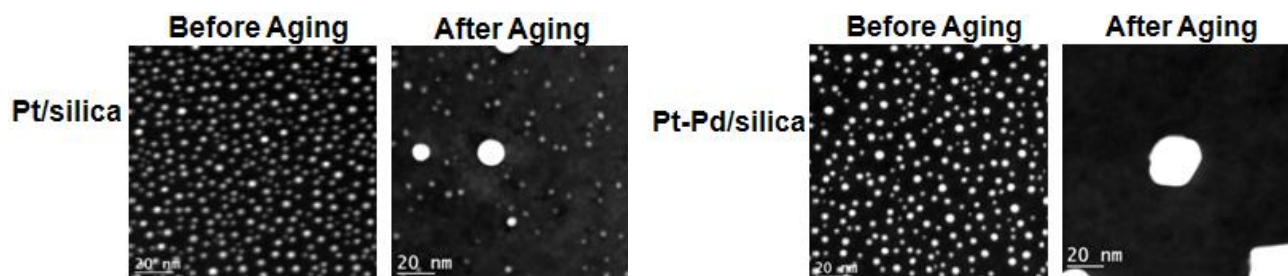


FIG. 1. HAADF-STEM images before and after aging of the Pt and Pt-Pd samples.

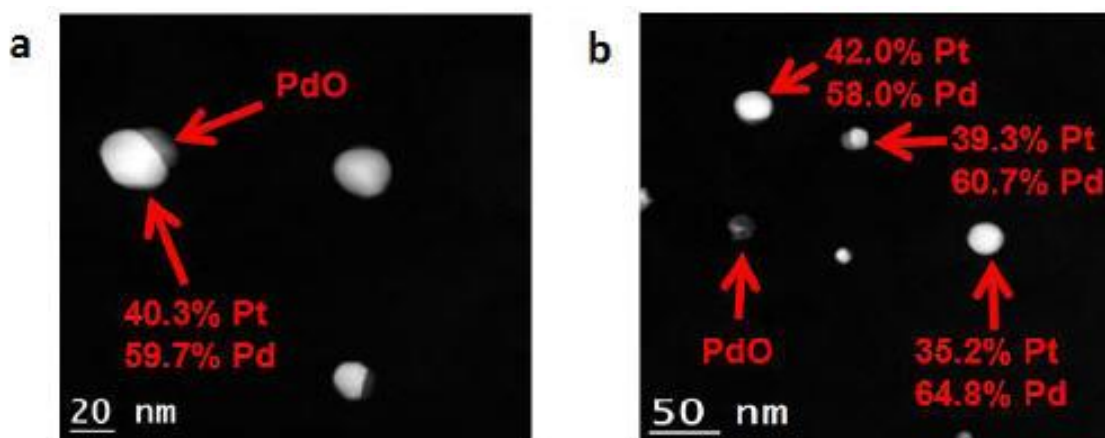


FIG. 2. HAADF-STEM images of the bimetallic sample after aging show that compositions almost remained the same and nanoparticles remained metallic and alloyed.