Adatom Emission from Pt-Pd Diesel Oxidation Catalysts: Implications for Ostwald Ripening

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Introduction

Pt and Pd are currently used in catalytic converters for the treatment of exhaust gases from gasoline and diesel engines. 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 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 Pt catalysts lose activity is through Ostwald ripening [1]. Several research groups have shown that Pt sinters readily under oxidizing conditions, leading to poor durability [1,2], but Graham et al. demonstrated that addition of Pd to Pt led to improved stability [2]. The factors that lead to this improved durability, however, are not well understood. Understanding the mechanisms by which Pd helps improve the performance of Pt catalysts is crucial for enhancing long term catalytic performance.

Materials and Methods

In automotive catalysts, the sintering phenomena can only be studied post-mortem, or after aging. Therefore, we have developed a novel approach using model catalysts where it is possible to perform direct measurements of the emission of atoms from nanoparticles. We used model catalysts that allow us to study the same region of the catalyst before and after treatment. The samples were prepared by electron beam evaporation. We studied Pt, Pd, and 40% Pt-60% Pd samples on SiO₂ TEM grids. The samples were reduced in 5% H₂/N₂ and then aged at elevated temperatures in air. TEM/STEM images and EDS spectra were acquired at each stage to determine the extent of particle growth and mass loss.

Results and Discussion

Ostwald ripening involves the transport of atoms from small to large particles. Atoms are emitted from a nanoparticle and can diffuse over the support surface, or they may be transported through the gas phase. It is suspected that volatile platinum oxides may be responsible for the rapid sintering of Pt catalysts, but the relative importance of the surface and gas phase processes is not known. With the model catalysts used in this work, we can determine the relative rates of vapor phase and surface diffusion processes. We are also able to deduce the nature of the mobile species- Pt, Pd, or both?

The Pt, Pd, and bimetallic Pt-Pd samples were reduced and then aged under oxidizing conditions at different temperatures ranging from 500°C to 795°C. We used a statistical approach to study thousands of nanoparticles as well as a microscopic approach to track the behavior of individual nanoparticles.

Our results also show that the primary process of interparticle transport is through surface diffusion of adatoms rather than vapor phase transport. Similar compositions were found in the aged nanoparticles despite significant growth in particle size. This suggests that Pt and Pd have similar mobility on the silica surface under oxidizing conditions. The Pt-Pd samples remained metallic under oxidizing conditions, while Pd transformed to PdO. Our results show that Pd impedes the emission of the volatile Pt oxides in the bimetallic samples. However, the lowering of the emission of Pt is not caused by a core shell structure. The morphologies of the particles observed in this work are shown in the figure below. Our work suggests that Pd does not help to slow the rate of sintering of Pt, but Pt allows the Pd to remain metallic. It is the presence of metallic Pd alloyed to Pt that accounts for enhanced reactivity in bimetallic catalysts.

Significance

The treatment of pollutants in the exhaust from high efficiency lean-burn automobiles is an important challenge. Catalyst sintering plays an important role on the low temperature light off. Understanding the key mechanisms during sintering will be helpful in the improving the performance of these catalysts.

Figure 1. A schematic diagram of the processes during aging of catalysts. The figure on the right shows how vapor phase emission processes can be studied by using the model catalysts. Here Pt/SiO₂ and Pt-Pd/SiO₂ are imaged before and after aging for 1.5 hours at 795°C in air. Addition of Pd to Pt led to almost an 82% decrease in the emission of volatile Pt oxides; however, the impact on the rates of Ostwald ripening was minimal.

References