Sintering Studies on Model Catalytic Systems

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Introduction

Sintering is one of the most important deactivation mechanisms for heterogeneous catalysts. Automotive emission control catalysts utilize costly precious metals as the active component. The metal phase is present in the form of nanoparticles, which help provide a high surface area. With closed-coupled catalysts being placed closer to the engine, automotive catalysts are being subjected to more extreme environments. At elevated temperatures nanoparticles sinter via an Ostwald ripening process (see Figure 1) leading to a loss of surface area and catalyst activity.

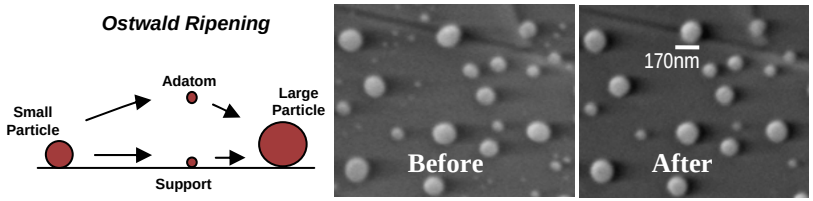

Figure 1. (a) Left: Schematic illustration of Ostwald Ripening behavior. Ad-atoms are emitted by small particles are captured by the larger particles. (b) Right: Observations of Pd on alumina, before and after ageing at 900°C for 24 hours in 1 bar N_2.

Direct electron microscopy observations of commercial catalysts are inherently difficult due to the tortuous pore structure of such materials. Model catalytic systems consisting of Pt and Pd particles on flat oxide substrates provide a means for improving the visibility of metal particles and to improve counting statistics. We use high resolution scanning electron microscopy (HRSEM) to observe the metal particles in the nano-size regime relevant to heterogeneous catalysis. Samples were aged in various gas environments to elucidate the mechanisms of metal particle growth.

Materials and Methods

Flat model samples of Pt and Pd on Al_2O_3 (sapphire) were made via evaporation. The 5x5mm Al_2O_3 single crystal substrates had a thin film of Pt and Pd deposited on the surface (~1.5nm in thickness), which then went through an oxidation reduction process to yield a uniform distribution of nanoparticles. The samples were subjected to isothermal aging at 900°C for designated periods of time.

Results and Discussion

The initial experiments were performed in vacuum to gain insight into the relative role of vapor phase versus surface transport of adatoms (see transport processes A & B in Figure 2b). Figure 2a shows the results of aging the sample for 30 minutes and 48 hours in vacuum at 900 °C. We observe a dramatic loss of Pd due to evaporation caused by the high vapor pressure of Pd at this temperature. The rate of metal evaporation predicted by the Langmuir model [1] was compared to the observed loss of Pd and the results suggest that the surface transport pathway is dominant even in vacuum. Hence, measurements of metal particle loss from these model catalysts provide a simple approach to investigate the role of the support on catalyst sintering. In this presentation, we will report on the role of the support modification via CeO_2, ZrO_2, and BaO on the transport of Pd adatoms during sintering at elevated temperatures. We compare the behavior of the model catalysts with those of conventional supported catalysts to relate these fundamental studies to rates of catalyst sintering.

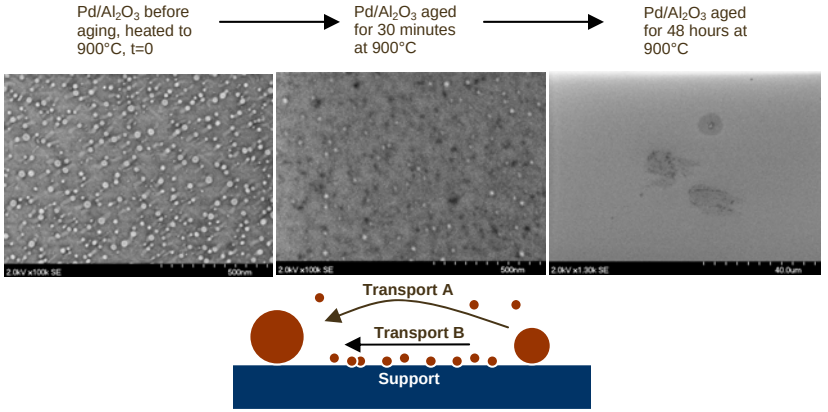

Figure 2. (a) Top: HRSEM images of Pd/Al_2O_3 at different stages of the aging process in vacuum. Eventually all the Pd is lost via evaporation. (b) Lower: Schematic illustration of ad-atom transport on an oxide support through the vapor phase (A) and surface diffusion (B).

Significance

A fundamental understanding of the mechanisms of sintering will help suggest methods to make catalysts more resistant towards sintering.

References

1. Irving Langmur "The Vapor Pressure of Metallic Tungsten", *The Physical Review*, November, 1913

Acknowledgements We acknowledge financial support from the NSF GOALI program grant CTS-05-00471 and from the industry members of the Ceramic and Composite Materials Center.

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