Support Effects on Adatom Emission from Palladium Nanoparticles

Levi R. Houk[1], Andrew DeLaRiva[1], Ron Goeke[1], Sivakumar R. Challa[1], Benjamin Grayson[2], Paul Fanson[2], and Abhaya K. Datye[1]*

[1]*University of New Mexico, Albuquerque, New Mexico 87121 USA*

[2]*Toyota Motor Engineering & Manufacturing, Ann Arbor, MI 48105, USA*

*datye@unm.edu

Introduction

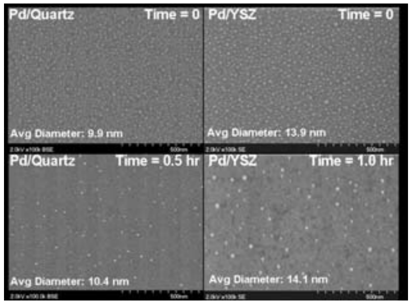
Sintering plays a major role in the deactivation of heterogeneous catalysts. However, there is limited understanding of the underlying mechanisms. The two accepted mechanisms are coalescence, due to the migration of smaller particles, or Ostwald ripening, the movement of atoms (or mobile species) preferentially emitted from smaller particles due to their higher surface energy. Direct measurements of atom emission from nanoparticles are difficult due to the tortuous pore structure of industrial catalyst supports. In this work, we have used model, single crystal oxide supports on which metal nanoparticles have been deposited. Heating these model catalyst samples causes the metal to evaporate and provides a direct measure of the atom emission rate. The objective of these experiments is to determine the role of the support on the rates of metal evaporation and ultimately on the rates of metal particle sintering. Fundamental understanding of this process will allows us to develop better predictive models for catalyst sintering and develop strategies to control sintering.

Materials and Methods

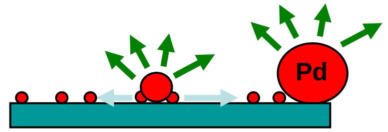
Three different (single crystal) model oxide supports were chosen for this study, quartz, sapphire, and yttria stabilized zirconia (YSZ). A nominal thickness of 1.5 nm of Pd was deposited by evaporation; the samples were then oxidized in air at 700°C to form a palladium oxide layer. Heating the sample in vacuum to 900°C caused dewetting of the Pd to form spherical particles on the support (time zero VTZ). Samples were then aged in vacuum at $1x10^{-6}$ Torr and 900 °C and imaged at 30-minute intervals.

Results and Discussion

The SEM images of the Pd particles before and after vacuum ageing show a dramatic influence of support. The loss of mass from the quartz sample is considerably faster than predicted by direct evaporation, while on YSZ the experimental measurements are in very good agreement with predictions. In 30 minutes we have lost more Pd from the quartz sample than we lose in one hour from Pd/YSZ. The particle size distributions also do not agree with the predictions of direct evaporation. These results suggest that surface mediated evaporation plays a significant role (atoms are emitted onto the support and are evaporate from there). This is borne out by the particle size distributions which do not show the drop in mean particle size that would be expected from direct evaporation. These results provide direct mechanistic insight into the adatom emission and surface diffusion steps on supported catalysts. In the presentation, we will compare the data on adatom emission with the rates of Pd sintering on model supports and with a parallel series of experiments on high surface area supported catalysts.



Proposed evaporation mechanism



Small particles losing mass due to evaporation while Ostwald ripening causes growth of larger

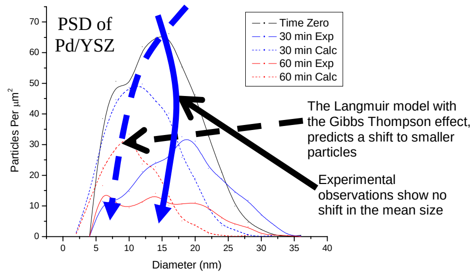


Figure 1.(top left) SEM images of Pd/quartz and Pd/YSZ after ageing in vacuum at 900 C. The quartz sample showed no Pd left behind after 1 hr, hence we show data after only 30 min of ageing. A schematic model for the processes responsible for the observed changes is shown (top right). The particle size distribution (PSD) of Pd on YSZ and the calculated curves based on direct evaporation and experiments are compared. It is evident that Ostwald ripening leads to the observed invariance in particle diameter, even though there is a loss in mass of Pd on the sample.

Significance

Measurements of adatom emission and transport can provide critical information for understanding the rates of Ostwald ripening. These studies provide direct evidence for the role of the support on catalyst. Previous work that found that direct evaporation from the metal explained the rates of metal loss on carbon supported particles[2].

Acknowledgements

This work is supported by the NSF GOALI grant CTS-05-00471 and the NSF I/UCRC grant EEC 04-36455 with additional support from Toyota Motor Engineering and Manufacturing.

References

1. Langmuir, I, *The Vapor Pressure of Metallic Tungsten*, The Physical Review, Vol.II, #5: p331, 1913
2. N.D. Lisgarten et al. *Vapour Pressure over Curved Surfaces – The Kelvin Equation*. Contemp. Phys., 1971, Vol. 12, 575-593