

Stable Sub-Nanometer Pd Species on Alumina Surfaces

Eric J. Peterson,¹ Barr Halevi,¹ Andrew De La Riva,¹ Hien Pham¹, Lawrence F. Allard², and Abhaya K. Datye^{1*}

¹University of New Mexico Center for Microengineered Materials, Albuquerque, NM 87131 USA,

²Oak Ridge National Laboratory, Oak Ridge, TN 37831-6064 USA

*datye@unm.edu

Introduction

Our studies of supported Pd/alumina catalysts reveal a systematic discrepancy between particle sizes derived from techniques such as Extended X-ray Absorption Fine Structure (EXAFS), X-ray Diffraction (XRD), and high-angle annular dark-field (HAADF) imaging in a Scanning Transmission Electron Microscope (STEM). In this work, we show how the newly available technique of aberration-corrected electron microscopy (ACEM) allows us to reconcile these discrepancies. To determine crystallite sizes, we used three techniques that are complementary to each other but sensitive to differing ranges of metal particle sizes. Notably, EXAFS is sensitive to particle sizes ranging from clusters of a few atoms to particles that are a few nanometers in size, whereas XRD sensitivity ranges from a few nanometers to hundreds of nanometers. While conventional HAADF-STEM has a size sensitivity lower-limit of about 1 nm, ACEM now provides the capability to reliably image single atoms of a heavy metal on an oxide surface. Hence, it is now possible to combine these three techniques to gain a comprehensive picture of the nature of the metal phase in a supported catalyst. In the present study, we applied these three techniques to study the evolution of a Pd/alumina catalyst as it was treated at elevated temperatures to cause sintering of the Pd metal phase. The catalytic significance of these sub-nm Pd species for CO oxidation and for selective hydrogenation will be presented in this work.

Materials and Methods

Alumina-supported Pd was produced using Pd-nitrate and the incipient wetness method to produce powder with a 2.5% Pd loading on gamma alumina. The sample was calcined and then treated in flowing N₂/H₂ at temperatures ranging from 300-900 °C, producing a series of samples having a range of Pd crystallite sizes.

Results and Discussion

Average crystallite sizes obtained from the EXAFS data were found to be significantly smaller than those obtained from XRD and STEM. Similar discrepancies have been observed in the past [1] and not fully resolved. This suggests that the presence of particles in the 0-1 nanometer size range is weighting the EXAFS-obtained average size to smaller values than those obtained from XRD and STEM. For the EXAFS average size to be brought into line with the TEM and XRD average sizes, these samples must have 0-1 nm size fractions comprising 10-20% of the Pd present. Further examination of these samples by ACEM confirmed the presence of an abundance of single atoms and small clusters of atoms on the support. The weight fraction of this highly dispersed phase was estimated from the ACEM images and was found to be in excellent agreement with the predictions of EXAFS/STEM.

Significance

The results demonstrate that alumina can stabilize a dispersed Pd phase even after sintering to temperatures as high as 900 °C. These anchoring sites may help explain the relative sinter-resistance of alumina-supported catalysts. The work also demonstrates that ACEM is critical in understanding dispersed metal phases on oxide supports.

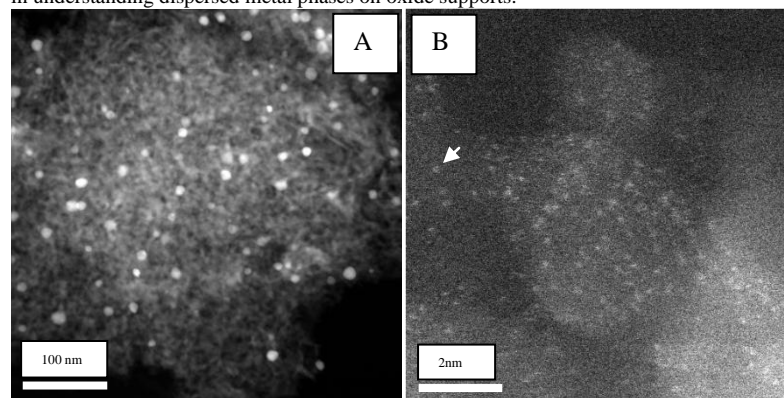


Figure 1. Images from sample reduced at 900 °C for 3.3 hrs in N₂/H₂.

(A) Conventional HAADF-STEM image showing Pd crystallites >1nm in diameter.

(B) ACEM image showing single atoms and atom clusters. The arrow indicates a typical Pd atom.

(C) Histogram showing the size distribution as obtained from HAADF-STEM images for the sample that was reduced at 900 °C for 3.3 hrs in N₂/H₂, and corresponding XRD and EXAFS-derived diameters.

Acknowledgments

This work has been supported by the United States Department of Energy, Office of Basic Energy Sciences under contract number DE-FG02-05ER15712 (University of New Mexico), and by the Asst. Sec. for Energy Efficiency and Renewable Energy, Office Of Vehicle Technologies, at ORNL, managed by UT-Battelle LLC for the U.S. Department of Energy, under contract # DE-AC05-00OR22725.

References

1. Calvin, S., Riedel, C.J., Carpenter, E.E., Morrison, S.A., Stroud, R.M. and Harris, V.G. *Physica Scripta* T115, 744 (2005).