

## Title: Dynamic anomalies in the nanoscale structure and disorder of supported metal nanoparticles

F.D. Vila (Univ. of Washington, Seattle, WA, USA), A.I. Frenkel (Stony Brook Univ., Stony Brook, NY, USA), R.G. Nuzzo (Univ. of Illinois, Urbana, IL, USA), J.J. Rehr (Univ. of Washington, Seattle, WA, USA).  
[fdv@uw.edu](mailto:fdv@uw.edu)

Supported metal nanoparticles (NP) are ubiquitous in heterogeneous catalysis, and there is broad interest in their physical properties. However, spectral probes such as EXAFS and XANES mostly reveal ensemble properties. For example, EXAFS studies of Pt/g-Al<sub>2</sub>O<sub>3</sub> reveal anomalous behavior in ~1 nm NPs, such as short Pt-Pt bonds that contract with increasing temperature, and that disappear in larger NPs. In addition, these NPs exhibit unusually large Pt-Pt mean square relative displacements (MSRD), quantities used in EXAFS analysis to estimate bond strengths from their temperature dependent vibrational component. Large corrections to the zero-point MSRD are conventionally interpreted as “static” disorder due to NP inhomogeneity. However, this interpretation is problematic, since for 0.9 nm NPs, it predicts mean force constants that are larger than those observed for the strongest known Pt-Pt bonds. We have shown using DFT/MD simulations that bond contraction and large disorder arise from the fluctuating nature of structure at the nanoscale or “dynamic structural disorder” (DSD). In this talk I show that a full interpretation is more complex, and that the DFT/MD MSRDs include long-time equilibrium fluctuations or “anomalous structural disorder” (ASD).

To show this we carried out 10 ps ab initio MD simulations of Pt[10,20]/g-Al<sub>2</sub>O<sub>3</sub>, unsupported Pt[10,20] clusters, and bulk Pt for temperatures ranging from 165 to 573 K. To acquire adequate statistics we averaged over six independent trajectories for each temperature. We partition the MSRD into three components according to their dynamic timescales: Vibrational disorder, associated with fast nuclear motion with frequencies higher than 1 THz; DSD, arising from slower dynamics in the 0 to 1 THz range; and ASD, associated with mean quasi-static Pt-Pt disorder.

We find that the vibrational component arises from local Pt-Pt vibrations controlled by the number of neighboring atoms, and behaves normally, increasing linearly with temperature. The DSD also behaves normally with temperature, but arises from the coupling between the NPs center of mass dynamics to local bond fluctuations. The ASD is due to the fraction of bonds that remain “frozen” at a given temperature and anomalously decreases with temperature. This decrease is due to two effects: i) The activation of the longer, weaker Pt-Pt bonds and ii) the stretching of shorter bonds.

In conclusion, the usual procedure of fitting the MSRD to normal vibrations plus static disorder is inadequate for these systems. Since these anomalous properties arise from effects of limited dimensionality, intra-particle heterogeneity, and support interaction, they are likely to exist in other particle-support systems.

This work was supported by U.S. Department of Energy, Office of Science CSGBD Grant No. DE-FG02-03ER15476, with computational support from NERSC, a DOE Office of Science User Facility, under Contract No. DE-AC02-05CH11231. A.I.F. acknowledges support from Program Development funding at Brookhaven National Laboratory under U.S. Department of Energy Contract No. DE-SC0012704.