

Séminaire

Jeudi 21 mai 2015 - 14H00
Salle LLR (05-2021)



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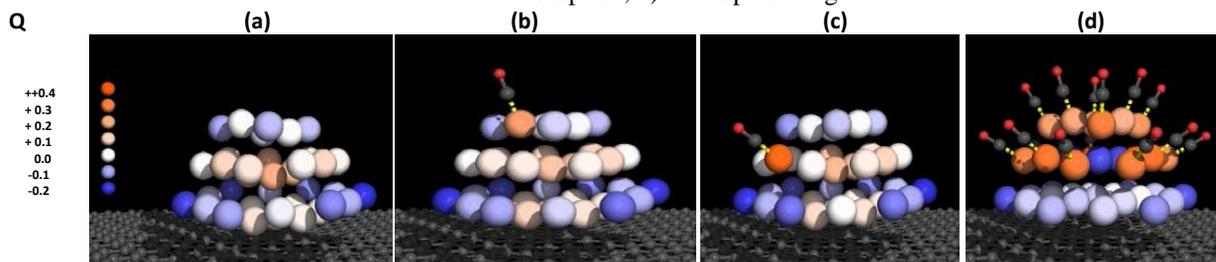
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Dynamic structural disorder in supported Pt nanoclusters under *operando* conditions*

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Supported nanoparticle catalysts are ubiquitous in heterogeneous catalytic processes, and there is broad interest in their physical and chemical properties. However, global probes such as XAS and XPS generally reveal their ensemble characteristics, obscuring details of their fluctuating internal structure. We have previously shown [1] that a combination of theoretical and experimental techniques is needed to understand the intra-particle heterogeneity of these systems [2], and their changes under *operando* conditions [3]. For example, ab initio DFT/MD simulations revealed that the nanoscale structure and charge distribution are inhomogeneous and dynamically fluctuating over several time-scales, ranging from fast (200-400 fs) bond vibrations to slow fluxional bond breaking (>10 ps). In particular the anomalous behavior of the mean-square relative displacement is not static, but rather is driven by stochastic motion of the center of mass over 1-4 ps time-scales. The resulting large scale fluctuations are termed “dynamic structural disorder” (DSD) [2]. Moreover, the nanoparticles tend to exhibit a semi-melted cluster surface, which for alloy clusters can be atomically-segregated. Recent studies of CO- and H-covered Pt nanoclusters on C and SiO₂ supports show a variety of spectral and structural trends as a function of temperature. DFT simulations show that adsorption drives local electronic structure changes that are responsible for the opposite energy shifts vs temperature, of the absorption edge and off-resonant emission line. Moreover, desorption results in local bond contraction, thus explaining the negative thermal expansion observed in XAS experiments. For example, upon single CO adsorption, the Pt-Pt bonds formed by coordinated Pt atoms are locally expanded by ~5%, with little change in the rest of the particle. Coordination also has a large effect on the net charge of the Pt atoms (Figure 1), with a net loss of charge upon adsorption. Finally, we show how high coverage inverts the charging structure of the cluster, turning the negative surface (positive interior) of the clean cluster to positive surface (negative interior) in the fully covered case.

Figure 1: Net charge changes upon CO adsorption for a Pt₃₇ cluster on carbon. a) Clean cluster, b) edge adsorption, c) face adsorption, d) full-top coverage



*Supported by DOE grant DE-FG02-03ER15476, with computer support from DOE-NERSC.

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[3] F. D. Vila, J. J. Rehr, S. D. Kelly and S. R. Bare *J. Phys. Chem. C* 117, 12446 (2013).