

# Theory of heterogeneous oxidation of carbon monoxide by sub-nano surface-deposits: from electronic structure to catalysis

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Small clusters of transition metals deposited on supporting surfaces are among the most promising but least understood catalytic materials. Their catalytic properties depend unpredictably and nonlinearly on cluster size and composition, and cannot be extrapolated from those of the extended surfaces or larger nanoparticles. We use and develop a full array of multi-scale modeling techniques, ranging from electronic structure to statistical mechanics, to gain insight into these dependencies, and enable rational design of highly active surface-deposited clusters.

- We assessed structure, stability, and mobility of selected small Pd clusters on titania surfaces.
- We developed a model for simulating the process of sintering of deposited clusters via the mechanism of Ostwald ripening. We are now able to predict cluster size-distribution over a range of temperatures (Fig. 1 shows the concentration of the Pd<sub>2</sub> dimer as a function of T).
- We realize electronic reasons for preferred structures of deposited clusters. In particular, we found that clusters change shape upon deposition, from 3D in the gas phase to 2D. Matching with surface O atoms for partially covalent bonding, and additional acquisition of the aromatic character of chemical bonding (Fig. 2) drives the transition.
- We study the activity of these clusters toward the reaction of CO oxidation as a function of cluster size.
- We used our insight into the electronic structure of these systems to rationally choose Au as a low-concentration dopant for deposited Pd clusters, for more efficient catalysis (Fig. 3).

We also presently develop new methods for

- unbiased search for the global minima of clusters
- statistical mechanical modeling of catalytic solid/gas interfaces at high temperatures and pressures
- Machine-learning guided Wannier Functions method for the analysis of electron transport pathways in surface-deposited clusters in catalysis

Fig. 1

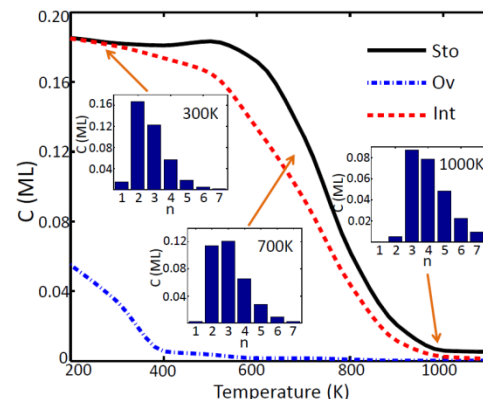


Fig. 2

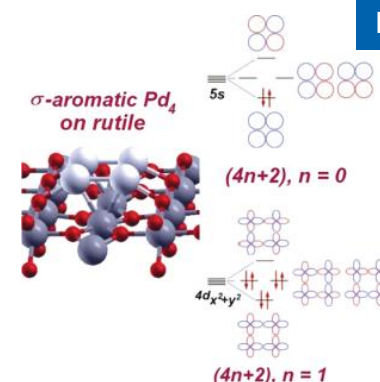


Fig. 3

