

Structure and reactivity of metal nanoparticles

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Properties of transition metal nanoparticles vary significantly with size and shape, a well known example of quantum size effects. From density functional calculations on the adsorption of CO probe molecules at Pd nanocrystallites, we concluded that mainly the size-dependence of lattice parameters affects the adsorption properties of nanoparticles in the scalable regime. The average Pd-Pd distance in nanoclusters of about hundred atoms is ~3% shorter than in Pd bulk. This results in a weaker adsorption compared to an extended Pd(111) surface. On going to smaller Pd clusters, to the non-scalable regime, the CO adsorption energy becomes even smaller, down to species of about 40 atoms. Below that size range the adsorption energy increases again rather significantly. This behavior can be rationalized by a second trend in the non-scalable regime.

We also report on a study of scaling properties with respect to a crucial element of technique, namely different exchange-correlation functionals: LDA, GGA, and MGGA. While the geometries of the clusters are reproduced within the expected trends, the energetics turned out to show variations among the functional groups. Finally, we address the so-called “ligand-free” catalysis where palladium particles are used in the synthesis of fine chemicals, e.g. in Heck coupling. A study of CO adsorption at high coverage offers insights into the controversy whether catalytic reactions occur on the surface of metal particles or after metal “leaching” in solution.