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DFT study of Pd₁₃ isomers in gas-phase and on (100)-TiO₂ Anatase

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The nonzero spin magnetic moment in small palladium clusters, unlike the bulk Pd, has been documented since long ago from measurements using the Stern–Gerlach experiment¹ and photoemission² and susceptibility measurements³ and from numerous recent theoretical studies.⁴ Despite the overall agreement about the nonzero spin in clusters with size <105 atoms, the magnetic moments and the associated ground state structures with variation of the cluster size are still under debates.

In this poster we present our results of a systematic study on the magnetic property variations of Pd₁₃ particles as a function of particle sizes and structures, and of Pd₁₃ interactions with the (100) TiO₂ anatase surface.⁵ Calculations were carried out with standard density functional theory (DFT) based method with periodic boundary conditions.

The biplanar Pd₁₃ structure with the spin state quintet is obtained to be the ground state in the gas-phase and on the anatase surface, being more stable than the compact icosahedral configuration. The preferred particle nucleation on the anatase surface is that with the largest possible contacts between Pd₁₃ and the oxide surface oxygens. The supported Pd₁₃ particles are better stabilized by 0.3 eV compared to the isolated ones. The profiles of the relative energies as a function of the spin state reveal that the Pd₁₃ magnetic isomers, belonging to the same cluster topology, become closer in energy and nearly degenerate on the anatase surface compared to their gas-phase counterparts. Quenching of the magnetism occurs only for the three-dimensional cluster topologies and not for the biplanar structure. Both the geometrical and electronic features were found to be important for the Pd₁₃-anatase interactions as analyzed in view of the energy profiles, electrostatic properties, and charge density distribution. The role of geometry and electronic structures on the reactivity of Pd₁₃-gas-phase clusters was examined for the adsorption reactions of acetylene and ethylene. Inversion of their magnetic isomer stability occurs upon adsorption of acetylene, whereas it remains unaffected upon adsorption of ethylene.

References

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