Size-dependent activity of platinum nanoparticles: Theoretical insights from CO adsorption and methanol dehydrogenation

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Size and shape of metal nanoparticles (NPs) determine their properties including the chemical activity. A detailed understanding if and how the reactivity of such NPs scales with size is crucial for the rational design of new nanosized catalysts with enhanced catalytic properties [1,2].

Using DFT calculations, the size dependence of CO adsorption was studied on Pt_n clusters with n = 38−314 atoms. These computational results suggest that a nanosized transition to a pronounced higher (comapred to single-crystal) adsorption activity occurs for Pt NPs at particle size about 200 Pt atoms. To elusidate the structural effects connected to low-coordinated sites on particle edges and vertexes the concept of generalized coordination numbers was adapted to include of second coodination sphere [2].

Further, the size and structure effects on Pt nanoparticles were studied using methanol dehydrogenation as a model surface reaction [3]. The effect of cluster morphology is manifested by higher adsorption energy of COH_x intermediates on vertexes and edges of model nanoparticles compared to the close-packed terraces. Moreover, due to the size effect, adsorption sites of Pt_{79} nanoparticles (1.2 nm in diameter) exhibit considerably higher adsorption activity than the same sites of Pt_{201} (1.7 nm). Thus, particles with a size of about 1 nm are shown to be more active due to the superposition of two effects: (i) higher surface fraction of low-coordinated adsorption sites, and (ii) higher activity of these sites compared to particles with a size of about 2 nm.

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