

EINLADUNG

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von

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**Towards More Realistic Density-Functional Modelling of
Nanostructures Relevant to Heterogeneous Catalysis**

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Abstract:

Active components present in heterogeneous catalysts as nano-aggregates of thousands atoms remain inaccessible for density-functional methods. However, such species can be quite realistically represented by computationally tractable smaller model nanoparticles (NPs), whose surface sites only slightly change the reactivity with increasing particle size. We illustrate this for reactions of methane,¹ methanol,^{2,3} and olefins^{3,4} on Pt and Pd catalysts as well as building of active sites on Pt/ceria catalysts.^{5,6} We show that using common slab models and thus neglecting the nanoscopic effects in these and similar systems could lead to severe misrepresentation of the surface reactivity.⁷ Methane decomposition on Pt NP is more exothermic than on Pt(111) surface and proceed via much lower activation barriers for the rate-limiting steps.¹ Pt activation by nanostructuring is due to stabilization of CH_x species on NP edges, converting the initial steps of CH₄ decomposition from endothermic on Pt(111) to exothermic on Pt₇₉ NP. Comparative analysis of these reactions on single-crystal Pd(111) surface and the corresponding sites on terraces of Pd₇₉ NP is also performed. The metal structural flexibility was found to affect not only adsorption properties of sites with low-coordinated atoms but also nearby terrace sites. It is most pronounced for strongly bound adsorbates, e.g atomic C – common by-product in reactions on Pd,² able to modify catalyst properties upon exothermic migration subsurface.³ The most spectacular effect of flexibility of Pd NPs is on the subsurface migration barriers of surface C. Near NPs edges these barriers essentially vanish. Presence of subsurface C makes Pd NPs more transparent for subsurface diffusion of adsorbed hydrogen,³ which in turn enables sustainable hydrogenation of olefins on Pd

FWF SFB F45 „Functional Oxide Surfaces and Interfaces (FOXSI)“

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catalysts.4 Strong metal-support interactions can radically modify surface chemistry. Due to catalysts complexity the microscopic origin of such effects is usually unresolved. However, our study on models of Pt-ceria catalysts uncovered atomic details of interactions in this system.5 Two types of oxidative Pt-ceria interactions were identified: electron transfer from a Pt particle to the support and O transport from ceria to Pt. The former is favorable on ceria supports regardless their morphology. But the O transfer requires the presence of Pt in close contact with nanostructured ceria, being inherently a nano-effect. Both effects were subsequently detected by monitoring the Ce³⁺/Ce⁴⁺ ratio using resonant photoelectron spectroscopy on Pt-CeO₂ model catalysts.5 Presented case studies reveal very significant differences in the surface reactivity derived from customary slab model calculations and those employing dedicated NP models. The latter expose a rich variety of active sites, whose structure and geometric flexibility notably better match those of the sites present under experimental conditions. Thus, we advocate much broader usage of suitable NP models in “catalysis from first principles”.

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