

Dynamics of truly monodisperse clusters under the STM

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The use of clusters promises to revolutionize our ability to design and control the selectivity and efficiency of catalytic processes owing to the unique chemical and physical properties of these structures [1]. Nanostructures and molecular clusters behave quite differently than bulk materials due to quantum size effects that become dominant upon reducing the dimensionality of the material grains. Every atom counts and thus size becomes a third dimension to the periodic table. A deeper understanding of the interplay between morphology and electronic structure as function of the cluster size will guide the development of a new generation of atomically designed nanostructures for catalysis. In order to access the ultimate fundamentals of the non-scalable size regime of supported cluster chemistry, we developed the preparation of truly monodisperse cluster-assembled materials, i.e. with every cluster of same size and adsorption site and thus chemical environment. To this purpose, we deposited size-selected, soft-landed Pd_N clusters ($7 \leq N \leq 31$) on epitaxial graphene films. Moiré moieties formed on graphene films have been shown to be good candidates for the stabilization of clusters [2]. Such well defined samples allow for the first time to fully complement these local with integrating measurements on cluster reactivity and electronic structure and to study isomer effects at the atomic scale. Our STM measurements show that the Pd clusters are well-dispersed on the graphene surface at room temperature, without any preferential aggregation at the step edges, contrary to what occurs upon physical vapour deposition [3]. Pd₂₀ clusters show a 2-3 monolayer high atomic structure, comparable to that of free-standing clusters in the gas phase. Neither cluster fragments nor surface damage is observed, confirming a well-controlled soft-landing on the graphene surface. On graphene, the clusters are exclusively adsorbed on one of the two ring hollow registries of the superstructure, indicating a strong carbon-metal interaction and a softening of the carbon-carbon bonding at this local registry. Different isomers of Pd₂₀ are observed, and isomerization processes can occur during continuous STM scanning. Clusters can be manipulated by the Push mode or can be removed in a controlled way, leaving behind the pristine surface. The STM study reveals that the cluster mobility/stability depends not only on the cluster size, but also on the footprint specific to isomers of different height. An investigation on the thermal stability of larger, Pd₂₀ clusters

by annealing clearly indicates different mechanisms in the sintering process: cluster diffusion dominates at temperatures below 500 K, Ostwald ripening at temperatures above 500 K. Two approaches are currently implemented in order to increase the STM time resolution for the study of these cluster-assembled materials under reactive gas environments [4].

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