

***In Situ* Studies of Working Catalysts at the Mesoscopic Level.**

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Advanced electron microscopy and catalysis are today mostly related through ultra-high resolution observations of atomistic details of periodic and aperiodic structures. The interest in such images is motivated by the desire to “see” active sites and to obtain a visual impression of the atomic details of nanostructures. ETEM is advocated as the ultimate solution to obtain the structure of active catalysts. Catalysis, however, is a multi-scale phenomenon that is related to its observable performance by a very large scaling factor of the dimension of Avogadro’s number (6×10^{23}). The minimum ensemble of active sites that we can observe by chemical analysis is of the order of 10^{10} and thus never accessible with atomic resolution. Problem-oriented electron microscopy for catalysis should thus consider the mesoscopic unit of analysis with the same level of attention that it provides for the level of atomic resolution. This is, according to our observation, not the case providing the motivation for the present contribution.

The catalytic oxidation of carbon monoxide is a test reaction [1] for all aspects of catalysis. In the present context we study the structure sensitivity of the reaction over various grains of Pt and Pd with differing orientation all subject to the same reaction conditions. The experimental evidence for structure-sensitivity is controversial pointing to a sensitivity of the reaction on mesoscopic transport phenomena. In addition it is interesting to study two active metals Pt and Pd in immediate comparison to substantiate the meaning of an intrinsic “activity” as function of the chemical element. Such activity differences are often quantitatively related to theoretical studies in which “details” of structure sensitivity are not considered. We observed through photoelectron emission microscopy (PEEM) that both elements exhibit indeed strong structure sensitivity [2] in agreement with prior single crystals studied. Minute restructuring through Ar ion sputtering that did not change the crystal grain structure completely altered the reaction behavior. The origin of this unexpected sensitivity was the formation of microfacets on the mesoscopic facets of the metal foil as evidenced by post-reaction scanning probe microscopy. The data will be discussed in the light of “universality” of catalytic activities for given elements.

The second example of mesoscopic *in situ* electron microscopy with catalysts concerns the formation of graphene over Ni and Cu surfaces through CVD [3, 4] from ethylene. This reaction is not only of considerable actual interest for obtaining large amounts of true single layer graphene samples. It further allows with one single technique to image the dynamics of the catalysts in exactly the same unit of analysis as the product is being formed. The research questions to be studied concern the observation that Ni does often not lead to single layer carbon and that copper leads to single layer carbon but not to continuous large carbon sheets.

Ni is a case where carbon dissolution and segregation control the carbon formation. The participation of the bulk makes it challenging to limit the carbon growth to a single layer. Restructuring of the Ni under

the lattice strain of the dynamically inserted and segregated carbon atoms modifies the growth geometry. In addition, nucleation at the surface of carbon segregating from the bulk is such a rapid process that control of a single layer formation is virtually impossible. We observe a continuous top graphene layer followed by a disordered and irregular grown multilayer nanostructure on which the top graphene is supported. The chemistry of carbon growth on Ni was followed *in situ* and time-resolved using NAP-XPS. An atomic carbon species as nucleating species was clearly discernible from the growing graphene product. After some seconds of growth time substantial concentrations of C-H terminations become detectable explaining the slowed kinetics and the critical choice of the C:H ratio of the feed gas for optimized growth without too many defects and without too much non-graphenic carbon.

The much-advocated Cu catalyst has indeed the advantage of growing preferentially a single layer of graphene. Its reactivity towards carbon atom formation is, however, low, so that high temperatures close to the melting point of Cu need to be used for relevant growth velocities and sufficient internal ordering of the graphene. We have observed the growth kinetics of graphene (Fig.1), and identified an increasing curvature of the carbon with respect to its substrate as a limiting factor for growth. The origin of the curvature as well as of many subtle ordering phenomena during cooling lies in the fact that Cu that is not covered by carbon tends to evaporate during graphene CVD. Hence a hill-and-valley structure with a most interesting faceting of the underlying Cu is formed. The nucleation seems to be heterogeneous in nature, but is not structure-sensitive, as the graphene grows as individual flakes across grain boundaries of the Cu catalyst. These grain boundaries are mobile during CVD growth as are segregates of Si impurities dissecting graphene layers.

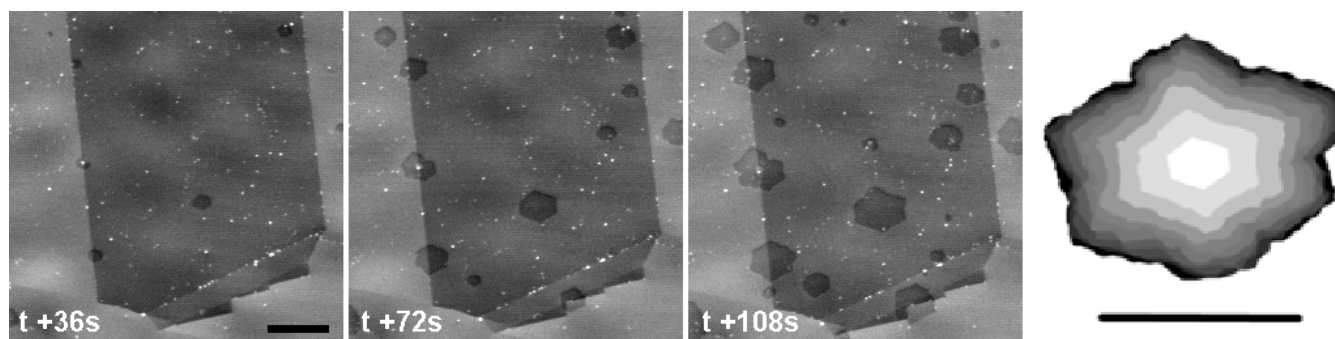


Figure 1: Snapshots taken during the initial stages of graphene growth on a Cu foil at 1000°C using an environmental scanning electron microscope. Time intervals are 36s, scale bars corresponds to 5 μ m.

The present examples of mesoscopic *in situ* observations of catalysts at work highlight the dynamical nature of operating catalysts. Structure-sensitive and structure-insensitive reactions were detected. It will be discussed if these categories do exist indeed or are only artifacts of insufficient consideration of the multi-dimensionality of catalysis. In any case without a full range of microscopic techniques the analysis of catalytic materials remains elusive.

References:

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