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Review of Habilitation Thesis entitled "Quantitative morphological information in model catalysis" authored by Mgr. Josef Myslivеček, PhD

Dear Prof. Holý,

Thank you very much for inviting me to review the habilitation thesis of Mgr Josef Mysliveček, PhD as part of his tenure application process.

Dr Mysliveček has currently authored 51 publications (as listed in Scopus) and holds an h-index of 18 with a total of about 900 citations. Interestingly, the number of citations has been steadily and significantly increasing over the past 10 years, clearly documenting his increasing visibility and impact in his research area. Of these publications, he has selected 21 original articles and one review article as representative of his scientific contribution. In addition to the majority of papers published in well-respected, more specialized journals as, e.g., The *Journal of Physical Chemistry C* and *Physical Review B*, some articles have been merited with extra visibility as provided by premier journals such as *Nature Materials*, *Angewandte Chemie International Edition*, *The Journal of Physical Chemistry Letters*, and *Physical Review Letters*. This quite wide range of scope, spanning the range from hard condensed matter and basic surface science through materials science to physical chemistry nicely reflects the breadth of the research presented by Dr Mysliveček in his thesis.

The habilitation thesis deals with the topic of model catalyst preparation and characterization by atomic-level surface science methodology and, in particular, by scanning tunneling microscopy, which is intended to contributing to the larger goal of reaching a fundamental understanding of the structure-reactivity relation in heterogeneous catalysis. As such, the general subject is timely and constitutes another important step beyond the seminal efforts of the 2007 Nobel laureate in Chemistry, Gerhard Ertl, the founder of the research field.

In the following paragraphs, I will go through the individual chapters of the thesis and highlight the individual strengths and weaknesses as appropriate. At the very end, I will summarize my assessment of the scientific merits and offer a recommendation to the habilitation commission.

After introducing the composition of the thesis in the first chapter, Dr Mysliveček briefly presents the main ideas of model catalysis and its intimate connection to surface science in the second chapter. Emphasis is put on the quantitative characterization of surface morphology and atomic structure using microscopy, which is soundly argued to be crucial for an accurate investigation of catalytic functionality of model systems on the nanoscale as derived from quantitative, yet spatially averaging chemistry techniques, as, e.g., thermal desorption spectroscopy. Consequently, the main part of his thesis is divided into three sections, focusing first on the capabilities of scanning tunneling microscopy (STM) for quantitative surface analysis, second on the preparation of suitable model systems for investigating catalytic chemistry, and finally on a number of studies highlighting the insights that may be gained in metal-oxide heteroepitaxial systems.

In the third chapter, the methodology of quantitative STM and its potential for investigating local electronic structure by means of scanning tunneling spectroscopy (STS) are summarized and illustrated by experimental studies taken from Dr Mysliveček's work targeting nucleation and growth processes of semiconductor nanostructures on silicon surfaces and molecular adsorbates on a Cu(111) metal surface. Starting from the clean, (7x7) reconstructed Si(111) surface, it is shown how local electronic and chemical properties may be explored. Molecular properties are elucidated by applying inelastic electron tunneling spectroscopy (IETS), a delicate method suitable to unraveling local vibrational properties and the influence of dopants on molecular electronic structure. Unfortunately, this powerful tool was not applied in the later studies targeting the local chemical properties of, e.g., prominent defect structures found in the ceria model catalysts, most probably due to the unavailability of a suitable low-temperature STM in Prague.

The fourth chapter is intended to illustrate the capability of STM investigations in the study of begins with an overview of the different growth modes identified in heteroepitaxy under ultrahigh-vacuum conditions, which are exploited for the intentional preparation of self-assembled nanostructures, whose structure and morphology may be effectively addressed by STM. One significant example discussed by Dr Mysliveček comprises the investigation of fundamental kinetic processes in surfactant mediated epitaxy (SME), a prominent route pursued in Ge/Si heteroepitaxy for the bottom-up creation of self-assembled Ge nanostructures of selected size and shape. It is convincingly demonstrated that additional elementary surface processes, extending the at the time widely accepted standard description, have to be considered to account for the experimental observations, namely the diffusive transport of the adsorbate through the surfactant layer, with important qualitative consequences for the island size distribution. Further studies comprise the quantization of the template effect of the faulted/unfaulted halves of the surface unit cell within the dimer-adatom-stackingfault model of the Si(111)-(7x7) reconstruction, which is found to distinctly modify the adsorption and nucleation behavior of Ag adatoms. A similar phenomenon is identified, exploited, and quantitatively modeled in the growth of metal clusters on the moiré pattern formed by single-layer graphene on an Ir(111) single crystal surface, which readily acts as a nanoscale template efficiently facilitating a bottom-up structural design.

The largest part of the habilitation thesis is devoted to illustrating the quantitative potential of STM in view of its relevance to the further conceptual development of heterogeneous model catalysis. A particular focus is laid on the study of the properties of epitaxial films and nanostructures of cerium oxide, a widely-used material that, in combination with, e.g., transition metals and other oxides, is fruitfully employed in heterogeneous catalysis and other subject areas. Owing to the multiple valence states of the cerium cations and the relative ease at which it may switch between them, the reducibility of cerium oxide is one of its key materials properties. For studying the relation between structure and chemical reactivity, Dr Myslivеček and his team have devised ways of growing epitaxial cerium oxide model systems of tunable thickness on copper single crystal surfaces. Specifically, recipes have been developed to systematically change the oxide stoichiometry and to study concomitant structural and chemical properties by applying a variety of surface science techniques, including resonant X-ray photoemission spectroscopy as a very sensitive probe to quantify surface reduction. These works are very well received by the scientific community and continue to be frequently cited in the literature on cerium oxide surface chemistry. Further notable examples are the recent studies on electronic metal support interactions and the peculiar defect chemistry of ceria-supported Pt single atom catalysts, which have been enabled by an impressive collection of experimental and theoretical techniques conducted in close collaboration with renowned foreign research groups. These results have been published in high-impact journals and, in the meantime, have grasped quite a bit of attention, as they may provide viable routes to more cost-effective designs of polymer electrolyte membrane fuel cells in the future. This particular project is very interesting because of the possibly direct impact of the results of academic research on the development of actual industry-compatible devices, which more often than not remains a dream to many surface scientists.

Summarizing my assessment, both the intellectual design and the excellent overall quality of the presented academic work are fully convincing and represent crucial aspects of a successful habilitation. Therefore, I am happy to recommend Mgr Josef Mysliveček, PhD for the appointment as associate professor to the review panel.

Sincerely,

Jan Ingo Flege