

Date: April, 2017
From: Darío J. Stacchiola
Subject: Opponent's review for Mgr. Josef Myslivecek, Ph.D, Habilitation Thesis

Dear Evaluation Committee:

I have reviewed Mgr. Josef Myslivecek, Ph.D, Habilitation Thesis and believe that the work he has presented is of very high quality and impact for the field of Catalysis. The 22 manuscripts included in the Thesis have been published in high impact journals dedicated to both general and specialized fields, with 8 of them having Dr. Myslivecek as the corresponding author. This production is consistent with expectations for granting Tenure at research universities in the USA.

Dr. Myslivecek initial scientific formation was in the application of low temperature Scanning Tunneling Microscopy (STM) applied to the study of Si surfaces. STM is considered one of the most demanding surface science techniques, and it is crucial to the atomic understanding of surface processes. He successfully introduced this technique in the Department of Surface and Plasma Science, leading to the formation of the Surface Physics Group. A system consisting of a modified commercial STM microscope including capabilities for XPS, LEED and TPD analysis was built and used for most of the work presented in the thesis. The initial work focused on the detailed study of Si surfaces by STM and scanning tunneling spectroscopy (STS). He later studied encapsulated Ce dimers in fullerenes by Inelastic Electron Tunneling Spectroscopy (IETS), one of the most demanding modalities of the demanding STM approach. As he describes in the thesis, the study of molecules by IETS is limited to very few groups, primarily working on metals, due to its challenging implementation, but I would point out that this could also be an opportunity to advance the field in the study of molecules with atomic resolution on oxides in the future. Studies on the growth of nano-structures on Si and some preliminary work related to monolayer grapheme are also presented.

The core of the Thesis and the main focus of the current research relate to the synthesis and atomic characterization of ceria films used as models of ceria based catalysts. The most important contribution in this regard has been the preparation of atomically resolved ceria films with a high level of control on their oxidation state and oxygen content, spanning from Ce₂O₃ to CeO₂(111) grown on Cu(111). This was achieved by using a novel strategy of preparing stoichiometric CeO₂(111) films and reducing them by controlled deposition of Ce. These films were used as supports for the deposition of Platinum both as small metal nanoparticles and isolated ionic species. Using metallic nanoparticles, charge

transfer and reverse oxygen spill over between Pt and ceria nanoparticles was clearly demonstrated. There has been increasing interest in the importance of isolated single atom ionic species for catalysis. Using stoichiometric CeO₂(111) films, Dr. Myslivecek and his group in collaboration with theoretical calculations, were able to clearly identify the presence and stabilization of Pt²⁺ species.

The atomistic view of model systems provided by the Surface Physics Group initiated by Dr. Myslivecek is a key element in linking theoretical modeling with practical catalysts. In the future, Dr. Myslivecek is planning to move towards operando STM and XPS studies with the implementation of new instruments already acquired. This will allow to identify the dynamic transformation of model catalysts during reaction conditions. Transferring highly defined model catalysts prepared and characterized by surface science methods in vacuum into electrolyte for the subsequent electrochemical characterization will position his team as one of the few in the world with these capabilities.

The work presented in the Thesis was carried in conjunction with the formation of Education on several students including 1 bachelor, 1 master, and 5 Ph.D. students. The implementation of techniques devoted to the new operando capabilities will open the possibility to the formation of students on state of the art capabilities.

In short, Dr. Myslivecek has proven himself to be a talented scientist in every facet and he will be a valuable permanent addition to your institution. I strongly endorse the work presented in his Thesis and will be happy to discuss any aspect of it further if necessary.

Sincerely,



Dario J. Stacchiola
Group Leader
Interface Science and Catalysis
Center for Functional Nanomaterials
Brookhaven National Laboratory

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