Friedrich-Alexander-Universität
Naturwissenschaftliche Fakultät

FAU

Ich bewerte die Dissertation von | I grade the thesis of

LUKÁŠ FUSEK

mit der Note | with the grade

Bitte ankreuzen: | Please tick:

| | | |
|---|---|---|
| O | sehr gut (1; summa cum laude - die Dissertation gehört zu den **besten 10%** aller Dissertationen) | very good (1; summa cum laude - this thesis belongs to the best **10% theses** I have seen) |
| ☒ | sehr gut (1; magna cum laude) | very good (1; magna cum laude) |
| O | gut (2; cum laude) | good (2; cum laude) |
| O | genügend (3; rite) | sufficient (3; rite) |
| O | abgelehnt - keine wissenschaftlich ausreichende Leistung | reject - the thesis does not represent a scientific achievement |

Ich füge dieser Bewertung eine ausführliche Begründung bei. | I am attaching an extensive written evaluation of the thesis.

PRAGUE, 5TH SEPTEMBER 2024

Ort, Datum | Place, date

doc. Mgr. Josef MYSLIVEČEK, Ph.D. Myslivecek

Unterschrift | Signature

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Prague, 5th September 2024

**Report on the Doctoral Thesis**

submitted by

**Lukáš Fusek**

entitled

**"Model Metal-Oxide Catalysts for Energy Conversion"**

Chemical or electrochemical conversions of suitable vector molecules are considered key technologies enabling a large-scale utilization of renewable energy sources. Using energy surplus from renewable sources, vector molecules can be reacted and stored in the form of higher energy products. The stored energy can be subsequently released at the time of energy demand.

A successful application of energy conversion technologies critically depends on the availability of stable, active, and selective catalysts or electrocatalysts. A knowledge-based catalyst design relies on obtaining atomically-resolved information on the activation, chemical reaction and destabilization processes at the interface between reaction environment and catalyst surface. Traditionally, and for gas reaction environments, such information has been provided by experimental techniques of surface science on atomically flat – or "model" – surfaces of catalytically active materials. State-of-the-art research in model catalysis however requires answering questions on chemically and structurally complex model catalysts in realistic gas, liquid and electrolyte environments, which is the scope of the doctoral thesis submitted by Lukáš Fusek.

The main motivation for Lukáš Fusek is investigating properties of model catalysts related to utilization of so-called Liquid Organic Hydrogen Carriers (LOHC) – organic molecules,

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that can be reversibly hydrogenated and dehydrogenated, and, thus, serve as energy vectors. Model catalysts are single crystals of Pt, clean or activated with oxide ($CeO_2$) nanoparticles, and structurally and chemically more complex catalysts composed of epitaxial thin films of $Co_3O_4$(111) activated with organic modifiers, or with Pt or Pd nanoparticles. The investigated properties include atomic-level structure of the as-prepared catalysts, changes of the catalyst structure exposed to realistic reaction environments (gas, moisture, electrolyte), and adsorption geometry and reaction pathways of the interacting organic molecules. The scope of the involved complementary analytical techniques includes Scanning Tunneling Microscopy (STM), laboratory and synchrotron photoelectron spectroscopy (XPS, SRPES), and electron diffraction (LEED) in vacuum, combined with near-ambient pressure XPS (NAP-XPS) for gas reaction environments and electrochemical infrared spectroscopy (EC-IRRAS), and ex-situ electrochemical cell (EC) for electrolyte environments.

Lukáš Fusek is presenting the motivation and scope of the thesis, selection of the investigated model catalysts and reaction environments, and the employed experimental techniques in a clear and concise manner. Placement of the investigated topics into a broader context of current research in catalysis is illustrated using references to relevant and up-to-date scientific literature.

Results presented in the Thesis are original and novel. Of particular interest seem to be the results on the stability and structure of $Pd/Co_3O_4$ and $CeO_2/Pt$ model catalysts in electrochemical environments, and on the electrooxidation of cyclohexylethanol to acetophenone on Pt(111) surface. The obtained results are summarized in seven publications in international peer-reviewed journals. Lukáš Fusek is the first author on four publications, and the second author or a shared first author on three publications.

Publication 1: **Atomistic Picture of Electronic Metal Support Interaction and the Role of Water** Fusek, L.; et al., *Journal of Materials Chemistry A* 2024, *12* (6), 3258–3264 DOI: 10.1039/D3TA06595B

Publication 1 is devoted to the structure of the as-prepared $Pt/Co_3O_4$(111) model catalyst. Interesting observation is that at the lowest Pt coverage, Pt atoms accommodate on $Co_3O_4$ as single atoms substituting Co atoms. At intermediate temperature this process is promoted by the presence of surface OH.

Publication 2: **$Pd/Co_3O_4$(111) Interface Formation** Kastenmeier, M.; Fusek, L.; et al., *The Journal of Physical Chemistry C* 2023, *127* (12), 6034–6044. DOI: 10.1021/acs.jpcc.3c00261

Publication 3: **Stability of the $Pd/Co_3O_4$(111) Model Catalysts in Oxidizing and Humid Environments** Schuschke, C.; Fusek, L.; et al., *The Journal of Physical Chemistry C* 2021, *125* (5), 2907–2917 DOI: 10.1021/acs.jpcc.0c08915

Publication 4: **Particle Size and Shape Effects in Electrochemical Environments: Pd Particles Supported on Ordered $Co_3O_4$(111) and Highly Oriented Pyrolytic Graphite** Kastenmeier, M.; Fusek, L.; et al., *The Journal of Physical Chemistry C* 2022, *126* (30), 12870–12881 DOI: 10.1021/acs.jpcc.2c03109

Publications 2, 3, and 4 are devoted to the structure and properties of the as-prepared Pd/$Co_3O_4$(111) model catalysts (Publication 2), and to the structure, chemical state and stability of these catalysts in oxygen and water atmospheres (as a function of temperature, Publication 3), and in electrolyte (as a function of electrochemical potential, Publication 4). Particularly interesting is the observation and evaluation of electrooxidation and electroreduction of the supported Pd nanoparticles.

Publication 5: **A Model Study of Ceria–Pt Electrocatalysts: Stability, Redox Properties and Hydrogen Intercalation** Fusek, L.; et al., *Physical Chemistry Chemical Physics* 2024, *26* (3), 1630–1639 DOI: 10.1039/D3CP03831A

Publication 5 is devoted to the structure and properties of the as-prepared Pt(111) model catalysts activated with $CeO_2$ nanoparticles, and to the stability and redox properties of Pt-supported $CeO_2$ nanoparticles in alkaline electrolyte. Interesting observations include size effect in the stability of $CeO_2$ nanoparticles and intercalation of underpotentially deposited H atoms between Pt support and $CeO_2$ nanoparticles.

Publication 6: **Anchoring of Porphyrins on Atomically Defined Cobalt Oxide: In-Situ Infrared Spectroscopy at the Electrified Solid/Liquid Interface** Fusek, L.; et al., *Surface Science* 2021, *718* (October 2021), 122013 DOI: 10.1016/j.susc.2021.122013

Publication 6 is devoted to activation of model $Co_3O_4$(111) surface with monophosphatophenyl-triphenyl porphyrin (MPTPP) molecules. Adsorption geometry of MPTPP and a stability range of the adsorbed molecules with respect to the applied electrochemical potential are determined.

Publication 7: **Toward High-Energy-Density Fuels for Direct Liquid Organic Hydrogen Carrier Fuel Cells: Electrooxidation of 1-Cyclohexylethanol** Fusek, L.; et al., *Journal of Physical Chemistry Letters* 2024, *15* (9), 2529–2536 DOI: 10.1021/acs.jpclett.3c03331.

Publication 7 is devoted to the study of electroreduction of cyclohexylethanol on Pt(111), Pt(110), and Pt(100) surfaces. Important observations are that Pt(111) represents the most active surface, and that the electroreduction of cyclohexylethanol can yield up to 8 H atoms per molecule without breaking the molecule C-C bonds.

Following a detailed discussion of the obtained results, Thesis of Lukáš Fusek is concluded with a comprehensive summary, a comprehensive list of references, and an Appendix containing copies of the included publications as they appear in print, together with the accompanying documents containing supplementary information to the publications.

Lukáš Fusek has conducted his doctoral studies under Cotutelle agreement jointly at the Faculty of Natural Sciences of the Friedrich-Alexander University in Erlangen-Nürnberg, Germany (3 semesters), and at the Faculty of Mathematics and Physics of the Charles University in Prague, Czech Republic (5 semesters). Doctoral studies of Lukáš Fusek were supervised jointly by Prof. Dr. Jörg Libuda from the Friedrich-Alexander University, and by myself. For all publications included in his Thesis, Lukáš Fusek was involved in preparation of the model catalyst samples, in performing surface science and electrochemical measurements, and in evaluating and interpreting the obtained experimental data with a special attention to understanding links among the atomically resolved morphology of the as-prepared catalysts (STM), the chemical state and electronic metal-support interactions in the catalysts (XPS, SRPES), and the stability and electrochemical response of the catalysts (XPS, SRPES, EC, EC-IRRAS). Lukáš Fusek was involved in the preparation of all publications included in his Thesis, for some he has written the original drafts. Throughout the time of his studies, Lukáš Fusek has rendered himself as a very active and productive student, understanding quickly the research topics and techniques and obtaining quickly all necessary laboratory skills. His understanding and scientific discussion have always been very deep and rational and based on a thorough knowledge of literature as well as the experimental data. Lukáš Fusek is a real team player always ready to help other students and colleagues. During his studies he was able to extensively use the complementarity of the research topics and experimental techniques of his home laboratory in Prague (model catalysis and surface science) and the host laboratory in Erlangen (model electrocatalysis and electrochemistry) and to integrate electrochemical and electroanalytical techniques into the model catalysis research in Prague. During his studies, Lukáš Fusek has proven his ability to perform standalone and independent scientific work.

Based on the above assessment I would like to recommend that the Doctoral Thesis of Lukáš Fusek is accepted. I grade the Doctoral Thesis of Lukáš Fusek

**very good (1; magna cum laude).**

Josef Mysliveček