Friedrich-Alexander-Universität
Naturwissenschaftliche Fakultät

An die Promotionskommission
der Naturwissenschaftlichen Fakultät
Prof. Dr. S. Tsogoeva
Halbmondstr. 6-8
91054 Erlangen

Department Physik

Lehrstuhl für Festkörperphysik

Prof. Dr. M. Alexander Schneider

Staudtstraße 7, 91058 Erlangen
Telefon +49 9131 85-28405
alexander.schneider@fau.de
www.fkp.physik.nat.fau.eu

Erlangen, den 24.09.2024

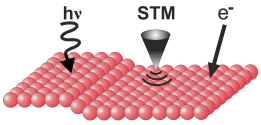
Report on the doctoral thesis
"Model metal-oxide catalysts for energy conversion" by Lukáš Fusek

Lukáš Fusek submits his cumulative thesis presenting a colaborative work between Charles University, Prague, and FAU. It is concerned with the analysis of four model catalysts Pt and Pd on Co_3O_4, CeO on Pt(111) and Pt single crystal surfaces. The thesis provides important insight into the systems, their atomic structure in ultra-high vacuum but also in near-ambient or electrochemical environments. The thesis is based on seven publications, all published in respected journals. Of six of them Lukáš Fusek is first author or equivalent to first author.

I should mention that I do not know Lukáš Fusek personally and was not involved in the work presented. Therefore I can only rely on the submitted documents including the co-author statements and the journals' statements with respect to the author contributions. Unfortunately they are not very precise. I therefore assume that Lukáš Fusek is primarily the person responsible behind sample preparation and STM experiments and their evaluation and was part of a team of investigators of the synchrotron data for publications P1-P4. In publications P5-P7 he is also responsible for the EC-IRAS experiments and their evaluation.

This preamble has to be seen in view of my criticism of the introductory chapters 2 and 3. Unfortunately, they do not convey very well for which experimental methods Lukáš Fusek really stands out as an expert. This is particularly important since the numbers of coauthors is on average 12, but ranges beween 18 (P1) and 7 (P6), reflecting of course the intense usage of different methods in tackling the scientific problem. While I can see the conflict between writing concise and detailed, it is not really useful to present textbook style knowledge (albeit correct). It would have been more important to point out the special assumptions and considerations that have arisen from the intensive work that Lukáš Fusek has undoubtedly spent on his thesis.

For the STM part, I would have expected at least a mentioning of the particular requirements when probing metal particles or clusters on a semiconducting surface like the thin Co_3O_4 film on Ir(100) (choice of bias voltages, path of electrons from tip to Ir(100) substrate) or what the typical sources and magnitude of errors are when determining the numbers of atoms in a metallic nanocluster and how to avoid them. In view of the identification of surface defects observed by



FKP Lehrstuhl für Festkörperphysik

STM with the help of DFT image simulations also a little more detail (choice of bias voltages, repeatability of imaging properties) would have been beneficial.

Similarly, how reliable is the determination of film thickness by XPS or by the quartz-crystal microbalance (QCM)? For the former one needs a reliable value for the inelastic mean free path of the electrons in Co_3O_4. If that has been used (Eq. 3.3), what is its value and origin? The latter can be influenced by numerous factors invalidating the Sauerbrey formula. The QCM is a decisive factor in determining the cluster sizes in P1 and P2. What are the expected errors of this analysis?

Concerning the EC-IRAS method, I would have wished to find more explanatory words on how one should interpret reflectivity changes with changing electrolyte potential (to better understand the data presented e.g. in Fig. 4.17).

Despite of this criticism, I see the following important results of Lukáš Fuseks work:

- Publication P1 deals with the interaction between a metal (atom or cluster) and its metal-oxide support exemplified at the case of Pt on Co_3O_4. STM data of very high quality allowed to follow the atomic scale evolution of the system with Pt amount and also as function of environment (ultra-high vacuum vs. humid). STM in combination with XPS and DFT allowed to identify charge transfer and formation of different Pt oxidation states.

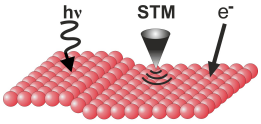
- Publication P2 in principle is similar to P1 only using Pd instead of Pt.

- Publication P3 details on P2 and investigates the stability of the Pd on Co_3O_4 system. Here it is shown conclusively that at certain temperatures and particularly in the presence of oxygen in a near-ambient experiment, Pd not only gets oxidized to PdO diffuses into the oxide and even beyond into the Ir(100) substrate.

- Publication P4 compares the electrochemical properties of Pd particles on Co_3O_4 with those of Pd on HOPG. It turns out, that the hemispherical particles on sputtered (!, unfortunately only mentioned in the original publication) HOPG are less prone to oxidation than their cylindrical counterparts on Co_3O_4. Here, the STM identification of nanoparticle morphology was key to this result.

- Publication P5 stands a bit aside as it rather deals with the morphology of a metal-oxide (CeO) on Pt(111), a inverted model catalyst. Again the determination of the electrochemical stability of the oxide is based on high-quality STM data.

- Publication P6 seeks to elaborate on the anchoring of a phosphonated prophyrin on the Co_3O_4(111) surface as function of electrochemical potential and solvent. This study is based on EC-IRAS data which shows the stability of a chelating adsorption on the surface in a certain potential range. Further it could be shown that certain solvent constitutes can block adsorption sites.



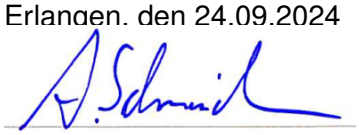
- Publication P7 finally establishes the link to “energy conversion” of the thesis albeit only at the example of differently oriented Pt surfaces for the use with electrochemically active liquid organic hydrogen carriers. Again a major contribution is the EC-IRAS data acquired.

I consider the presented work as a very valuable contribution to unraveling the structure and functioning of oxide supported metal catalysts.

In conclusion, I rate the contributions of Lukáš Fusek to the publications and his work as worthy of a PhD and recommend the acceptance of the thesis by the faculty. Even though I am not happy with Ch. 2 and 3, I rate the careful work that constitutes in fact the basis of the presented publications as very good in comparison to other theses and therefore grade the thesis with:

very good (1, magna cum laude).

Erlangen, den 24.09.2024



Prof. Dr. M. Alexander Schneider

Friedrich-Alexander-Universität
Naturwissenschaftliche Fakultät

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)
X	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.

Erlangen, 24.09.24

Ort, Datum

Place, date

A. Schmid

Unterschrift

Signature