Referee report on the doctoral thesis "Model Metal-Oxide Electrocatalysts for Energy Conversion" by Lukáš Fusek

The doctoral thesis by Lukáš Fusek is a summary of several carefully elaborated studies on model electrocatalytic metal and metal-oxide based catalysts for application in energy relevant reactions and hydrogen economy. The author used UHV surface science methods and electroanalytical methods to investigate properties and stability of a model metal-oxide catalysts combining the rare metals (Pt, Pd) with reducible oxides (Co_3O_4, CeO_2). Among using of well established surface science techniques author implemented EC cell designed at Department of Physical Chemistry at the Friedrich-Alexander University (FAU) into the experimental setup at Department of Surface and Plasma Science at Charles University (CU).

The structure of doctoral thesis is well designed and it incorporates up to date approaches frequently used in model heterogeneous catalysis. Although individual chapters are solely based on published papers their connection is clearly presented. Perhaps only last two chapters about porphyrins on atomically defined cobalt oxide and electrooxidation of cyclohexylethanol on platinum did not quite fit in previous parts. Enclosed full publications can help readers to understand line of reasoning of that parts which are in main text too concise.

The thesis begins with general introduction of role of catalysis in prospective chemical energy storage and continues in explanation of model catalyst approach and role of reducible oxides. After introduction working principles of characterization techniques are explained, next chapter describes experimental setup in FAU, CU and Material Science Beamline.

The main results chapter is divided into 7 subsections. The first and the second subsection is focused on Pt/Co_3O_4(111) and Pd/Co_3O_4(111) model system prepared in UHV. The third and fourth subsection study stability of Pd/Co_3O_4(111) under humid and oxidizing conditions and in electrochemical environment. 5th subsection presents study on stability of inverse catalyst ceria/Pt in electrochemical environment. The results chapter is completed by interaction of porhyrins to Co_3O_4(111) and electrooxidation of 1-cyclohexylethanol on Pt single crystals.

The author used variety of experimental characterization methods, carefully analyzed the data, as well as he interpreted them on the basis of DFT calculations made by collaborating theoretical groups. The results were finally published in reputable journals and therefore I am convinced that Mgr. Lukáš Fusek has met all necessary requirements for the doctoral degree.

I recommend that the dissertation committee to accept doctoral thesis and award grade "1 = very good" to Mgr. Lukáš Fusek.

Further questions for the defence

1. **Section 4.4. Particle size and shape effects in electrochemical environments: Pd particles supported on ordered Co_3O_4(111) and highly ordered pyrolytic graphite**

   Page 54 The intensity analysis of Pd 3d spectra shows a drop of intensity after the first emersion at 0.5 V_{RHE}. The drop is explained by attenuation of the signal by adsorbed carbon and residues of electrolyte. Approximately 15 % of the intensity loss is related to dissolution of Pd.

This finding raises the general question about applicability of thin layers in electrochemical environments. How can it be stabilized and how to prevent passivation of surface by carbon a residues from electrolyte?

2. **Section 4.5. Stability, redox properties, and hydrogen intercalation in ceria-Pt model electrocatalyst**

   Page 59, Figure 4.16 shows that the charge contribution in the CVs of H adsorption/desorption do not decrease with increased ceria coverage which is explained by the H_{upd} intercalation at the ceria/Pt interface. This charges are higher for low-temperature (LT) sample. However, whereas as high-temperature (HT) samples, show large flat islands, LT samples, results in small but still flat ceria nanoislands. Does it mean that intercalation in LT samples is more effective? How charge contribution from Figure 4.16 depends on number of CV cycles?

3. **Section 4.6. Anchoring of porhyrins on atomically defined cobalt oxide: In-situ infrared spectroscopy at the electrified solid/liquid interface**

   Page 61 Figure 4.17 The band at 970 cm^{-1} which is assigned to phosphonates appears at applied potential. Does it mean, that porhyrins are anchored to Co_3O_4(111) surface only when potential is applied? Is it this behaviour specific only for Co_3O_4(111) surface?

4. **Section 4.7 Direct fuel cell liquid organic hydrogen carriers: The electrooxidation of cyclohexylethanol**

   Page 65 In comparison to other low-index Pt surfaces Pt(111) shows the highest activity towards 1-cyclohexylethanol oxidation. How it is connected to surface structure of Pt(100), Pt(110) and Pt(111) ? Does Pt(111) surface undergoes some surface reconstruction during this reaction?

Minor comments

- Main motivation in introduction part is development of chemical methods for hydrogen storage, however it is not explained how anchoring of porhyrins to Co_3O_4(111) and electrooxidation of 1-cyclohexylethanol is connected to chemical energy storage.
- Part "Theory and fundamentals" is rather description of general principles of used experimental techniques.
- Although some important conclusion are based on peak fitting of XPS spectra the fitting procedures are not well explained. Namely, it is not mentioned type of used background, using of symmetrical or asymmetrical lines for Pt^0 or Pd^0, presence of shift attributed to final state effects as a consequence of the particle size, and presence of Co LMM Auger peaks in XPS Co 2p spectra.

Prague 24. 10. 2024

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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 24.10.2024

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