Referee report on the doctoral thesis "Reactivity of transition metals – influence of the degree of oxidation of active substrate" by Mgr. Miroslav Kettner.

The submitted doctoral thesis represents a comprehensive study of the properties of cerium oxide doped with fluorine. In particular, the author investigated an impact of fluorine on the morphology, the reactivity, and oxygen storage capacity of cerium oxide films. The most important finding concerns the influence of the fluorine on the electronic structure of cerium oxide. In the unique fashion, the corresponding approach allows controlling the electronic metal-oxide interaction as a function of fluorine concentration and, thus, tailoring the activity and selectivity of the ceria-based catalysts on the knowledge driven basis.

The thesis begins with detailed overview of the current state of research in the field of heterogeneous catalysis. In particular, the authors highlighted the role of cerium-based catalysts in the treatment of automotive exhaust gases. The author introduced the concept of model catalyst for systematic investigation of fluorine interaction with cerium oxide based systems. The thesis continues with the description of experimental techniques and methods.
The results are organized into six sections, each preceded with a preface, an introduction, and experimental details and summarized with a brief conclusion. The corresponding structure provides a reader with immediate information about the results presented in particular section without a need to read general introduction and experimental sections. However, among the main disadvantages of this format are multiple repeating and partially overlapping details.
In Section 3.1, the author describes the structure of Ce 3d core level spectra of fluorine doped cerium oxide and suggests the deconvolution procedure based on the linear combination of the peak envelopes determined on reference samples. In Sections 3.2 and 3.3, the author reports the changes in the morphology, electronic structure, and chemical state of CeO_2(111) films caused by doping with fluorine. In Section 3.4, the author suggested a preparation method for new model system, a CeO_2(110) film epitaxially grown on Rh(110). In the following Sections 3.5 and 3.6, the author consistently compared the influence of fluorine on the oxygen storage capacity of CeO_2(111) and CeO_2(110) films in the presence and in the absence of supported Rh nanoparticles. Finally, the results are summarized providing important information on the experimental control over the properties of cerium based model catalysts.
The major part of the reported results has been published in recognized journals. However, in order to increase the visibility and scientific relevance of the thesis it would be beneficial to provide the list of the publications at the end of the thesis or as a separate supplement.

In summary, the author has demonstrated the ability to conduct extremely high quality experimental work, to plan and carry out the research in cooperation with international teams, and report his results in clear communication.
Thereby, I recommend Mgr. Miroslav Kettner to be awarded the title PhD.

To the content of the Thesis I have following questions sorted in the order of their importance below.

More important:

1) Section 3.1.4. The author developed fitting procedure of Ce 3d core level spectra which employs constant intensity ratios between the contributions from different final states in Ce^{4+}

cations denoted as v-u, v”-u”, and v”’-u”’ doublets. Under this conditions, the amplitude of u”’ component determines the total Ce^{4+} area (page 28, top). Is the corresponding fitting approach justified in view of the strong influence of the fluorine on the electronic structure of cerium oxide described in Section 3.3.3? In particular, considering the changes in the coordination shell of Ce^{4+} caused by fluorine and resulting changes of the degree of Ce-O bond covalence and screening of 3d core hole (discussed on page 53), will the intensity ratios between the contributions from different final states of Ce^{4+} cations remain the same in the Ce 3d spectra of fluorine-doped cerium oxide?

2) Section 3.3.3. The author identified a new feature at 3.4 eV in the valence band of fluorine doped cerium oxide obtained with photon energy corresponding to resonant condition in Ce^{3+} cations (Figure 24G on page 52). Nevertheless, the author assigned the corresponding feature to Ce^{4+} states altered by the fluorine. With respect to the nature of this feature, do the intensities of the resonant features scale with the corresponding contributions in Ce 3d spectra and support the assignment? It would be informative to explore the resonant intensity and binding energy of this feature as a function of photon energy.
3) Section 3.5.2, Figure 28. The author explains the shift of Rh 3d core levels on Rh/CeOxFy system by the electronic metal-support interaction. How the author rule out the size effect which would basically lead to a similar shift in Rh 3d spectra.
4) Section 3.6.4. Did author consider the formation of oxygen difluoride (OF_2) upon exposure of fluorine doped cerium oxide to mixture of hydrogen and oxygen?
5) Section 3.1.3. The author introduced a term of 1 MLE (monolayer equivalent) for the thickness of the studied films based on the CO adsorption and LEED characteristics. What is the actual thickness of MLE in terms of nanometers?

Less important notes and corrections:

1) Page 13. “death time” of the detector should be written as “dead time”
2) Page 16. The author writes: „... NAP-XPS allows the studies of dynamics of catalytic reactions.“ In view of the classic understanding of the reaction dynamics, the sentence seems incorrect.
3) Page 30. Figure 10. The description of “x” axis labeled as “Experiment number” is missing.
4) Page 44. In the sentence “… in Figure 19 is the decrease of produced CO_2 with the increase of the Rh(111) coverage.” The corresponding trend in Figure 19 is opposite.
5) Page 44. Apparent error in calculations: The author claims that 4 CeO_2 surface units occupy 9 Rh(111) units. Considering the (1.4x1.4) epitaxy, the 4 CeO_2 occupy 8 Rh(111) units.

Erlangen, 7.11. 2017

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