To whom it may concern,

I accept the honor to critically review the thesis "Interaction of simple molecules with reducible oxides: model studies of H2O/CeOx and CO/CuOx" written by Mgr. Filip Dvořák, the PhD. applicant. Therefore I would like to offer my comments and questions for consideration by the committee and the applicant.

The thesis gives a generally good impression and all the parts fit well within the scope of the title. The topic is at the peak of interest, the choices of the measurement and analysis methods are appropriate. Every major part of the thesis brings some important contribution to the field.

The introduction and the methods sections are well-written and concise, the language is simple and clear. The experimental techniques are explained to sufficient extent. The references are abundant and leave no doubt about the efforts made to find the relevant sources of information. The applicant decided to present his results in form of scientific papers, inserted into the thesis along with brief comments. Since most of the papers are already published (and cited) in high-impact journals with peer review, it ensures certain level of quality and professional editing. It also demonstrates the ability of the applicant to work in a large team of both young and seasoned researchers. His experience with work at a synchrotron beamlines and in laboratories abroad definitely improves his career prospects.

The results reveal some highly interesting properties of ceria catalyst model systems, that can have direct consequences for the applications in catalysis. Exactly such kind of precise understanding is the advantage that research can offer to technology. In particular, it is the influence of growth conditions on the morphology of ceria/Cu thin films and controlling the level of ceria reduction and following the reaction with water. The facts and conjectures drawn from the experiments have a potential impact in the catalysis industry. In addition, the study of reduction dynamics of Cu2O surface in near-atmospheric pressure STM is an excellent example of using this technique to visualise mesoscopic processes in surface chemistry. The thesis supplies sufficient evidence that the applicant is able to come up with new ideas and conduct an independent scientific research of high value.
As I was explicitly asked to, I provide some critical remarks. Since the scientific approach and logic seems valid in most cases, the criticism is rather about technicalities and the questions are mostly driven by interest. In particular, the formatting of the thesis is inhomogeneous and the typesetting is of an average quality. Second, the number of coauthors of the presented works hides the individual contribution of the applicant. Third, there are several minor issues with the content; a question is added whenever I felt it deserves an explanation.

1) Formatting

It was not stated which program was used for typesetting, however the result is not optimal. Mainly as a result of article printout inclusion, the thesis suffers with some typographical errors. In particular, the page number positioning, margin layout and references are inconsistent. Also, some references are duplicated and thus dispersed around the book. Included article printouts are very dense, and therefore difficult to read. The text would gain much better homogeneity with hyphenation. Occasionally, some paragraphs span over entire pages.

2) doi://10.1021/jp1121646

This article is experimentally characterizing the growth of ceria films with average thickness of 5ML. under specific temperature dynamics and O2 treatment. The authors claim to gain control over step density (related to terrace sizes). The story appears well-thought, the results are good-quality. The text contains a lot of comparisons to other works. That is not an error, however, I find this style of writing more appropriate for a review paper than for an experimental report.

There are other few minor issues commented below, with questions:

Q1: I found no note in the entire text about the reproducibility. Can you comment on that?

p.7498: ...The reduced diffusion rate on the the interfacial layer is most likely a consequence of an increased binding energy of ceria on ceria..

Q2: Although this seems believable, I'd appreciate a detailed explanation, why for this case such relation is valid. Is there a general relation between a diffusion barrier landscape and the binding energy between an adsorbate and a substrate? Do you know any examples, where the diffusion barrier is directly related to the binding energy and where it is not?

p.7498: ..., a deviation of about 5% is expected. The moire pattern is observed also in the second and third layer..
Q3: Clearly this is quite mysterious. While the 3:2 lattice const. ratio ensures that ceria layer has i) to reconstruct or ii) create a decoupled structure, the observed Moire periodicity is extended: 60A. Considering that the possible Moires can vary a lot with subtle changes of the lattice const. ratios, it is not quite clear how the requirement for the enormous 5% deviation from the 1.5 ratio was obtained? What are the possible Moires and why the 60A one is realised?

p.7499, 7500: Captions of Figs.4,5 - the notion of O2 treatment is missing for 650C annealing.

Q4: In the Figs.4 and 5 there is not the same treatment set - is it because of a lack of data?

p.7500: The LEED patterns qualitatively reflect the characteristic lateral sizes of the ceria islands...

Q5: The LEED images at the first glance show a varying width of the spots. (This seems as a suggestion for a decent SPA-LEED study) However, in the presented LEED images, the varying width cannot be fully recognized. Can the author show the averaged spot profiles (using the video camera images) for each case?

3) doi://10.1021/jp409220p
The central point of this study is a systematic STM, LEED and XPS characterization of ceria reduction and oxidation. The level of oxidation is varied using O2 treatment and Ce deposition. The networks of vacancy determine the reconstruction observed in the LEED. LEED patterns are linked to XPS/RPES ratios of Ce3+ to Ce3+ and Ce4+ oxidation states. ISS is used to detect cracks in ceria layers, attributed to oxidation. The vacancy gradient from the surface to the bulk is discussed. The study is written clearly and brings a sound message. It is particularly convincing, since a combination of complementary techniques is used to obtain a full picture. Unfortunately, the proposed model of the 3x3 structure is lacking symmetry and in this work it is not supported by any theoretical calculation, although the stoichiometry fits well the experimental results.

Q6: At the end of the experimental section, STM instrument is said to lack the sample heating option. Does it mean that the samples were transferred from other instruments? How?

Q7: Let's assume that XPS stoichiometry can't serve as a primary means to determine that the surface is exactly in one of the 4x4, 3x3, 1x1, r7 structures. If only the LEED is used, what is the uncertainty (value/percentage) of the stoichiometry determination? Can the Ce deposition/O2 treatment be used to estimate this kind of information?

Q8: The proposed model for the stoichiometry of the 3x3 reconstruction is quite peculiar. What are the alternative models? Is it possible, that the structure is not maintaining the same number of vacancies in all the unit cells?

Q9: Is some kind of real depth-profiling possible, e.g. by SIMS?
4) Manuscript "Reaction pathways for reversible and irreversible decomposition of water on reduced ceria", intended for JPCC

Following the previous works, the authors use the four ceria stoichiometries to investigate the adsorption, reaction and desorption of water on this substrate. Using a combination of TPD, SRPES (core level components+RPES) and LEED they gather data that allow a mindful discussion about the chemical and physical processes, which H2O undergoes on the catalyst surface. The measurements can distinguish whether the water adsorption is dissociative or molecular and how the hydroxyl groups are recombined, depending on the temperature and ceria stoichiometry. The H2 production on ceria with reduced stoichiometry is linked to its reoxidation, as shown mainly by repeated adsorption-recombination-desorption cycles on variable-thickness layers.

This work deserves publication in the intended journal beyond any doubt. It represents a solid experimental approach to the description of such complex scenario and certainly brings new substantial information. However amendments are needed, since there are some concerns arising from the style of writing and certain statements.

First, there is some space for improvement in the introduction, which is quite complex and inaccessible for a newcomer. It could be a result of a too-big emphasis on providing a complete overview of all available sources and viewpoints on water interaction with ceria. I recommend shortening it by a paragraph or two and adding more focus on the questions that the results in the paper can answer. Second, there is a discussion section in the manuscript. However the experimental parts (i), (ii), and (iii) contain a number of interpretations and "minidiscussions" already. Third, the language suffers from some complicated constructions. I can understand that, since none of the authors is a native speaker. On the other hand a typical journal editor/referee could have a problem with that.

Examples of expressions:

a) ...and the reactivity of reduced ceria towards water.
b) The average stoichiometry of ceria obtained from XPS .. is related ..., which generally depends on ..., the ..., the ... and the thermal treatmnt.
c) ..is related to the absence of possibility..
d) The further indication of the lowered adsorption energy of the molecular water on reduced ceria..
e) The driving force for the .. of the recombinative water channel from ... can be associated .. -the readiness of ceria to ..., here, particularly ..

Finally, some questions arise:

p.16: The slow regime is connected to minor production of hydrogen on non-specific surface defects.
Q10: This interpretation points out a water-H2 conversion. However, the Fig.2 the TPD H2 signal seems to be copying the trend of the H2O production. Can the H2 signal simply originate from ionization of H2O in the QMS, as explained on p.9, at the end of section Results (I)?

Q11: What are the possible configurations of the "non-specific defects"?

Q12: Can the author evaluate the applicability of the findings to use ceria as a water-hydrogen converter?

5) doi://10.1021/ja408506y

This nanoscopic and mesoscopic study joins multiple surface-characterization techniques to image Cu2O exposed to reducing conditions (atmosphere of CO). Especially remarkable is the use of AP-STM in the mTorr range, which is a challenging experiment. The local measurements with atomic resolution is complemented by space-averaging AP-XPS and AP-IRRAS measurements under comparable conditions. An independent LEEM and u-LEEM dataset is shown in attempt to provide a mesoscopic perspective. Development of the surface morphology, phase transitions and their development in time are shown with atomic resolution. The paper is a substantial piece of work, demonstrating the great potential of the AP-STM in surface chemistry and catalysis. I have some minor objections and a question:

This part of the thesis gives an impression that the paper has been added in a hurry. I was somehow missing a Cu2O/hex and Cu2O/5-7 models and explanation in the introduction preceding the paper. The introduction is maybe too short. The expression "massive mass transfer" sounds exaggerated. It is difficult to distinguish the phases in Fig.2. and designations are missing.

Q13: How is the total oxygen amount on the observed area developing with time? How would the percentage of phases (Fig.2h) look like as a function of the total oxygen mass instead of time?

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