

**Review of the doctoral thesis:**

**Chemical reactivity of metal-supported ceria thin films: a density functional study**

by dr. Lucie Szabová

In this study computational techniques are used to investigate the catalytic system formed by an ultrathin film (1 or 2 monolayers, ML) of (111) cerium dioxide ( $CeO_2$ , ceria) deposited onto a copper substrate exposing the (111) surface.

More specifically, the following systems have been considered:

- stoichiometric 1 ML ceria film
- defective 1 ML ceria film with oxygen vacancies
- stoichiometric 2 ML ceria film
- defective 2 ML ceria film with oxygen vacancies

Moreover, the reactivity towards water adsorption of the above systems has been addressed.

The subject of the thesis is very topical, as there is currently a great research focus on ceria based materials, due to their very important technological applications in the fields of environmental protection and clean energy production.

The influence of both the metallic substrate and the finite thickness of the oxide layer on the atomistic and electronic structure of the oxide component is thoroughly analyzed.

The computational methodologies of which use has been made are of state-of-the-art level. In particular, the DFT +U technology has been applied to overcome the strong correlation between the  $f$  electrons in reduced  $Ce^{3+}$  centers, thus allowing the correct treatment of both the charge transfer from the metallic support to the oxide component and the simulation of defects in the form of oxygen vacancies.

This is the first study in which the connection between the experimentally observed peculiar properties of the  $Cu(111)/$  ultrathin ceria film system (which were addressed in previous work by the same author at the Charles University in Prague) and its atomistic and electronic configuration is analyzed.

The obtained results point out the most critical factors determining the different behavior of ultrathin ceria films as compared to more conventional thick films on  $Cu(111)$ , namely:

- an important strain of the first ceria ML, which can be partially relaxed by the creation of oxygen vacancies and/or reduced  $Ce^{3+}$  centers
- the preference of oxygen vacancies to “float” on the ceria film (they tend to migrate at the outer  $O$  layer in the 2 ML system); this is well explained with the charge transfer from the metallic support to the first

layer of  $Ce$  ions which leads to their complete reduction; then, if a second unreduced  $Ce$  layer is present, oxygen vacancies will prefer to localize there, since the extra electronic charge left behind by them can be better transferred to a  $Ce^{4+}$  center

- the stronger adsorption energy of water on the 2ML ceria film with respect to unsupported thicker films, which is explained in terms of the electrostatic effect brought about by the underlying copper/ceria interface where all the cerium ions of the first ML are in the +3 reduced form
- the striking preference of water to adsorb molecularly on the 1ML system, as compared to both the 2ML and unsupported thicker ceria films

The scope of these fundamental points is not limited to the system considered here, but can be of significant help in the study of other metal/thin film oxide systems.

The thesis is well written, the pertinent literature has been thoroughly reported and critically evaluated. The goals, work done and obtained results have been clearly exposed and developed, suggesting that the author has a good ability to produce original scientific work.

Overall, my opinion about this thesis is very positive.

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Yours faithfully  
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