

### 3P079

#### Chemical reactivity of metal-supported ceria thin films: A DFT+U study

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#### [Introduction]

Environmental protection together with the attempts for finding new, cleaner sources of energy gains more and more importance in the present time. Polymer electrolyte membrane fuel cells (PEMFC) are among the most promising technologies for portable energy sources. Highly efficient catalysts are necessary to operate efficiently these fuel cells as well as to produce the necessary fuel. The most used technology to produce H<sub>2</sub> for fuel cells is steam reforming with water gas shift reaction (WGS) or alcohol decomposition.

The development of new, cheaper and more effective catalysts is focused on heterogeneous catalysts composed of noble metal materials supported on or dispersed in metal-oxides. Cerium oxides are frequently used as a support for catalysts for WGS [1] or preferential CO oxidation [2]. The present work is focused on investigating the physical and chemical properties of ultrathin ceria films supported by Cu(111).

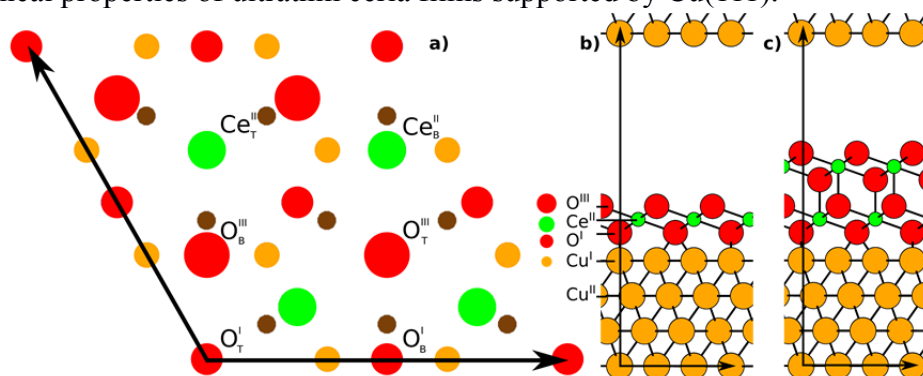


Figure: Top view of the 1 ML CeO<sub>2</sub>/Cu(111) interface (a). Side view of a supercell for calculations of 1 ML (b) and 2 ML (c) CeO<sub>2</sub>/Cu(111) systems

#### [Method]

The calculations are based on DFT using PBE exchange-correlation functional. The plane wave pseudopotential method is used as implemented in the PWscf code of the Quantum ESPRESSO distribution employing Vanderbilt ultrasoft pseudopotentials. In order to provide the correct insulating description of Ce<sub>2</sub>O<sub>3</sub>, we use GGA functional with addition of the Hubbard-U term in the implementation of Cococcioni and de Gironcoli.

### [Results and Discussion]

We provide evidence of the influence of film thickness on the electronic and structural properties as well as on the reactivity of new system consisting of ultrathin ceria films supported on Cu(111). The theoretical calculations together with STM experiments show that one monolayer (ML) thin film of ceria on Cu exhibits differences in strain buildup, charge and the structure of oxygen vacancies compared to thicker ceria layers on Cu. In particular the experiment revealed a 2x2 pattern of bright spots in the STM image of 1 ML film in contrast with simple 1x1 pattern in thicker films, in agreement with simulated STM images shown in the figure. The distinct properties of the 1 ML film are ascribed to pronounced finite size effects when the limiting thickness of the oxide and the proximity of the metal substrate cause significant rearrangement of charges and change in preferential site for oxygen vacancies formation compared to thicker ceria slabs [3].

Figure 2: Simulated STM image of 1 and 2 ML CeO<sub>2</sub>/Cu(111)

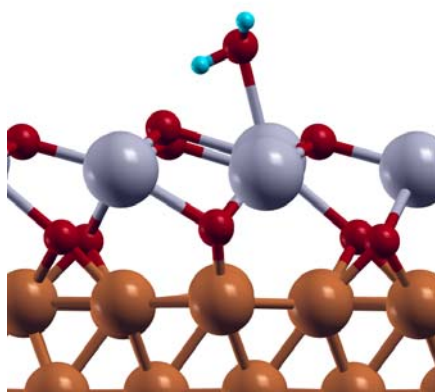
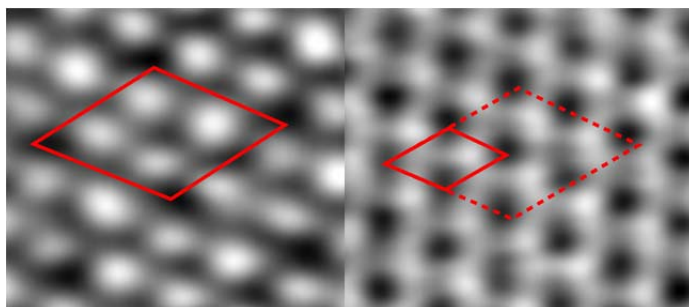


Figure: Molecular water adsorption on 1 ML CeO<sub>2</sub>/Cu(111)

The thickness of the film is important also for the reactivity of thin ceria films. The adsorption and dissociation properties of water are strongly affected by the size and electronic effects. The water adsorption is more stable on 2 ML film than on 1 ML ultrathin film or thick ceria slabs. In contrast with thicker ceria films, the unique structural flexibility and electronic properties of the ultrathin 1 ML ceria film supported by Cu strongly prefers molecular adsorption of water to dissociative adsorption and allows for strong structural and electronic relaxation upon water adsorption.

### [References]

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