

ORIGIN OF THE SURFACE-ORIENTATION DEPENDENCE OF THE REDUCTION KINETICS OF ULTRATHIN CERIA

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Performance of catalytic redox reactions depends crucially on the oxygen storage and release capability of the catalyst and with that the catalyst's defect chemistry. Here, we show that the surface defect chemistry of cerium oxide, a prototypical reducible oxide, differs markedly between two surface terminations. The results are in good agreement with density functional theory calculations and provide important guiding factors for rational design of industrially relevant catalysts. The study is conducted by preparing (100) and (111) terminated nanoislands of cerium oxide next to each other on Cu(111). Leveraging the benefits of full-field imaging capability of photoemission electron microscopy (PEEM), we follow the structural and chemical properties of the nanoislands under reducing hydrogen atmosphere simultaneously and in situ. The results, summarized in Figure 1, directly reveal different overall reducibility that can be traced to equilibrium oxygen vacancy concentrations via a kinetic model. The density functional theory calculations provide further details regarding the equilibrium co-ordination of oxygen vacancies for both surface planes. Conjoining the two, the unique simultaneous nature of the PEEM-facilitated structure–activity relationship study allows us to separate the thermodynamics of reduction from the kinetics of oxygen exchange, revealing the fact that the difference in reducibility of the two surfaces of ceria is not determined by the kinetic rate constants of the reduction reaction, but rather by the equilibrium concentration of oxygen vacancies, an information that has not been provided by the isolated model system approach to date. Surprisingly, the reason for the different reducibilities is a purely geometric one: the creation of nearest neighbor oxygen vacancies.

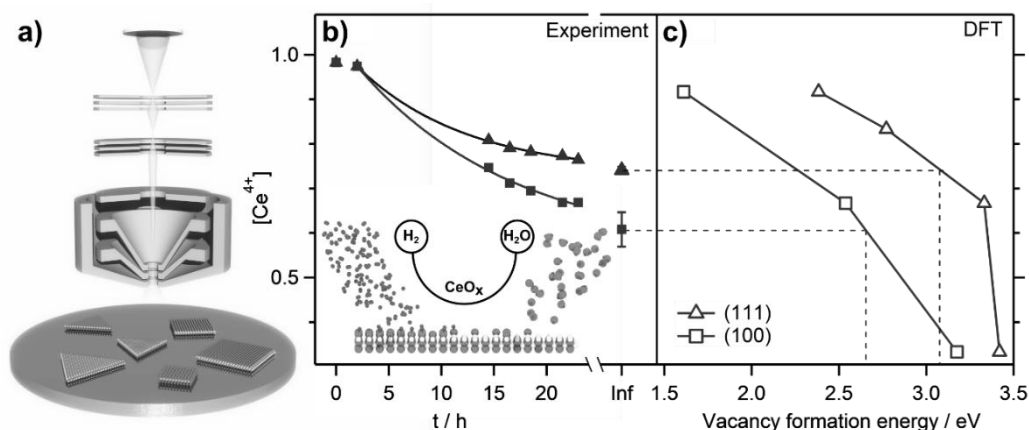


Figure 1 – (a) Schematics of the experimental layout. (b) Ce⁴⁺ content of ceria islands over time in hydrogen and fits to a kinetic model. (c) Oxygen vacancy formation energies as a function of Ce⁴⁺ content calculated using DFT from a 3ML slab.