

## ***In situ* monitoring of chemical processes at cerium oxide model catalyst surfaces using low-energy electron microscopy**

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The versatility of the reducible oxide  $\text{CeO}_2$  leads to a wide variety of applications, e.g., in the growing fields of renewable energy harvesting, storage, and chemical conversion. Knowledge based optimization of the catalyst performance for the desired usage requires a fundamental grasp of both the intrinsic materials properties of the oxide as well as its exerted functionality in the physical and chemical processes that take place in reactive environments. This approach calls for a full *in situ* methodology including (i) its controlled synthesis under well-defined experimental conditions and (ii) its characterization in a reactive environment mimicking the essential features of the intended application.

Here, we present our efforts in achieving this ambitious goal based on low-energy electron microscopy and photoemission microscopy studies of inverse model catalyst architectures involving  $\text{CeO}_2$  microparticles on transition metal surfaces under near-ultrahigh vacuum conditions. Starting from the growth of well-defined ceria on single crystal surfaces such as Ru(0001), Cu(111), and Pt(111), we demonstrate a strong oxide-metal support interaction governing both oxide morphology as well as chemical reactivity. Depending on interfacial structure and growth kinetics, both ceria(111) and ceria(100) facets develop, exerting different chemical properties and thermal stability. In reactive atmospheres involving methanol or  $\text{H}_2$  exposure at elevated temperatures, we are able to follow the reduction and transformation of the oxide microparticles into cubic and hexagonal  $\text{Ce}_2\text{O}_3$  locally and in a time-resolved fashion. Furthermore, while the oxide is particularly stable at ruthenium surfaces maintaining an abrupt interface to the support, a higher oxide reducibility as well as pronounced surface alloying is observed for ceria/Pt(111), leading to a dynamical reorganization process of the oxide involving substantial mass transport during reoxidation by exposure to  $\text{O}_2$ .