

In situ study of the identification of the active sites during oxidation of Ce₂O₃ on Ru(0001) by CO₂

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Cerium oxide is of great technological interest due to its relevance in various catalytic applications. An inverse model catalyst such as cerium oxide on Ru(0001) can be used to understand the fundamentals behind catalytic processes. For the production of methanol from CO₂ and H₂, oxygen vacancies, as found on reduced ceria, are necessary to activate the CO₂ molecules [1]. Ceria reduction may be achieved by, e.g., exposure to H₂ at elevated temperatures [2] or by thermal treatment [3]. We have studied the interaction of CO₂ with thermally reduced cerium oxide islands on Ru(0001) in situ with low-energy electron microscopy (LEEM) and spatially resolved x-ray absorption spectroscopy (XAS-PEEM) at the ELETTRA nanospectroscopy beamline. The structure and composition of the islands were analyzed by XAS-PEEM and dynamic (real-time) intensity-voltage (I(V))-LEEM measurements. In particular, the oxidation state was derived from specific islands by fitting the data by a linear combination of reference spectra of Ce₂O₃ and CeO₂. Partial reoxidation by exposure to CO₂ was achieved at 550 °C, which agrees well with other studies that oxidized cerium oxide on other metal substrates [4,5]. From this analysis we derive a correlation of the oxidation state and the size of the island, revealing that larger islands are reduced less throughout this process. We attribute this finding to a larger thickness of these islands (Fig. 1). Furthermore, the different electron escape depths from I(V)-LEEM and XAS-PEEM allow comparing the oxidation state of the topmost layers and the bulk. Also, fitting the I(V)-LEEM data by a linear combination of reference spectra was used to derive a pixel resolved map of the oxidation state providing further insight into the distribution of active sites of the cerium oxide islands on the few nanometer scale.

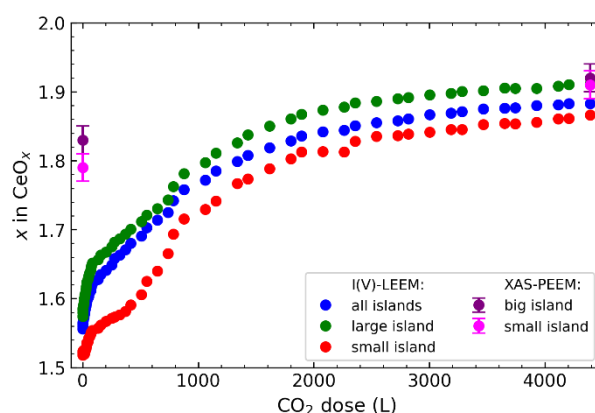


Fig. 1. Reoxidation of cerium oxide islands by exposure to CO₂ at 550 °C obtained from XAS-PEEM and I(V)-LEEM.

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