In situ identification of the active sites during oxidation of Ce_2O_3 on Ru(0001) by CO_2

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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 CO_2 and H_2, oxygen vacancies, as found on reduced ceria, are necessary to activate the CO_2 molecules [1]. Ceria reduction may be achieved by, e.g., exposure to H_2 at elevated temperatures [2] or by thermal treatment [3]. We have studied the interaction of CO_2 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 Ce_2O_3 and CeO_2, respectively. Partial reoxidation by exposure to CO_2 was achieved at 550 °C, which agrees well with previous 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, which is possibly related to the higher thickness of these islands (Fig. 1). Furthermore, the different probing depths of 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 cerium cation oxidation state providing further insights and enabling statistical analysis of the distribution of reactive sites of the cerium oxide on the few nanometer scale.

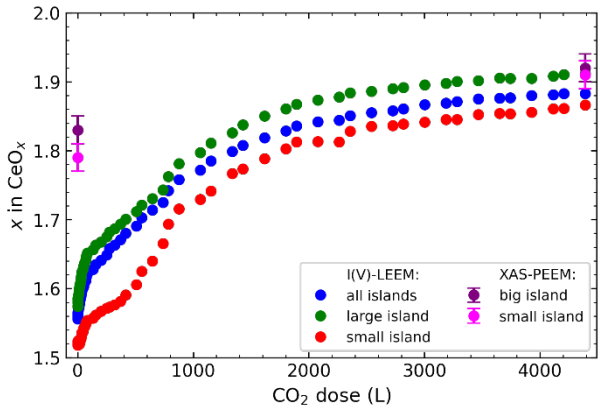

Figure 1: Reoxidation of cerium oxide islands by exposure to CO_2 at 550 °C obtained from *in situ* XAS-PEEM and I(V)-LEEM analyses.

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