Growth dynamics and chemical reactivity in Sm-doped cerium oxide inverse catalytic model systems

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Cerium oxide has been successfully employed in heterogeneous catalysis for several decades due to its attractive chemical properties and high oxygen-storage capacity. Fundamentally, these properties are closely linked to its flexible cubic crystal structure, allowing facile changes between the cerium cations' +4 and +3 oxidation states and the creation of oxygen vacancies, which have been associated with an increased activity in many chemical reactions. These findings suggest a route for further enhancing its activity by promoting the formation of Ce^{3+} species through alloying using transition or rare-earth (RE) metals.

Here, we present our efforts to characterize the structural and chemical transformations in Sm-doped CeO_x inverse catalytic model systems during growth and under reaction conditions using in situ low-energy electron microscopy and micro-diffraction (LEEM/µ-LEED), along with X-ray absorption spectroscopy combined with photoemission electron microscopy (XAS-PEEM). On the Ru(0001) surface, comparing sequential RE metal evaporation to co-evaporation shows that the nanoparticle shape, morphology, and chemistry are strongly influenced by the choice of synthesis method, resulting in a modification of the reducibility of the nanoislands and an increased catalytic activity in CO_2 activation, as determined by near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) [1].

Utilizing a similar preparation approach for Sm-CeO_x on the Cu(111) surface, which enables the selective growth of CeO_2(111) and CeO_2(100) nanoislands through a suitable choice of growth parameters, reveals an increased chemical complexity in the mixed oxide model system. Specifically, we demonstrate that the interaction between the post-deposited Sm metal and the CeO_2 nanoislands is influenced by their facet orientation. Furthermore, we have found that the growth characteristics differ markedly from those in the ruthenium case, highlighting a significant influence of the dopant-support interaction that leads to the formation of metastable Sm-rich structures [2]. These observations have motivated an in-depth study of the "pure dopant" Sm_2O_3 material system on both Ru(0001) [3] and Cu(111) [4] surfaces, with the latter case revealing a rather unexpected structural variety of the sesquioxide both during growth and under oxidizing and reducing conditions.

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