Correlating LEEM and NAP-XPS in ceria-based model catalysts for CO_2 activation.

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Reducible oxides play an important role in catalysis because of their ability to store oxygen and undergo redox changes. Cerium oxide is commonly used in various fields of heterogeneous catalysis due to its ability to change between Ce^{4+} and Ce^{3+} states under reducing and oxidizing conditions [1]. Additionally, Ce^{3+} cations are known to actively participate in methanol synthesis, where they have been suggested to be the active phase [2]. Therefore, catalytic activity can be improved by increasing the Ce^{3+} sites and stabilizing them through alloying with trivalent, catalytically active rare-earth metals that also form cubic sesquioxides (RE_2O_3), such as Sm [3].

Using low-energy and X-ray photoemission electron microscopy (LEEM/XPEEM), we explore how Sm modifies the properties of the well-known CeO_2 islands on Ru(0001) [4,5]. We show that Sm incorporates into the CeO_2 ceria lattice, causing a lattice expansion that, along with charge compensation due to the lower oxidation state of Sm, promotes the formation of intrinsic oxygen vacancies. Additionally, the incorporation of Sm stabilizes the reduced ceria lattice, promoting the phase transition to hexagonal Ce_2O_3. Complementary in situ near-ambient-pressure x-ray photoemission spectroscopy (NAP-XPS) measurements have shown the presence of a component associated with the carboxylate species $CO_2^{\delta-}$, a signature of CO_2 molecule activation, only in samples containing Sm. Therefore, the presence of Sm at the surface enhances the activation of CO_2 compared to undoped CeO_x/Ru(0001). This finding is supported by DFT calculations, which show a negative adsorption energy for the CO_2 molecule on the doped ceria.

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