

The role of samarium in the catalytic activation of CO₂ over cerium oxide nanoparticles supported on Ru(0001)

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In cerium-based inverse catalyst systems, the Ce³⁺ states have been shown to be the active sites for methanol synthesis [1,2]. This suggests that the activity can be enhanced by promoting those through alloying with trivalent, catalytically active rare-earth metals that also form cubic sesquioxides (RE₂O₃), as Sm [3].

Here, we present a structural and chemical investigation by low-energy and X-ray photoemission electron microscopy (LEEM/XPEEM) of the Ce_{1-x}Sm_xO_{2-δ}/Ru(0001) model system, measured at the Nanospectroscopy beamline at the synchrotron Elettra (Trieste, Italy). Further characterization at more realistic conditions was performed by near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) at the CIRCE-NAP beamline at the synchrotron ALBA (Barcelona, Spain).

We show that, with the deposition of Sm, the CeO₂ (111)-oriented islands undergo a structural change, concomitant with a partial conversion from Ce⁴⁺ to Ce³⁺. Subsequent exposure to reducing (H₂) and oxidizing (CO₂) conditions at moderate pressures (1×10⁻⁶ mbar), results in enhanced ceria reduction and reoxidation as compared to undoped CeO₂/Ru(0001) [4]. NAP-XPS measurements at higher pressures (up to 1 mbar) show similar results under H₂ and CO₂ exposure. Furthermore, when exposing the sample to different mixtures of H₂/CO₂, the spectra show features associated with the carboxylate species CO₂^{δ-} [1], i.e., a fingerprint of CO₂ molecule activation, that significantly increase in the presence of Sm. The presence of more Ce⁴⁺ in the Ce3d spectra at the same time as the active phase appears suggests that the Ce³⁺ is participating in the activation of the CO₂^{δ-} molecule and, thus, rapidly oxidizing to Ce⁴⁺ in a dynamic equilibrium where Sm prompts the facile and fast exchange of Ce³⁺/Ce⁴⁺ cations compare to bare CeO₂. Therefore, the complex Ce_{1-x}Sm_xO_{2-δ} surface likely promotes the activation of the CO₂ molecule compared to the undoped CeO_x/Ru(0001).

Keywords: Samaria, model system, NAP-XPS, LEEM

References

- [1] J. Graciani et al. *Science* 345, 546 (2014)
- [2] S. D. Senanayake et al. *J. Phys. Chem. C* 120, 1778 (2016)
- [3] Y. Wang et al., *Top. Catal.* 61, 1227 (2018)
- [4] D. C. Grinter, S. D. Senanayake, and J. I. Flege, *Appl. Catal. B: Environmental* 197, 286 (2016)