

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

Raquel Sánchez-Barquilla^{1*}, Carlos Morales¹, Rudi Tschammer¹, Lars Buß¹, Dominic Guttman¹, Virginia Pérez-Dieste², Tefvik Onur Mentés³, Lilia Cojocairu³, Matteo Jugovac³, Andrea Locatelli³, Jens Falta⁴, Fabian Rachow¹, Jan Ingo Flège¹

¹*Applied Physics and Semiconductor Spectroscopy, Brandenburg University of Technology Cottbus-Senftenberg, 03046 Cottbus, Germany*

²*ALBA Synchrotron Light Source, 08290 Cerdanyola del Vallès, Barcelona, Spain*

³*Elettra-Sincrotrone, AREA Science Park 34149 Basovizza, Trieste, Italy*

⁴*Institute of Solid State Physics, University of Bremen, 28359 Bremen, Germany*

**sanchez@b-tu.de*

1. Introduction

The interaction between metal and oxide is critical when considering the hydrogenation of CO₂ into hydrocarbons. In this context, the inverse catalyst architecture, where the metal oxide is anchored on a metallic support, has shown higher activity than its traditional counterparts due to the strong metal-oxide interaction, which shows its maximum complexity in this configuration as reactants can interact with defect sites from the metal oxide nanoparticles, the metallic support, or the metal-oxide interface. For example, in cerium-based inverse catalyst systems, the Ce³⁺ states have been shown to provide active sites for methanol synthesis [1,2], suggesting that the activity can further be enhanced by promoting those through alloying with trivalent, catalytically active rare-earth metals, such as Sm [3].

Here, we present an *in situ* near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) study of the effect of Sm doping on the CeO_x/Ru(0001) model system, measured in the CIRCE-NAP beamline at the synchrotron ALBA (Barcelona, Spain). We also present low-energy and X-ray photoemission electron microscopy (LEEM/XPEEM) experiments performed at the Nanospectroscopy beamline at the synchrotron Elettra (Trieste, Italy), which give real-time insights into the formation and structure of the CeO_x(111)/Ru model system and the effect of Sm alloying.

2. Material and methods

Epitaxial thin films of Ru(0001) grown on Al₂O₃(0001) were used as substrates in this study. These samples can be cleaned in ultra-high vacuum (UHV) conditions by successive cycles of annealing up to 500°C in an oxygen atmosphere ($P_{O_2} = 5 \times 10^{-7}$ mbar). Metallic cerium was evaporated using an e-beam evaporator under an oxygen atmosphere at 5×10^{-7} mbar in a preparation chamber with a base pressure of 7×10^{-10} mbar. During evaporation, the samples were heated between 500°C and 800°C. Low-energy electron diffraction (LEED) measurements show epitaxially grown CeO₂ islands in (111) orientation. Finally, metallic samarium was evaporated at room temperature onto these samples using an e-beam evaporator under UHV conditions. At ALBA, *in situ* XPS and X-ray absorption spectroscopy (XAS) measurements were carried out at pressures between UHV conditions and 1 mbar, including exposure to H₂, CO₂, and a mixture of both gases. At Elettra, the samples were structurally and chemically characterized *in situ* by XAS and LEEM intensity-voltage curves.

3. Results and conclusions

The ceria growth dynamics and chemistry [4] and subsequent alloying with metallic Sm were studied by LEEM and XPEEM, observing an initial reduction of as-grown, almost fully oxidized CeO₂(111) islands. Subsequent exposure to H₂ at 400°C and moderate pressure (1×10⁻⁶ mbar) reveals notable changes in the Ru(0001) surface and enhanced ceria reduction as compared to undoped CeO₂/Ru(0001), while exposure to CO₂ at the same conditions promotes ceria oxidation.

In situ NAP-XPS measurements allow more realistic conditions typically used in catalysis reactors and to follow reaction intermediates adsorbed at the catalyst surface. Figure 1 shows the O1s and Ru3d+C1s XPS spectra of Sm_xCe_{1-x}O_{2-δ}/Ru(0001) under UHV conditions at 400 °C and under 1 mbar with different H₂/CO₂ ratios. In the O1s region (left), at 537 eV, a component appears in the presence of CO₂, which further increases when more CO₂ is added to the mixture. This component is associated with the carboxylate species CO₂^{δ-} [1], i.e., a fingerprint of CO₂ molecule activation, and can also be seen in the Ru3d + C1s region (Fig.1, right) at 290 eV, increasing with the presence of CO₂ in the same way. The insert in Fig. 1 shows the C1s region for the CeO_x/Ru(0001) sample, where the CO₂^{δ-} active phase cannot be seen. Therefore, the presence of Sm at the surface likely promotes the activation of the CO₂ molecule compared to the undoped CeO_x/Ru(0001).

Combining multiple techniques helps to understand each constituent's role and their synergistic interaction in the activation and hydrogenation of CO₂ molecules, thereby facilitating the rational design of a powder-based, highly efficient catalyst as the next logical step.

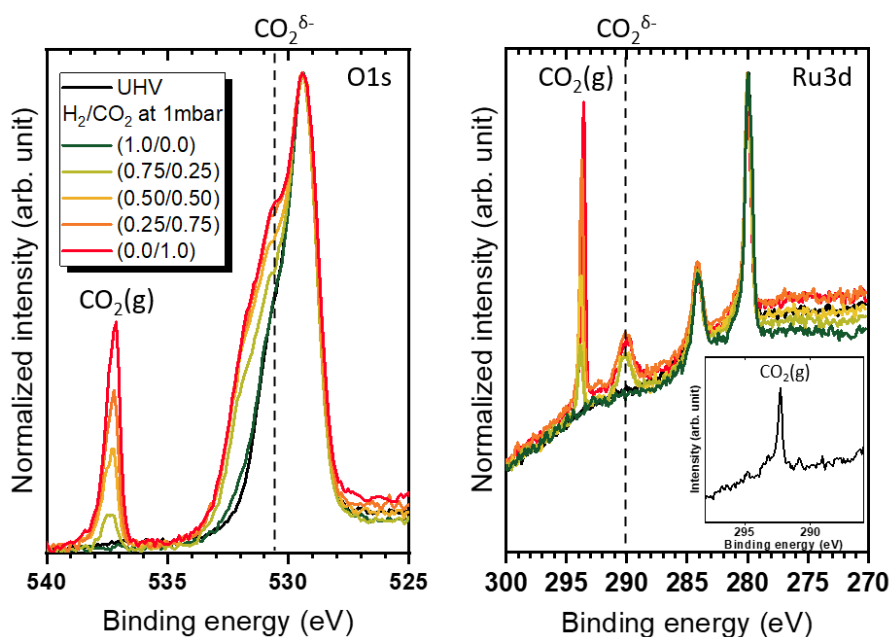


Figure 1. O1s (left) and Ru3d+C1s (right) XPS spectra measured in UHV and at a total gas pressure of 1 mbar, with different H₂ and CO₂ mixtures.

5. 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, S. Hu, Q. Xu, H. Ju, and J. Zhu, *Top. Catal.* 61, 1227 (2018)
- [4] D. C. Grinter, S. D. Senanayake, and J. I. Flege, *Appl. Catal. B: Environ.* 197, 286 (2016)