# Combining X-ray absorption and diffraction to relate structure to the activity in catalysts for $CO_2$ valorization reactions

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The development of effective catalytic processes for the conversion of $CO_2$ into value-added chemicals or fuels, such as methanol synthesis or the dry reforming of methane (DRM) relies strongly on a rational catalyst design, which in turn requires an in-depth understanding of structure-activity relationships. Due to the inherent complexity of heterogeneous catalytic systems, an arsenal of complementary techniques is required to characterize the catalytic structure (and dynamics thereof) from the atomic-to-nanoscale (under reaction conditions). In this talk, we show how the application of combined X-ray powder diffraction (XRD) and X-ray absorption spectroscopy (XAS) allows obtaining the oxidation state, the local and (nano)crystalline structure of the catalysts providing the basis for the formulation of structure-performance relationships in catalysts for $CO_2$ valorization reactions.

In the first example, we demonstrate how a combined *operando* XAS-XRD experiment allowed us to relate the evolution of the structure of $In_2O_3$ nanoparticles (NPs) to their activity for $CO_2$ hydrogenation to methanol.[1] The experiments revealed a reductive amorphization of the $In_2O_{3-x}$ nanocrystallites with time on stream (TOS), leading ultimately to an over-reduction of $In_2O_{3-x}$ to (molten) $In^0$, in a process that is linked to catalyst deactivation. When the $In_2O_3$ NPs were supported on a nanocrystalline monoclinic $ZrO_2$ support, we observed the stabilization of the oxidation state of In via the formation of a solid solution m-$ZrO_2$:In.[2] In the second example, we explore a Ni-Fe-based catalyst for the DRM. Combined, *operando* XAS-XRD experiments allowed us to probe the dynamics of Ni-Fe alloying/dealloying with the formation of FeO to explain the superior stability of the NiFe catalysts compared to a Ni-based analogue, due to a Fe-$FeO_x$-based redox cycle.[3] In the last example, combined XAS–XRD experiments are used to shed light on the formation of $Ru^0$ nanoparticles (ca.1 nm) via their exsolution from defective, fluorite-type $Sm_2Ru_xCe_{2-x}O_7$ solid solutions. The resulting exsolved nanoparticles show a high activity and stability for the DRM.[4]

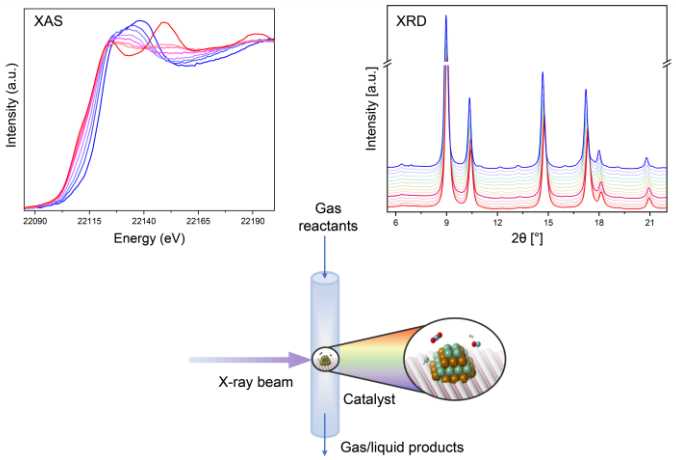


**Figure 1**. Top: Ru K-edge XAS and XRD (0.5 Å) data collected in situ under the reductive treatment of $Sm_2Ru_xCe_{2-x}O_7$, (10 % $H_2/N_2$). Bottom: Schematic illustration of the combined XAS-XRD experiments using a capillary flow reactor.

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