



	Experiment title: Unveiling structural and electronic properties of ZrZnCeO_x catalysts for CO₂ valorization: a combined XAS/PXRD study	Experiment number: A-31-1-161
Beamline: BM31	Date of experiment: from: 05/10/2021 to: 11/10/2021	Date of report:
Shifts: 9	Local contact(s): Dragos constantin Stoian, Wouter Van beek	<i>Received at ESRF:</i>
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Report:

In a waste-to-value perspective, CO₂ direct conversion to hydrocarbons and olefins is generating a great interest in the scientific community in the last decade[1]. In this regard we are investigating tandem catalysts formed by physically mixed ZrO₂/CeO₂ based oxides with zeolites/zeotypes[2]. The former catalyst hydrogenates CO₂ to methanol, immediately converted to propane/propene by the latter catalyst. Whilst methanol to hydrocarbons (MTH) reaction has been widely investigated, CO₂-to-methanol is of great interest since being the limiting reaction of the tandem catalyst. This reaction requires a catalyst able to successively split H₂ molecule and parallelly activate CO₂. The latter step is catalysed by presence of oxygen vacancies (V_O) forming reactive carbonates.

In the last years we then prepared and characterized Zn-doped ZrO₂ catalyst[3,4]. For these catalysts, while PXRD presented a single phase diffractogram, thus suggesting a solid solution scenario, Zn and Zr K-edge XAS unveiled Zn segregation as ZnO nanoclusters embedded in the ZrO₂ matrix. The so formed ZnO/ZrO₂ interface rich in V_O was then ascribed to the active phase towards CO₂ hydrogenation. Recently Wang et al. successfully prepared ZnCeZrO_x catalysts which, compared with ZnZrO_x, improved CO₂ conversion and propene and butene selectivities when combined with H-RUB-13 catalyst[5]. The promising CO₂ activation properties were ascribed to the high oxygen vacancies content of the catalyst solid solution.

Guided by the knowledge gained on ZnZrO_x catalysts, in experiment A-31-1-161 we deeply investigated the nature of the ZnCeZrO_x active phases after H₂ treatment at 400°C by performing combined PXRD/XAS measurements at Zn, Zr and Ce K-edges under in situ conditions for Zn_{0.5}Ce_{0.2}Zr_{1.8}O₄ catalyst.

In particular, the experiment A-31-1-161 at BM31 was aimed to investigate structural (average and local) and electronic variations of the catalyst as prepared and activated (H₂/400°C) by PXRD and XAS. The catalyst was loaded in quartz capillaries (φ=0.5/1.0 mm) and heated with an heat blower. Gas flow was provided by gas mixing set-up available at the beamline whilst products (mainly H₂O from surface reduction) were measured by

a downstream mass spectrometer. Diffraction cones were detected by a CCD camera whilst I_0 and I_1 were recorded by two ionization chambers. A third ionization chamber (I_2) was used for measuring reference materials (Zn/Zr metal foils and pure CeO_2 pellet) for energy alignment.

We performed high quality XAS measurements (EXAFS analyzable up to $k=14\text{\AA}^{-1}$) during steady states including :I) as prepared catalyst, II) after H_2 activation, III) prior and after reaction. Faster XAS scans (EXAFS analyzable up to $k=12\text{\AA}^{-1}$) followed by PXRD measurements were collected during H_2 activation and under $\text{CO}_2:\text{H}_2$ interactions.

In Figure 1a PXRD data measured for the as prepared and activated catalysts showed as the ZrO_2 tetragonal ($\text{P4}_2/\text{nmc}$) structure is preserved under activation. Hexagonal ZnO reflections, previously not observed from laboratories measurements can be distinguished from ZrO_2 one (Figure 1a inset), suggesting the presence of bigger ZnO clusters.

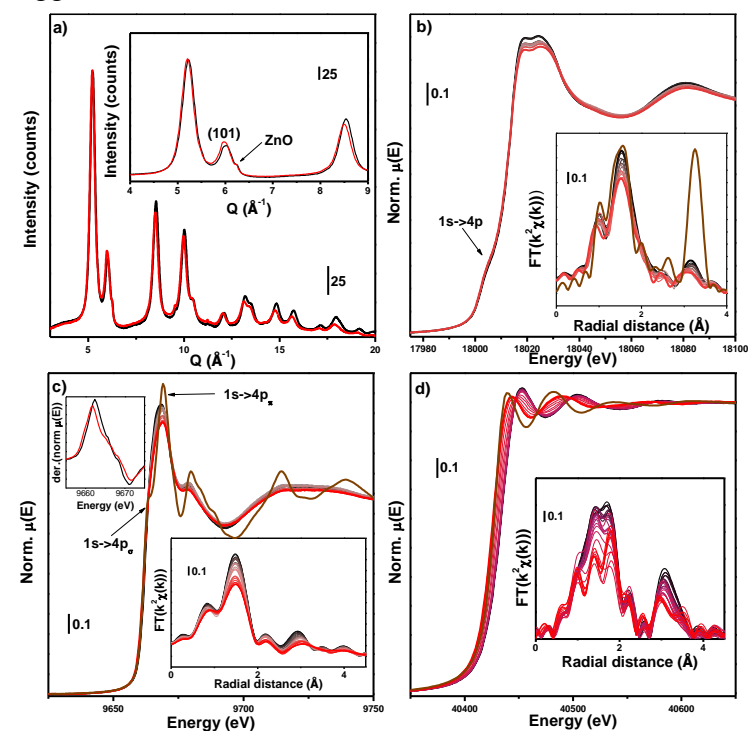


Figure 1 ZnCeZrO_x H₂ activation a) PXRD, b) Zr K-, c) Zn K- and d) Ce K-edges. Reference ZrO₂, ZnO and Ce(III)NO₃ are reported in brown. FT-EXAFS spectra transformed in the 2.5-11.0 Å⁻¹ range are reported in insets. Temperature increases from black to red colours.

solutions with ZrO_2 , Ce local structural reorganization might be related to the PXRD (110) Bragg peak intensity (Figure 1a) which counterintuitively increases at higher temperature.

These results are of outstanding quality from both XRD and XAS viewpoint and will be the basis on further studies on doped ZrO_2 catalysts. Moreover, the wide energy range reachable at BM31 allowed us to have a complete view of the as prepared and active catalyst structure: this outstanding dataset represents the core of a manuscript currently in preparation. It would be now of great interest to combine this multi-edge study approach with the BM31 PDF set-up (available from autumn 2022) under operando conditions during the CO_2 hydrogenation reaction. For this reason a dedicated proposal will be submitted in one of the next rounds.

References

- 1) Liu, Q., Wu, L., Jackstell, R. *et al.*, *Nat Commun*, 2015, 6, 5933
- 2) Ojelade, O. A., *et al.* *Journal of CO₂ Utilization*, 2021, 47, 101506.
- 3) Ticali *et al.*, *Catal. Sci. Technol.*, 2021, 11, 1249-1268
- 4) Salusso *et al.*, *J. Phys. Chem. C* 2021, 125, 40, 22249–22261
- 5) Wang *et al.*, *Chem*, 2020, 6, 12, 3344–3363

Zr K-edge (Figure 1b) presented a $1s \rightarrow 4p$ pre-edge associated to the ZrO_8 double tetrahedral coordination confirming the presence of tetragonal polymorph. EXAFS Zr-Zr second-shell intensity is dampened with respect to pure t- ZrO_2 suggesting the presence of Zr-Zn scattering path, as observed in ZnZrO_x case. Zn K-edge had similar whiteline as observed for ZnZrO_x catalysts: not well structured $1s \rightarrow 4p_{\sigma,\pi}$ transitions and weak EXAFS Zn-Zn second shell. Moreover Zn second shell presented a broadening towards higher radial distances during activation, evidence, as showed in ZnZrO_2 case, of the ZnO/ ZrO_2 interface. Differently from ZnZrO_x , a slight shift of Zn edge to lower energies under H_2 treatment was observed (Figure 1c), particularly visible in the spectra first derivative, suggesting an electronic variation of Zn in the ZnCeZrO catalyst. Interestingly, Ce K-edge showed a substantial Ce^{4+} reduction, reaching an edge energy lower than that observed for Ce^{3+} , suggesting formation of $\text{Ce}^{\delta+}$ ($0 < \delta < 3$) species. Moreover, Ce K-edge EXAFS presents a complex second shell dynamic, suggesting important variations of Ce local environment under activation. Since Ce is known to form solid