	Experiment title: CO_2 reduction over GaZrOx oxide: disclosing catalyst structure and V_O contribution through MES-PSD operando-XAS/PD	**Experiment number**: CH 6463
Beamline: BM31	**Date of experiment**: from: 20/02/2023 to: 28/02/2023	**Date of report**:
Shifts:	**Local contact(s)**: Dragos constantin Stoian ; Wouter Van Beek	*Received at ESRF:*

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Report:

In a sustainable CO_2 recycling economy, we are developing a combined catalyst for CO_2 direct conversion to high value products i.e., propane and propylene. After a thorough investigation of Zn-containing systems, we are currently exploring a GaZrOx/H-SSZ-13 bifunctional catalyst, guaranteeing an even higher performance while solving issues related to Zn mobility in tandem systems. Ga, being substitutional in ZrO_2 lattice, increases oxygen vacancies dispersion and catalyst stability whilst H-SSZ-13 acidity and pores dimension guarantees an extremely high C3 selectivity. Nevertheless, connecting catalytic properties to structural/electronic environment requires a deep understanding of this complex system.
Guided by the knowledge gained on ZnZrOx catalysts, in the experiment CH6463 we combined MES-PSD with operando-XAS/PDF at Ga K-edges during catalyst activation at 400C under H2/1bar and CO_2 hydrogenation to methanol under 10 bar of CO_2:H_2 (1:3).
High pressure reaction was performed by putting pressed and sieved catalyst in a 1mm quartz capillary. 10 bars were reached by using a portable box containing 4 mass flow controllers, 2 back-pressure regulators and 1 4-way valve prepared in our laboratories while heating was provided with an heat blower. XAS signal was recorded with two ionization chambers (I0 and I1) and a Fluorescence detector (I fluo). High energy PXRD patterns were measured with a 2M pylatus CdTe detector.
The experiment consisted in 3 main steps :

I) Sample activation. The catalyst was heated at 5C/min under He:H_2 (1:1, 50mL/min, 1bar) flow to 400C and it was kept at 400C for 30'.

II) Steady state reaction. Afer reaction we build up pressure in H_2 up to 10 bar and we switched to CO_2:H_2 atmosphere (1:3, 10 bar) for 1h in order to ensure to have reached steady state. CH_3OH production was observed with an online MS connected to the gas outlet.

III) Modulation. After having reached the steady states we started modulating between CO_2:H_2 and He:H_2. The total period length wa sof 40 minutes and we repeated 30 periods for a total of 22h experiment.

This protocol was repeted also with CO_2:H_2 (1:1) which is the ratio for CO_2 conversion to CO in order to distinguish different active sites. Moreover the experiment was repeated separately for Ga K-edge and PXRD measurements, leading to a total of 4experiments of 22h each.

The obtained results are of outdtanding quality from both XAS and XRD viepoints. An initial XAS data analisis showed as during modulation periods spectra changes were recorded in-phase with the modulation. The observed changes are in line with our first hypothesis were Ga tetrahedral and octahedral sites had different contributions towards CO_2 hydrogenation. Moreover a preliminar demodulation analysis showed a clear relation between the two Ga sites and the periods frequency.

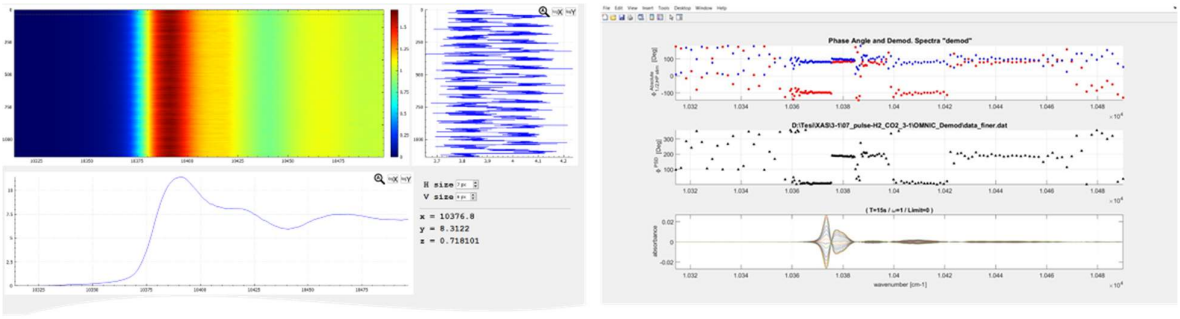

Figure 1 Left) Series of ga K-edge XAS data collected during CO2:H2 modulation. Right) Preliminar demodulation analisis of the obtained spectra

It is worthy to point out as the obtained high-quality/impact results were possible only thanks to the support of BM31 staff. The new PDF/XAS set-up lead to results unreachable anywhere else.

The obtained results will clarify the role of guest atom/host matrix and oxygen vacancies relation towards CO_2 conversion to hydrocarbons.