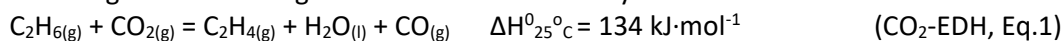




	Experiment title: Unravelling the role of low Z elements for Fe-based catalysts during CO ₂ -assisted ethane dehydrogenation	Experiment number: CH-6657
Beamline: ID20	Date of experiment: from: 03/05/2023 to: 09/05/2023	Date of report: 24/05/2023
Shifts: 15	Local contact(s): Dr. Alessandro Longo	<i>Received at ESRF:</i>
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Report: Summary

Ethylene is a petrochemically derived monomer and the largest from the olefins market, with an estimated annual increase rate of 4% per year. It is mainly produced through an energy demanding process, named steam cracking. The **on-purpose ethylene production** via the ethane oxidative dehydrogenation (EDH) route, implementing a catalyst, is considered the most attractive alternative to the conventional industrial process [1]. In EDH, the use of CO₂ as a soft oxidant (Eq. 1) is gaining more attention due to its environmental effects, mild oxidizing nature, compared to O₂ and its advantage in moderating the reaction exothermicity.



Our 5wt% Fe catalyst, supported on a mixed oxide of 10wt%NiO-MgO-ZrO₂, calcined at 700°C for 5 h, was found to be selective for C-H bond scission during CO₂-EDH at 650°C and atmospheric pressure, attaining 90% selectivity at C₂H₆ conversion level of ~23% [2]. However, the **role of the support**, mainly consisting of low Z elements, such as Mg and O, still awaits clarification. The aim of this proposal is to identify in situ, under reaction conditions, the electronic modifications occurring at the support structure, as they define the activity, selectivity and stability of the whole catalyst.

Experimental conditions

An operando XRS/XES study was performed in ID20, for three main samples: 1) 5 wt%Fe impregnated on previously synthesized MgO-ZrO₂ support (named **Fe/MgZr**) 2) 5 wt%Fe impregnated on previously synthesized 10 wt% NiO-MgO-ZrO₂ (named **Fe-two pot**) and 3) 5Fe-10NiO-MgO-ZrO₂ synthesized in one step (named **Fe-one pot**). The aforementioned catalysts were calcined at 700°C for 5 h (Fe-two pot) and 800°C for 4h (Fe-one pot).

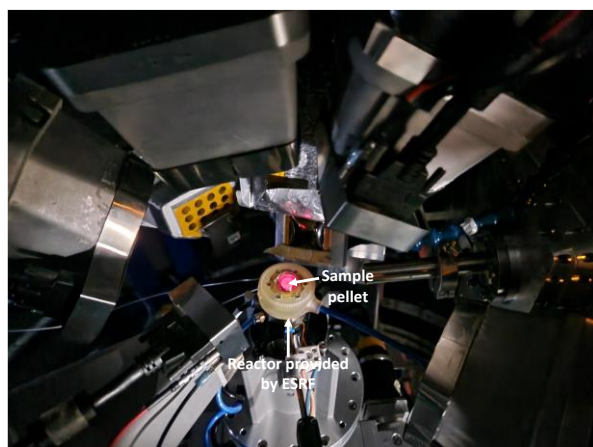


Figure 1 : Reactor cell and XRS/XES detectors configuration during CO₂-EDH reaction conditions (650°C).

XRS spectra were collected both ex-situ and in-situ. For the in-situ experiments, a reactor cell with a spherical Kapton dome that allows the x-rays access, provided by ESRF, was used (Figure 1), while the XRS/XES measurements were performed at four edges: O K- and Mg L_{2,3}- edges for the former and Fe- and Ni- edges for the latter. CO₂-EDH reaction conditions were imposed: 9 vol% C₂H₆, 9 vol% CO₂ and the rest He, T_{reac}=650°C, 10-20 ml/min of total flow rate using calibrated mass flow controllers (brought by the users). During a typical experiment, the catalyst was placed in the reactor cell as a pellet, while the time-on-stream (TOS) during the CO₂-EDH reaction was between 4-7 h. Unfortunately, the combination of high reaction temperatures (>600°C) and beam radiation for long TOS (>2 h) resulted in sample damage. To enable the in-situ measurements without beam damage, it was suggested by the local contact to collect the XRS spectra at low temperature (room temperature, RT) and under pure He flow. The latter was successful as data of good quality were collected, after the CO₂-EDH reaction

step, facilitating the monitoring of electronic modifications during reaction conditions. The XRS/XES measurements were coupled with kinetic measurements based on gas-phase compositions obtained during CO₂ EDH reaction, from a mass spectrometer (MS) provided by ESRF. Ex-situ measurements were also performed over 7 reference and 4 used materials (used during experimental campaign in AUTH for chemical looping CO₂-assisted EDH at 600°C); reference samples: pure MgO, 5wt% Fe/MgO, Fe₂O₃, Fe₃O₄, support MgO-ZrO₂, support 10wt% NiO-MgO-ZrO₂, pure ZrO₂; used samples: after 4, 8, 10 and 12 cycles of chemical looping and after 1 h under C₂H₆/He flow, i.e., absence of CO₂ in the feed stream. A mechanical mixture of the same composition as the examined samples was also tested for comparison purposes.

Experiments performed and first results for Mg L_{2,3} signals

Mg L_{2,3} edge spectra of Fe-one pot and Fe-two pots samples were recorded in-situ at RT in He after 3 and 5 h of CO₂-EDH. Figure 2-left compares the abovementioned spectra with the sample treated for 1h under C₂H₆/He flow. All the spectra exhibit three main peaks at ~52.5, ~56 and ~57.5 eV. Concerning the ratio of the peak intensities, some differences can be highlighted, originating mainly from the peak at 52.5 eV: the longer TOS results in structural modification of the one-pot catalyst. More specifically, by comparing the spectrum after 3 h with the spectrum after 5 h, a higher peak intensity at 52.5 eV can be seen. The latter peak corresponds to Mg at tetrahedral coordination. Thus, under CO₂-EDH reaction conditions, Mg obtains a more tetrahedral coordination.

Figure 2-right compares ex-situ samples that were previously used during CO₂-EDH in a chemical looping feed mode. The abovementioned experiments were performed in Aristotle University of Thessaloniki and the samples were brought to ESRF for ex-situ measurements. Strong differences can be seen from the peak at 52.5 eV.

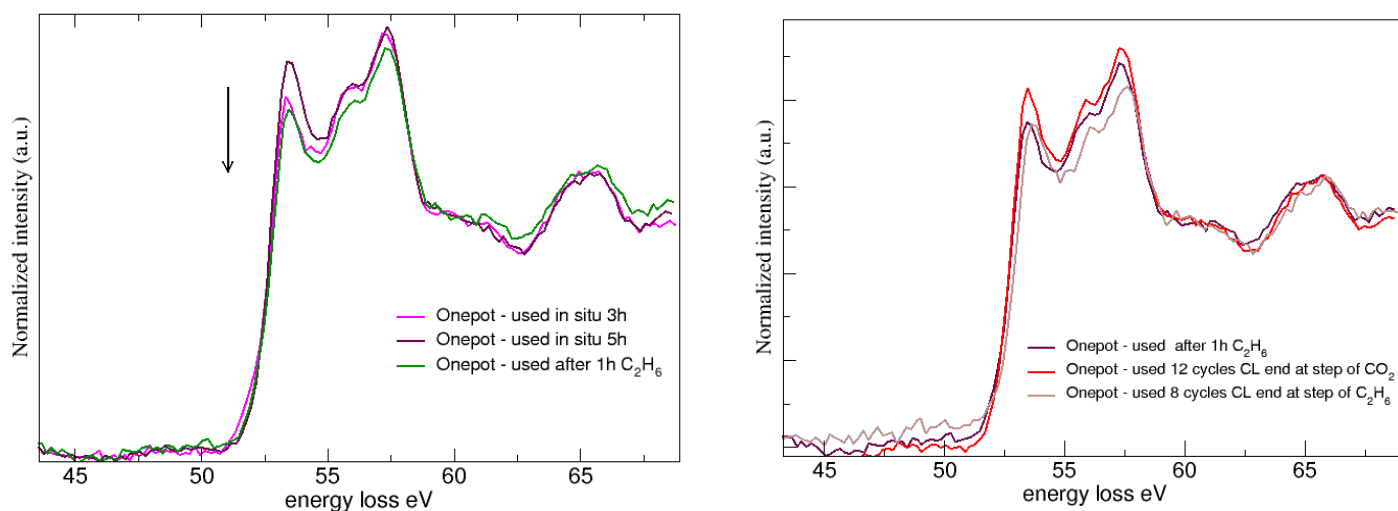


Figure 2: (left) in-situ measurement at Mg L_{2,3} edge of 5 Fe-one pot after 3 and 5 h time-on-stream during CO₂-EDH and after 1 h time-on-stream during only C₂H₆ flow. (right) ex-situ measurement at Mg L_{2,3} edge of previously used 5 Fe-one pot during CO₂-EDH at a chemical looping feed mode.

In-situ and ex-situ measurements were also performed at O-K edge and Fe- and Ni- edges (XES measurements), but the data analysis is still in-progress.

Concluding, we have performed combined XRS and XES in-situ and ex-situ measurements on three Fe-based catalytic materials. The in-situ CO₂-EDH measurements were coupled with a MS to follow the reaction progress as a function of time-on-stream. Fortunately, the problem that we faced with the beam damage was quickly solved by the local contact and there was no significant waste of beamtime. At the current state, we see that our results shed light on the role of the NiO-MgO-ZrO₂ on the C-H bond scission selectivity and thus we foresee a publication in the future.

References

- [1] C.A. Gärtner, A.C. van Veen, J.A. Lercher, *ChemCatChem*, 5 (2013) 3196-3217.
- [2] M. Tasioula, E. de Clermont Gallerande, S.A. Theofanidis, A. Longo, K.A. Lomachenko, C. Sahle, A.A. Lemonidou, *ACS Catalysis*, 13 (2023) 2176-2189.