

Experiment Report Form



	Experiment title: Nucleation and growth of MOFs	Experiment number: A31-1 173
Beamline: BM31	Date of experiment: from: 11.06 to: 14.06	Date of report: 12.10.2022
Shifts:	Local contact(s): Dragos Stoyan	<i>Received at ESRF:</i>
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Report:

The goal of the proposed experiment was to identify local structure around Zr^{4+} in early stages of Zr-based MOFs synthesis and the effects of synthesis conditions on this structure. It was planned to utilise a home-built reactor where the synthesis reaction could be followed in situ at elevated temperature (100 – 120 C) and after constant heating. We envisaged to carry out measurements at Zr- and Ce- k-edges for these two reactions.

The trial of the reactor was partially successful. After the consultation with the beamline scientists, it was realised that Ce should be measured at L-edge. However, for that low energy, the window in the glass reactor was too thick. The local contact(s) attempted to improve the reactor construction by cutting a hole in the glass and closing it with kaption foil. We managed to carry out two reactions in this way measuring the Ce- L-edges and Zr k-edge during the same reaction run. For the rest of the reactions, only Zr K-edge was measured in the intact glass reactor. The heating was rather unstable varying within 10 °C. Taking into account this experience, the reactor will be modified for the future use. The trial of the reactor in this experiment, however, can be considered as successful.

We obtained very good data, in EXAFS range for Zr and XANES range for Ce k-edge for a few in-situ reactions. The data are being analysed at the moment. In several reactions, MOF was obtained, which was and dried at the beamline with the subsequent XAS analysis.

We could not measure simultaneous XRD as planned in the proposal.

In addition to the in-situ reactions, we have measured a great deal of ex-situ pellets:

- Ce, Zr references
- MOFs and other porous materials after metal uptake to identify the adsorption sites
- Nb additives in TiFe alloys
- V additives in TiFe alloys and metal vanadates.

It total, about 70 pellets.

In this report we present the data from the in-situ reactions. The reports for other series of measurements were also prepared as requested but we have not found the opportunity to submit three reports. These reports are available upon request.

1) Ce-Zr fumerate mixed cluster and MOF series

In this series, we have investigated the formation of mixed Ce-Zr clusters and MOFs by varying Ce:Zr ratio of the precursors. The Figure 1 below shows the in-situ data in XANES and EXAFS region for 0.75:0.25 ratio of the Ce-Zr cluster formation. The data were obtained in-situ at Zr k-edge during heating and continuous mixing of the precursor solution. The data show gradual formation of the second-neighbour peak at 3.2 Å responsible for the Zr cluster formation in the solution.

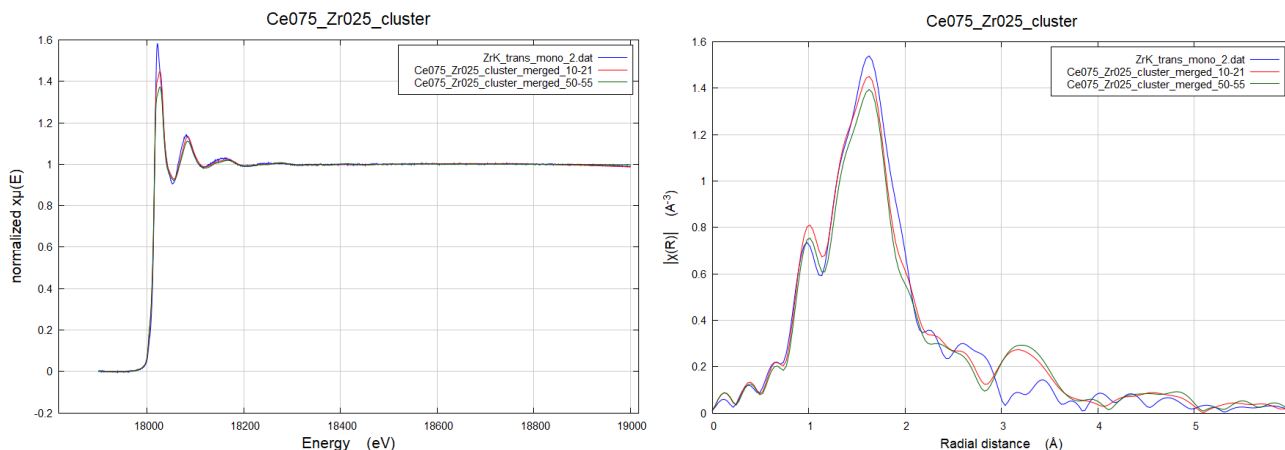
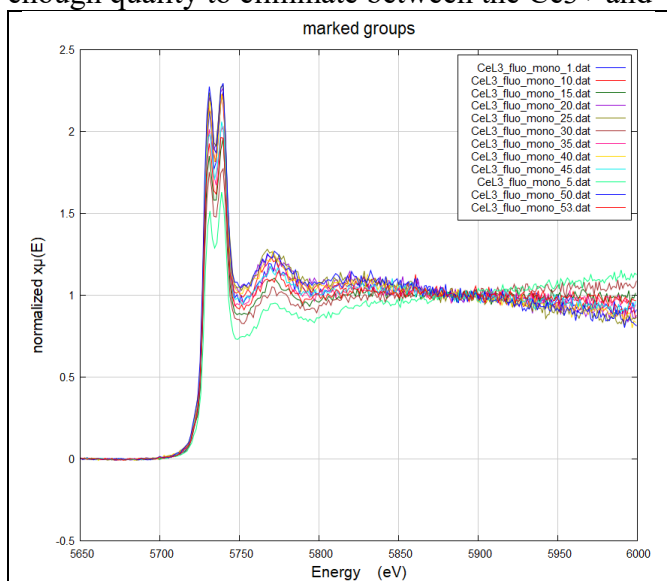


Figure 1. Ce-Zr cluster formation from the precursors in 0.75:0.25 concentration.

We have found that the metal precursor ratio has an effect on the formation of MOF, for some ratios powders were obtained at the end of the measurements, which upon washing, drying and measuring an XRD, shown the formation of Zr-MOF. For other concentrations, gel was obtained on the contrary.

Figure 2 below shows the in-situ data at Ce L-edge for one of the experiments. The XANES data are of a good enough quality to eliminate between the Ce³⁺ and 4⁺ oxidation states.



Data analysis is on progress. In parallel, we have completed the additional characterisation of the MOFs obtained in these experiments with TGA, XRD, BET, Raman and SEM. The main aim will be to conclude whether the formation of the mixed MOF was achieved.

Figure 1. Ce-Zr cluster formation from the precursors in 0.75:0.25 concentration.