



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Revealing structure-activity relationships during selective olefin oxidation by operando X-ray diffraction	Experiment number: CH 6051
Beamline: BM01	Date of experiment: from: 28.10.2021 to: 01.11.2021	Date of report: 28.02.2022
Shifts: 12	Local contact(s): Charles McMonagle	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Linda Klag ^{1*} , Matthias Stehle ^{1*} , Mariam Schulte ^{1*} , Thomas L. Sheppard ^{1,2*} , Jan-Dierk Grunwaldt ^{1,2} . ¹ Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany. ² Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany.		

Report:

Selective oxidations are key reactions for the functionalization of hydrocarbons in chemical industry [1]. These include the selective oxidation of propylene and isobutene to acrolein and methacrolein (respectively). However, catalytic processes that occur during selective oxidations are still not entirely understood. Thus, establishing relationships between catalyst structure and activity/selectivity is required for a knowledge-based catalyst design and improvement.

Most commonly, research focuses on simplified model systems (e.g. 2-component Bi-Mo, Fe-Mo, Co-Mo) to get a fundamental understanding of catalytic function [2,3]. However, such model studies cannot relate sufficiently to the complex structure of the superior 4-component Bi-Mo-Co-Fe-O systems used in the light olefin oxidation reactions. Such 4-component Bi-Mo-Co-Fe-oxides show indeed excellent catalytic performance, but their complex crystalline phase composition is still challenging to characterise, particularly the role and interplay of individual metal oxide phases [4,5]. An *operando* synchrotron XRD approach is therefore crucial.

This study involves the structural investigation of complex 4-component Bi-Mo-Co-Fe-oxide catalysts during selective isobutene oxidation by means of *operando* XRD. Using our capillary microreactor system, we investigated seven Bi-Mo-Co-Fe oxide catalysts prepared with flame spray pyrolysis or hydrothermal synthesis, containing various amounts of bismuth, molybdenum, cobalt and iron. In this way both the influence of preparation method and that of chemical composition on catalytic performance were investigated. For this purpose, we focused on phase formation and phase stability of each catalyst, using the following conditions:

- i) **Phase formation** experiments were performed in a temperature range of 25 – 600 °C (2 K/min) under reaction atmosphere (80% He, 12% O₂, 8% C₄H₈).
- ii) **Phase stability** experiments were performed at 430 °C, switching in a successive manner between oxidizing, reducing and reaction atmosphere.

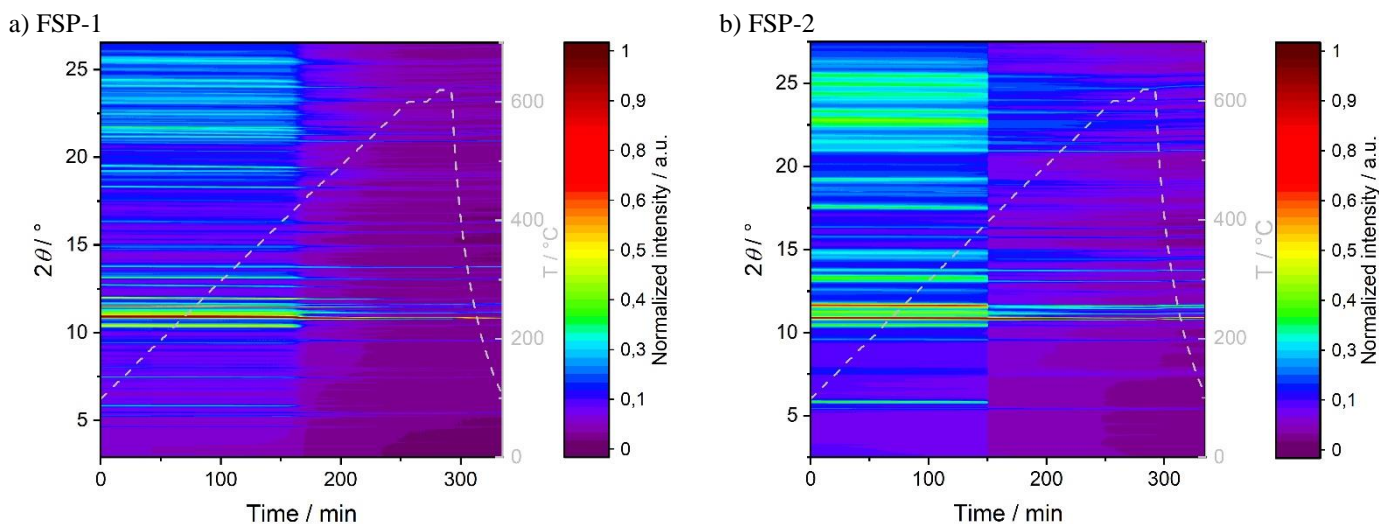


Fig. 1: Structural evolution of two Bi-Mo-Co-Fe-O catalysts derived from XRD during phase formation experiments (25 – 600 °C, 2 K/min, 80% He/ 12% O₂/ 8% C₄H₈).

Fig. 1 shows exemplarily the acquired XRD patterns during phase formation experiments of two catalysts prepared via flame spray pyrolysis that differ in their amounts of Bi, Mo, Co and Fe. Here, a strong influence of chemical composition on the metal oxide phases present could be observed, as the initial XRD patterns of the two catalysts strongly differed from each other. Moreover, heat-up from room temperature to 600 °C lead to several structural changes taking place during selective isobutene oxidation (e.g. formation of ternary phase Bi₃FeMo₂O₁₂). A pronounced structural change was observed in similar ranges for both catalysts (T= 400 – 420 °C). As the simultaneously collected activity data (via mass spectrometry) showed, this strong change in catalyst structure took place as the catalyst was activated. However, further qualitative and quantitative data analysis will be required to assign the changes in the XRD patterns to the formation of the particular phases present in such complex systems (e.g. Co_xFe_{1-x}MoO₄, α-Bi₂Mo₃O₁₂). Here, especially using Rietveld refinement (Fig. 2) will enable to determine and quantify the individual metal oxide phases present.

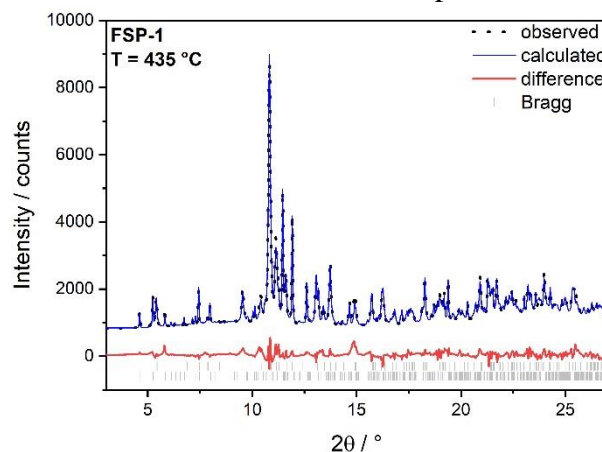


Fig. 2: Selected pattern at 435 °C and corresponding fit during sequential Rietveld refinement of Bi-Mo-Co-Fe-O.

In conclusion, the phase formation and phase stability experiments need to be analyzed in detail for final conclusions on the seven investigated catalyst systems. First results showed us that synchrotron XRD with (sequential) Rietveld refinement will allow to deconvolute the complex crystalline phase structure of Bi-Mo-Co-Fe oxides as it evolves under reaction conditions, while simultaneous mass spectrometry data monitors the catalytic performance. Thus, correlations between the role of individual catalyst phases, their dynamic behaviour, and interaction with other phases and their effect on catalytic performance can be determined. Together with complementary characterization methods (*operando* XAS, Raman spectroscopy) this will allow us to more accurately define catalyst functionality in terms of active, inactive or spectator phases. In turn this promotes optimisation of catalyst synthesis and process conditions for greater efficiency and sustainability.

We thank the beamline staff, especially Charles McMonagle, for their support.

References

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- [3] P. Sprenger, M. Stehle, A. Gaur, et al. ACS Catal. **2018**, 8, 6462-6475.
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