



|   |   |                                     |
|---|---|-------------------------------------|
|   | <b>Experiment title:</b><br>Time-resolved HE-XRD during methanol-to-olefins under pulsed conditions | <b>Experiment number:</b><br>MA5630 |
| <b>Beamline:</b><br>ID15A   | <b>Date of experiment:</b><br>from: 17/04/2023 to: 21/04/2023                                       | <b>Date of report:</b>              |
| <b>Shifts:</b><br>13  | <b>Local contact(s):</b><br>Stefano Checchia  | <i>Received at ESRF:</i>            |
| <b>Names and affiliations of applicants</b> (* indicates experimentalists):<br>Luca Maggiulli, * PSI, Switzerland<br>Davide Ferri, * PSI, Switzerland |   |                                     |

## Report:

We performed operando powder x-ray diffraction experiments to study the structural changes of zeolite catalysts in the methanol-to-olefins process at ID15A beamline.

We performed 11 experiments in which the type of zeolite, type of reagent (CH<sub>3</sub>OH vs CD<sub>3</sub>OD) and mode of operation (continuous flow vs pulsed flow) were changed. Experimental conditions were: T= 300/350°C, total gas flow 20 mL/min, catalyst loading varied between 10-20 mg, the total pressure was 1 bar. A custom-built spectroscopic cell that was previously used for high energy XRD was employed as reactor and was interfaced with an online gas chromatograph and a mass spectrometer to analyse the gas effluents.

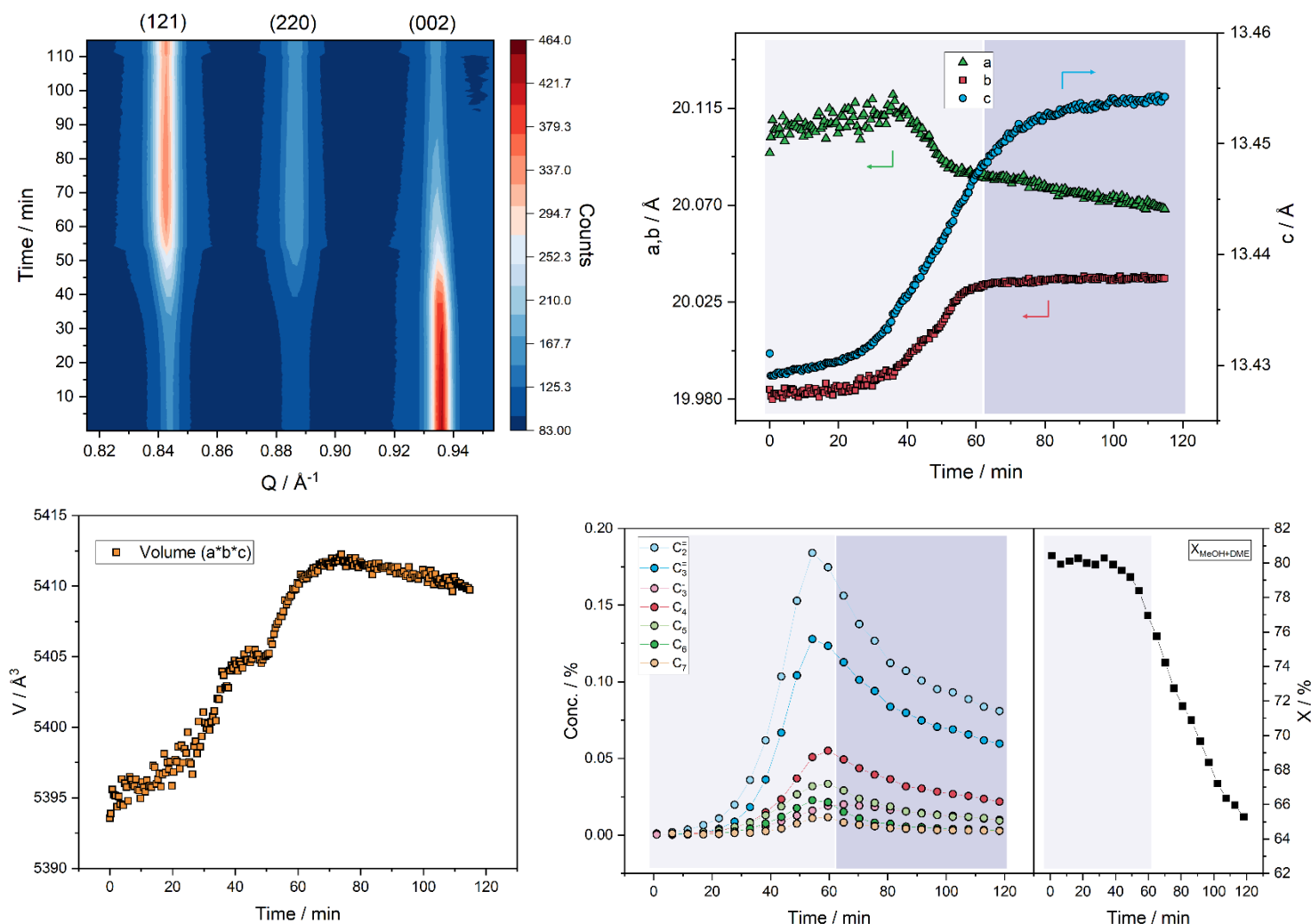
On Monday 17<sup>th</sup>, the set-up, including dosing system, catalytic reactor, on-line analytics, was installed; the gas lines were checked together with the gas flow.

On Tuesday 18<sup>th</sup>, the x-ray beam was converged and aligned. The distance of the 2D Dectris Pilatus detector from the sample was adjusted by using the reference CeO<sub>2</sub>, and was set to 1.8 m with an acquisition range between  $0.2 < Q (\text{\AA}^{-1}) < 3.4$  with x-ray energy of  $\lambda = 0.194 \text{ \AA}$  (64 keV).

A reference Si needle was placed between the catalytic reactor and detector, through which it was possible to follow the Si (111) and (200) reflections. This was needed to be able to account for any undesired fluctuations of the beam energy during the experiments because of the nature of the changes object of this study. We also did not overlook the potential of beam damage: in the continuous flow experiments 1 pattern per second was collected while during the pulsed flow experiments, and from the cycle n. 2 we reduced the acquisition frequency to 10 patterns per minute, condensed in 10 s while maintaining the beam shutter on for the rest of the time.

On the same day, we started the proposed experiments. The continuous flow experiments took 3 h, including 1 h for activating each zeolite sample at 400°C under Ar flow. The pulsed experiments took more than 4 h including 1 h for activating the zeolite catalyst and 20 cycles of intermittent methanol flow.

The results from the experiment on ZSM-5 are presented in Figure 1. The position and intensity of all reflections related to the zeolite framework experienced changes in different directions. Given our interest in the structural changes, specifically of the unit cell parameters, along methanol conversion we left aside the analysis of the intensities that on a first approximation can be associated to the modification of the structure factor as a consequence of the formation of hydrocarbon species in the zeolite pore volume.



**Figure 1.** a) time dependent change in intensity and position of selected peaks during methanol conversion on ZSM-5; b) change of lattice parameters a, b, c of the orthorhombic unit cell of ZSM-5; c) total unit cell volume change; d) products concentration and methanol conversion.

Analysis of the orthorhombic structure of the unit cell of ZSM-5 highlights the gradual modification of the structure along the 2 h experiment. In particular, three independent reflections were followed that showed both intensity and position changes (Figure 1a), as mentioned above. By converting Q values into the direct space quantities a, b, c we can understand the behaviour of the zeolite in the process. Figure 1b shows a first induction period, lasting ca. 20-25 min, in which there was no significant change of the unit cell vectors. After this initial period a sudden and exponential increase of these occurred with an increase of b and c parameters and decrease of a parameter. The expansion/contraction continued till 60 min for a and b parameters and 10 min longer for c parameter, after which the final values of b and c parameters stabilised, while a parameter kept decreasing (cell contraction) gradually. These changes are mirrored by the variation of the total unit cell volume, as shown in Figure 1c, which increased relatively till 40 min, then dwelled for 10 min and increased again before starting decreasing likely as a result of the contraction along the c direction.

The structural behaviour described so far followed the catalytic behaviour characterized by the analysis of products and methanol conversion (Figure 1d). The first period features a stable methanol conversion at around 80%, but with an initial induction period (20 min) where no products formation were observed at relevant concentrations. Then, an exponential spike of products can be observed, which mirrors well the expansion/contraction along different crystallographic directions of the unit cell of ZSM-5. This behaviour is in line with expectations based on reaction mechanism considerations, and by an autocatalytic model of this process. The sudden decrease in products concentration after ca. 60 min on stream is associated to the parallel decrease in conversion, possibly due to evolution of active sites into an inactive form and space limitation after reaching maximum stretch of along the three directions. Ongoing analysis of the experimental data of this type will progress the understanding of zeolite in methanol conversion processes, in view of future endeavours towards more stable catalysts.