


Experiment title:

Combined μ XRD-XEOL Study of Large H-ZSM-5 Zeolite Model Catalyst Particles: Towards "Single-Shot" Structure-Activity Relationships in Heterogeneous Catalysis

Keywords: μ XRD, Zeolites, Crystallography, Intergrowth, XEOL

Experiment number:

CH3706

Beamline: ID01	Date of experiment: from: 30.04.2013 to: 06.05.2103	Date of report: 06.12.2013
Shifts: 15	Local contact(s): Dr. Tobias Schülli	<i>Received at ESRF:</i>

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1. μ XRD of large H-ZSM-5 crystals after dealumination treatment

A series of μ XRD measurements of post-synthetically treated ZSM-5 zeolite crystals started in beamtime CH3498¹, were completed addressing structural heterogeneities induced by a steaming treatment of the crystals. Steam treatment leads to the removal of Al from the zeolite framework with impact on acidity, porosity and crystallinity of the zeolite. With μ XRD imaging it was possible to analyze the location and impact on crystal structure on a single zeolite particle level.

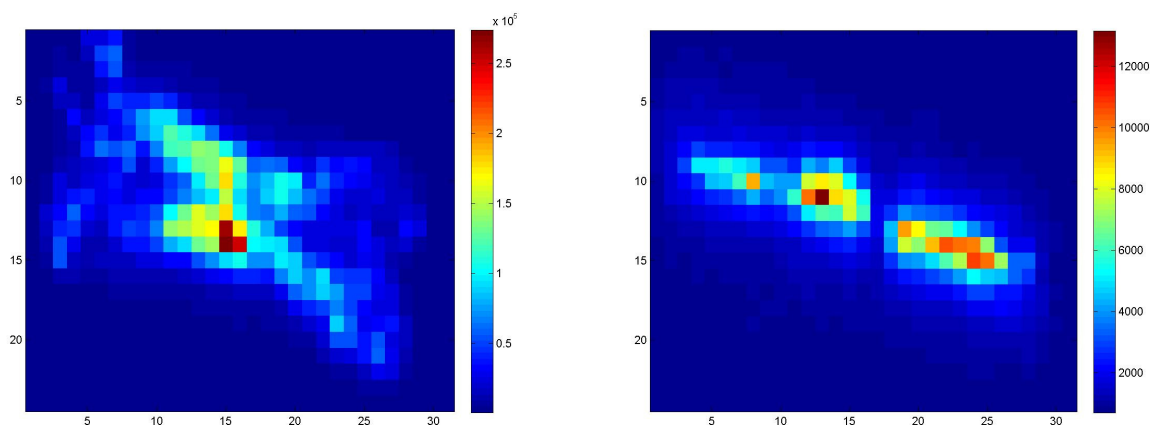


Fig. 1 Diffraction intensity maps of a steam-treated ZSM-5 crystal showing the distribution. Left: 16 0 0 reflection, right: 0 16 0 reflection. Scan size is $96 \times 44 \mu\text{m}^2$.

¹ part of data of beamtime CH3498 recently published in:

Z. Ristanovic, J. P. Hofmann, U. Deka, T. U. Schülli, M. Rohnke, A. M. Beale, B. M. Weckhuysen "Intergrowth Structure and Aluminium Zoning of a Zeolite ZSM-5 Crystal as Resolved by Synchrotron-Based Micro-X-ray Diffraction Imaging" *Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.201306370, online, **2013**.

2. Spectral analysis of XEOL signal in UV/vis and NIR region

The initial idea of the proposal was to record simultaneously lateral maps of the X-ray diffraction response (crystal structure) and the X-ray excited optical luminescence (presence of Brønsted acid sites) of large, styrene oligomer labeled H-ZSM-5 zeolite crystals. To proof the origin of the light emission presumably in the visible range as recorded in a proof-of-concept experiment during beamtime CH3498 (June 2012), it was necessary to characterize the emission spectroscopically. We applied standard UV/Vis and NIR fiber optics based spectrometers with room-temperature CCD detectors. However, it turned out that neither collection of light by a tube microscope nor directly mounting the samples on top of optical fibers led to a signal above noise in the spectrometers. The intensity of the emitted light was so low, that in all cases the dark noise of the spectrometers' CCD detectors was larger than the potential emission signal. A more sensitive CCD camera and optimized collection optics turned out to be mandatory to analyze the XEOL signal spectroscopically.

3. Collection of XEOL emission by CCD camera

Nevertheless, with a standard CCD camera mounted to a tube microscope as present at ID01, XEOL signal could be detected, when preamplifier gains were set to high levels. Despite of the noise level, we could observe emission in the CCD camera image and could move on with important testing to determine the XEOL behavior of the labeled crystals and study the dependence on experimental parameters, although without spectral characterization.

4. Proof of chemical species responsible for emission

To check which requirements need to be fulfilled by the sample and whether the presence of styrene oligomers is related to the observation of an optical emission, several different samples have been tested as shown in Table 1. Empty zeolites did not yield emission at all, while crystals impregnated with methoxy styrene – which reacts at Brønsted acid sites already at room temperature to form fluorescent oligomers – and fluoro styrene after heat treatment led to an optical emission followed in the CCD camera-tube microscope combination. Fluoro styrene labelling without heating did not result in an emitting sample because of the lower reactivity of fluoro styrene. Furthermore, that observation proofs that indeed the oligomeric species are responsible for the observed light emission and not the unreacted styrenes themselves.

Table 1. Optical emission resulting from different zeolite H-ZSM-5 batches and different labelling precursors.

Crystal type / pretreatment	Empty	Methoxy styrene	Fluoro styrene, not heated	Fluoro styrene, heated to 120 °C
Parent H-ZSM-5	No	Yes	No	Yes
Steamed at 500 °C	No	Yes	No	Yes
Steamed at 700 °C	No	Yes	No	Yes

5. Time profiles of photobleaching

Having confirmed styrene oligomers as the emitting species, we analysed subsequently the photobleaching behavior of these species under focused 9 keV X-ray illumination. Figure 2 shows the decrease in integrated emission intensity over irradiation time. This experiment has important consequences for subsequent mapping/spectroscopy studies in that we could assess how much time is available to accumulate signal or how fast scanning either in lateral dimension for imaging or in spectral domain for spectral imaging needs to be achieved.

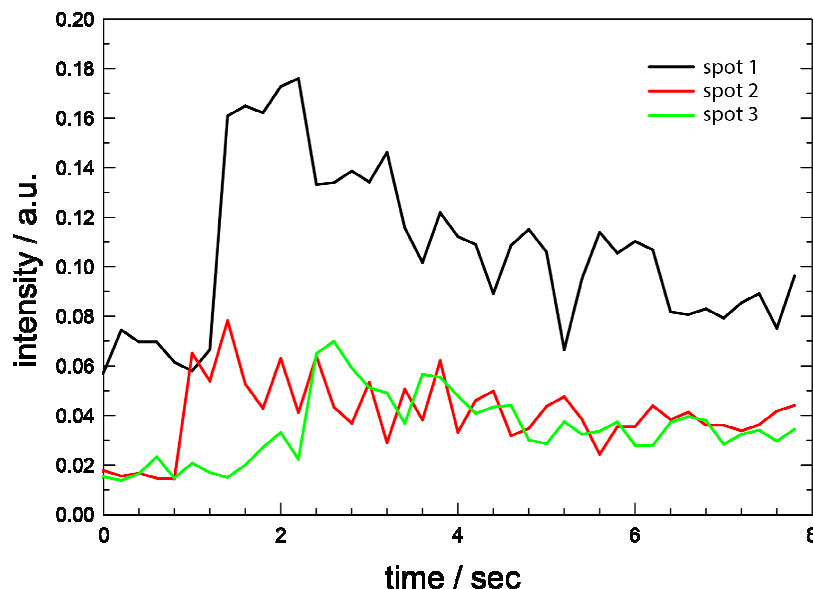


Fig. 2. Photobleaching of XEOL signal of methoxy styrene labeled parent H-ZSM-5 as recorded from the CCD camera integrated signal; region of interest defined around emitting spot. Three different spots on a labeled H-ZSM-5 have been followed subsequently.

Within maximum 8 sec a complete decay of the emission signal could be observed. Despite the low S/N ratio, a clear trend is visible. The relatively fast decay of the emission due to photobleaching further proofs the necessity of having a more sensitive CCD detection/spectrometer device.

6. Conclusion

The objects of study during beamtime CH3706 have been large zeolite H-ZSM-5 crystals. Important information about crystallinity and possibly zoning of Al in dealuminated H-ZSM-5 samples could be obtained by μ XRD imaging. Fast scanning enabled for a decrease of beam induced damage, the possibility to study a larger sample set to account for interparticle heterogeneities and to probe diffraction response of the crystals with a higher resolution in incident angles.

For the intended XEOL- μ XRD experiments we could make important steps forward by *i)* determining the emitting species, *ii)* recording time-resolved photobleaching curves, *iii)* determining the required sensitivity of a light collection optics for XEOL spectral imaging and *iv)* confirming the mapping possibilities of combined μ XRD-XEOL response of large H-ZSM-5 zeolite crystals. All four points are important prerequisites for a successful follow-up beamtime.