ESRF	**Experiment title:** Combined AFM and X-ray micro-diffraction study of large ZSM-5 zeolite crystals: Intergrowth structure and characterization of highly reactive heterogeneities	**Experiment number**: CH3498
Beamline: ID01	**Date of experiment**: from: 07.06.2012 to: 12.06.2012	**Date of report**: 31.08.2012
Shifts: 15	**Local contact(s)**: Dr. Tobias Schülli	*Received at ESRF:*

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Report:

The objects of study during beamtime CH3498 have been large zeolite H-ZSM-5 crystals. Main goals were *i)* to proof their proposed intergrowth structure crystallographically and *ii)* to study the influence of crystal structure, defects and surface heterogeneities on catalytic activity. Room temperature, gas phase oligomerization of 4-methoxy styrene has been employed as a labeling reaction to fluorescently label Brønsted acid sites at the zeolite surface and in the bulk, respectively.

Due to the availability of a video microscope with 20x and 50x magnification, the location of the zeolite crystals could be easily achieved. The use of an atomic force microscope (AFM) was not indicated.

X-ray diffractograms on spots of large parent (as-synthesized, detemplated) H-ZSM-5

Using the available video microscope and the xyz piezo scanning stage, the zeolite crystals could be aligned properly with the incident X-ray beam (see Fig. 1). Diffraction was taken for ZSM-5 (2 0 0) and related higher order Bragg reflections. Going to higher order reflections, a splitting became visible indicating differences in the d-spacings of the crystal lattice. This was a first hint of two different phases or 90° rotated intergrowth building units present in the crystals. Referring to the lattice constants of ZSM-5 (a=19.879 Å, b=20.107 Å, c=13.369 Å, α=90°, β=90.67°, γ=90°), the observed splitting most probably can be ascribed to the presence of 90° rotated intergrowths. Further analysis and mapping of the large zeolite crystals was based on splitted 16 0 0 and 18 0 0 Bragg reflections (Fig. 1). Those reflections have been sampled by x,y-maps with a step size of 0.4-0.8° in an interval of 2-3° 2Θ.

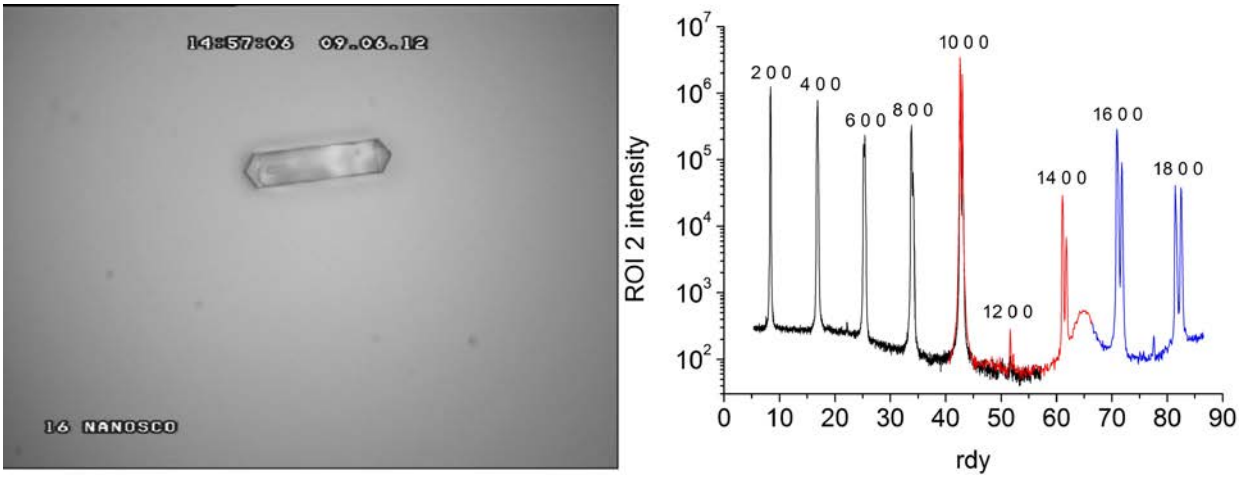

Figure 1. Left: Optical image of an H-ZSM-5 crystal, size approximately 20x20x100 µm³. Right: XRD of ZSM-5 showing 2 0 0 and corresponding higher order Bragg reflections.

µ-XRD mapping of parent H-ZSM-5 crystals

The zeolite crystals were in a next step subjected to x,y-mapping based on scattering intensity at fixed angles. The spatial intensity distribution maps for a parent H-ZSM-5 crystal are shown in Fig. 2b and c for two different 2Θ angles. Fig. 2b shows the scattering intensity distribution at lower angles of the 18 0 0 reflex corresponding to the domain with the higher d-spacing value whereas Fig. 2c shows the domain with the lower d-spacing. Intensity maps display integrated CCD detector counts.

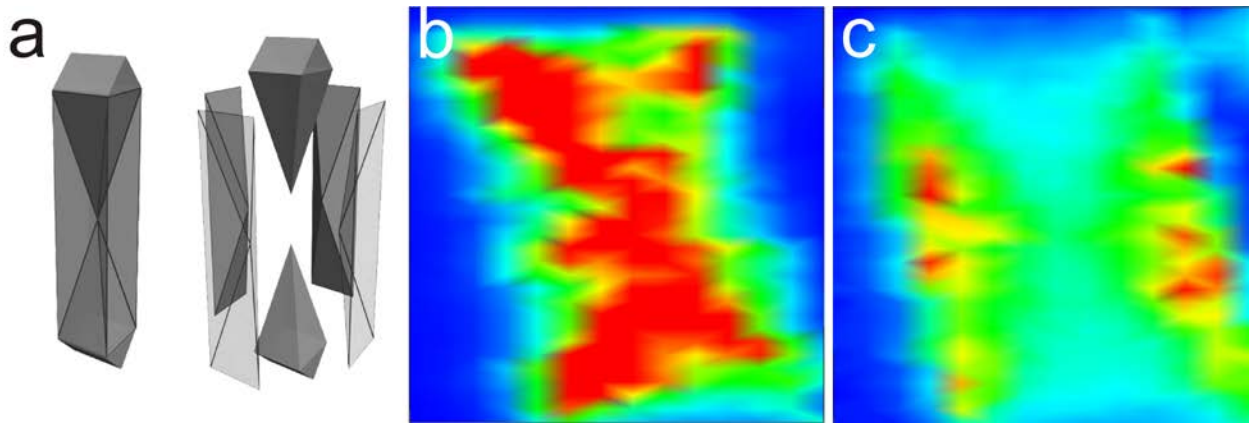

Figure 2. a) scheme of ZSM-5 intergrowth structure and building units, b) µ-XRD (CCD integrated intensity) map of parent H-ZSM-5 based on 18 0 0 Bragg reflection revealing an inverse hourglass pattern, c) µ-XRD map at higher 2Θ angle, revealing an hourglass pattern.

To study the dependence of relative alignment of crystals and incident beam and with that the orientation of the intergrowth units, crystals have been mapped in flipped orientation and 90° rotated to the incident X-ray beam, respectively. With this data set, the recently proposed intergrowth structure of large H-ZSM-5 – obtained from confocal fluorescence microscopy and electron backscatter diffraction experiments – will get a crystallographic foundation.

Influence of dealumination treatment by post-synthesis steaming treatment

In a further mapping series, steamed H-ZSM-5 have been studied. Depending on the steaming treatment conditions, mesoporosity is introduced to the crystals. At low temperature (500 °C) steaming introduces mainly surface mesoporosity, 700 °C steaming leads to a

pronounced mesoporosity throughout the crystal bulk. With this mapping data will show the influence of dealumination on crystallinity and d-spacing as well as the formation of amorphous parts of the single intergrowth units.

Proof-of-concept: Combined µXRD-XEOL experiments for structure-activity relationships of heterogeneous catalysts

8.5 keV X-rays passing through the zeolite sample impregnated with methoxy styrene – a selective probe for the distribution of Brønsted acid, catalytically active sites – induced an optical luminscence signal in the visible spectral range. The very basic CCD camera of the video microscope installed at ID01 thus was read out and the total integrated intensity was mapped along the x,y-translation of the sample stage (Fig. 3a). In that way, we were able to obtain – along with scattering intensity maps (Fig. 3b) – maps of the spatial distribution of optical luminescence signal indicating the presence of fluorescent molecules and with that the presence of Brønsted acid sites. The obtained patterns resemble those, which were obtained by standard confocal fluorescence microscopy experiments. The collection of the XEOL signal thus provides a way to acquire simultaneously combined µXRD scattering data and spatial distribution of fluorescent species, which – in this case – indicate catalytically active sites.

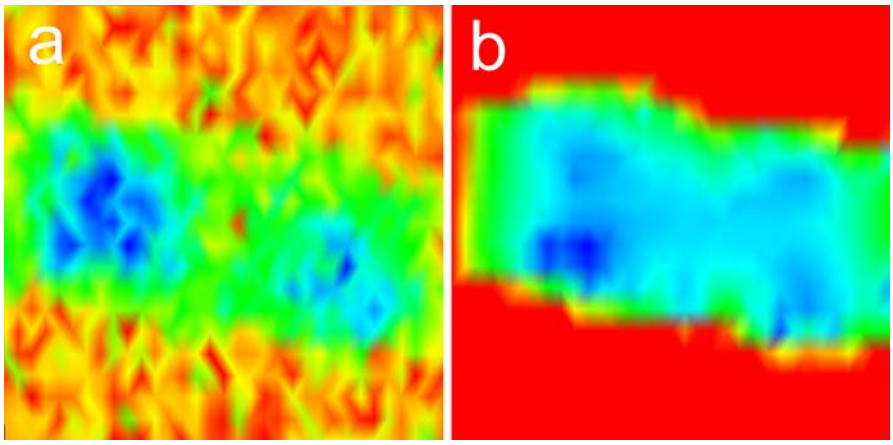

Figure 3. a) XEOL map via video microscopy CCD camera integrated intensity b) corresponding X-ray diffraction map based on 16 0 0 Bragg reflection intensity for a fixed 2Θ angle. Inverse color code to Fig. 1.

Further data treatment is in progress. Publication of the µXRD mapping data with respect to the intergrowth structure of large H-ZSM-5 is targeted. A further publication of combined µXRD and XEOL to establish structure-activity relationship requires a follow up beamtime, which will be applied for in the upcoming round October 2012.