

MS14-03 **Watching the MTO process with time and space resolved X-ray diffraction.** David S. Wragg,^a Matthew G. O'Brien,^b Francesca Bleken,^a Unni Olsbye,^a Marco Di Michiel^c and Helmer Fjellvåg^a ^a*inGAP Centre for Research Based Innovation, Centre for Materials and Nanotechnology and Department of Chemistry, University of Oslo, 0315 Oslo, Norway,* ^b*Department of Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, University of Utrecht, Sorbonnelaan 16, 3584 CA Utrecht, Netherlands,* ^c*European Synchrotron Radiation Facility, 1 Rue Jules Horowitz, BP 220, F-38043 Grenoble Cedex*
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The direct catalytic nature of the industrial methanol to olefin (MTO) conversion process is hotly debated. We have tracked the progress of the reaction over SAPO-34 in a fixed bed reactor in real time using high energy, time and space resolved synchrotron powder X-ray diffraction (PXRD). The results give strong evidence that the “hydrocarbon pool” (HCP) intermediates are formed by direct conversion of methanol after a specific residence time in the catalyst bed. A new kinetic model, developed alongside the data, gives excellent agreement with our observations. The *c*-axis of SAPO-34 expands by up to 3% as intermediates develop in the chabazite cages and we have used this property to produce *in situ* images of the reactor during the reaction by extracting unit cell parameters with parametric full profile Rietveld refinements. The images produced from fast, repeated scans up the reactor under MTO conditions show that development of the HCP, believed to be necessary for the reaction, begins at a point part-way up the reactor and diffuses back against the flow of reactants. The point of appearance of the intermediates depends on the flow rate through the reactor; supporting the theory that the hydrocarbon pool develops directly from methanol. The scans show that the reactor bed is not evenly filled with intermediates after several hours of reaction, in agreement with mass spectra collected in parallel with the PXRD data. Furthermore we will present a kinetic model, based on simple reaction steps, which predicts a spreading pattern of reactants in excellent agreement with the XRD data. The formation and spread of heavy coke, which causes deactivation of the catalyst, is also observed. The kinetic model not only gives good agreement with the observed data for this stage of the reaction, but also links coke formation to methanol input for the first time. By using a novel synchrotron based mapping technique we have revealed a significant level of new information about the mechanism of the MTO process, potentially settling the argument over whether the reaction can be initiated by direct methanol conversion. The kinetic model developed to give chemical meaning to the results shows the link between back diffusion, methanol and heavy coke for the first time.

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MS14-04 **In-situ diffraction determination of the structural response of GaAsO₄ submitted to an applied electric field.** Pierre Fertey,^{ab} Paul Allé,^b Emmanuel Wenger,^b Bernard Dinkespiler,^c Claude Lecomte,^b ^a*Synchrotron Soleil, France,* ^b*CRM2, Nancy, France,* ^c*imXPAD, La Ciotat, France*
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In-situ diffraction experiments performed when a sample is subject to an electric field *E* (i.e. applying an electric field to a sample during the diffraction experiment), gives the opportunity to obtain information on the induced response. The interaction between a crystal and an external electric field is the basis of many fundamental physical phenomena. Among them, piezoelectricity and its converse effect are widely used in many technological applications such as ultrasonic transducers, frequency filters and resonators, actuators, sensors. A deeper understanding of these important physical properties of crystals at the atomic scale is compulsory to manufacture materials with enhanced piezoelectric responses.

However, applying a static electric field may induce spurious effects (charge migrations, charge accumulations), leading to a decrease of the applied field strength inside the sample and the possible vanishing of the induced response. The remedy is to periodically reverse the direction of the applied electric field at a frequency high enough to avoid charge build up and low enough to consider the electric field to be quasi-static. In these so called field switching experiments, the field exciting the sample is maintained during the short-time probe step (typically few tens of ms). Several amplitude strength of the field excitation can be chained successively, giving access to the measurements of the corresponding (structural) states of the sample quasi simultaneously.

Several setups have been developed to allow such kind of field-switching studies [1, 2]. In all of them, Bragg intensities are sequentially measured with a high accuracy (better than 0.3%). However, long data collection times are needed to obtain a minimum set of independent data to be able to determine a (generally oversimplified) structural model of the field-induced response.

The advent of the new generation of X-ray detectors, the hybrid pixel array detectors based on single-photon counting processes and their advantageous properties (fast readout time and programmable electronic architecture flexibility) has opened new prospects. Using a XPAD detector [3] we have upgraded our field-switching experimental setup to take advantage of the 2D detection surface (i.e. significant increase of the number of measured reflections/decrease of the data collection time) and reduce the number of stored images to the strict minimum (data storage and processing). This provides new opportunities to structural properties modeling in more realistic conditions (less constrained structural models).

We will present this new transportable setup which has already been installed on our laboratory diffractometer or at the diffraction beamline Cristal at synchrotron SOLEIL. First results measured on the *a*-quartz isotype GaAsO₄ will be presented. The piezoelectric tensor has been determined. Bragg intensity changes induced by the applied electric field have also been measured and are interpreted within a deformed structural model.

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