ESRF	**Experiment title:** Catalysts at work: *In-situ* XAS andPowder diffraction studies of catalysts at real working conditions.	**Experiment number**: 01-02-785
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Report:

Preliminary studies of the MTO (Methanol to olefin) catalyst under operating conditions were performed at the European Synchrotron Radiation Facility (ESRF) at the Swiss Norwegian Beam Lines (SNBL). For the first time an *in situ* powder diffraction study was performed of methanol conversion over a SAPO-34 catalyst at conditions close to real operating conditions.

SAPO-34, a silicon substituted microporous aluminophosphate, was put into a micro reaction cell consisting of a quartz glass capillary mounted in a Swagelok fitting using a ferrule. The capillary was heated using a hot air blower. Utilizing the new gas-flow and switching system which has been constructed at SNBL, methanol saturated helium was passed through the sample at temperatures of 430-440°C at pressures between 1 and 4 atm. Powder diffraction patterns were collected using a MAR345 imaging plate system, with an exposure time of 20 seconds, giving a time resolution of 107 seconds. The product formation for the catalytic reaction was followed using a mass spectrometer connected to the reaction cell. In addition Raman spectra were collected at the same time.

Surprisingly, significant changes in the powder diffraction pattern were observed in the first ca. 20-30 minutes after exposure to methanol. Figure 1 shows parts of the powder diffraction patterns collected after switching to methanol saturated helium. In the three dimensional representation, a significant change in the intensity of some of the reflections is observed. After 20-30 minutes the intensities become constant. Seemingly correlated to this, a significant anisotropic change in the unit cell parameters (mainly elongation of the *c*-axis) was observed.

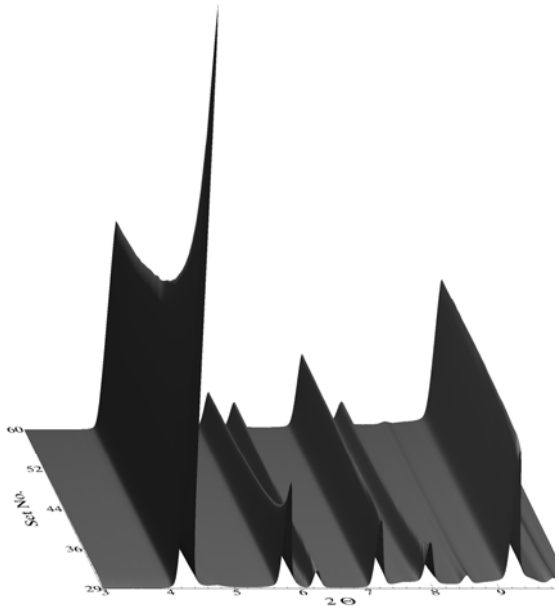

Figure 1. A three-dimensional representation of the powder diffraction patterns during the MTO reaction.

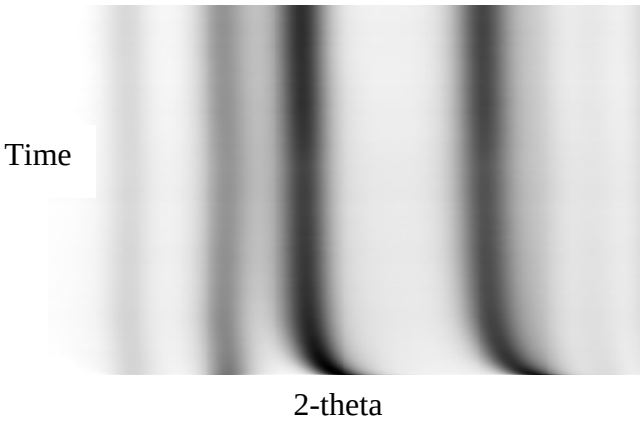

Figure 2. Part of the powder diffraction patterns as a function of time during the MTO reaction.

This change is visible in Figure 2, where a shift toward lower diffraction angle is observed for some reflections, while others are less influenced. The shifts are consistent with an increase mainly in the langth of the *c*-axis, Figure 3.

The observations indicate that significant structural changes takes place during the early stages of the catalytic reaction. The changes are too slow to result from adsorption effects. The suggested mechanism for the catalytic MTO reaction involves formation of organic molecules, which will act in a carbon pool mechanism. The large impact on diffraction intensities and the anisotropic change in unit cell parameters indicate that localized species

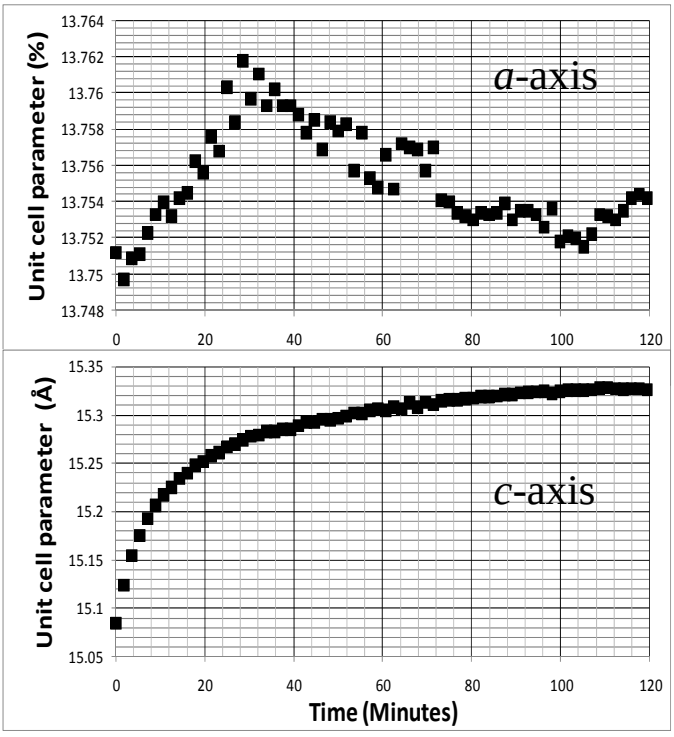

Figure 3. Unit cell parameters as a function of reaction time.

are involved.

Further *in situ* and *ex situ* experiments will be performed in order to identify and localise the species.