

Report for Proposal Code 01-02-1114; Proposal Title Time and Space resolved in operando XRD studies of methanol conversion with zeolite ZSM-5

This was a very successful session. We were able to record the data for zeolite catalyst deactivation that we anticipated. The deactivation of zeolite catalyst H-ZSM-5 by coking during the conversion of methanol to hydrocarbons was monitored by high energy space- and time- resolved operando X-ray diffraction. Space resolution was achieved by continuous scanning along the axial length of a capillary fixed bed reactor with a time resolution of 10 seconds per scan. Using real structural parameters obtained from the XRD we can track the development of coke at different points in the reactor and link this to a kinetic model to correlate catalyst deactivation with structural changes occurring in the material. The “burning cigar” model of catalyst bed deactivation is directly observed in real time. For the regeneration of coked zeolites, we could observe in real time the local structural transformations of the H-ZSM-5 catalyst during the removal of coke under variable temperature oxidative conditions. We were able to study this transformation with unprecedented detail by operando high time- and space-resolved synchrotron XRD. The coke removal occurs suddenly, and the removal itself is associated with a stable plateau in the value of the unit cell volume.

This experiment has resulted in 2 publications and contributed significantly to one PhD:

“Deactivation of Zeolite Catalyst H-ZSM-5 during Conversion of Methanol to Gasoline: Operando Time- and Space-Resolved X-ray Diffraction” D. Rojo-Gama, L. Mentel, G. N. Kalantzopoulos, D. K. Pappas, I. Dvogluk, U. Olsbye, K. P. Lillerud, P. Beato, L. F. Lundegaard, D. S. Wragg, S. Svelle, *Journal of Physical Chemistry Letters* 9 (2018) 1324-1328.

“Real-time regeneration of a working zeolite monitored via operando space resolved X-ray diffraction: How coke flees the MFI framework” Georgios N. Kalantzopoulos, Daniel Rojo Gama, Dimitrios K. Pappas, Unni Olsbye, Karl Petter Lillerud, Pablo Beato, Lars F. Lundegaard, David S. Wragg, Stian Svelle in preparation.

Dani Rojo-Gama, “Investigations of the Long Term Catalytic Activity and Stability of Zeolite-Based Catalysts in the Conversion of Methanol-to-Hydrocarbons” PhD thesis, University of Oslo, 2017