

Heterogenization of Homogeneous Catalysts onto Solid Supports: Potential and Challenges

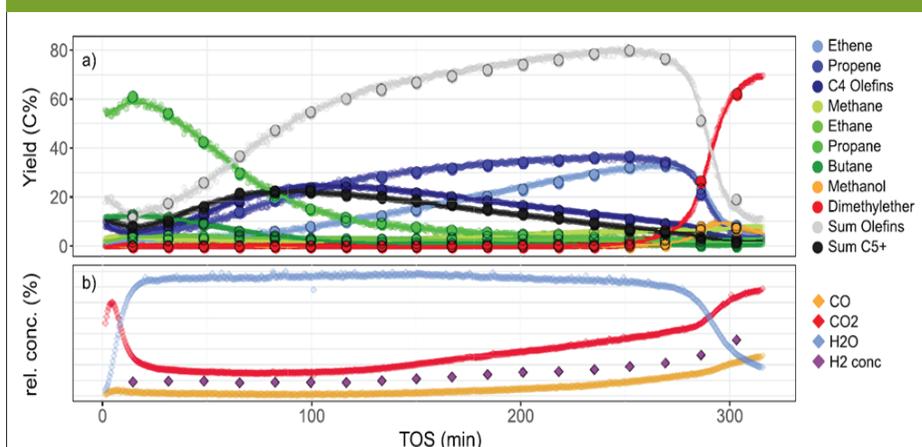
Image reference: Dr. Sylvain Antoniotti, ICN Institut de Chimie de Nice

Time-Resolved Product Analysis of Dimethyl Ether-to-Olefins Conversion on SAPO-34...

Conversion of methanol and dimethyl ether to hydrocarbons (MTH) continues to attract significant attention. The process is catalyzed by various zeolites in which the microenvironment (topology and Brønsted acidity) plays a significant role in the product distribution and catalyst lifetime. In the case of the methanol-to-olefins (MTO) reaction, the silica-alumino phosphate SAPO-34 with a chabazite (CHA) framework and small 8-ring pore windows is very selective toward the formation of lower olefins. Linear reaction products can exit, while larger molecules such as branched and aromatic products are retained within the pores leading to the formation of hydrocarbon residues which, in turn, restrict the pores and lead to relatively fast deactivation. However, the high selectivity of SAPO-34 toward lower olefins has led to its successful commercialization in a fluidized-bed reactor-regenerator configuration with continuous regeneration.

Herein, the authors focus on the detailed product analysis during induction, steady state, and deactivation in a fixed-bed using high time resolution. In order to follow the rapidly changing product distribution, gas-phase FTIR spectroscopy was applied in measurement intervals down to 5 s. Multivariate analysis of the FTIR spectra and correlation to the online product analysis by GC was used for *in-situ* training of chemometrical models for all major products between C₁ and C₅. These models were used for the prediction of product selectivities from the FTIR spectra in high time resolution giving valuable insights into the product formation during the induction, steady-state, and deactivation periods of the catalyst. The results indicate that the product distribution on SAPO-34 depends on the time-on-stream (TOS) deactivation and coke content (Figure 1).

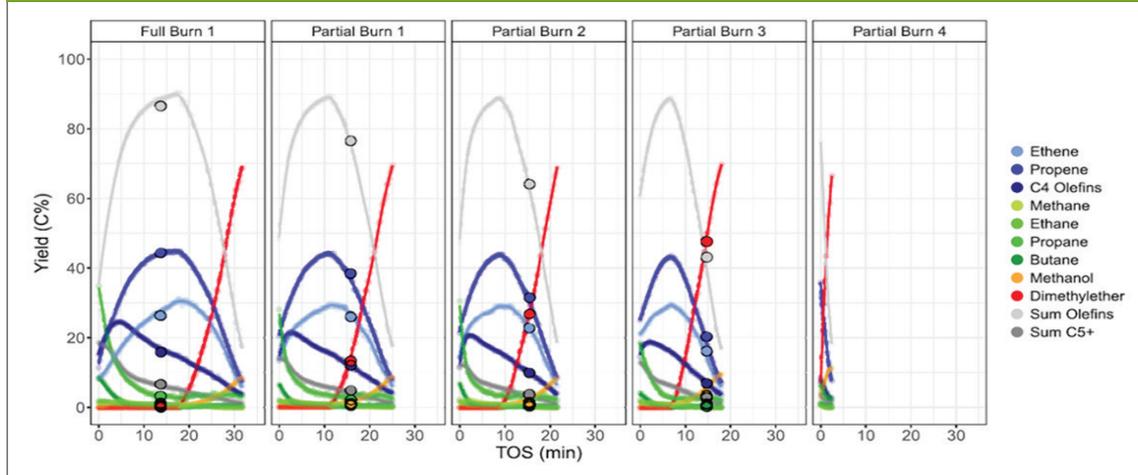
Figure 1. (a) Product distribution at WHSV = 0.2 h⁻¹ and 400 °C versus TOS. The big symbols show the GC data, whereas the smaller symbols show the predicted data from the FTIR spectra. (b) Not quantified values for H₂O, CO, and CO₂ by FTIR and hydrogen by GC TCD analysis.



It was found that interfering water absorptions in the FTIR limited the identification of species indicative of the first C–C coupling although initial CO₂ may indicate decomposition products of oxygenates during the induction period. In addition, high initial

hydrogen transfer activity to paraffins may indicate aromatics buildup during hydrocarbon pool formation. During the subsequent steady-state period, detailed selectivities provided information on the development of ethene, propene, butene, and C₅₊ yields and confirmed product shape selectivity of SAPO-34. For the deactivation period, the product yields were followed at partial conversion enabling the determination of primary

Figure 2. Product distribution at WHSV = 1.6 h⁻¹ at 400 °C with a horizontal split by completeness of the coke burn. The big symbols show the GC data, whereas the smaller symbols show the predicted data from the FTIR spectra. The solid line indicates a local regression (LOESS) for the FTIR data.



and secondary stable or unstable products. By burning-off coke partially, the effect of selectivation by coke was studied, and the initial selectivities after regeneration indicate that the maximum olefin yield can be obtained directly when bringing the catalyst back on stream while leaving the right amount of coke on the catalyst during regeneration. This provides further evidence of the concept of product shape selectivity (Figure 2). Source: Haas A., Hauber C., and Kirchmann M. (2019). ACS Catal., 9: 5679–5691.

Florian Huber, PhD

Head of Hydroprocessing R&D Services, hte GMBH, Heidelberg, DE



Florian received his M.Sc. degree in chemical engineering from the University of Erlangen-Nuremberg, Germany in 2002 and his Ph.D. from the Norwegian University of Science and Technology in Trondheim in 2006, where he concentrated on heterogeneous catalysis. He then worked for Haldor Topsoe for five years developing, up-scaling, and introducing new catalysts for environmental applications in the chemical and energy industries. In 2011, he joined hte – the high throughput experimentation company, working on syngas conversion, CO₂ valorization, and bio-feedstock conversion. For the last five years, his focus has been on developing high throughput technology into applied R&D for refinery applications, as well as on bio-feedstock conversion to biofuels and biochemicals, bringing expertise and added value to catalyst vendors, end users, and companies developing new catalytic processes. He is convinced of the enormous creative power that resides in self-driven and independent teamwork. He can be reached at florian.huber@hte-company.de.

The Catalyst Review asked Dr. Huber to provide his insights into accelerated aging as a useful tool for industrial catalyst evaluation.

While fresh catalyst testing (start-of-run performance, SOR) is straightforward, evaluating catalyst deactivation reflecting the industrial lifecycle (end-of-run performance, EOR) is more challenging. If the cycle length is short – of the order of days or weeks – testing over the whole lifespan is not very time-consuming. However, when the cycle length lasts several months or even years and catalysts must be improved continuously to stay competitive (e.g., in refineries, chemical, or environmental applications), evaluating the lifetime performance poses real-time constraints. Traditionally, pilot or side-stream tests are performed, or new catalysts are installed in baskets in the industrial unit to assess catalyst stability.

Consider the following example from the oil refinery sector: Catalytic hydrocracking is a process where the low-value heavy oil fractions are upgraded into high-value fuels or lubricants by means of hydrogen addition. A typical cycle length is in the range of two to three years. A new or improved catalyst system that generates only a few percent more of the high-value products may contribute with additional revenue in the order of several million per year. At the same time, choosing the wrong catalyst may cause economic damage far greater than that. To ensure that they are less reliant on paper studies and to mitigate the risk of a wrong choice, refineries are increasingly tending toward testing potential catalyst candidates under industrially relevant operation conditions and feedstocks.

When the time scale required for catalyst selection – from evaluation to delivery – is compared with the cycle length, there is not much time left for extensive stability testing. Therefore, refineries and catalyst vendors have two options for assessing the catalyst stability besides the traditional, rather slow ways. One option is to focus on quantifying the SOR performance difference and to assume a similar deactivation behavior – clearly a simplified approach. The other option is to accelerate the deactivation. Accelerated aging means forcing catalyst deactivation by applying higher severity operation conditions. The key question here is whether the applied severity is representative of the extent of deactivation observed under industrial conditions. For this purpose, an industrial benchmark is required that has seen the full industrial cycle length and acts as a reference for the development of an appropriate accelerated aging protocol. The protocol aims to generate a deactivation that corresponds to industrial conditions and to give an indication of the EOR performance. Accelerated aging does not give a perfect reflection of the industrial SOR-EOR catalyst deactivation. However, with a thoroughly calibrated protocol, it is a reasonable way to get an estimate of the catalyst stability ranking and the critical product characteristics defining the catalytic EOR.

Our group has had good experience with utilizing accelerated aging in refining and environmental applications, enabling a fast and pragmatic but also industrially relevant assessment of catalyst stability and hence adding value to catalyst development and selection. It needs to be stressed that accelerated aging protocols are only as good as their calibration against the industrial reference. It is an applied research tool supporting industrial operation and constitutes a time-saving and cost-efficient supplement to fundamental research studies.

The Catalyst Review - Subscribe Today!

<http://www.catalystgrp.com/tcg-resources/studies-and-publications/the-catalyst-review/>