High throughput testing of catalysts with fast deactivation for Methanol-to-Hydrocarbons (MTH)

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Abstract: State-of-the-art catalysts SAPO-34 and ZSM-5 were tested for the reaction of Methanol-to-Hydrocarbons. In order to capture the rapidly changing product spectrum during deactivation, suitable test methods were developed such as a low severity protocol which prolongs the deactivation timescale and a commercially relevant high severity protocol.

Keywords: Methanol-to-olefins, high-throughput experimentation

1. Introduction (11-point boldface)

In this article we will focus on the Methanol-to-Hydrocarbons (MTH) reaction that has been thoroughly investigated with current state-of-the-art catalysts based on ZSM-5 (slow deactivation) and SAPO-34 (fast deactivation). This process represents a challenging application for parallel testing of catalysts which was met by appropriate test protocols for both types of catalysts and an advanced analytical setup to detect complex multi-component products in connection with a fully automated data evaluation.

2. Experimental (or Theoretical)

All experiments were carried out in 16-fold parallel fixed bed reactor systems. The unique process control guarantees constant pressure (2-30 barg), flow, feed concentration and temperature (up to 570°C) for very long run-times and allows sequential start-up of the reactors and product analysis. This means that catalysts with different deactivation time-scales can be compared at constant time-on-stream.

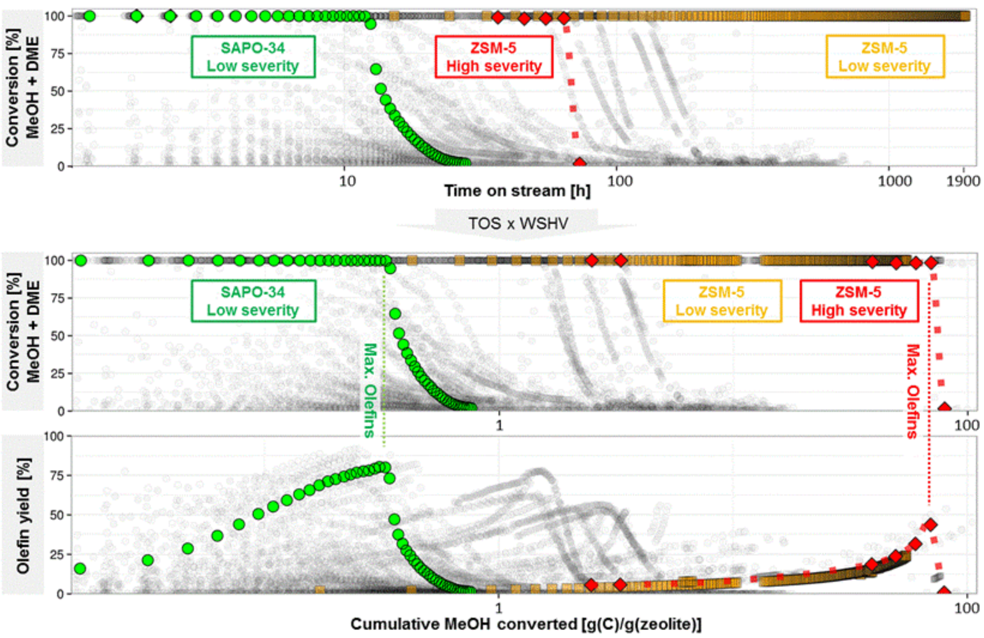

Figure 1. . Breakthrough curves for MTH conversion versus TOS (top) and versus cumulated carbon on zeolite (middle). The corresponding olefin yields versus cumulated carbon on zeolite are shown in the bottom chart. Reference catalysts SAPO-34 (green) and ZSM-5 (orange /red) are highlighted. Grey data points demonstrate the results of various zeolites.

3. Results and discussion

Especially for fast deactivating catalysts such as SAPO-34, a low severity protocol with low MeOH concentration (3.3 vol %) and WHSV (0.05 h-1) was developed. The common variable to compare activity, selectivity and deactivation of both protocols is cumulative MeOH converted on zeolite and the activity, selectivity and deactivation can be differentiated as a function of cumulative MeOH converted on zeolite and reaction parameters (temperature, WHSV, MeOH partial pressure). This is demonstrated in Figure 1, in which the effect of using TOS or cumulative MeOH converted on zeolite as an x-axis is shown for the deactivation curves and the olefin yields of various zeolites and mesoporous materials (grey data points) in comparison with state-of-the-art catalysts SAPO-34 and ZSM-5. It is very clear that the maximum olefin yield is obtained at close to 100% conversion at the MeOH / DME breakthrough while the full bed is utilized for feed conversion.

4. Conclusions

Testing of catalysts with fast decay can be done in parallel fixed-beds by starting up reactors sequentially and comparing conversion and yields during TOS. More recently, catalysts can be tested at short contact times under high severity conditions using a fast analytical setup. Data with high statistical significance and screening of broad parameter ranges can be done by cyclic operation of feed conversion, purge and regeneration.

References

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