**Green Aromatics: Catalytic Valorisation of bio-derived 2,5-dimethylfuran over Zeolites and Zeotypes**

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**INTRODUCTION:** In a fossil-free future, the production of commodity chemicals from alternative feedstocks is necessary. Benzene, toluene and xylene (BTX) aromatics can be obtained from naturally abundant (hemi)cellulose by catalytic valorization. Five-membered ring furans have been used as relevant model compounds and been upgraded to BTX [1]. However, catalyst materials need to be adapted to the new bio-derived feedstock and need further improvements. A deep understanding of the reactant-catalyst interaction is needed, which relies on the ability to monitor the product stream and its dynamic response to stimuli such as temperature change or deactivation processes.

**METHODS:** We developed an on-line analysis method that allows compositional analysis of the complex product stream by gas phase FTIR spectroscopy (MKS MultiGas 2030) and ion-molecule reaction mass spectrometry (V&F Airsense Compact) [2]. The method operates with a time-resolution on a per-second scale, compared to several minutes for commonly used collection- and separation-based GC-FID/MS approaches [2]. This method was successfully applied to a range of zeolite and zeotype catalysts, of BEA and MFI type in H-form with different Si/Al ratio, as well as Cu-ZSM-5 [3]. Thanks to the on-line analysis, the product distribution and selectivity changes can be followed in high time resolution, allowing the observation of transient phenomena, such as a pre-oxidation effect of Cu species and catalyst deactivation due to coking and the use of temperature programmed experiments.

**RESULTS:** Besides effects from a metal in ion exchanged zeolites, we also observe a selectivity change from BTX and olefins towards isomers of 2,5-dmf such as 2,4-dimethylfuran and cyclic ketones with increasing time on stream for all zeolites. P-xylene can be produced much more selectively via temperature programmed experiments.

**DISCUSSION & CONCLUSIONS:** We attribute this phenomenon to the availability change of specific active sites. Initially, certain active sites are available for BTX and olefin formation, which get deactivated due to coking and different acid sites remain or become available for 2,5-dmf isomerization. This led to the assumption that not only the amount of acid sites plays a significant role, but also their nature (Lewis vs Brønsted) and strength. Experiments investigating a Ga-Silicate, show much increased selectivity towards benzene when converting 2,5-dmf as depicted in Fig. 1. Compared to Al containing ZSM-5.

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**REFERENCES:**