Kinetic modeling of the dehydration of a complex bioalcohol feed: towards more rational catalyst design

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The need to shift from fossil feedstocks towards bio-based feedstocks for the chemical industry is now more urgent than ever [1]. In order to accelerate this shift, progress has to be made in the ways to utilize biomass as a feedstock to produce short-chain olefins, which are essential platform molecules. A possible way is the ABE-fermentation. In this process biomass, e.g. municipal waste, is fermented to form 1-butanol, ethanol and acetone in a fixed ratio (6:1:3). From these alcohols, it is possible to produce butene and ethene via dehydration. Performing the dehydration of both molecules simultaneously, without having to separate them in advance, would save a lot of time and energy. Therefore, the dehydration of a 6/1 1-butanol/ethanol mixture, which is a typical composition for alcohols obtained from the ABE-fermentation, over χ -Al₂O₃ was studied.

When alcohols are converted individually over γ -Al₂O₃, there are clear trends in reactivity and selectivity. Increasing the carbon chain length increases reactivity, similar as increasing the branching of the carbon to which the hydroxyl group is connected [2]. The difference in reactivity is observed when this alcohol mixture is dehydrated over a Brønsted acid, for example HZSM-5. Oddly enough, when alcohols are processed as mixtures over γ -Al₂O₃, a Lewis acid, this reactivity difference is attenuated [3]. In this study, this interesting phenomenon is studied through kinetic modelling to unravel what causes this behaviour, see Figure 1. A possible explanation is the formation of cross-ethers which provide a pathway that facilitates the ethanol conversion. Different reaction mechanisms will be modelled. The method of least squares will be used to select the model that best predicts the experimental data. Relating the experimentally observed results to catalyst descriptors, such as acid strength and pore geometry at the active site, allows fundamental insights, which in turn enables a more rational catalyst design for the production of bio-based platform molecules.



Figure 1: Using microkinetic modelling to gain in depth understanding of reaction mechanisms

[1] IPCC: Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press (2021)

[2] Kang et al.: Kinetics and Mechanism of Alcohol Dehydration on γ -Al2O3: Effects of Carbon Chain Length and Substitution. ACS Catal. (2015) 5, 602 – 612

[3] de Reviere et al.: Sustainable short-chain olefin production through simultaneous dehydration of mixtures of 1-butanol and ethanol over HZSM-5 and γ -Al2O3. Journal of Industrial and Engineering Chemistry (2020) 89, 257 - 272