

Difference in the Reactivity of Methanol and Dimethylether in ZSM-5 and Its Role in the Autocatalytic Formation of Olefins

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Abstract

The catalytic conversion of methanol into lower olefins (MTO), gasolines (MTG) or aromatic compounds (MTA) provides an alternative route to conventional crude oil based pathways.^{1,2} A main feature of the methanol conversion is the segregation of the reaction into three zones: the formation of the first C-C-bonds, the methylation of the already formed hydrocarbons and finally the interactions of hydrocarbons in the absence of MeOH. It is furthermore a characteristic that the educt comes as a mixture of MeOH, dimethylether (DME) and water, given by the methanol dehydration equilibrium and the fact that in many industrial applications water is used to dilute the hydrocarbons. Consequently, the differences in the reactivity between MeOH and DME as well as the influence of the presence of water in MTO have been subject of study.³

In this work, we studied the reactivity of DME and MeOH in the hydrogen transfer (HT) reactions that finally leads to the formation of the first C-C bonds. It has been established a correlation between the catalyst amount necessary to form a certain amount of C-C bonded products and the HT rate in this stage of the reaction. The rate increased linearly with the formation rate of the first C-C bond products, confirming that the HT reactions under study are necessary steps in the initiation of olefins in the MTO process. The impact of methanol dehydration to DME and the presence of water was also investigated. DME was found to decompose into methane and, among other components, into formaldehyde, leading to a C₁ reacting mixture similar to the mixture formed from methanol feeds, however with a 10 times higher rate constant than methanol. In parallel, it was also noted that DME is more reactive than MeOH in both the initiation of the MTO reaction and the carbon chain growth.

These findings will not only help to understand the underlying mechanism of the MTO process but will also provide knowledge to optimize the applied feed composition with respect to catalyst activity and product distribution.

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