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Understanding zeolite-catalyzed benzene methylation reactions by methanol and dimethyl ether at operating conditions from first principle microkinetic modeling and experiments

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ABSTRACT

In methanol-to-hydrocarbon chemistry, methanol and dimethyl ether (DME) can act as methylating agents. Therefore, we focus on the different reactivity of methanol and DME towards benzene methylation in H-ZSM-5 at operating conditions by combining first principles microkinetic modeling and experiments. Methylation reactions are known to follow either a concerted reaction path or a stepwise mechanism going through a framework-bound methoxide. By constructing a DFT based microkinetic model including the concerted and stepwise reactions, product formation rates can be calculated at conditions that closely mimic the experimentally applied conditions. Trends in measured rates are relatively well reproduced by our DFT based microkinetic model. We find that benzene methylation with DME is faster than with methanol but the difference decreases with increasing temperature. At low temperatures, the concerted mechanism dominates, however at higher temperatures and low pressures the mechanism shifts to the stepwise pathway. This transition occurs at lower temperatures for methanol than for DME, resulting in smaller reactivity differences between methanol and DME at high temperature. Our theory-experiment approach shows that the widely assumed rate law with zeroth and first order in oxygenate and hydrocarbon partial pressure is not generally applicable and depends on the applied temperature, pressure and feed composition.

1. Introduction

In industrial chemical reactions such as the methanol-to-hydrocarbons (MTH) or xylene production, zeolite-catalyzed methylation reactions are crucial reaction steps [1–3]. In recent years, many theoretical and experimental groups studied methylation reactions of alkenes and aromatics by several methylating agents to gain insight into the mechanism, kinetics and the effect of the zeolite characteristics and operating conditions [3–14]. During the early stages of the MTH reaction, a mixture of methanol (MeOH) and dimethyl ether (DME) is formed. However, MeOH-DME equilibrium is not always established because the rate of MeOH dehydration to DME is similar to the rates of methylation reactions over strong Brønsted acid sites (BAS) [15]. Hence, under MTH conditions, both MeOH and DME act as methylating agents.

It is well-known that zeolite-catalyzed methylations can occur via two distinct mechanisms (Fig. 1) [3]. In a concerted reaction step the oxygenate transfers its methyl group directly to the hydrocarbon, with the simultaneous formation of methanol or water. The stepwise mechanism goes through a framework-bound methoxide, formed by the oxygenate. For both mechanisms it is assumed that the oxygenate adsorbs first, as it can form strong hydrogen bonds with the BAS, and that the hydrocarbon co-adsorbs.

Both mechanisms are assumed to occur during zeolite-catalyzed methylation reactions and the occurrence of one or the other mechanism was found to critically depend on the zeolite topology and the applied reaction conditions [10,14,16–19]. Similar conclusions were drawn for methanol dehydration to form DME [17,20,21]. The coverage of the surface by methoxides becomes increasingly important with increasing temperature due to the entropic gain associated with

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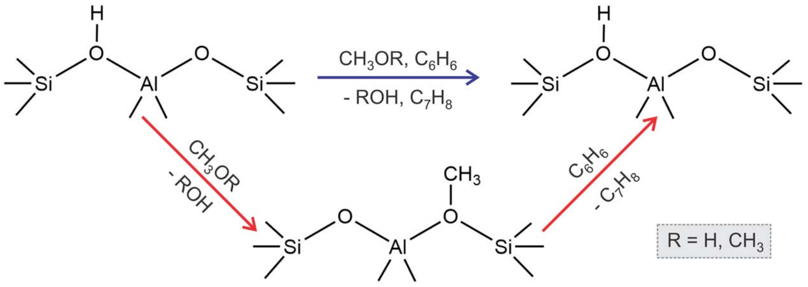

Fig. 1. Schematical representation of the concerted and stepwise methylation mechanisms with MeOH or DME as reactant.

the intermediate release of a water molecule [10,16,17].

Even though most of the methylation kinetic studies are performed under low conversion levels to minimize by-product formation, it remains challenging to limit the occurrence of unwanted secondary reactions. Typical by-products formed during co-feeding of oxygenates with aromatics are polymethyl benzenes (polyMBs), light olefins and the recently reported diphenylmethanes (DPMs) [14]. While polyMBs and olefins are formed by over-methylation and the MTH reaction according to the dual cycle concept [1,2,22], DPM was found to result from Prins-type reactions between benzene and formaldehyde. Formaldehyde is a typical hydrogen-transfer product from methanol–methanol reactions [23–25], or as recently proposed from methanol-alkene reactions at Brønsted or Lewis acid sites [13,26]. While hydrogen transfer between methanol and isobutene and isobutene methylation were found to exhibit similar reaction rates, DME forms a methoxymethyl cation which is higher activated [13]. This results in high DPM selectivities only when using methanol as methylating agent. It should be mentioned that only few studies report on the differences between methanol and DME as methylating agents. Although the chemistry of hydrocarbon methylation with both agents is very similar, there does not seem to be a straightforward trend in reactivity differences between the two. While Maihom et al. report a higher reactivity for methanol [27], other studies conclude that DME is more reactive in H-ZSM-5 [16,28]. Using advanced molecular dynamics simulations, Van der Mynsbrugge et al. concluded that methoxide formation from methanol or dimethyl ether can follow different pathways when assisting molecules are present in the pores of H-ZSM-5. However, methoxide formation from DME was found to exhibit a lower activation energy than from methanol [19].

Recently, systematically higher rates for benzene and isobutene methylation were measured when DME instead of MeOH was used as methylating agent in various zeolites [12,13]. Moreover, also the MTH activity and carbon conversion capacity were found to be higher with a DME feed [15]. While the different deactivation behavior for MTH with a DME and MeOH feed can be explained by different rates of formaldehyde formation and subsequent Prins-type reactions, the higher methylation rates with DME remain an intriguing observation. Therefore, this work focusses on calculating benzene methylation rates at operating conditions from a first principle microkinetic modeling perspective corroborated by detailed kinetic experiments on zeolite nanosheets.

It is striking that many theoretical studies in zeolite catalysis are solely based on (free) energy diagrams, often giving limited insights into the actual performance of the catalyst at operating conditions. In the last years significant progress has been made by introducing the use of advanced molecular dynamics (MD) methods such as metadynamics for zeolite catalysis to study the effect of reaction temperature, pressure, feed composition and zeolite characteristics on elementary reaction steps [10,11,14,19,29,30]. While advanced MD studies led to many unprecedented invaluable insights, they are very time consuming and – especially when using DFT – limited to relatively short time- and length scales. Inspired by the work of Brogaard et al. [16] we instead opt for a microkinetic modeling approach, giving direct access to experimentally measurable rates.

While microkinetic models are nowadays routinely applied in metal (oxide) surface catalysis [31–38], the use of microkinetic models is not widely spread within computational catalysis in nanoporous materials due to often highly complex reaction mechanisms and the high computational expense [39–41]. Moreover, many steady-state microkinetic models make use of a mean-field approximation. By eliminating all possible attractive or repulsive interactions between adsorbates, a uniform coverage of all active sites is assumed, irrespective of their specific location in the catalyst. The only required information is the types of active sites and the elementary processes that can take place at each of them. This simplification is only justified when it can be assumed that there is a perfect mixing of the reaction intermediates over the active sites, e.g. when there is fast diffusion. It is clear that this might be a very limiting approximation in some zeolite materials and if the mean-field assumption breaks down, one has to resort to much more complex kinetic Monte Carlo (kMC) schemes [35,42]. Due to the computational expense and complexity of kMC models, applications have to date been restricted to some seminal works in metal surface catalysis [35,42,43]. In nanoporous materials, kMC applications are currently mostly limited to force-field based diffusion studies [44–48].

In most experimental and theoretical kinetic studies, it is assumed that the oxygenate − either physisorbed on the Brønsted acid site, either converted into a methoxide − completely covers the surface, after which the hydrocarbon weakly co-adsorbs. This, in turn, leads to a representation of the rate law for this elementary reaction step as

$$r = k p_{oxygenate}^{n_{ox}} \; p_{hydrocarbon}^{n_{HC}} \qquad (1)$$

in which it is typically assumed that the rate is zeroth order in oxygenate partial pressure ($n_{ox} = 0$), and first order in hydrocarbon partial pressure ($n_{HC} = 1$) [4–7,9,49,50]. Given that the adsorption of the oxygenate, which included the formation of one or more hydrogen bonds, is usually stronger than the co-adsorption of the hydrocarbon, which is mainly driven by long-range dispersion interactions, this is a fair assumption. However, in this work our calculations and kinetic measurements show that this rate expression is only valid in a limited range of temperatures, pressures and feed compositions.

2. Materials and methods

2.1. Computational details

Periodic Density Functional Theory (DFT) calculations were performed using the Vienna Ab Initio Simulation Package (VASP 5.3) with the PBE functional [51–54]. To account for attractive London dispersion interactions, Grimme's D3 corrections were added [55]. During the calculations, the projector augmented wave (PAW) method was used [56,57], a plane-wave cutoff of 600 eV was adopted and the self-consistent field (SCF) convergence criterion was set to 10^{-5} eV. The Brioullin zone sampling was restricted to the Γ-point. Transition states were initially optimized with the improved dimer method and then refined with a quasi-Newton algorithm as implemented in VASP. For the optimization of stable states, a conjugate gradient algorithm was applied.

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