Benzene co-reaction with methanol and dimethyl ether over zeolite and zeotype catalysts: Evidence of parallel reaction paths to toluene and diphenylmethane

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ABSTRACT

The reactivity of methanol (MeOH) and dimethyl ether (DME) toward benzene was studied over zeolitic materials with different topology and acid strength (H-ZSM-5, H-SSZ-24, and H-SAPO-5) at 250–350 °C. Higher rates of methylation, and subsequent de-alkylation reactions, were observed with DME compared to MeOH. In addition, significant differences in product distribution based on the choice of methylating agent were observed. For reactions between MeOH and benzene a fraction of diphenylmethanes (DPMs) was formed, while this product group was nearly absent during reactions between DME and benzene. A range of co-feed and isotopic labeling experiments was performed, mainly over H-ZSM-5, in order to elucidate mechanistic information on the pathway from methanol and benzene to DPMs. Overall, these studies revealed that DPM formation involves the dehydrogenation of methanol to formaldehyde on the Brønsted acid site, followed by subsequent reaction with two benzene molecules. Theoretical calculations confirmed the higher reactivity of DME compared to MeOH toward benzene methylation and suggested a plausible route from formaldehyde and benzene to DPM.

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1. Introduction

Zeolite-catalyzed methylation reactions are important in a number of large scale petrochemical industrial processes such as xylene and 2,6-dimethylnapthalene production [1,2]. Methylation reactions are also key steps in the increasingly relevant Methanol-To-Hydrocarbons (MTH) reaction, which include the Methanol-To-Gasoline (MTG), Methanol-To-Olefins (MTO) and Methanol-To-Propene (MTP) processes [3–6].

Zeolitic catalysts provide suitable environments for shape selective catalytic hydrocarbon transformations and methylations due to their large surface areas, strong Brønsted acidity and pore systems of molecular dimensions [7–10], which can be exploited to control the product distribution. Recent studies of the MTH reaction over micron-sized H-ZSM-5 crystals and 2–4 nm thick H-ZSM-5 nanosheets revealed that the product distribution is mainly maintained when diffusional constraints are eliminated [11,12],

indicating that the confinement in zeolite pores dominates the observed product distribution of the MTH reaction in H-ZSM-5.

Hydrocarbon methylation over zeolitic catalysts has been the topic of numerous fundamental studies over the past decades. These studies have aimed at disclosing the effect of hydrocarbon size and class, zeolite topology, acid strength and active site environment on the intrinsic and apparent activation energies as well as pre-exponential factors for the different reaction steps involved. Svelle et al. measured the rates of ethene, propene and *n*-butene methylation with methanol (MeOH) over H-ZSM-5 at high space velocities to minimize by-product formation [13,14]. An increase in alkene size consistently increased the rate and decreased the intrinsic activation energies, being 135, 110 and 90 kJ/mol for ethene, propene and *n*-butene, respectively. The apparent rate constants follow the trends in theoretical studies carried out by means of a small cluster model consisting of four T-atoms [15], and also with *a posteriori* work by Van Speybroeck et al. and Svelle et al. with state of the art computational methods [16,17], reflecting the effect of alkene size in zeolite-catalyzed methylation reactions. A higher methylation rate with increased size and branching of the hydrocarbon molecules has also been found with dimethyl ether
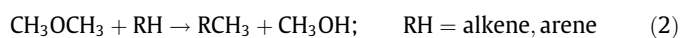

(DME) as methylating agent for H-FER, H-ZSM-5, H-MOR, H-BEA* catalysts [18,19]. Analogous trends have been reported for arene methylation with apparent activation barriers decreasing with the number of methyl substituents connected to the aromatic ring [2,20–23]. For instance, the rate of methylation of benzene, toluene and xylenes over microporous and mesoporous H-ZSM-5 crystals becomes faster for larger arenes. However, xylene rates were strongly influenced by the reaction conditions and this phenomenon was ascribed to possible diffusion limitations or a distinct methylation mechanism at play with respect to benzene and toluene methylation [21]. A diffusion limitation effect has been proposed by Lercher and co-workers who studied toluene, xylene and tri-methylbenzene methylation in large pore-size (H-BEA*, H-MOR) and medium pore-size (H-ZSM-5, H-ZSM-11) zeolites. They suggested that reaction rates can decrease if the size of products is bulky enough to slow down product diffusion as observed in the narrower pores of H-ZSM-5 and H-ZSM-11 [24]. Lesthaege et al. pointed out that the deviations in methylation rate for larger molecules also can be due to a change in the reaction mechanism due to a transition-state-shape selectivity [25].

The effect of zeolite topology during benzene methylation by MeOH was studied in H-ZSM-5 and H-BEA* by Van der Mynsbrugge and co-workers [26]. Two-fold higher methylation rates were observed in H-ZSM-5 compared to H-BEA* zeolite. Theoretical calculations suggest that the stronger stabilization of the transition state is the cause for the higher activity in H-ZSM-5. Van der Mynsbrugge et al. pursued the effects of zeolite topology by studying very distinct zeolites, H-ZSM-58, H-ZSM-22 and H-ZSM-5, as alkene methylation catalysts using DFT methods [27]. They predicted that the methylation rates of ethene, propene and 2-butene were 3 orders of magnitude higher over H-ZSM-5 than over H-ZSM-58 or H-ZSM-22. The high enthalpy barriers in the large cavities of H-ZSM-58 (weak transition-state stabilization) and the high entropic barriers in the narrow channels of H-ZSM-22 (steric hindrance) were reported as responsible for the pronounced differences. The role of acid strength on zeolite-catalyzed methylation reactions has been recently studied by Westgård Erichsen et al. by comparing propene and benzene methylation over highly acidic H-SSZ-24 and weakly acidic H-SAPO-5 [28]. While both hydrocarbons were methylated at similar rates over H-SAPO-5, benzene methylation was significantly faster than propene methylation over H-SSZ-24.

Even though most of the methylation kinetic studies are performed under low conversion levels to minimize by-product formation, the microporous structure and high reactivity of zeolitic materials promote the rapid arousal of secondary reactions. For instance, typical by-products observed during co-reactions of MeOH/DME with benzene or toluene are polymethyl benzenes (polyMBs) and light olefin products, following the dual-cycle mechanism (*i.e.* the mechanism found to dominate the MTH reaction under steady-state conditions, see Scheme 1 [3,24,26,29]). Very recently, the formation of diphenylmethanes (DPMs) has

been reported during benzene methylation reactions by MeOH over H-SSZ-24 and H-SAPO-5, although its origin was not identified [28].

The two methylation agents, MeOH and DME, may be interconverted on Brønsted acid sites [31,32] by dehydration of MeOH to form DME and water (Rx. 1). Furthermore, MeOH is formed during methylation of a hydrocarbon by DME (Rx. 2). When MeOH is the methylating agent, a higher hydrocarbon is formed together with water (Rx. 3).

$$2CH_3OH \leftrightharpoons CH_3OCH_3 + H_2O \qquad (1)$$

$$CH_3OCH_3 + RH \rightarrow RCH_3 + CH_3OH; \qquad RH = alkene, arene \qquad (2)$$

$$CH_3OH + RH \rightarrow RCH_3 + H_2O; \qquad RH = alkene, arene \qquad (3)$$

Only a few studies exist that have compared methylation reactions by MeOH and DME. Apart from one theoretical study by Maihom et al. [33], these studies report DME as more reactive than MeOH over H-ZSM-5 [34,35]. This difference in reactivity is not fully understood yet, as the chemistries of MeOH and DME in zeolite-catalyzed hydrocarbon reactions are closely related. An analogous mechanistic role is generally assumed for MeOH and DME during methylation reactions [33,34,36]. Two alternative pathways have been proposed: the concerted and the stepwise mechanisms [2,20,26,37], as shown in Scheme 2. In the concerted mechanism, MeOH or DME react directly with the hydrocarbon in a single step to form a methylated product and H_2O or MeOH respectively. Alternatively, in the stepwise mechanism, MeOH or DME first react unimolecularly on the acid site to form water and a methoxy group. This methoxy group can subsequently act as a methylating agent.

DFT calculations on alkene methylation reactions in H-ZSM-22 have shown that DME stabilizes the methylation transition states to a larger extent than MeOH during a concerted methylation due to an increased entropy effect and additional electrostatic stabilization in comparison to MeOH when the gas phase reactants are the reference state, again leading to faster methylation rates [35]. Regarding the stepwise methylation, the methoxide formation is the distinct step between both oxygenates. Van der Mynsbrugge et al. reported slightly higher free energy barriers for unassisted methoxide formation for MeOH (160 kJ/mol) than for DME (143 kJ/mol) at 397 °C over H-ZSM-5 [38], and this effect might lead to different coverages of methoxy groups when using DME or MeOH. However, the second step of the methylation is identical by reacting methoxide with the alkene/arene. Both mechanisms are assumed to occur during zeolite-catalyzed methylation reactions and the occurrence of one or the other mechanism has been shown to depend on the zeolite topology and reaction conditions. Further work regarding the competition of both mechanisms is found in [20,28,31,35,38].

Apart from the higher methylation activity for DME, a recent contribution regarding the MTH reaction showed a slower catalyst
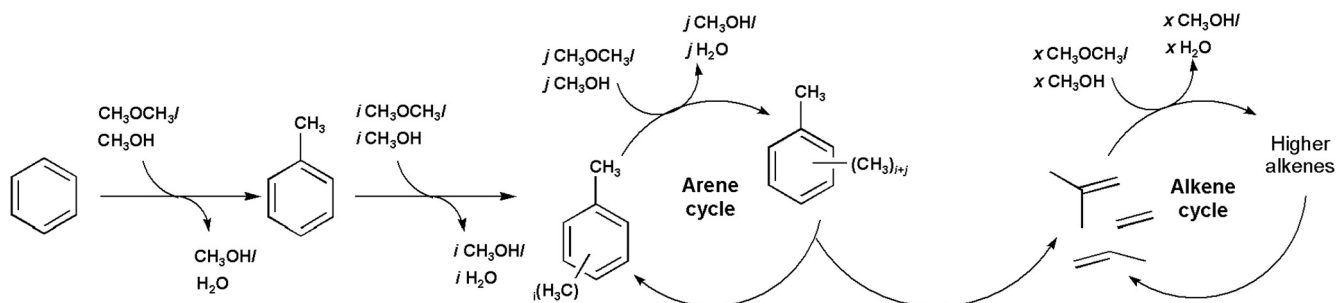
Scheme 1. Expected reactions during co-feed of benzene and MeOH/DME according to the dual-cycle mechanism. Adapted from [28,30].