

Effects of Zeolite Framework Topology for Conversion of Methanol/Ethanol to Hydrocarbons: Towards Computer-Directed Synthesis

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Proton-from zeolites, for example H-MFI, contain Brønsted acid sites capable of catalyzing reactions such as hydrocarbon methylation, alkene oligomerization, and alcohol dehydration—all of which are reactions that occur during methanol-to-hydrocarbon (MTH) processes. During MTH reactions, alkenes can grow through repeated methylation reactions to a size capable of cracking (C_{6+}) to form C_2 – C_4 alkenes which can egress from zeolite crystals as products or re-alkylate in the alkene cycle (Figure 1, blue). Alternatively, alkenes can undergo hydride transfers to form dienic compounds and which can subsequently cyclize to form aromatic species. These aromatics can be methylated during MTH to form one of thirteen distinct C_6 – C_{12} methylbenzene species which can undergo isomerization and dealkylation reactions (Figure 1, pink) to produce light alkene products that can egress or incorporate into the alkene cycle—thus making this process auto-catalytic. The complexity of these reaction pathways convolutes experimental kinetic studies, thus making theoretical approaches crucial to understanding the mechanisms involved during MTH processes.

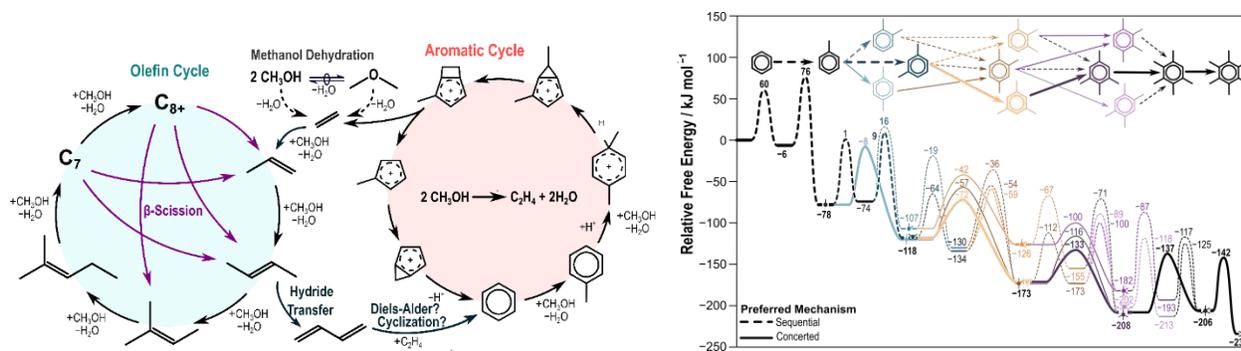


Figure 1. (Left) Dual cycle mechanism of MTH reactions. **Figure 2.** (Right) Reaction coordinate diagram showing the best methylation scheme (concerted or sequential) to form all possible methylbenzenes (top). Concerted methylation is shown in solid lines and sequential methylation is shown with dashed lines. Colors correspond to the methylbenzene species being formed (as shown in the top scheme). The most favorable pathway to form hexamethylbenzene is shown with thicker lines. Free energy values (kJ mol^{-1}) are reported at 473 K.

Previous experimental reports suggest that the aromatic cycle is responsible for the formation of C_2 alkenes in H-MFI, while the alkene cycle is the main mechanism to form C_{3+} species. Additionally, aromatic species can form large poly-aromatics which deactivate the catalyst by blocking access to the Brønsted acid site. Therefore, understanding the mechanism through which aromatic species grow during MTH processes is necessary to understand the formation of precursors for both ethene formation and catalyst deactivation. Arene methylation reactions occur via one of two distinct mechanisms: a sequential mechanism (also known as the dissociative or indirect mechanism) in which methanol (CH_3OH) or dimethyl ether (CH_3OCH_3) first methylate the zeolite surface to form a surface methoxy species preceding the methylation of the arene; or a concerted mechanism (also known as the associative or direct mechanism) in which CH_3OH or CH_3OCH_3 directly reacts with the arene. There are no significant increases in methylation barrier as the number of methyl-substituents on the aromatic species grows (Figure 2). Additionally, the formation of higher methylated arenes is thermodynamically favorable suggesting that C_{10+} methylbenzene species are likely to be the predominant species during MTH processes. The predominant pathway to form hexamethylbenzene involves sequential methylation of benzene to toluene then to meta-xylene, and then repeated concerted methylation of meta-xylene, to form 1,3,5-trimethylbenzene, 1,2,3,5-tetramethylbenzene, and finally penta- and hexamethylbenzene (Figure 2, denoted with thick lines)—suggesting that predominant arene species will be 1,2,3,5-tetra-, penta-, and hexamethylbenzene. The most favorable pathway to form hexamethylbenzene involves both the sequential and concerted methylation mechanisms indicating that both mechanisms occur during MTH processes and the preference is dependent on the number and position of methyl-substituents on the aromatic species.

Once aromatic species are formed in the zeolite, they can undergo isomerization and dealkylation reactions to produce light alkenes—predominantly ethene in H-MFI. There are three proposed mechanisms in which alkenes are produced via the aromatic cycle: side-chain, expansion-contraction, and contraction-expansion. The side-chain

mechanism involves direct methylation of an exocyclic C-substituent until the side-chain is large enough to detach as an olefin. The expansion-contraction and contraction-expansion mechanisms form side chains through methylation and manipulation of the aromatic ring, and these cycles will therefore incorporate ring C-atoms into product alkenes. The three mechanisms can occur via a multitude of different pathways (Figure 3).

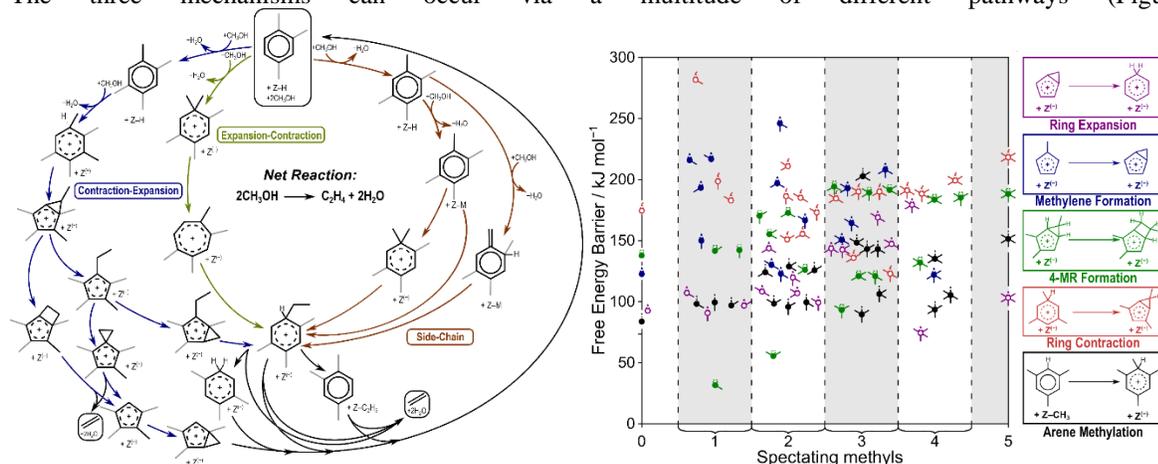


Figure 3. (Left) Mechanisms attempted for the contraction-expansion (blue), expansion-contraction (green), and side-chain (brown) pathways. **Figure 4.** (Right) Effects of methylation on free energy barriers of elementary steps involved in the aromatic cycle of MTH reactions.

Each pathway in Figure 3 was modeled in the MFI framework using all thirteen aromatic co-catalysts and the results suggest that the most favorable pathway and mechanism change based upon the selection of co-catalyst—similar to the results of arene methylation reactions. With benzene as the co-catalyst, the minimum energy pathways for expansion-contraction and side-chain routes have similar energy barriers (138 kJ mol^{-1} and 143 kJ mol^{-1} respectively). However, when 1,2,4-trimethylbenzene serves as the co-catalyst, the barrier for the side-chain mechanism is $> 20 \text{ kJ mol}^{-1}$ lower in energy than contraction-expansion and expansion-contraction—suggesting that the favorability of different routes changes between co-catalysts.

Overall, the barriers of ethene formation via benzene are lower than those of ethene formation via 1,2,4-trimethylbenzene, supporting that the identity of aromatic co-catalyst alters the preferred pathway. There are no simple trends, such as steric or electronic confinement, to describe the effects of extent and location of methyl-substituents on the aromatic co-catalyst (Figure 4). Therefore, all elementary steps must be modeled with all thirteen methylbenzene co-catalyst species to yield accurate conclusions.

Reaction coordinate diagrams are insufficient to analyze 500+ elementary steps involved ethene-forming pathways. Thus, kinetic Monte-Carlo (KMC) simulations are employed to assess the efficacy of different co-catalysts, mechanisms of co-catalyst interconversion, and preferred pathway to form ethene. Using KMC we can reduce the reaction network by identifying surface intermediates, quasi-equilibrated steps, and dominating chemical cycles. Using this method to identify the primary ethene formation route, we find that benzene repeatedly methylates to form 1,2,3,5-tetramethylbenzene which then proceeds through the side-chain mechanism to eliminate ethene and re-form 1,2,3,5-tetramethylbenzene.

This work will be expanded to involve all critical steps of alkene-forming mechanisms during MTH processes (e.g., alkene cracking, diene formation, and diene cyclization). This large reaction network will be reduced by KMC as demonstrated by the ethene-forming reaction network which reduced 529 total reactions into 11 reactions that make $>90\%$ of C_2 . Once the key structures in these reaction networks are identified, the investigation will expand to include all 12 unique T-sites in H-MFI to evaluate a variety of confining environments on the reactivity of different intermediate species. Finally, state-specific forcefields will be developed to rapidly predict confinement effects and reactive intermediates in a large subset of zeolites to identify potentially transformational materials within the complete set of synthesized (>200) and theoretical ($>300,000$) zeolite frameworks. This multiscale modeling approach combining DFT, SSFF/ML, and KMC will generate fundamental understanding of the impacts of acid strength, site location, zeolite framework and crystal size on MTH reactions and ultimately enable the rational design of novel zeolites to improve MTH selectivity and stability.