Mechanism and Kinetics of Methylating C_6−C_12 Methylbenzenes with Methanol and Dimethyl Ether in H-MFI Zeolites

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ABSTRACT: This study uses periodic density functional theory (DFT) to determine the reaction mechanism and effects of reactant size for all 20 arene (C_6−C_12) methylation reactions using CH_3OH and CH_3OCH_3 as methylating agents in H-MFI zeolites. Reactant, product, and transition state structures were manually generated, optimized, and then systematically reoriented and reoptimized to sufficiently sample the potential energy surface and thus identify global minima and the most stable transition states which interconnect them. These systematic reorientations decreased energies by up to 45 kJ mol^{-1}, demonstrating their necessity when analyzing reaction pathways or adsorptive properties of zeolites. Benzene−CH_3OCH_3 methylation occurs via sequential pathways, consistent with prior reports, but is limited by surface methylation which is stabilized by coadsorbed benzene via cooperativity between the channels and intersections within MFI. These coadsorbate-assisted surface methylations generally prevail over unassisted routes. Calculated free energy barriers and reaction energies suggest that both the sequential and concerted methylation mechanisms can occur, depending on the methylating agent and methylbenzene being reactant; no single mechanism prevails for these homologous reactions. Intrinsic methylation barriers for stepwise reactions of benzene to hexamethylbenzene remain between 75−137 kJ mol^{-1} at conditions relevant to methanol-to-hydrocarbon (MTH) reactions where such arene species act as cocatalysts. Intrinsic methylation barriers are similar between CH_3OH and CH_3OCH_3, suggesting that both species are equally capable of interconverting methylbenzene species. Additionally, these methylation barriers do not systematically increase as the number of methyl-substituents on the arene increases and the formation of higher methylated arenes is thermodynamically favorable. These barriers are significantly lower than those associated with alkene formation during the aromatic cycle, suggesting that aromatic species formed during MTH reactions either egress from the catalyst—depending on that zeolite’s pore structure—or become trapped as extensively substituted C_10−C_12 species, which can either isomerize to form olefins or ultimately create polyaromatic species that deactivate MTH catalysts.

KEYWORDS: surface methoxy (CH_3−Z), kinetics, zeolites, coadsorbate interactions, methanol-to-olefins, methylation

1. INTRODUCTION

Brønsted-acid-catalyzed alkylation reactions are ubiquitous, occurring during alcohol dehydration, and alkene oligomerization, and methanol-to-hydrocarbon (MTH) reactions. Methanol does not directly couple to form C_3−C bonds during MTH reactions or does so at low rates. Instead, zeolite surfaces, alkenes, and arenes are methylated by a combination of methanol (CH_3OH) and dimethyl ether (CH_3OCH_3), both present at MTH conditions. Alkenes can grow through repeated methylation reactions (reacting with surface methoxy (CH_3−Z) species or directly with methylating agents such as CH_3OH and CH_3OCH_3). Larger C_6 arenes can crack into C_3−C_6 alkenes which can desorb as products or realkylate in the alkene cycle, in which olefins are alkylated and crack to form other alkene species of varying lengths. For example, three CH_3OH molecules may sequentially methylate propene to form hexene which could crack into two propene molecules; as such, this olefin-forming process can be “auto-catalytic” as alkenes are both cocatalysts and products of MTH. Alkenes may, instead of cracking, undergo hydride transfer reactions with other alkenes (to form alkanes and dienic compounds) or with methanol (to form alkanes, formaldehyde, and ultimately dienes) and then cyclize in mono- or bimolecular routes to ultimately form aromatic compounds (arenes). These arenes can be methylated during MTH to form one of 12 distinct C_6−C_12 methylbenzene species, shown in Figure 1. Many of these methylbenzene species can undergo isomerization and dealkylation reactions to produce light alkene products that can egress from the zeolite crystal or join the alkene cycle; thus, the alkene products from methylbenzenes may be incorporated into other aromatic compounds, again leading to autocatalytic behavior. Therefore, under-
standing how arene cocatalysts interconvert is key to understanding the larger MTH reaction network. Arene methylation, in addition to its role in MTH, is also important in the formation of toluene from benzene, toluene disproportionation to xylenes, and other transalkylation reactions.\textsuperscript{22–25} Despite the ubiquity of arene methylation reactions in industrial processes, there are few studies contrasting arene methylation mechanisms with CH$_3$OH and CH$_3$OCH$_3$ and fewer studies elucidating methylation mechanisms across a wide range of methylbenzene reagents.

Brønsted-acid-catalyzed alkylation reactions occur via one of two distinct mechanisms:\textsuperscript{2,6,26–31} a sequential mechanism (also known as the dissociative or indirect mechanism) or a concerted mechanism (also known as the associative or direct mechanism). In the sequential mechanism, the methylating agent first methylates the zeolite to form CH$_3$–Z preceding the methylation of an alkene, alkane, or arene:

$$\text{ROCH}_3 + \text{H}–\text{Z} \rightarrow [\text{ROH} \cdots \text{CH}_3^+ \cdots \text{Z}^-]$$\textsuperscript{‡}

$$\rightarrow \text{ROH} + \text{CH}_3–\text{Z}$$ (1)

$$\text{C}_n\text{H}_6 + \text{CH}_3–\text{Z} \rightarrow [\text{C}_n\text{H}_6 \cdots \text{CH}_3^+ \cdots \text{Z}^-]$$\textsuperscript{‡}

$$\rightarrow \text{C}_n\text{H}_8 + \text{H}–\text{Z}$$ (2)

In the concerted mechanism, the methylating agent directly reacts with an alcohol, alkane, or arene:

$$\text{ROCH}_3 + \text{C}_n\text{H}_6 + \text{H}–\text{Z}$$

$$\rightarrow [\text{ROH} \cdots \text{CH}_3^+ \cdots \text{C}_n\text{H}_6 + \text{Z}^-]$$\textsuperscript{‡}

$$\rightarrow \text{ROH} + \text{C}_n\text{H}_8 + \text{H}–\text{Z}$$ (3)

Surface methoxy species are a reactive intermediate in the sequential pathway but not the concerted pathway, and their presence is commonly used to differentiate between these pathways. The purging of C$_6$H$_6$–CH$_3$OCH$_3$ after reaction in a pillared MFI framework zeolite (H-SPP, 358 K) followed by a subsequent heat treatment (423 K) and titration with H$_2$O formed CH$_3$OH in a 1:1 ratio with Al, suggesting high surface methoxy coverages.\textsuperscript{28} Benzene and toluene d$_0$, DME/DME switching experiments demonstrate a 1:2:1 ratio of d$_0$:d$_1$:d$_2$ indicating rapid C–O bond breaking and formation at reaction conditions,\textsuperscript{28} consistent with alkene methylation studies.\textsuperscript{29}

However, CH$_3$–Z species were not identified by FT-IR during the coreaction of benzene and CH$_3$OH at 623 K at steady state—conditions that better represent those of MTH processes\textsuperscript{27}—suggesting that the presence of an arene at reaction conditions may alter the amount of surface methoxy species formed. The absence, presence, or abundance of CH$_3$–Z, however, does not rule out either methylation mechanism. For instance, the absence or scarcity of CH$_3$–Z species can indicate that the concerted mechanism occurs (i.e., they are not formed) or that ring methylation consumes CH$_3$–Z too fast for them to accumulate to detectable levels. Similarly, high coverages of CH$_3$–Z species do not preclude the concerted mechanism from occurring, as CH$_3$–Z species may be unreactive spectators in arene methylation or react predominantly with oxygenates.

The sequential and concerted mechanisms may also differ by the kinetic dependencies of the methylating agent (CH$_3$OR), the leaving group (ROH), and the species being methylated (alcohol, alkene, or arene). Kinetic studies (0.002–0.05 bar aromatic, 0.29–0.68 bar CH$_3$OCH$_3$, 0.1% conversion) of benzene (373 K), toluene (403 K), and xylene (473 K) methylation with CH$_3$OCH$_3$ have shown rates independent of CH$_3$OCH$_3$ pressure and linearly dependent on arene pressure.\textsuperscript{28} Coupled zero-order effects of CH$_3$OCH$_3$ and first-order effects of arene reagents suggest that sequential methylation pathways prevail and are limited by arene methylation steps on surfaces covered by CH$_3$–Z species; however, coadsorbate-assisted surface methylation reactions have not been considered.\textsuperscript{28} Density functional theory (DFT) calculations on a cluster of four tetrahedral sites (T-sites) and ab initio molecular dynamic studies indicate concerted methylation barriers are >30 kJ mol$^{-1}$ lower than those of sequential methylation with CH$_3$OCH$_3$.\textsuperscript{32,33} These theoretical data suggest that benzene methylation proceeds via concerted methylation;\textsuperscript{26,29} however, small cluster models fail to differentiate between these mechanisms across a wide range of methylbenzene reagents.

Theoretical and experimental work has demonstrated that CH$_3$OCH$_3$ methylates alkenes and arenes at a faster rate than CH$_3$OH. CH$_3$OCH$_3$ methylates propene at a rate 2.5 times faster than CH$_3$OH in H-ZSM-5 (523 K, 0.02 bar propene, 0.025–0.075 bar CH$_3$OH or CH$_3$OCH$_3$).\textsuperscript{11} DFT calculations on cluster models with four T-sites similarly predict that concerted methylation of both propene and toluene occur with lower barriers from CH$_3$OCH$_3$ than with CH$_3$OH.\textsuperscript{11} Computational and experimental studies generally agree that CH$_3$OCH$_3$ is the dominant methylation agent at typical arene methylation conditions (low conversions, 400–600 K).\textsuperscript{35–37} These comparisons between CH$_3$OH and CH$_3$OCH$_3$ are limited to methylations of C$_6$–C$_{12}$ arenes; larger, extensively substituted methylbenzene species, however, may crowd out CH$_3$OCH$_3$ molecules in favor of smaller CH$_3$OH, thereby limiting the effectiveness of CH$_3$OCH$_3$ during methylation.

Few studies investigate the effects of arene substitution on methylation barriers and preferred methylation mechanisms. DFT calculations of p-xylene, 1,2,4-trimethylbenzene, and 1,2,3,5-tetramethylbenzene on larger 66 T-sites of H-ZSM-12 and H-ZSM-22 suggest that barriers of concerted methylation by CH$_3$OH remain relatively constant for C$_6$ and C$_9$ species but increase for C$_{10}$ species—suggesting that strong repulsive interactions limit methylation in these zeolites.\textsuperscript{38} Additionally, this work demonstrated that in H-ZSM-22 geminal methyl-
methylation barriers of smaller arenes through non-covalent interactions. Conversely, the rates of methyl substituents increases. Conversely, the rates of methyl substituents increases.39 Conversely, the rates of methyl substituents increases. Conversely, the rates of methyl substituents increases. Conversely, the rates of methyl substituents increases. Conversely, the rates of methyl substituents increases.

Reorientations of Reactant, Product, and Transition States. All DFT-optimized reactant, product, and transition states were systematically reoriented and reoptimized to increase the likelihood that optimum transition states were accurately sampled. Reorientations of Reactant, Product, and Transition States. All DFT-optimized reactant, product, and transition states were systematically reoriented and reoptimized to increase the likelihood that optimum transition states were accurately sampled.

2. METHODS

2.1. Computational Methods. DFT calculations were carried out using the Vienna ab initio simulation package (VASP)40–43 in a fully periodic MFI unit cell. Plane waves were constructed using projector augmented-wave (PAW)44,45 potentials with an energy cutoff of 400 eV. The Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation (GGA) was used to determine exchange and correlation energies.46–48 The DFT-D3 method with Becke and Johnson damping accounted for dispersive interactions.49–51 The Brillouin zone was sampled at the Γ-point for all calculations.52

The MFI structure was obtained from the IZA database53 and annealed using ab initio molecular dynamics (AIMD) to generate a low-energy state for these DFT settings. The structure was heated from 200 to 800 K over 3000 fs, held at 800 K for 3000 fs, and then cooled over 15000 fs. During these AIMD studies, the wave function for each step was converged to within 10−4 eV and one atom was fixed to prevent bulk translation. The final structure obtained after annealing and optimizing is 23 kJ mol−1 more stable than the directly optimized IZA structure (Figure S1, in the Supporting Information, SI). These calculations were done to ensure stability within the baseline framework and prevent framework restructuring from altering calculated activation and reaction energies, as described in detail elsewhere.54

Previous work investigating methanol dehydration on sites T3, T10, T11, and T12 in MFI suggests that surface methylation occurs with the lowest barriers at T11;5 therefore, all calculations were performed at the T11 T-site in MFI, which gives access to both the straight channel and the channel intersection where arenes prefer to adsorb.

All reactant, product, and transition states were optimized with static DFT calculations until the maximum force on any atom was <0.05 eV Å−1. Wave functions were converged to within 10−4 eV, and all forces were computed using a fast Fourier transform (FFT) grid with a cutoff twice the planewave cutoff. No atoms were constrained in any DFT optimization, pathway, or transition state calculations while the lattice parameters (a = 20.090 Å, b = 19.738 Å, c = 13.142 Å) and orthorhombic shape were fixed.

Minimum energy pathways were estimated using the nudged elastic band (NEB)55,56 method. NEB calculations used 16 images, and wave functions converged to 10−4 eV with an FFT grid 1.5 times the size of the plane-wave cutoff. The maximum force on each atom in all images was converged to <0.5 eV Å−1. This estimate of the minimum energy pathway was used to generate initial transition state structures and reaction modes for the Dimer method,57 which optimizes a pair of structures to determine the local curvature of the potential energy surface until ultimately converging on a saddle point. The same convergence criteria were used for optimization and dimer calculations (e.g., maximum forces on any atom <0.05 eV Å−1).

Frequencies were calculated for all reactant, product, and transition states using a fixed displacement method where the adsorbates (e.g., CH3OH and benzene) and AlO4H of the acid site are displaced while all other framework atoms are fixed. Low-frequency modes (<60 cm−1) were replaced with 60 cm−1, similar to previous work58,59 because low frequencies are inaccurate and contribute significantly to vibrational entropy terms. These frequency calculations are used to determine temperature-corrected (373–673 K) enthalpies and free energies according to harmonic oscillator approximations for vibrational partition functions and ideal gas treatments of rotational and translational partition functions for bulk gas species.

2.2. Reorientations of Reactant, Product, and Transition States. All DFT-optimized reactant, product, and transition states were systematically reoriented and reoptimized to increase the likelihood that optimum transition states were accurately sampled.
state structures were obtained via static (nondynamic) DFT calculations. Species were first optimized from manually generated structures and then reoriented based on the nature of the interaction between the adsorbate and the zeolite; all reoriented structures are subsequently reoptimized to identify minimum energy states. Adsorbed species and transition states can interact with the zeolite in several ways: forming covalent bonds (e.g., CH$_3$−Z), forming H-bonds with Bronsted acid sites (e.g., CH$_3$OH*), or purely through nonspecific dispersive and electrostatic interactions (e.g., C$_6$H$_6$*, C$_7$H$_9$*). Three reorientation schemes are used here: acid site reorientations, internal reorientations, and spatial reorientations (Figure 2 gives examples of all three).

Adsorbates that covalently bind to the framework or form H-bonds with protonated Bronsted acid sites, such as adsorbed oxygenates and alkoxides, underwent acid site reorientations (e.g., CH$_3$OCH$_3$* in Figure 2a). Structures and acid sites are rotated by altering the dihedral angle formed between an O atom of the acid site (O$_a$), the Al atom, the Si atom closest to the acid site, and the O to which the proton or alkoxide is bound (O$_t$) in O$_t$−Al−Si−O$_a$ rotations. This motion effectively sweeps the adsorbed species around the acid site (Figure 2a), as done previously for Bronsted acid site calculations. The O$_t$−Al−Si−O$_a$ angles were varied by 30° increments from 30° to 330°, and each 30° increment was optimized using the parameters discussed in Section 2.1. The angle between the Al atom, the O$_t$ atom, and the adsorbate itself (A$_1$) can also be varied (Figure 2a) to move the adsorbate above the acid site parallel to the Si−O$_a$−Al bridge, and this Al−O$_t$−A$_1$ angle was varied by −30°, −15°, 15°, and 30° from the initial optimized position and optimized at all of these increments. Finally, the dihedral angle between a T-site, the O$_t$ atom, and two adsorbate atoms (A$_1$ and A$_2$) can be altered to spin the adsorbate around the O$_t$ atom, as shown in Figure 2a; the dihedral angles were varied by 30° increments from 30° to 330°, and each 30° increment was optimized using the parameters discussed in Section 2.1.

Large transition state complexes associated with surface methylation, sequential methylation of the arene ring, or concerted methylation of the arene ring have multiple fragments that can rotate about breaking or nascent bonds. Concerted benzene methylation by CH$_3$OCH$_3$*, for example, involves CH$_3$OH, methyl, and arene fragments (Figure 2b), and these species can be reoriented relative to one another to isolate more stable transition state structures. The orientation of the ring relative to the attacking methyl group (ring-CH$_3$ angle) was altered so that the two species were coplanar. Furthermore, the ring was rotated about the axis of the oxygen of the CH$_3$OH group (O$_n$), the carbon of the attacking methyl species (C$_i$), and the carbon on the ring being attacked (C$_j$) so that the orientation of the ring changes without affecting the incipient bond of the transition state. Rotations about the O$_n$−C$_i$−C$_j$ axis were performed from 30° to 330° in 30° increments, and each 30° increment was optimized using the parameters discussed in Section 2.1. This transition state complex, furthermore, can be rotated spatially as it interacts nonspecifically with the zeolite framework and the deprotonated Bronsted acid site. Each transition state reorientation is reoptimized using the Dimer method. The mode and internal geometry of the initial structure is preserved during reoptimization (Figure S5), and all reoriented structures demonstrate a single strongly negative frequency associated with the expected bond-breaking or forming events.

Adsorbate species that interact nonspecifically through a combination of dispersive and electrostatic interactions and without H-bonds to a protonated acid site were rotated in spatial reorientations (e.g., methylbenzene in Figure 2c). Arenes were also rotated around the axis perpendicular to the ring (Figure 2c). Species were rotated and then optimized in 30° increments from 30° to 330° during these spatial reorientations; rotations resulting in collisions with the zeolite framework were discarded.

All reorientations described above are used as initial structures—they are not intended to determine torsional barriers or generate intramolecular potential energy surfaces; they are instead fully optimized in unconstrained calculations. As such, these reorientations serve to extensively seed a potential energy surface with multiple initial structures—each optimized—to potentially many local minima. These local minima are compared, and the minimum potential energy structures are used in further analysis. The relationship between the potential energy and free energy was tested for two states (C$_6$H$_6$* and surface methylation near 1,2,4-trimethylbenzene transition state) by running frequency calculations for all reoriented structures. The results suggest that there is generally a strong correlation between potential energy...
energy and free energy (Figure S6 and S7). These reorientation techniques result in energies more accurate than those obtained from a single or small ensemble of DFT optimizations; however, they are not guaranteed to isolate global minima.

3. RESULTS AND DISCUSSION

3.1. Identifying the Most Stable Orientations and Locations of Arene Methylation Species. The T11 T-site is used for all reactions in this study and is connected to four unique O-sites: O14 (straight channel), O16 (intersection), O24 (beneath intersection), and O25 (intersection) (see Figure S8 in the Supporting Information). The O24 site is inaccessible for species larger than −CH3, and therefore, all other reactions were studied only at O14, O16, and O25, except for surface methylation, which was modeled at all sites. Systematic reorientations can find structures drastically lower in energy than initial optimizations (Figure 3). Three types of systematic reorientations were performed on guest species using static DFT calculations as appropriate: acid site, spatial, and internal reorientations. Each type of reorientation produced structures that were more stable than their manually generated counterparts. Figure 3 shows a subset of the results of the reorientations performed for CH3OCH3*; C6H6--CH3OCH3*; C7H8*; the transition state for surface methylation (e) in the presence of benzene, the transition state for benzene methylation from a surface methoxy, and concerted benzene methylation on each accessible O-site on T11.

Acid site reorientations were performed on adsorbates that covalently bind to the framework and those that form H-bonds to surface protons (e.g., CH3OCH3*) as described in Section 2.2. Structures were reoriented by altering the Ot−Al−Si−Oa, Al−Oa−A1, and Ot−Oa−A1−A2 angles (Figure 2a). These reorientations resulted in average energy decreases of 6.5 kJ mol−1, 6.1 kJ mol−1, and 11.3 kJ mol−1 compared to manually generated optimized structures for species relevant to benzene methylation (Figure 3a) shows reorientations of CH3OCH3 about O14, O16, and O25 resulting in energy decreases of ∼6 kJ mol−1 at each acid site.

Spatial reorientations were performed on species that do not strongly interact with the Brønsted acid site (e.g., toluene). The subset of structures relevant to benzene methylation were rotated about the a-, b-, and c-axes of the unit cell resulting in an average decrease in energy of 8.5, 7.2, and 8.4 kJ mol−1, respectively. Species with one or more methyl-substituents on the benzene ring (toluene to hexamethylbenzene) were also rotated about the axis perpendicular to the center of the ring resulting in <5 kJ mol−1 energy decreases for C7H8* at O14 and O16 but a ∼45 kJ mol−2 decrease at O25 (Figure 3c).

States with coadsorbed species, such as C6H6--CH3OCH3* (Figure 3b), may contain both acid-site interacting fragments (CH3OCH3*) and noninteracting fragments (C6H6). These two fragments were rotated independently of each other. Benzene was rotated with spatial reorientations (e.g., Figure 2c), and CH3OCH3 was rotated with acid site reorientations (e.g., Figure 2a). The reorientation that located the minimum
value is the rotation about the c-axis angle at O14, the a-axis at O16, and Al−O−A1 at O25, suggesting that no single reorientation scheme consistently finds the minimum energy state. Internal reorientations are specific to ring methylation transition states (concerted or via methoxy species, Figure 3ef). Both ring methylation transition states, \([C\text{H}_2\cdots\text{CH}_3\cdots\text{Z}\]^+\) (sequential) and \([\text{CH}_3\text{OH}−\text{CH}_2\cdots\text{CH}_3\]^+\) (concerted), underwent internal reorientations (e.g., Figure 2b) in addition to the other appropriate reorientations (acid site reorientations in sequential methylation and spatial reorientations in concerted methylation). The orientation of the ring was changed independently of the transition state (about the O−C−C axis); these reorientations resulted in an average decrease of 12 kJ mol\(^{-1}\) for transition states relevant to benzene methylation. The internal coordinates of the CH3OH and attacking methyl species were also altered about the O−C−C−C axis, resulting in energy decreases of 16 kJ mol\(^{-1}\) and 19 kJ mol\(^{-1}\).

Initial optimizations or transition states formed by manually generated structures or pathways are consistently less stable than the best structures obtained after their systematic reorientation. These energy shifts can be as high as 45 kJ mol\(^{-1}\) and are not consistent across all adsorbates, indicating that ground-state activation barriers and reaction energies are overpredicted absent these reorientations. Performing these systematic reorientations leads to major shifts in DFT-predicted reaction mechanisms, kinetics, and surface coverages. No consistent reorientation schemes or types (e.g., acid site) locate the lowest energy state; therefore, when using static DFT reorientations to probe a potential energy surface, all appropriate reorientation schemes should be utilized to obtain the lowest energy state.

Surface methylation reactions were modeled on all four T11 O-sites (O14, O16, O24, and O25) with both CH3OH and CH3OCH3 (Figure 4). Observed free energy barrier trends for both methylation agents are identical with regard to O-site preference (O16 < O14 < O25 < O24), suggesting methylation transition states on sites near the straight channel are more stable. Initial calculations (pre-reorientation) followed different trends for transition state stabilities on these O-sites (Figure S9). These results further demonstrate the necessity of seeding the potential energy surface with systematically reoriented structures to find the lowest energy transition states. These data also suggest that reaction energies cannot predict the kinetically active site, as reaction energies do not trend with activation barriers.

The transition states on O14, O16, and O25 sit in the straight channel (Figure 5), where stabilizing interactions between the framework and transition state complex are maximized. The transition state for surface methylation with CH3OH at O16 forms the strongest H-bonds with the framework (182 pm, Figure 5b), leading to the most stable transition state for surface methylation with CH3OH. Similarly, the transition state from CH3OCH3 at O16 forms H-bonds with the framework (192 pm) which are shorter than those found in transition states at O14 and O25 (221 and 215 pm respectively, Figure 5ad). Both transition states at O24 form H-bonds (192 pm for CH3OH and 188 pm for CH3OCH3, Figure 5c), but because O24 does not share a void with O14, O16, and O25, the transition state nearly collides with framework atoms. As a result, repulsive forces outweigh the stabilization conferred by H-bonding, leading to a barrier >200 kJ mol\(^{-1}\) higher than the barrier at all other O-sites.

Examining these reactions at all O-site combinations and reorienting optimized reactant, product, and transition state structures results in activation free energies varying from 82 to 126 kJ mol\(^{-1}\) (neglecting the nearly inaccessible O24 site). Furthermore, systematic reorientations (e.g., Figure 2) shift energies by ~10 kJ mol\(^{-1}\) on average and up to 45 kJ mol\(^{-1}\) compared to calculations optimized “manually” generated structures, typical of DFT examinations. These reorientations were done for all calculations in this text, although only discussed in this section. Differences in reactant, transition state, and product orientations may create reorientation barriers that must be overcome to connect reactant and product states to the transition state; however, these reorientation barriers are not kinetically relevant and do not change the rate of the reaction (Figure S10). These efforts demonstrate the complexity of the potential energy surface for zeolite-catalyzed reactions, in contrast to metal surface reactions, for example, which have relatively few binding modes of interest for each adsorbate. While ab initio molecular dynamics have been used previously to determine low-energy states in MTH studies,\(^{33}\) we feel these systematic reorientation studies offer a less computationally expensive approach for determining ground state energetics of adsorbates and transition states within zeolites for thermodynamic and kinetic analyses.

3.2. Kinetics of Benzene Methylation. Arene methylation can occur through two well-defined mechanisms: sequential and concerted methylation (Figure 6). Rate equations for each possible rate-determining step are used to employ a maximum rate analysis which asserts, one at a time, that a step is rate-determining and that all preceding steps are quasi-equilibrated. This method of rate analysis can be used to predict the maximum net rate for each elementary step using DFT-calculated energies. These rate equations and assumptions made with maximum rate analysis are defined and derived in Section S2 of the Supporting Information. The maximum rates of the concerted and sequential pathways are

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**Figure 4.** Reaction coordinate diagram of surface methylation by (a) CH3OH and (b) CH3OCH3 (right) at O14 (red), O16 (yellow), O24 (blue), and O25 (green). The most favorable pathway, determined by the lowest energy transition state, occurs at O16 and is traced with lines. Free energy values relative to a proton at O14 are reported at 373 K in kJ mol\(^{-1}\).
compared to determine the preferred mechanism. Maximum rate analyses can be used to compare reactions that occur in parallel, for example surface methylation in an empty pore versus surface methylation with a spectating arene, by identifying the mechanism with the highest maximum rate which is most likely to form the product. Alternatively, the maximum rate of reactions that occur in series—for example surface methylation followed by ring methylation of the sequential mechanism—is determined by identifying the step with the lowest maximum rate which limits the rate of that pathway. Maximum rate analysis also allows for comparison of DFT-derived rates and experimentally measured rates. We compare our predictions (Figure 7) to measurements obtained from kinetic studies of benzene methylation by CH$_3$OCH$_3$ (373 K, 0.02 bar aromatic, 0.68 bar CH$_3$OCH$_3$, 0.1% aromatic conversion).$^{28}$

Surface methoxy formation, the first step of the sequential mechanism, was investigated in an empty zeolite and with a spectating benzene ring with CH$_3$OH and CH$_3$OCH$_3$ at all four O-sites surrounding T11. Site O16, which is located in the channel intersection, has the lowest surface methoxy formation barrier with CH$_3$OH and CH$_3$OCH$_3$ (Section 3.1). At 353–463 K, surface methylation with spectating benzene occurs with a higher maximum rate than surface methylation in an empty pore by CH$_3$OH and CH$_3$OCH$_3$, demonstrating that benzene enthalpically stabilizes the surface methylation transition states (Figure 7b). The rate increase with a spectating benzene is accompanied by concomitant decreases in the intrinsic free energy barriers at these temperatures:

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**Figure 5.** Lowest energy orientation of the surface methylation transition state at (a) O14, (b) O16, (c) O24, and (d) O25 looking down the straight (top) and sinusoidal (bottom) channels for CH$_3$OH and CH$_3$OCH$_3$. Enthalpy (kJ mol$^{-1}$), entropy (J mol$^{-1}$ K$^{-1}$), and free energy (kJ mol$^{-1}$) values are reported at 373 K and relative to a protonated zeolite and stoichiometric amounts of gas-phase CH$_3$OH or CH$_3$OCH$_3$ molecules, as appropriate. Relevant H-bond lengths are reported in pm. Additional viewing angles for the methylation of O24 are provided in Figure S11 in the Supporting Information.

**Figure 6.** Scheme of benzene methylation pathways showing surface methylation with no spectating species, surface methylation with spectating benzene, concerted methylation, and deprotonation (left to right). Associated rate constants (K and k values) are shown adjacent to each arrow and are used in eq 4.
Surface methylation by CH$_3$OH occurs with an intrinsic barrier of 144 kJ mol$^{-1}$ in the absence coadsorbed benzene and 105 kJ mol$^{-1}$ its presence (Figure 8), and a similar decrease from 129 kJ mol$^{-1}$ to 114 kJ mol$^{-1}$ is observed for CH$_3$OCH$_3$ at 373 K. Benzene provides enthalpic stabilization for surface methyl-ation transition states at all temperatures; however, at higher temperatures, entropic gains from benzene desorption outweigh the enthalpic stabilization it confers. Surface methylation by CH$_3$OH has maximum rates that are slightly higher than CH$_3$OCH$_3$ when coadsorbed benzene is present. These barrier differences, however, are within the uncertainty associated with DFT calculations ($\sim 10$ kJ mol$^{-1}$). Therefore, it is reasonable to assume that both CH$_3$OH and CH$_3$OCH$_3$ are equally capable of methylating the MFI surface at site T11 in the presence of a coadsorbed benzene.

Here, systematic reorientations (Section 3.1) provided valuable insight into the cooperativity between coadsorbates and the different voids of MFI—aspects that were unapparent on initial structure input. The surface methylation transition states occur with the lowest barriers when positioned in the straight channel, rather than the channel intersection, because the tighter confinement by the framework offers more dispersive stabilization (Section 3.1). When benzene is coadsorbed during surface methylation, the transition states (CH$_3$OH and CH$_3$OCH$_3$) remain in the straight channel while the benzene caps the intersection of the straight and sinusoidal pores (Figure 8b,c). This orientation of benzene creates a pocket that increases dispersive stabilization without preventing diffusion and transport as the benzene can shift to allow ROH egress. The MFI framework thus offers a unique environment for catalysis as small transition states can be confined in the straight channel, while larger species can reside in the channel intersection, thereby maximizing stabilization for small species and minimizing steric repulsions for large species. This cooperativity between the smaller channels and larger intersections makes MFI ideal for reactions involving disparately sized species such as those involved in benzene, toluene, and xylene (BTX) methylation and MTH reactions.

Benzene methylation via CH$_3$Z is rapid compared to the formation of CH$_3$Z species, occurring at rates over 100× higher at 373 K. Ring species are methylated most favorably from CH$_3$Z bound to O16, which is also the most favorable

Figure 7. (a) Reaction coordinate diagram with free energies (kJ mol$^{-1}$, 1 bar, 373 K) relative to a proton at O16 for benzene methylation by CH$_3$OH (solid lines) and CH$_3$OCH$_3$ (dashed lines) with surface methylation (green), surface methylation near arene (red), concerted arene methylation (blue), arene methylation (gray), and deprotonation (black) steps. (b) Maximum rates of arene methylation by CH$_3$OH (solid) and CH$_3$OCH$_3$ (dashed) at 0.01 bar C$_6$H$_6$, 0.68 bar CH$_3$OR, 0.1% aromatic conversion, ranging from 353–493 K using surface methylation of O16 (green), surface methylation of O16 near arene (red), concerted arene methylation (blue), and arene methylation (gray) as the rate-determining step.

Figure 8. Lowest energy orientation of (a) empty surface methylation with CH$_3$OH, (b) empty surface methylation with CH$_3$OCH$_3$, (c) surface methylation with spectating benzene with CH$_3$OH, (d) surface methylation with spectating benzene with CH$_3$OCH$_3$, (e) benzene methylation via surface methoxy, (f) concerted methylation with CH$_3$OH, and (g) concerted methylation with CH$_3$OCH$_3$ with views down the straight (top) and sinusoidal (bottom) channels. Enthalpy ($\Delta H$ in kJ mol$^{-1}$), entropy ($\Delta S$ in J mol$^{-1}$ K$^{-1}$), and overall free energy barriers ($\Delta G$ in kJ mol$^{-1}$) are reported at 373 K and relative to a proton at O14. Intrinsic free energy barriers for each transition state ($\Delta G_{\text{int}}$ in kJ mol$^{-1}$) are also reported at 373 K.
energies of these ROH species—maximum rates. Di benzene conversions above reactions (e.g., alcohol dehydration). This inhibition via Le those experimental studies for this and similar methylation dependent on the pressure of ROH), lending importance to low conversion are only observed if sequential arene breakthroughs are dependent on ROH pressures and thus dependent on conversion, can alter the rate-determining step of the sequential mechanism.Arene methylation reactions are typically run at low arene conversions (0.1% here), and thus the pressure of ROH leaving group (0.00002 bar) is very low relative to the pressure of CH3OR (0.68 bar). Rates of surface methylation are not dictated by ROH pressures at negligible conversions, where equilibrium effects need not be considered. Rates of arene methylation via CH3Z, however, are inhibited by ROH pressures and thus dependent on conversion, X

\[ r = k_{\text{CH}_3\text{OR}} K_{\text{CH}_3\text{OR}}^z K_{\text{CH}_3\text{OH}} P_{\text{CH}_3\text{OH}} \left(1 - X \right) \frac{P_{\text{CH}_3\text{OR}}}{P_{\text{CH}_3\text{OR}} + X} \]  

(4)

Increasing the conversion from 0.1% to 0.2% would cause a ~2x decrease in the rate of ring methylation via the sequential mechanism whereas the same conversion increase would negligibly impact rates if the concerted mechanism or surface methylation were the rate-determining steps (rate constants for eq 4 are defined in Figure 6 and derived in Section S2). As the pressure of the ROH group increases with increasing conversion, the formation and subsequent desorption of the ROH leaving group results in an inhibition of the benzene methylation through the action of Le Chatelier’s principle. The rate of surface methoxy formation will approach equilibrium, thus limiting consumption of surface methoxy species by benzene and decreasing the rate of arene methylation (Figure 9, gray). This kinetic behavior is also observed, for example, in the hydrogenolysis of alkanes on metal surfaces, in which H2(g) is formed in quasi-equilibrated dehydrogenation steps prior to the rate-determining C–C bond activation. At benzene conversions above ~20% for CH3OH and CH3OCH3, the rate of CH3Z consumption by benzene becomes limited to the extent that benzene methylation becomes rate determining in the sequential pathway (Figure 9). At very high benzene conversions (>75%) for CH3OCH3, the concerted pathway occurs with nearly identical rates to the sequential pathway. These strong effects of ROH pressure at low conversion are only observed if sequential arene methylation is the rate-determining step (i.e., the rate is dependent on the pressure of ROH), lending importance to those experimental studies for this and similar methylation reactions (e.g., alcohol dehydration). This inhibition via Le Chatelier’s principle, unlike site-blocking inhibition, is observable across all pressure ranges of the ROH leaving group, indicating that it can be observed or ruled out by simple space velocity experiments, rarely published but often performed.

Concerted methylation and surface methylation with spectating benzene demonstrate the same pressure dependencies in the rate equation (eqs S7 and S19), rendering kinetic experiments incapable of differentiating the two mechanisms, thus motivating this DFT study. The most favorable orientation of the concerted methylation transition state involves a hydrogen bond between deprotonated O16 and the leaving group species (H2O or CH3OH, Figure S8f,g). Concerted methylation of benzene by CH3OCH3 (122 kJ mol\(^{-1}\)) is slightly more favorable than methylation by CH3OH (129 kJ mol\(^{-1}\)); however, these values fall within the uncertainty of DFT, indicating that the relative rates of methylation by these two species should be nearly proportional to their pressure ratios. Free energy barriers of concerted methylation can be directly compared to those of the rate-determining surface methylation step as the two reactions demonstrate the same pressure dependencies. Barriers of concerted methylation are 20 kJ mol\(^{-1}\) higher for CH3OH and 30 kJ mol\(^{-1}\) higher for CH3OCH3 than the barriers of surface methylation (Figure 7a), indicating that sequential methylation is the preferred mechanism at benzene methylation conditions. However, at conversions above 75% for CH3OCH3 the maximum rate of the sequential mechanism (determined by the maximum rate of arene methylation, Figure 9) is limited and the concerted mechanism becomes preferred as arene methylation rates from CH3Z decrease.

Only direct proton donation from C7H15 to the zeolite surface was modeled to approximate ring deprotonation barriers. In a real system, CH3OH and H2O can act as proton shuttles and facilitate proton transfer to the zeolite surface and the barriers in the presence of these species could be lower. The rate of deprotonation, however, is significantly higher than the rate of other possible rate-determining steps for benzene methylation (Figure S12). Deprotonation benefits from relatively low barriers (Figure 7) coupled with entropic contributions of oxygenate desorption. As such, it does not limit methylation rates and will not be discussed in the remainder of this work because of its kinetic irrelevance.

Most abundant surface intermediates (MASI) were calculated using a Langmuir adsorption model, using DFT-obtained adsorption energies to identify abundant surface.
intermediates. Possible MASIs are limited to CH₃O⁻*, C₆H₆⁻*, CH₃−Z, C₆H₆−CH₃OR⁻, and C₆H₆−CH₃−Z in this analysis. CH₃OH⁻ is the predominant MASI from 353−473 K when CH₃OH serves as the methylation agent. At temperatures above 473 K, the MASI becomes CH₃−Z, suggesting that surface methylation occurs in an empty pore at these temperatures, likely because adsorption of C₆H₆ is limited as the temperature increases (Figure S13). When CH₃OH serves as the methylation agent, C₆H₆−CH₃OH⁻ is the MASI between 353−373 K, suggesting that adsorption of C₆H₆ is facile at low temperatures. Between 383 and 493 K, the MASI becomes predominantly CH₃OCH₃, because C₆H₆ adsorption is less favorable at high temperatures. At temperatures above 473 K, CH₃−Z species begin to appear on the surface (20−40%); however, the formation of CH₃−Z is kinetically limited at low temperatures. Maximum rate analyses do not predict that CH₃−Z species are the MASI between 353 and 493 K−only at temperatures above 503 K are CH₃−Z species observed to cover the surface (Figure S13). This result agrees well with previous DFT studies in MFI that suggest that CH₃−Z formation becomes more facile at high temperatures. Previous experimental studies of C₆H₆−CH₃OCH₃ reactions used kinetic data, isotopic labeling studies, and postreaction titration studies to conclude that benzene methylates via the sequential pathway and that the arene alkylation step is rate determining on sites covered by CH₃−Z species. However, previous theoretical studies predict that concerted methylation is facile compared to the formation of CH₃−Z species and that CH₃−Z species are not a MASI at low temperatures. Kinetic studies showed a linear dependence on benzene pressure (Figure 10), indicating that benzene adsorption occurs prior to CH₃OCH₃ at benzene methylation conditions, there is 1:2:1 d₀:d₃:d₆ suggesting facile C−O bond cleavage, and our calculated barriers concur. However, the low CH₃OH content prevents scrambling via reversible surface methylation reactions and this scrambling is more likely explained by the formation and decomposition of trimethyloxonium species (TMO⁺) through a sequential route:

\[
CH₃OCH₃ \rightarrow CH₃−Z
\]

(5)

\[
CH₃OCH₃ + CH₃⁻ \rightarrow \{[(CH₃)₂O...CH₄⁺...Z]⁻\}² \rightarrow (CH₃)₂O⁺ + Z⁻
\]

(6)

or a concerted route

\[
2CH₃OCH₃ + H−Z \rightarrow (CH₃O)₃O⁺ + CH₃OH + Z⁻
\]

(7)

Both sequential and concerted trimethyloxonium formation occur with low barriers (124 and 60 kJ mol⁻¹ for sequential and 80 kJ mol⁻¹ for concerted TMO⁺ formation). This indicates rapid exchange of CH₃ between CH₃OCH₃ and the zeolite surface, resulting in the observed d₀:d₃:d₆ ratios, as shown in Section S3. These TMO⁺ species can also contribute to surface and ring methylation, further discussed in Section S3. Postreaction titration studies (H-SPP heated to 423 K to remove physisorbed species) with flowing H₂O form CH₃OH in a 1:1 ratio with Al content, indicating that the heated material was covered with CH₃OH⁻ or CH₃−Z, with the former being more likely. The concentration of CH₃−Z, however, is very sensitive to the pressure of C₆H₆, CH₃OH, and H₂O in the system. The heat treatment to remove physisorbed species could have created a surface covered in CH₃−Z; these purge treatments are typical of zeolite methylation protocols for this reason. Instead, our DFT calculations suggest that a mixture of CH₃OCH₃⁻ and coadsorbed C₆H₆−CH₃OCH₃⁻ dominates the surface at benzene methylation conditions; this is consistent with the observed zero-order pressure dependence in CH₃OCH₃. However, this DFT analysis predicts sublinear kinetic behavior in C₆H₆ (rather than the linear behavior observed). This disagreement with experimental evidence is caused by the C₆H₆ binding free energy calculated here (−11 kJ mol⁻¹), which is approximately 4 kJ mol⁻¹ more exothermic than that found from experiments. Increasing the binding energy to −7 kJ mol⁻¹ ad hoc results in a linear dependence on benzene pressure, consistent with measured kinetic data. This thermodynamic correction does not cause CH₃−Z to become a predicted MASI, however, because with these altered data CH₃OCH₃⁻ are predicted as the lone MASI at benzene methylation conditions. This benzene-facilitated surface methylation pathway, which was not considered in previous theoretical or experimental studies, explains low CH₃−Z coverages predicted by DFT and linear dependence on benzene pressure predicted by kinetic studies—thus bridging the gap between previous theoretical and experimental results.

3.3. Mechanisms of Toluene Methylation. Toluene methylation yields three unique products: o-, m-, and p-xylene. p-Xylene has the highest industrial relevance as it is a precursor to terephthalic acid. m-Xylene is typically thermodynamically favored; however, zeolites, particularly H-ZSM-5, can shift this selectivity to favor p-xylene production through diffusive

![Figure 10. Comparison of DFT-obtained turnover rates with CH₃OCH₃ (solid) and experimentally obtained rates (circles) multiplied by a factor of 17 from ref 28. Data points are reported at 373 K, 0.02 bar C₆H₆, 0.68 bar CH₃OCH₃, and 0.1% aromatic conversion.](image-url)
Here, the mechanisms and rates of toluene methylation are analyzed using the previously discussed maximum rate analysis method to determine the intrinsic selectivities of the active site, uncorrupted by mass transport limitations (Figure 11). These insights can determine whether the observed preference for \( p\)-xylene is caused solely by mass transport limitations or if those limitations bolster a kinetically favored pathway.

Surface methylation in the presence of toluene demonstrates the same pore cooperativity as benzene (Section 3.2) to maximize noncovalent interactions and thus lower transition state barriers as compared to surface methylation in an empty pore. Surface methylation in the presence and absence of toluene occurs most favorably on O16. Toluene resides in the channel intersection and acts as a channel "cap" to maximize dispersive interactions (shown in Figure 12), and the surface methylation transition state resides in the straight channel to maximize favorable noncovalent interactions with the framework (such as H-bonding, cf., Figure 5). The presence of toluene lowers intrinsic barriers associated with CH\(_3\)OH surface methylation from 144 to 125 kJ mol\(^{-1}\) (Figure 13); similarly, the barrier for methylation by CH\(_3\)OCH\(_3\) decreases from 130 kJ mol\(^{-1}\) to 115 kJ mol\(^{-1}\) at 403 K and 1 bar of all species. At toluene methylation conditions (403 K, 0.03 bar C\(_7\)H\(_8\), 0.68 bar CH\(_3\)OR, 0.1% aromatic conversion), surface methylation with spectating toluene occurs at a higher maximum rate than surface methylation in an empty pore. This suggests that CH\(_3\)-Z is primarily formed with spectating toluene at these conditions. However, at temperatures above 503 K for CH\(_3\)OH and 423 K for CH\(_3\)OCH\(_3\), the rate of surface methylation in an empty pore occurs at a higher maximum rate than with spectating toluene. This likely occurs because strongly exothermic toluene adsorption (\( \Delta H_{\text{ads}} \) of \( -94 \) kJ mol\(^{-1}\)) becomes balanced by entropic losses as the temperature increases. Surface methylation by CH\(_3\)OCH\(_3\) occurs with rates only 1.5\( \times \) faster than those with CH\(_3\)OH at 403 K, suggesting that CH\(_3\)OCH\(_3\) and CH\(_3\)OH are equally capable of methylating the surface (Figure 11).

The rate of ring methylation via the sequential mechanism, like benzene methylation, occurs most favorably at O16 and has maximum rates \( >200\times \) higher than those of surface methylation at toluene methylation conditions (Figure 11b), indicating that the rate of ring methylation is limited by the formation of surface methoxy species. Therefore, surface methylation with spectating toluene is the rate-determining step of the sequential mechanism with CH\(_3\)OH and CH\(_3\)OCH\(_3\). Although ring methylation does not control the rate of sequential methylation, it does control the selectivity toward \( \sigma\)-, \( m\)-, or \( p\)-xylene. Ring methylation selectivity favors \( p\)-xylene, then \( \sigma\)-xylene, and finally \( m\)-xylene (Figure 11), suggesting that \( p\)-xylene is the kinetically preferred product of the sequential mechanism; this neglects additional effects of mass transport that would prevent egress of \( \sigma\)- and \( m\)-xylene in practical studies. Such high \( p\)-xylene selectivity is not observed in experimental studies (573 K, 0.015 bar CH\(_3\)OH, 0.06 bar C\(_7\)H\(_8\), and 4.3% C\(_7\)H\(_8\) conversion) which have demonstrated that \( p\)-xylene formation is only slightly favored, with distributions of 35\% \( \sigma\)-, 28\% \( m\)-, and 38\% \( p\)-xylene. At the same conditions, DFT results suggest the distribution is 13\%
o-, 4% m-, and 83% p-xylene; however, these distributions arise from arene methylation barriers that differ by only 12 kJ mol\(^{-1}\) (Figure 13), near the expected error in DFT calculations. Despite the uncertainties in these DFT-predicted selectivities, the trends suggested by DFT follow those found in experiment, where p-xylene is preferred over o-xylene and m-xylene. While DFT cannot accurately predict the selectivities of the products of these reactions, it can predict trends based on estimated free energy barriers and thus elucidate experimental results convoluted by mass transport limitations.

The concerted methylation of toluene has three possible transition states (forming each xylene) for each methylation agent, all of which H-bond with deprotonated O16 to stabilize the ROH leaving group. Here, intrinsic free energy barriers of concerted methylation can be directly compared to those of sequential methylation to form para-xylene (136 kJ mol\(^{-1}\)), meta-xylene (141 kJ mol\(^{-1}\)), and o-xylene (136 kJ mol\(^{-1}\)). The sequential mechanism occurs with barriers over 10 kJ mol\(^{-1}\) lower than those of the concerted mechanism when CH\(_3\)OH serves as the methylation agent, suggesting that sequential methylation is the predominant mechanism through which CH\(_3\)OH methylates toluene. When CH\(_3\)OCH\(_3\) is the methylation agent, the barrier to methylate the surface (115 kJ mol\(^{-1}\)) is less than concerted barriers to form o- (119 kJ mol\(^{-1}\)) and m-xylene (128 kJ mol\(^{-1}\)) but higher than the concerted barrier to form p-xylene (107 kJ mol\(^{-1}\), Figure 13). Therefore, when CH\(_3\)OCH\(_3\) is the methylation agent, p-xylene is formed via the concerted mechanism preferentially over CH\(_3\)-Z species and other xylene isomers. Barriers to form p-xylene are 7–21 kJ mol\(^{-1}\) lower than those to form o- or m-xylene, indicating that the intrinsic selectivity favors the formation of p-xylene and its formation is likely further promoted by mass transport restrictions disfavoring the desorption of o- and m-xylene from the catalyst compared to the more-linear para isomer.

p-Xylene is the most favorable product to form for both CH\(_3\)OH and CH\(_3\)OCH\(_3\); however, methylation to form p-xylene occurs through different mechanisms with CH\(_3\)OH (sequential methylation) and CH\(_3\)OCH\(_3\) (concerted methylation), suggesting that the preferred methylation mechanism is dependent on both the position of methyl-addition and methylation agent. Neither CH\(_3\)OH nor CH\(_3\)OCH\(_3\) has proven a noticeably superior methylaing agent among all methylation locations examined thus far (benzene and toluene); DFT-predicted barriers for each species differ by <20 kJ mol\(^{-1}\) (Figure S14).

Similar to Section 3.2, surface MASI were calculated using a Langmuirian adsorption model with the same potential MASI, except with toluene instead of benzene (prediction of surface MASI are shown in Figure S15), and are demonstrated to be both temperature and methylation agent dependent. When CH\(_3\)OH is the methylation agent, C\(_6\)H\(_5\)-CH\(_3\)OH\(^*\) is the MASI at temperatures below 413 K; however, as the temperature increases C\(_6\)H\(_4\)-CH\(_3\)OH\(^*\) is less favorable and the MASI becomes a mixture of C\(_6\)H\(_6\)-CH\(_3\)OH\(^*\) and CH\(_3\)OH\(^*\) at temperatures above 413 K. As with benzene, entropic effects for larger arene species limit adsorption at higher temperatures, where high-entropy gas-phase species are favored. When CH\(_3\)OCH\(_3\) is the methylation agent, CH\(_3\)OCH\(_3\)-CH\(_3\)OH\(^*\) is the MASI at all temperatures (353–493 K), because toluene does not adsorb as strongly next to CH\(_3\)OH (\(\Delta G_{\text{ads}} = -50 \text{ kJ mol}^{-1}\)) as it does near CH\(_3\)OH (\(\Delta G_{\text{ads}} = -68 \text{ kJ mol}^{-1}\)) (Figure 13).

The DFT results suggest that toluene methylation via CH\(_3\)OCH\(_3\) likely occurs via a concerted mechanism with barriers ~8 kJ mol\(^{-1}\) lower than those of surface methylation. This value falls within the uncertainty of DFT, so it is difficult to determine which, if any, mechanism prevails at these conditions. Similar to benzene methylation, DFT-predictions can be used to provide insight and alternative explanations for previously published kinetic, surface titration, and isotopic switching results during CH\(_3\)OCH\(_3\) and toluene coreaction conditions (403 K, 0.008–0.08 bar C\(_7\)H\(_8\), 0.68 bar CH\(_3\)OCH\(_3\), 0.1% conversion).\(^{28}\) Experimental kinetic results predict no dependence on CH\(_3\)OCH\(_3\) pressure and a linear dependence on toluene pressure, suggesting that the rate-determining step occurs after toluene adsorption, and thus the rate-determining step was toluene methylation. However, as we have shown with benzene and toluene methylation, surface methylation can occur in the presence of a spectating arene species, which explains the linear rate dependence on arene pressure. Furthermore, an abundance of CH\(_3\)OH\(^*\) on the surface explains a zero-order dependence on CH\(_3\)OCH\(_3\) pressure. DFT results predict a linear dependence on toluene pressure and no dependence on CH\(_3\)OCH\(_3\) pressure (Figure 14), confirming that this species is the MASI consistent with these previous kinetic studies. Isotopic switching studies also demonstrated a 1:2:1 mixture of \(d_0:d_3:d_6\) when \(d_0\) and \(d_6\) CH\(_3\)OCH\(_3\) were cofed during toluene methylation.\(^{28}\) Similar to benzene methylation, we suggest that this rapid exchange is likely to occur via trimethyloxonium species, not because surface methylation is a quasi-equilibrated step.

3.4. Mechanisms of Methylbenzene Methylation at Methanol-to-Hydrocarbon Conditions. Methanol-to-hydrocarbon (MTH) reactions typically occur at transient conditions because catalyst induction and deactivation
preclude steady state operation. Industrially, this is overcome by operating in fluidized bed reactors with low catalyst residence times. MTH occurs at higher temperatures (523–723 K) than arene methylation conditions (373–473 K, 0.1% conversion) and can form a range of substituted methylbenzene cocatalysts which produce light alkenes in the aromatic cycle. Here, we will analyze and interpret our arene methylation reactions at MTH conditions assuming 623 K, 0.04 bar C6H6, 0.08 bar CH3OR, and 10% conversion, similar to previous studies of MTH.

Surface methylation was the rate-determining step of the sequential mechanism at low-temperatures (373–473 K) and low conversions (<1%) and occurred near a spectating arene at benzene and toluene methylation conditions (373 and 403 K, respectively). However, this trend is not observed in the rates of surface methylation at higher temperatures and near larger arene species (C9+). Surface methylation in an empty pore is the preferred mechanism for all species at MTH temperatures (near 623 K), because arenes are less likely to coadsorb at higher temperatures and larger arenes adsorb more weakly because of steric hindrance.

The formation of higher methylbenzenes from benzene is of fundamental interest to determine active methylbenzene species during MTH reactions. Figure 15 shows the lowest methylation barriers and the most facile chemical pathways to reach hexamethylbenzene (structures shown in Section S6). The formation of hexamethylbenzene from benzene proceeds through p-xylene, 1,2,4-trimethylbenzene, and 1,2,3,5-tetramethylbenzene—all of which have been identified as possible intermediates of the aromatic cycle in MTH chemistry by previous DFT and kinetic studies. The formation of hexamethylbenzene from benzene proceeds through p-xylene, 1,2,4-trimethylbenzene, and 1,2,3,5-tetramethylbenzene—all of which have been identified as possible intermediates of the aromatic cycle in MTH chemistry by previous DFT and kinetic studies. The formation of hexamethylbenzene from benzene proceeds through p-xylene, 1,2,4-trimethylbenzene, and 1,2,3,5-tetramethylbenzene—all of which have been identified as possible intermediates of the aromatic cycle in MTH chemistry by previous DFT and kinetic studies.

Figure 15. Reaction coordinate diagram of hexamethylbenzene formation via repeated benzene methylation with CH3OH (solid lines) and CH3OCH3 (dashed lines). Overall barriers (relative to C6H6) are shown in bold, and intrinsic barriers are listed in italics and parentheses. Red lines indicate that the sequential mechanism is preferred, while blue lines indicate that the concerted mechanism is preferred. Barriers are reported at 623 K, 1 bar of all species.
MTH processes. This result contradicts previous theoretical studies which have predicted that methylation barriers decrease with additional methyl-substituents on the ring. However, these studies were performed on zeolite cluster models and only investigated four ring interconversion pathways via the concerted mechanism—an insufficient analysis for these complicated pathways. The formation of higher methylbenzene species is thermodynamically favorable, with average reaction free energies of $-34$ kJ mol$^{-1}$. These reaction free energies increase with additional methyl substitution. For example, the formation of pentamethylbenzene from 1,2,3,5-tetramethylbenzene has a positive reaction free energy ($+24$ and $+27$ kJ mol$^{-1}$ for CH$_3$OH and CH$_3$OCH$_3$, respectively). This indicates that extensively substituted rings start to encounter steric hindrance within MFI intersections, consistent with their less favorable adsorption energies (Table S2). Despite this, methylation reactions are generally thermodynamically favorable and occur with barriers significantly lower than those reported for arene isomerization and alkene formation. During these methylation reactions, several competing factors affect the energies of guest species: electron withdrawing groups, steric hindrance, van der Waals interactions, and repulsive effects. The absence of a monatomic trend in methylation barriers suggests that none of these factors dominate in stabilizing or destabilizing methylation transition states; thus, interpolation of barriers in MFI yields inaccurate results because no dominant factor governs transition state energies during methylation reactions. Overall, the relatively low barriers of methylation indicate that arenes either escape zeolite domains as aromatic products of MTH or become extensively substituted as C$_{10}$$-$$C_{12}$ species that are trapped within MFI intersections. These highly substituted arenes serve as cocatalysts in the aromatic cycle and produce light alkenes.

The formation of geminal methylated aromatic species is shown to be an important step in the aromatics-cycle of MTO. Previous reports comparing methylation and geminal methylation in H-ZSM-12 and H-ZSM-22 suggest that geminal methylation barriers are only competitive with methylation barriers for C$_{10+}$ species; similar results have been demonstrated in CHA, BEA, and H-ZSM-5. Here, we find that barriers of geminal methylation via the sequential mechanism are $50$–$90$ kJ mol$^{-1}$ higher than those of monomethylation (Figure S19). These results further support that large aromatic rings are cocatalyzing the formation of arenes via the aromatic cycle. These large aromatic rings will ultimately grow to polyaromatic species via deactivation mechanisms when trapped in zeolite pores.

4. CONCLUSIONS

Reactant, product, and transition state species involved in arene methylation reactions were systematically reoriented to probe the potential energy surface in an attempt to identify their respective global minima. These reorientations demonstrate that a single optimization of a user-generated structure is insufficient to obtain reliable ground state energies. Reorientations reduced energies by up to $45$ kJ mol$^{-1}$ for states tested here. Furthermore, these systematic reorientations provide valuable insight regarding the void and coadsorbate cooperativity, which are not immediately apparent. Through systematic reorientations of surface methylation transition states with coadsorbed arenes, we have demonstrated that MFI offers a unique environment for catalysis because small transition states (e.g., surface methylation) can reside in the straight channel to maximize dispersive interactions while larger arenes (e.g., benzene) can reside in the channel intersection to minimize repulsive interactions with the zeolite framework. The proximity and locations of these species creates a “capped” channel which resembles a side-pocket in which surface methylation is accelerated by noncovalent interactions among coadsorbates and by solvation by the zeolite framework. This cooperativity of pores makes MFI an ideal catalyst for housing transition states of different sizes, such as those in BTX methylation and MTH reactions.

Concerted and sequential arene methylations were studied with CH$_3$OH and CH$_3$OCH$_3$ for all methylbenzene interconversion pathways from benzene to hexamethylbenzene. Maximum rate analyses were used to determine the rate-determining steps of the sequential mechanism, compare the sequential and concerted mechanism, and compare DFT-predicted rates to previous kinetic studies. Benzene methylation is predicted to occur via sequential methylation at reasonable temperatures ($353$–$623$ K) and pressures ($0.02$–$1$ bar). Surface methylation facilitated by coadsorbed benzene is rate-determining at these conditions with low benzene conversion (0.1%). However, at higher ROH pressures (caused by higher conversions, above $20$%), the rate of surface methylation approaches equilibrium, thus limiting the rate of the subsequent arene methylation reaction and causing it to become rate-determining. DFT data demonstrate that coadsorbed benzene facilitates surface methylation by CH$_3$OH and CH$_3$OCH$_3$, resulting in rates that yield pressure dependencies identical to those observed experimentally. Additionally, isotopically labeled methyl groups in CH$_3$OCH$_3$ can be scrambled through trimethyloxonium cations, and surface methoxy species are only MASI in the absence of CH$_3$OH, H$_2$O, and C$_6$H$_6$ (i.e., can only be formed at high coverages by heating or flowing in an inert gas). These calculations shed new light on prior experimental studies leading to a more thorough understanding of BTX methylation reactions.

Concerted and sequential barriers tend to be within $20$ kJ mol$^{-1}$ of each other for the complete set of arene methylation reactions (from benzene to hexamethylbenzene), indicating that both mechanisms likely occur. Similarly, barriers for methylation by CH$_3$OH and CH$_3$OCH$_3$ are nearly identical, suggesting that either species can methylate arenes and that CH$_3$OH formed by CH$_3$OCH$_3$ reactions may itself react to form H$_2$O. Intrinsic methylation free energy barriers remain between $76$ and $137$ kJ mol$^{-1}$ during repeated methylation of benzene to hexamethylbenzene, suggesting that the number of methyl-substituents on the ring has no consistent trend with regard to raising or lowering activation barriers of methylation. Additionally, reaction free energies become less negative but generally remain low, suggesting that the formation of C$_{10}$$-$$C_{12}$ species is unlikely kinetically limited during MTH reactions. This suggests that an aromatic compound, once formed during MTH, likely either desorbs from the zeolite as a light aromatic product (C$_{6}$–C$_{8}$) or forms an extensively methylated species, such as tetra-, penta-, or hexamethylbenzene. This extensively methylated arene will serve as a cocatalyst for olefin production and eventually lead to catalyst deactivation via the formation of polyaromatic species. Overall, this study provides mechanistic understanding of low-temperature BTX alkylation and gives insight into the dominant aromatic species present during MTH reactions while employing a novel method of identifying global minima and stable transition state structures within
zeolite frameworks and revealing previously undescribed cooperativity between zeolite voids that enable the versatile chemistry of the MFI framework.

■ ASSOCIATED CONTENT

2 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b00650.

Formulas and details of frequency calculations for enthalpy and free energy approximations, detailed images showing structures and reorientation schemes, derivations for arene methylation rate equations, and all activation and reaction enthalpies and entropies (PDF).

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■ REFERENCES


