

# Methanol to Olefins Reaction Route Based on Methylcyclopentadienes as Critical Intermediates

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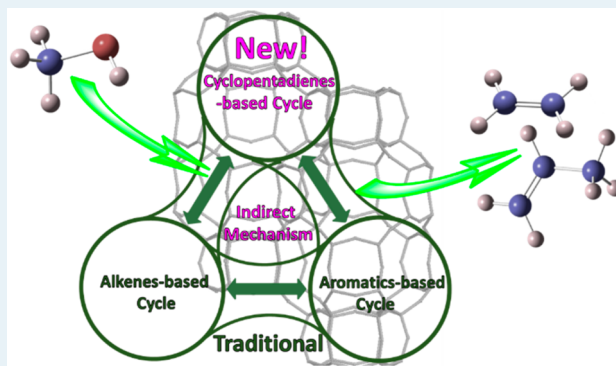
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## Supporting Information

**ABSTRACT:** Starting from C1 raw material, methanol conversion to hydrocarbons has been realized via a rather complicated pathway. In this contribution, we proposed an alternative methanol reaction route and provided a general understanding of such complex indirect mechanism. The methylcyclopentadienyl cations and their deprotonated counterparts (methylcyclopentadienes) were validated to appear on the working H-SAPO-34 catalyst by in situ <sup>13</sup>C MAS NMR spectroscopy and the GC-MS technique, and their catalytic reactivity was revealed by the <sup>12</sup>C/<sup>13</sup>C-CH<sub>3</sub>OH isotopic switch experiment. In this context, a cyclopentadienes-based cycle was established, in which light olefins were formed with methylcyclopentadienes as critical intermediates. The feasibility of this alternative route was confirmed by density functional theory calculations. Notably, the cyclopentadienes-based cycle runs in parallel with the traditional alkenes-based and aromatics-based cycles; these three mechanistic cycles are interrelated through interconversion of the involved intermediates, including alkene, cyclopentadiene, and aromatic species. All these three cycles work together for the C–C bond assembly in the methanol-to-olefins reaction system. These findings help to build a more complete methanol conversion network and advance the in-depth understanding of indirect mechanism of methanol conversion.

**KEYWORDS:** methanol-to-olefins, H-SAPO-34, indirect mechanism, methylcyclopentadiene, cyclopentadienes-based cycle



With the increasing demands for light olefins, as one of the key technologies for production of light olefins from non-oil sources such as coal or natural gas,<sup>1</sup> the methanol-to-olefins (MTO) process has been developed and industrialized successfully. Meanwhile, a thorough understanding of the mechanism of methanol conversion, especially the pathway of C–C bond assembly and the complete methanol conversion network, remains a challenge.

The well-known indirect mechanism has been proposed and accepted widely to explain the mechanistic origin of forming light olefins during the steady-state period of methanol conversion.<sup>2–6</sup> Light olefins are formed via an indirect pathway through hydrocarbon-pool (HCP) species, which consist of organic reaction centers (e.g., olefinic and cyclic species) accommodated in the cages or channels of the inorganic host.<sup>7–10</sup> Great efforts and systematic studies have been devoted to identifying these active intermediates using a wide

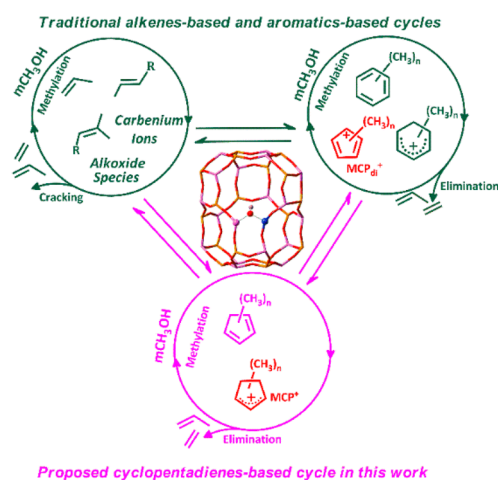
variety of experimental and theoretical approaches.<sup>11–17</sup> Several types of organic active species, such as cyclic alkenyl,<sup>12,13,16,18</sup> aromatic carbenium,<sup>13,14,17,18</sup> and the corresponding neutral species were captured and verified as active intermediates, which play a cocatalysis role in the zeolite-catalyzed MTO process. In the context of these active intermediates, the aromatics-based cycle including side-chain methylation<sup>19</sup> and paring<sup>20</sup> mechanisms, together with the alkenes-based cycle,<sup>15,21,22</sup> were considered to be responsible for the olefins formation as described in Scheme 1. However, given the complexity of the methanol reaction network, besides the above-mentioned reaction intermediates and reaction routes, whether the current findings reflect all the potential

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**Scheme 1. Traditional Dual Cycles (Alkenes-Based and Aromatics-Based Cycles<sup>21</sup>) and the Cyclopentadienes-Based Cycle Proposed in This Work for Methanol Conversion<sup>a</sup>**



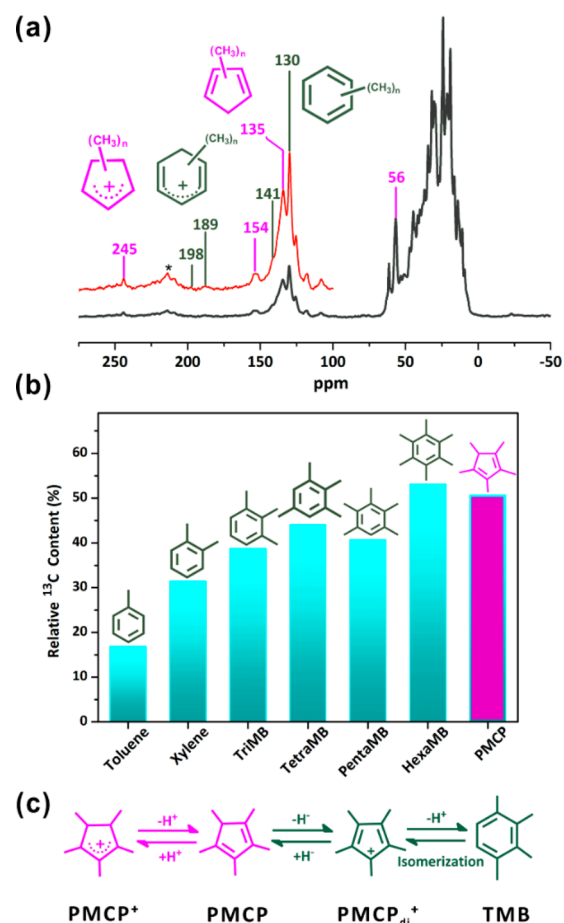
<sup>a</sup>Methylcyclopentadienyl cations,  $\text{MCP}_{\text{di}}^+$ ; methylcyclopentenyl cations,  $\text{MCP}^+$ .

active intermediates and all the possibilities of their participation in the reaction remain a question; the nature of the indirect mechanism involving active intermediates in the catalytic cycle for production of olefins is still puzzling. This status prompts us to further reveal the exact nature of the indirect mechanism and to unveil more details of how the active intermediates function through an indirect pathway.

The cyclic species with five-membered ring (5-MR), appearing as polyalkyl-substituted cyclopentadienyl cations, cyclopentenyl cations, and their deprotonated forms, have been discussed in zeolite or SAPOs.<sup>12,13,16,23–30</sup> When the researchers proposed the aromatics-based catalytic cycle, methylcyclopentadienyl cations ( $\text{MCP}_{\text{di}}^+$ , one isomer of the benzenium cations, as displayed in red in Scheme 1) are involved as one of the important intermediates in the paring mechanism.<sup>13,20,24,27</sup> As another kind of experimentally observed crucial 5-MR species, methylcyclopentenyl cations ( $\text{MCP}^+$ , as displayed in red in Scheme 1) and their neutral species (i.e., methylcyclopentadienes) were also identified by <sup>13</sup>C NMR,<sup>12,13,23–28,30</sup> UV–vis,<sup>16,31</sup> spectroscopy, and synchrotron infrared microspectroscopy.<sup>29</sup> The lower energy barriers of methylation reaction for MCP compared with olefinic and aromatic intermediates manifest their higher reactivity.<sup>12</sup> However, in contrast to  $\text{MCP}_{\text{di}}^+$  moieties, no complete catalytic cycle involving these methylcyclopentenyl cations as the critical intermediates to form light olefins was established.

In this work, with the aid of in situ <sup>13</sup>C MAS NMR, GC-MS, and <sup>12</sup>C/<sup>13</sup>C-methanol switch experiment,  $\text{MCP}^+$  cations and their deprotonated species (MCP) were captured on the working catalyst and identified as one kind of key active intermediate. Then, the cyclopentadienes-based cycle (Scheme 1), an energetically feasible cycle for methanol conversion on H-SAPO-34, was proposed. The feasibility and the contribution of such cyclopentadienes-based cycle were investigated by density functional calculation (DFT), in comparison with the traditional alkenes-based and aromatics-based cycles. This work generalizes the common nature of indirect mechanism in MTO reaction, characterized by the co-operating of multi-routes for methanol conversion over acidic catalysts.

Textural characterizations of H-SAPO-34 are shown in Figures S1–S3 in the Supporting Information. The catalytic performances of methanol conversion over H-SAPO-34 at 300 and 400 °C are shown in Figure S4–S5. <sup>13</sup>C MAS NMR and <sup>12</sup>C/<sup>13</sup>C-methanol switch experiments were conducted to identify the active intermediates. First, we acquired the <sup>13</sup>C MAS NMR spectrum of the organic intermediates retained in the H-SAPO-34 catalyst after <sup>13</sup>C methanol conversion at 300 °C for 10 min, as shown in Figure 1a. Both the



**Figure 1.** (a) <sup>13</sup>C MAS NMR spectrum of the organic intermediates retained in H-SAPO-34 after continuous-flow <sup>13</sup>CH<sub>3</sub>OH reaction at 300 °C for 10 min. (b) Relative <sup>13</sup>C content of the confined organic species in H-SAPO-34 after continuous-flow <sup>12</sup>C-methanol conversion at 300 °C for 25 min followed by switching <sup>13</sup>C-methanol for 1 min. (c) The interconversion between active intermediates.  $\text{PMCP}^+$ : pentamethylcyclopentenyl cation;  $\text{PMCP}$ : pentamethylcyclopentadiene;  $\text{PMCP}_{\text{di}}^+$ : pentamethylcyclopentadienyl cation; TMB: tetramethylbenzene.

polymethylbenzene species (characteristic of a broad band at 130–140 ppm) and the polymethylbenzenium ions (141, 189, 198 ppm) have been detected.<sup>13</sup> The relative weak peaks of polymethylbenzenium ions appearing at 189 and 198 ppm are due to the weaker Brønsted acidity of H-SAPO-34.<sup>13</sup> The appearance of peak at 135 ppm is attributed to cyclopentadiene species. The signals of 56, 154, and 245 ppm are assigned to pentamethylcyclopentenyl cation ( $\text{PMCP}^+$ ).<sup>13</sup> The identification of the  $\text{PMCP}^+$  is further consolidated by the observation of the corresponding neutral species (pentamethylcyclopentadiene,  $\text{PMCP}$ ) analyzed by GC–MS method as shown in Figure S6. Under a relatively higher temperature of

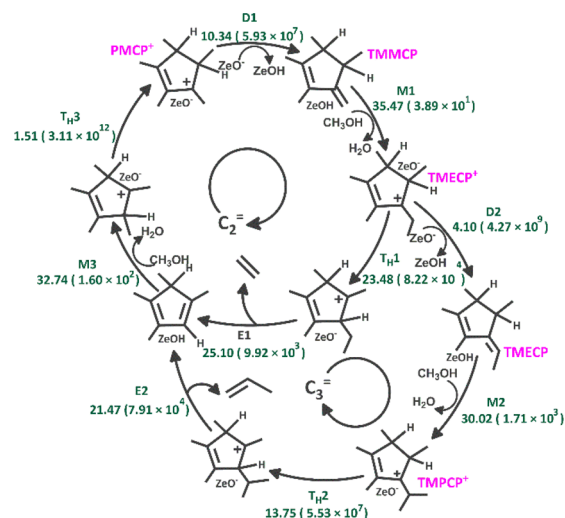
400 °C, in which full methanol conversion was realized (Figure S5), we can still successfully capture PMCP<sup>+</sup> cations and neutral PMCP as shown in Figure S7. All these detected carbenium and neutral intermediates may act as cocatalytic active centers for methanol conversion. In order to further investigate the roles of active PMCP<sup>+</sup> cations and PMCP, the presence and abundance of PMCP<sup>+</sup> and PMCP throughout the MTO reaction were probed and quantitatively calculated by <sup>13</sup>C MAS NMR spectra (Figure S8), GC-MS chromatograms (Figure S9), and UV-vis spectra (Figure S10). The spectra and chromatograms results show that PMCP<sup>+</sup> and PMCP are present across the whole MTO stage. The concentration evolving trends of PMCP<sup>+</sup> (Figure S8b and S10) and PMCP (Figure S9b) associated with hexaMB (Figure S10) with TOS are almost consistent with the methanol conversion profile (Figure S4). These observations further imply the participation of PMCP<sup>+</sup> cations and the neutral PMCP in the MTO reaction as one kind of important intermediate.

Subsequently, the <sup>12</sup>C/<sup>13</sup>C-methanol isotopic switch experiment was employed to evaluate the reactivity of the retained organics. When the feeding is switched from <sup>12</sup>C to <sup>13</sup>C-methanol, <sup>13</sup>C atom incorporation reveals the reactivity of the intermediates. Figure 1b displays the total <sup>13</sup>C content of the organic cyclic materials liberated from the catalyst by HF dissolution and CH<sub>2</sub>Cl<sub>2</sub> extraction<sup>32</sup> (Section 2.4 in Supporting Information) after the <sup>12</sup>C/<sup>13</sup>C-methanol switch experiments. Among the detected cyclic organics, PMCP exhibits very high <sup>13</sup>C content of 50.7%, close to that of hexamethylbenzene (HMB) (53.2%). The latter has been identified as the most active species for catalyzing methanol conversion.<sup>13,14</sup> The aromatic species, such as polymethylbenzenium cations and their isomerized counterpart (methylcyclopentadienyl cation) have been ascertained to participate in the aromatics-based cycle.<sup>13,14,19,20,23,24,27,33</sup> Notably, the experimental observation and high reactivity confirmation of PMCP<sup>+</sup> cation (Figure 1a), implied that PMCP<sup>+</sup> cation and PMCP (Figure 1c) may also function as critical active intermediates to convert methanol through a new pathway, parallel to the aromatics-based cycle and alkenes-based cycle.

These results, all together, prompt us to propose a reasonable and alternative reaction route to produce light olefins with the participation of MCP species as critical intermediates via methylation and elimination steps. To validate this proposal, DFT theoretical calculations were performed to examine the feasibility of this cyclopentadienes-based cycle from energetic perspective. Computational details are provided in section 2.4 in the Supporting Information. It should be noted that the 5-MR species (i.e., MCP<sup>+</sup> cations and their deprotonated counterpart) involved in our proposed cyclopentadienes-based cycle are different from the MCP<sup>+</sup> cations and their deprotonated form being involved in the pairing mechanism of the aromatics-based cycle (as compared in Figure 1c).<sup>13,20,24,27</sup>

The mechanism routes for ethene and propene formation in our proposed cyclopentadienes-based cycle, associated with the Gibbs free energy barriers and reaction rate constants at the real working conditions of methanol conversion of 400 °C, are shown in Scheme 2. The calculated enthalpic and entropic contributions to the free energy for all reaction steps are provided in Table S1 in Supporting Information. Before M1, M2, and M3 steps, the methanol molecules with the optimal methyl group origination adsorb in SAPO-34 pores, with free

**Scheme 2. Mechanism Routes Based on the Proposed Cyclopentadienes-Based Cycle for Ethene and Propene Formation over H-SAPO-34<sup>a</sup>**



<sup>a</sup>Calculated free energy barriers and reaction rate constants (in brackets) at 400 °C are given in kcal/mol and s<sup>-1</sup>, respectively. Reaction types: D (deprotonation), M (methylation), T<sub>H</sub> (Hydride-transfer), E (elimination).

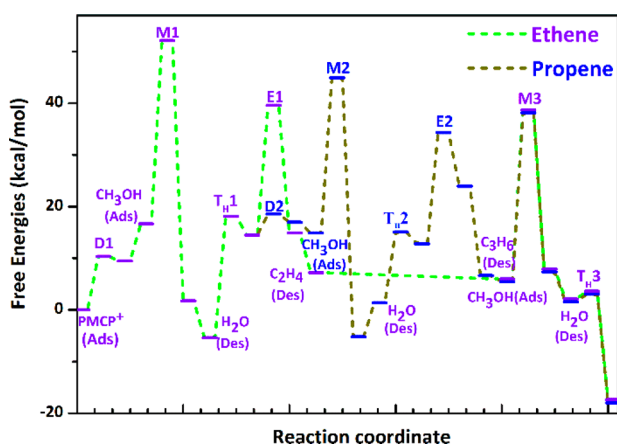
energy barriers of 7.19, -2.10, and -1.24 kcal/mol, respectively. The water molecules desorb after these methylation steps with free energy barriers of -7.13, 6.57, and -5.80 kcal/mol, respectively. Ethene and propene desorb with a free energy barrier of -7.68 and -17.33 kcal/mol. The differences of the molecular adsorption/desorption and desorption exothermically should be attributed to the differences in the chemical environments and the configuration transformation of the intermediates between the previous product and the subsequent reaction steps.<sup>33-35</sup> For the elementary reactions, first, PMCP<sup>+</sup> (the protonated form of PMCP) loses a proton via a faster deprotonation step (D1, 10.34 kcal/mol, 5.93 × 10<sup>7</sup> s<sup>-1</sup>) to form neutral tetramethylmethylenecyclopentene (TMMCP) with an exocyclic double bond. This step is crucial to form olefin precursor. Subsequently, 2, 3, 4, 5-tetramethyl-1-ethylcyclopentenyl cation (2, 3, 4, 5-tetraM-1-ECP<sup>+</sup>, TMECP<sup>+</sup>), ethene precursor, is formed by an exocyclic methylation step (M1, 35.47 kcal/mol, 3.89 × 10<sup>1</sup> s<sup>-1</sup>). The following hydride-transfer (T<sub>H</sub>1, 23.48 kcal/mol, 8.22 × 10<sup>4</sup> s<sup>-1</sup>) step results in the sp<sup>3</sup> hybridization of ring carbon atom connecting with ethyl side-chain. This weakens the C-C bond connecting the five-membered ring and ethyl side-chain, which is beneficial for ethene split-off.<sup>36,37</sup> A relative lower barrier of 25.10 kcal/mol and higher reaction rate constant of 9.92 × 10<sup>3</sup> s<sup>-1</sup> are predicted for ethene elimination (E1) through a concerted mechanism, where the cleavage of the C-C bond is accompanied with the return of the proton from the terminal methyl group of the ethyl side-chain to zeolite framework oxygen. Next, the simultaneously formed tetramethylcyclopentadiene gets methylated (M3, 32.74 kcal/mol, 1.60 × 10<sup>2</sup> s<sup>-1</sup>) to form pentamethylcyclopentenyl cation over the restored Brønsted acid sites. Eventually, PMCP<sup>+</sup> is recovered via a rapid hydride-transfer step (T<sub>H</sub>3, 1.51 kcal/mol, 13.11 × 10<sup>12</sup> s<sup>-1</sup>).

The formation of propene shares the same precursor, TMECP<sup>+</sup>, with ethene formation. TMECP<sup>+</sup> first undergoes deprotonation reaction (D2, 4.10 kcal/mol, 4.27 × 10<sup>9</sup> s<sup>-1</sup>) to



form tetramethylethyldienecyclopentene (TMECP) with an exocyclic double bond. Then the propene precursor, 2, 3, 4, 5-tetramethyl-1-propylcyclopentenyl cation (2, 3, 4, 5-tetraM-1-PCP<sup>+</sup>, TMPCP<sup>+</sup>) with propyl side-chain group is formed via methylation of TMECP (M2, 30.02 kcal/mol,  $1.71 \times 10^3$  s<sup>-1</sup>). Similar to the process of ethene formation, propene finally splits off after relatively fast hydride-transfer (T<sub>H2</sub>, 13.75 kcal/mol,  $5.53 \times 10^7$  s<sup>-1</sup>) and elimination steps (E2, 21.47 kcal/mol,  $7.91 \times 10^4$  s<sup>-1</sup>).

The energy profiles of elementary steps for ethene and propene formation at 400 °C and the optimized transition state structures for the ethene and propene precursors (methylcyclopentenyl cation with ethyl or propyl side-chain) formation are shown in Figure 2 and Figure S12 in Supporting

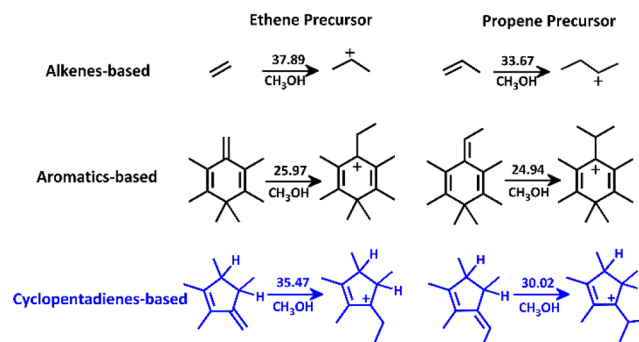


**Figure 2.** Gibbs free energy profiles of the ethene and propene formations over H-SAPO-34 based on the cyclopentadienes-based route starting from PMCP<sup>+</sup> at 400 °C. (The detailed transition state structures of all the elementary reactions are shown in Figure S11.)

**Information.** The free energy barriers (1.51–35.47 kcal/mol), reaction rate constants of all the elementary steps, and the energy span (ethene/propene formations, 52.13/50.31 kcal/mol, respectively) over the whole catalytic cycle are comparable to the values in the aromatics-based mechanism,<sup>13,34,38</sup> indicating the energetic feasibility of the cyclopentadienes-based reaction route. Besides, the energy barriers of the elementary steps for ethene and propene formation at 300 °C are 1.33–35.52 kcal/mol (Table S2), also suggesting cyclopentadienes-based cycle is energetically feasible. These results suggest that the cyclopentadienes-based cycle can operate as a feasible methanol conversion route and contribute for generation of light olefins. The critical steps for ethene and propene precursors (methylcyclopentenyl cations with ethyl or propyl side-chain) formation, via the methylation of TMMCP (M1) and TMECP (M2), exhibit relatively higher free energy barrier and lower rate constant relative to other steps. The free energy barrier of M1 step is 35.47 kcal/mol slightly higher than those of M2 step (30.02 kcal/mol).

As a key step for formation of light olefins, a methylation reaction to form olefin precursors in different catalytic cycles (Scheme 1) was predicted and compared theoretically. As shown in Scheme 3, formation of ethene and propene precursors, in the cyclopentadienes-based cycle, has the free energy barrier of 35.47 and 30.02 kcal/mol, relatively, which is higher than those in the aromatics-based cycle with the barrier of 25.97 and 24.94 kcal/mol and somewhat lower than those in the alkenes-based route with the barrier of 37.89 and 33.67

**Scheme 3. Ethene and Propene Precursors Formations via Various Reaction Routes on H-SAPO-34 (Alkenes-Based, Aromatics-Based, and Cyclopentadienes-Based Catalytic Cycles)<sup>a</sup>**



<sup>a</sup>Free energy barriers in kcal/mol at 400 °C are displayed.

kcal/mol. These results, together with MCP<sup>+</sup> cations detected by solid-state NMR and the high reactivity revealed by the isotopic switch experiment and the moderate energy span of the overall reaction cycle, convincingly show that cyclopentadienes-based cycle can play an important role in catalyzing methanol conversion to light olefins.

To form exocyclic double bond is a crucial step to form olefin precursor. In our proposed cyclopentadienes-based cycle as shown in Scheme 2, the exocyclic double bond is formed by deprotonation of PMCP<sup>+</sup>, from which construction of additional side chain C–C bond to form the precursors of ethene/propene can be realized by continuous methylation reaction on Brønsted acid site. This is different from the case of side-chain methylation mechanism of aromatics-based cycle that is realized by gem-methylation reaction to form the polymethylbenzenium ions with different substitution methyl groups.<sup>13,19,33</sup> An alternative cyclopentadienes-based cycle based on the pentamethylcyclopentadiene was calculated to further evaluate the feasibility of the proposed cyclopentadienes-based cycle. The cycle starts from the gem-methylation of PMCP (see Scheme S1 in Supporting Information) to form an exocyclic double bond, from which ethene and propene can be obtained via a series of methylation and elimination steps. The energy barriers of the elementary steps and the energy span for light olefins formation are 12.06–36.05 and 49 kcal/mol, respectively (see Table S3 and Figure S13 in Supporting Information), which are comparable to the respective barriers for cyclopentadienes-based route presented in Scheme 2 and the reported values for the aromatics-based cycle.<sup>13,34,38</sup> This evidently demonstrates that polymethylcyclopentadienes can act as the active intermediates, resembling alkene species or polymethylaromatic species in alkenes-based or aromatics-based cycles. In this sense, the cyclopentadienes-based cycle could be described as an alternative reaction route of indirect mechanism with the similar feature of active intermediates (i.e., intermediate methylation chain propagation with methanol to the form new C–C bond and elimination steps to form an olefin product).

To further examine the feasibility of our proposed cyclopentadienes-based mechanism, we next theoretically compare the free energy barriers ( $\Delta G^\ddagger$ ) of cyclopentadienes-based cycle with the traditional aromatics-based and olefins-based cycles at 400 °C, taking propene formation as a

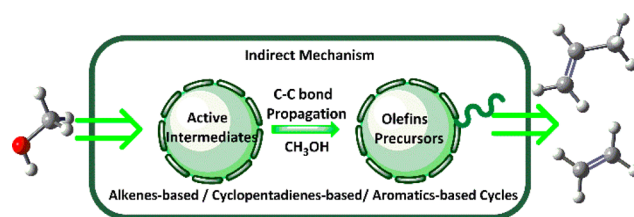
representative reaction. Considering that the paring mechanism plays a minor role in the MTO reaction because of its higher energy barrier,<sup>39</sup> a side-chain mechanism was taken to represent the aromatics-based cycle. The mechanism routes and the free energy barriers of all the elementary reactions for propene formation via these three cycles at 400 °C are compiled in Scheme S2 in Supporting Information. The rate-determining steps of the three cycles are methylation of hexamethylbenzene (M1a), elimination (E1b), and methylation (M1), respectively, and the free energy barriers of which are around 34–36 kcal/mol with the difference less than 2 kcal/mol. The comparable energy barriers clearly demonstrate that the cyclopentadienes-based cycle associated with other traditional cycles works together for olefins formation and that the aromatics-based cycle (side-chain mechanism) is slightly energetically more favorable, in accordance to the higher <sup>13</sup>C incorporation in (higher reactivity of) hexaMB than PMCP as shown in Figure 1b.

Next, we evaluate the correlations between these three catalytic cycles and reconsider the methanol conversion network. First, we discuss the role that cyclopentadiene played as a potential bridge to connect the three catalytic cycles. Cyclopentadiene can be readily formed from olefins via a series of reactions (i.e., oligomerization, cyclization, and hydride transfer reaction),<sup>12,40,41</sup> which are evidenced energetically feasible (<32.8 kcal/mol<sup>42</sup>) by theoretical calculation. Furthermore, we theoretically evaluate the transformation from cyclopentadienes-based cycle to aromatics-based cycle from an energetic perspective, exemplified by the conversion of PMCP<sup>+</sup> to tetramethylbenzene (see Figure 1c and Scheme S3 in Supporting Information). The results illustrated that PMCP converts to tetramethylbenzene fast with a relative lower energy barrier of 6.41–40.44 kcal/mol. Based on the above analysis, apparently, the origin and evolution of the cyclopentadiene can link the alkenes-based and aromatics-based cycles. Conclusively, the interconversion between active intermediates and their interdependent correlations in these three cycles are provided in Scheme S4. In addition to the well-discussed interlinkage between alkenes-based and aromatics-based cycles,<sup>2,3,21</sup> the cyclopentadienes-based cycle can, on one hand, run as a critical scaffold for converting methanol to light olefins as discussed before, and on the other hand, it can function as a bridge to link alkenes-based and aromatics-based cycles.

The proposed catalytic cycle based on cyclopentadiene intermediates in this work, together with the traditional alkenes-based cycle and aromatics-based cycle, gives rise to a unifying description of methanol indirect reaction mechanism: the active intermediates (including alkenes, cyclopentadienes, and aromatics) are gradually methylated with methanol to fulfill the propagation of the C–C bond, and then the extended entities (alkyl chain carrier) split off light olefins (see Scheme 4).

In summary, the methylcyclopentenyl cations and the methylcyclopentadiene were identified as the active intermediates by <sup>13</sup>C MAS NMR and GC-MS, and their reactivity was verified by the isotopic switch experiment and theoretical calculations. A catalytic cycle based on cyclopentadiene species as critical intermediates for ethene and propene formation was proposed. Cyclopentadiene species can directly participate the catalytic cycle and mediate the light olefins formation with a moderate energy barrier. Such unique cyclopentadienes-based cycle serves as a bridge to link the traditional alkenes-based

#### Scheme 4. Common Nature of the Indirect Mechanism in Methanol Conversion



and aromatics-based cycle, thus enriching and developing the indirect mechanism of methanol conversion. The present work not only provides a new methanol conversion route but also contributes to the general understanding of the indirect mechanism in the MTO reaction.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b02487.

Experimental and theoretical calculation details, catalyst characterization, and additional results (PDF)

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##### Notes

The authors declare no competing financial interest.

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