ACS Catalysis

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Methylcyclopentenyl Cations Linking Initial Stage and Highly Efficient Stage in Methanol-to-Hydrocarbon Process

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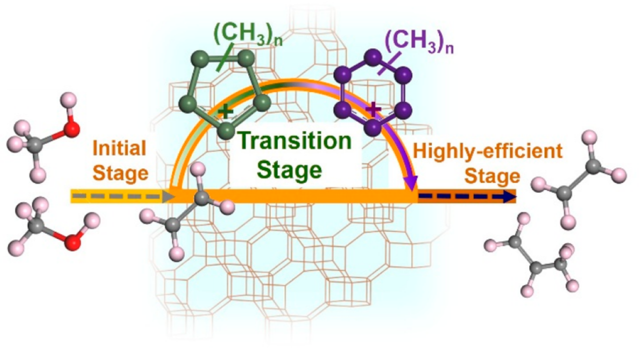
Cite This: *ACS Catal.* 2020, 10, 4510−4516 Read Online

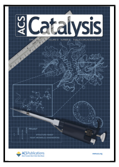
ABSTRACT: In the conversion of methanol to hydrocarbon (MTH), hydrocarbon pool (HCP) species have been observed and demonstrated as important intermediates for efficient formation of olefins in the steady-state stage. However, *in situ* observation on the formation and evolution of the hydrocarbon pool species at the initial stage is still a huge challenge. In this contribution, experimental and theoretical evidence on the origin and conversion of the methylcyclopentenyl cations (MCP^+) were obtained directly at the initial period of the MTH reaction. *In situ* solid-state NMR spectroscopies revealed that MCP^+ was formed preferentially than polymethylbenzenes (PMBs) species when the HCP species began to accumulate at the transition stage. Additionally, the relationship between MCP^+ and PMBs species was established by ^{13}C-isotope tracing experiments and theoretical calculations. Importantly, this contribution highlights the importance of the MCP^+ species in the whole methanol conversion process. Besides acting as an important active intermediate species for formation of olefins at the steady-state stage, MCP^+ species play a crucial role in bridging the direct mechanism at the inefficient initial stage and the highly efficient steady-state stage following the indirect pathway for methanol conversion.



KEYWORDS: *methanol-to-hydrocarbon, in situ solid-state NMR spectroscopy, methylcyclopentenyl cations, linking species, transition stage*

Light olefins production, through the non-petrochemical routes such as methanol-to-hydrocarbon (MTH) process, has attracted much attention from both academia and industry.[1−3] H-ZSM-5 zeolite with topology structure of MFI and SAPO-34 with topology structure of CHA exhibit excellent catalytic performance in the MTH reaction with high selectivity to light olefins (e.g., ethene and propene). Although the commercial MTH process has achieved great success, the mechanism of this reaction including the initial C−C bond formation and the detailed catalytic reaction routes for olefins formation remains elusive. In the past four decades, most studies have focused on the direct mechanism[4−10] at the initial stage and the indirect mechanism[11−18] at the steady-state stage. Researchers have been devoted to elucidate the formation of the initial C−C bond and the formation of products. Apart from 20 direct mechanisms proposed in the early studies, new developments in revealing the initial C−C bond formation in methanol conversion have been achieved recently.[19−23] With the aid of *in situ* IR spectroscopy, ssNMR, and theoretical calculation, the observed methoxymethyl carbocation ($CH_3OCH_2^+$),[19] surface-bounded acetyl group (Zeo-$OCCH_3$),[20] carbene-like species,[21] and surface methoxy species bound to an extra-framework Al,[22] among others, were responsible for the formation of the first C−C bond. Recently, our group observed a surface methyleneoxy-analogue that originated from the surface-activated dimethyl ether by *in situ* ssNMR, which was recognized to be the crucial intermediate for the initial C−C bond formation via the direct mechanism at the initial MTH process.[23,24] For the formation of olefins at the steady-state stage of the MTH process, methanol conversion will propagate via the efficient indirect mechanism[2,12,18,25−27] with the participation of the active organic compounds. In general, the active intermediates, including carbenium ions and their neutral species, can participate in the olefins formation via aromatics-based (side-chain methylation route and paring route), cyclopentadienes-based cycle, and alkenes-based routes.[26−30] Some carbenium ions in the MTO reaction, such as five-membered ring cations (methylcyclopentenyl cations, MCP^+) and six-membered ring cations (polymethylbenzenium cations, PMB^+), have been identified using the solid-state NMR technique via an *ex situ* method.[18,26,31] Direct observation of these carbenium ions under operando condition is a huge challenge because of their instability and relatively lower sensitivity of spectroscopy.

Received: February 17, 2020
Revised: March 16, 2020
Published: March 23, 2020



https://dx.doi.org/10.1021/acscatal.0c00799
ACS Catal. 2020, 10, 4510−4516

Additionally, it is noticeable that there is a very important transition stage linking the initial stage and the steady-state stage, which involves the formation and aggregation of hydrocarbon pool species.[3,24,32−37] After the initial C−C bond formation, the initial olefins and hydrocarbon pool species will be gradually aggregated, and then the reaction enters steady-state stage. Although the efficient formation of olefins via indirect mechanism has been widely accepted at the steady-state period, there are still some uncertain issues, such as the generation of initial HCP species and the relationship between the HCP species. Besides, establishing a bridge between the direct mechanism at the inefficient initial stage and the highly efficient steady-state stage following indirect pathway for methanol conversion is very important, including how initial olefins generate initial hydrocarbon pool species and the evolution of the initial hydrocarbon pool species. Herein, we observed that MCP^+, as the crucial intermediate, has bridged the direct mechanism at the initial stage and the indirect mechanism for olefins' formation at the steady-state stage. With the aid of *in situ* ^{13}C MAS NMR spectroscopy, we found that MCP^+ was formed earlier compared with PMBs at the initial stage. Furthermore, we provided the direct evidence on the formation and evolution of MCP^+ species by ^{13}C-isotope labeling experiments and theoretical calculations.

Structural characterizations of H-SSZ-13, H-ZSM-5, and H-Beta zeolites have been described in our previous work.[18,38,39] *In situ* ^{13}C MAS NMR spectra were carried on a high-temperature continuous-flow MAS NMR probe head. The experimental details can be found in the Supporting Information (SI). The methanol conversion and the effluent product distribution at 275 and 300 °C over H-SSZ-13 were provided in Figures S1 and S2. Figure 1 shows the *in situ* ^{13}C MAS NMR spectra (a) and the yield of ethene and propene in gas phase products (b) of methanol conversion at 275 °C with time on stream (TOS) over H-SSZ-13. At the very initial period from 0 to 9 min (Figure 1a), the main organic species consisting of methanol at 50 ppm and dimethyl ether (DME) at 60 ppm can be observed. The peak intensity of DME increases with the prolonging of reaction time, and methanol and DME are predominant products along with methane and ethene with lower quantities (Figure S2a), which suggest that methanol dehydration to DME is the primary reaction at this period, followed by the first C−C bond formation. In this stage, ethene is the first olefin product and propene appears later (Figure 1b), which indicates ethene and propene may be originated from different mechanisms at this period. From 9 to 30 min, both ^{13}C MAS NMR spectra and online GC results (Figure S2a) reveal that the amount of DME decreases obviously, accompanied by more light olefins' formation. Ethene presents higher yield than propene, although the ratio of $C_3^=/C_2^=$ keeps increasing, and methanol achieves the maximum conversion rate at 30 min. More importantly, some saturated species at 0−40 ppm and unsaturated species at 245, 154, and 131 ppm were confined in the CHA nanocage of catalyst. According to our previous study,[18,40] the saturated species at 0−40 ppm are assigned to the cycloparaffin such as methyl-submitted adamantane from polymerization and cyclization of initial olefins. Additionally, the characteristic signals at 245 and 154 ppm illustrate the formation of MCP^+, such as pentamethylcyclopentenyl cation (pentaMCP^+). The signal of the peak at 131 ppm can be identified as polymethylbenzenes (PMBs). The failure to capture the polymethylbenzenium cations under *in situ* condition is due to their extremely high reactivity.[18] These two unsaturated species accumulate gradually during this transition stage, which have been considered widely as active HCP species during the MTO reaction.[18,41] In this transition period, the MCP^+ species may transform to more active intermediates for ethene and propene formation. After the transition period, from 30 to 120 min, the MTO reaction went into a steady-state period. The yield of propene continues to increase while ethene maintains stability, leading to the increase of the ratio of $C_3^=/C_2^=$. The intensity of pentaMCP^+ increases first and then decreases during this period, but the signals of PMBs continuously increase. During the steady- state period, MCP^+ species via the cyclopentadienes-based cycle, together with the alkene and aromatic intermediates, were considered to be responsible for ethene and propene generation.[30] Then, with the decreases of methanol conversion and product yield, the reaction goes into deactivation stage after 120 min. Next, we also performed *in situ* reaction and detected the distribution of gas-phase products at 300 °C (see Figures S2b and S3). The reaction at 300 °C shows a similar phenomenon to that at 275 °C. The differences are the shorter reaction induction period and slower deactivation at 300 °C, which is due to the less aggregation of adamantane species at relatively higher temperature of MTO reaction on CHA catalyst.[40]

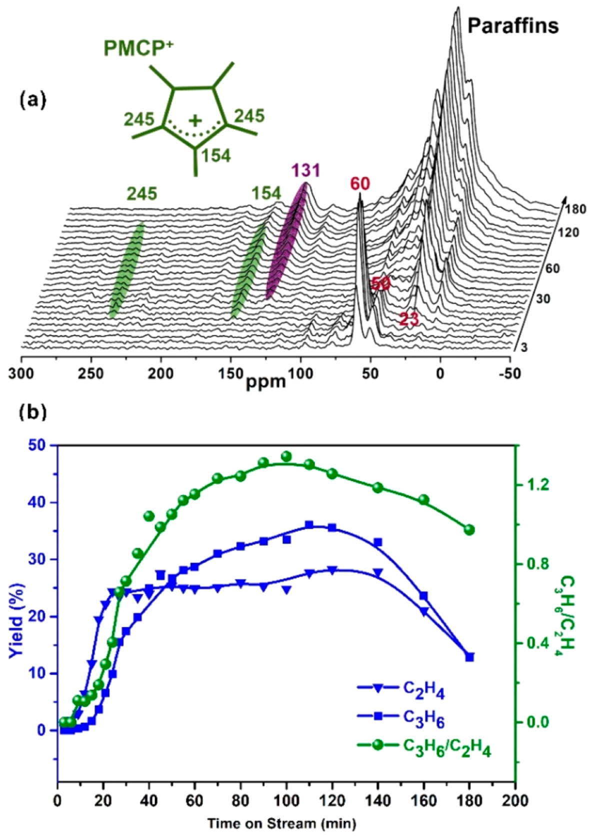


Figure 1. *In situ* ^{13}C MAS NMR spectra (a) and the yield of ethene and propene as well as their ratio (b) of $^{13}CH_3OH$ reaction over H-SSZ-13 catalyst at 275 °C with methanol weight hourly space velocity (WHSV) of 1.0 h^{-1}.

It is noteworthy that the apparent observation of pentaMCP^+ appears at 15 min earlier than PMBs at 21 min. This result is in accordance with our previous *ex situ* studies of MTO reaction on H-SSZ-13 that the appearance of highest concentration of pentaMCP^+ is earlier than heptaMB^+.[18]

Interestingly, besides the CHA zeolite, the similar phenomena were also found on other zeolites. *In situ* ^{13}C MAS NMR experiment of methanol reaction on H-ZSM-5 at 275 °C was present in the Figure S4. Similarly, MCP^+ is generated earlier than PMBs on H-ZSM-5. We failed to observe this phenomenon on H-Beta by *in situ* ^{13}C MAS NMR spectra (see Figure S5), but an *ex situ* ^{13}C MAS NMR experiment clearly found that MCP^+ appeared earlier than $heptaMB^+$ (see Figure S6). The failure of observation of carbenium ions on H-Beta under the *in situ* reaction condition may be attributed to the relatively larger 12-membered-ring pore size of H-Beta, which makes MCP species effuse from the channel, leading to a relatively lower concentration of MCP^+ retaining in the BEA cage. This interesting phenomenon reflects that the new insight of the mechanism exists in the formation of HCP species at the induction period. And MCP^+ and PMBs, as critical intermediates, have been considered to be responsible for the formation of olefins via indirect mechanism at the steady-state period of methanol conversion.[31,41,42] Therefore, it is necessary to explore the formation and evolution of MCP^+ and PMBs at the transition period, which links the direct mechanism at the initial stage and the indirect mechanism at the steady-state stage of methanol conversion.

According to the *in situ* continuous-flow $^{13}CH_3OH$ reaction on the H-SSZ-13 result, ethene is the first olefin product along with formation of methane and propane (Figure S2), which is consistent with our previous work on H-ZSM-5 zeolite during MTO reaction.[23] Then, to further investigate whether MCP^+ originates from ethene, we performed the reaction of adsorbed ^{13}C-ethene on H-SSZ-13 and H-Beta zeolites at 275 °C (Figure 2). When ethene reacted on the zeolite, the characteristic signals of MCP^+ species at 240−250, 140−150 ppm were observed along with the formation of aromatic species (130 ppm) and oligomers of ethene (0−50 ppm). The results are in accordance with the report of Haw that cyclopentenyl cations can be formed from ethene accompanied by alkanes formation on H-ZSM-5 using pulse-quench method.[31] Therefore, as shown in Scheme S1, the initial MCP^+ and MCP species can be formed via a series of reactions, such as oligomerization, cyclization, and H-transfer of initial olefins.

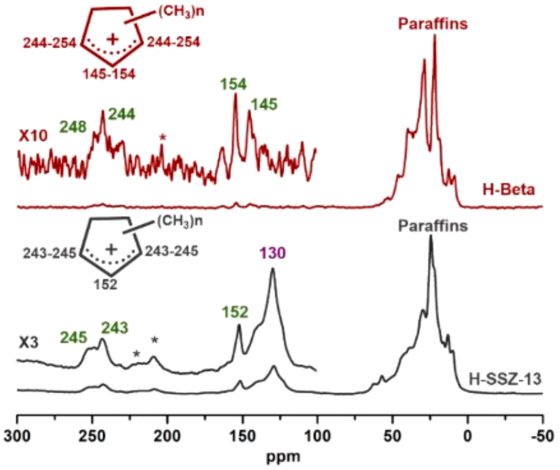


Figure 2. ^{13}C MAS NMR spectra of H-SSZ-13 and H-Beta zeolites on the reaction of adsorbed ^{13}C-ethene at 275 °C for 60 and 30 s, respectively. Asterisk denotes spinning sideband.

Next, the remaining question is the evolution of MCP^+ and whether there is a relationship between MCP^+ and initial PMBs? In the paring mechanism of aromatics-based cycle, the methylcyclopentadienyl cations (MCP_{di}^+, as displayed in the Scheme S2) can be converted to PMBs by ring contraction/expansion reactions.[18,42,43] The observed methylcyclopentenyl cation (MCP^+) by ^{13}C NMR deprotonates to form methylcyclopentadiene (MCP) that can further lose H^- to generate methlycyclopentadienyl cation (MCP_{di}^+).[31] Therefore, we proposed the reaction route for the formation of PMBs from MCP^+ on H-SSZ-13, as shown in Figure 3. Density functional theory calculations (DFT) were used to evaluate the feasibility of this reaction route. Computational details are provided in section 2.3 in the Supporting Information, and the calculation model of SSZ-13 was displayed in the Figure S7. With the fast deprotonation steps (20.83 kcal/mol) of $PMCP^+$, PMCP can be easily obtained. Then PMCP can lose H^- to cation (e.g., an alkoxy species (CH_3^+) derived from methane) to form pentamethlycyclopentadienyl cation ($PMCP_{di}^+$) with the energy barrier of 34.62 kcal/mol. This cyclopentadienyl cation (MCP_{di}^+) has been widely regarded as a critical intermediate in the paring mechanism, which undergoes hydride transfer (33.04 kcal/mol), ring expansion (17.22 k/mol), and deprotonation (5.09 kcal/mol) to form TMB.[18] Then, heptamethylbenzenium cation ($heptaMB^+$) can be formed through continuously methylation with an acceptable energy barrier (6.06−21.47 kcal/mol).[18] These theoretical calculations, combining with our *in situ* ^{13}C MAS NMR results, demonstate that the formations of initial PMBs at initial stage originate from MCP^+ with methanol reaction via deprotonation, hydride-transfer reactions, and ring-expansion.

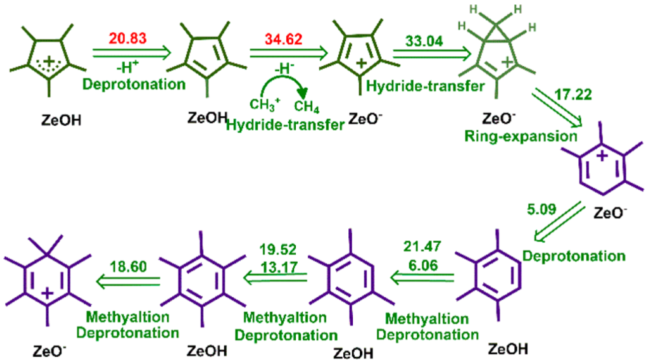


Figure 3. Proposed reaction route for the formation of initial PMBs from MCP^+ on H-SSZ-13. Calculated energy barriers are given in kcal/mol. The calculated energy barriers of methylation of PMBs (green font) on H-SSZ-13 have been obtained in our previous work.[18]

Furthermore, the direct experimental evidence for the PMBs formation were offered by the coreaction of MCP^+ and methanol. We choose H-Beta zeolite with 12-membered ring pore as a model catalyst because of its larger pore size, which allows the introduction of pure MCP species. Our previous study has demonstrated that $pentaMCP^+$ can be formed by adsorption of its deprotonated species (i.e., neutral pentamethylcyclopentadiene (pentaMCP) molecule).[18] In this work, first, the sample containing $pentaMCP^+$ was obtained by the adsorption of neutral pentaMCP on H-Beta zeolite at 80 °C. Then, the sample was sealed and heated at 275 °C in a NMR rotor for a certain time, and the rotor reactor was quenched immediately by liquid N_2. The confined organic species were analyzed by GC-MS after HF dissolution and CH_2Cl_2 extraction. Figure 4a,b provided the GC-MS chromatograms and the isotopic distributions of the confined organic species after the sole pentaMCP reaction and the coreactions of pentaMCP and $^{13}CH_3OH$ for different reaction time. When the sole pentaMCP reacts on the H-Beta, the main product is tetramethylbenzene (TMB) with small amounts of pentamethylbenzene (PMB) and hexamethylbenzene (HMB). Obviously, TMB can be easily generated from pentaMCP$^+$. Compared with only pentaMCP as a reactant, the retained organic products of PMB and HMB increase obviously while adding methanol. It indicates that TMB can be easily methylated with methanol to produce PMB and HMB. Additionally, the amount of HMB increases with the reaction time extending from 1 to 3 min (see Figure 4a). Next, the distribution of ^{13}C atoms of the confined organic species descripts the detailed reaction mechanism from MCP$^+$ to PMBs. First, the isotopic distributions of the confined pentaMCP, PMBs, and HMMC (hexamethylmethylene-cyclohexadiene, the deprotonated product of heptaMB$^+$) indicate that ^{13}C atoms from labeled methanol are incorporated into these organic species during the reaction. Importantly, the average number of ^{13}C atoms in these species is in good agreement with the ring expansion and methylation reaction between MCP and PMBs$^+$ (see Figure 4b,c). In addition, the ^{13}C MAS NMR spectra of the two H-Beta zeolites with coreaction of pentaMCP and $^{13}CH_3OH$ for 1 and 3 min exhibit a similar result in that the participation of pentaMCP enhances the reaction rate and promotes the production of the PMBs species (see Figure S8). On the basis of the above experiments, we confirm PMBs can be generated from MCP$^+$ with the help of methanol via deprotonation, hydride-transfer reactions, ring expansion, and methylation reaction.

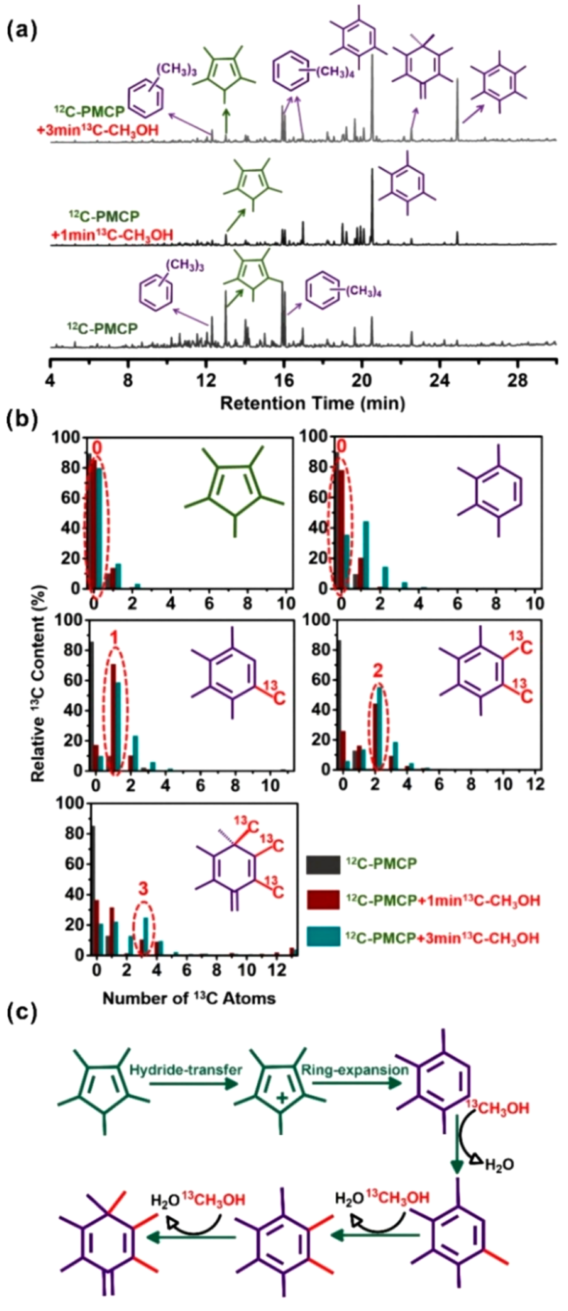
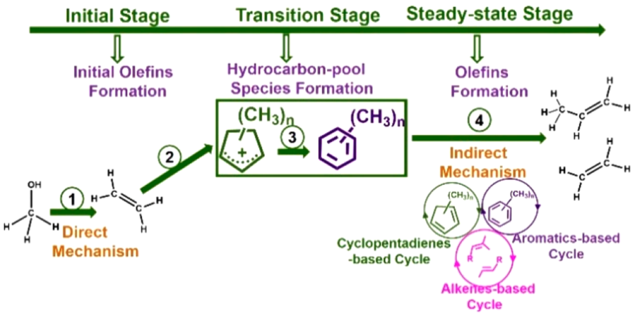


Figure 4. GC-MS chromatograms (a) and isotopic distribution (b) of the organic species retained in H-Beta catalyst after coreaction of ^{12}C-pentaMCP and $^{13}CH_3OH$ at 275 °C for 1 min (red line or column) and 3 min (blue line or column); the black line or column is the control experiment of ^{12}C-pentaMCP reaction for 1 min. The evolution process from pentaMCP to PMBs was shown in (c).

This experimental evidence, together with the theoretical results, reveal the relationship between MCP$^+$ and PMBs and offer a rational explanation of the priority formation of MCP$^+$ species compared with PMBs. Importantly, this contribution provided a detailed formation process of HCP species at the transition stage, and a whole mechanism from direct mechanism at the initial stage to indirect mechanism at the steady-state stage was proposed in Scheme 1. At the initial period of reaction, methanol can generate initial olefin (ethene) via direct mechanism.[19−23] Subsequently, the reaction enters the transition stage. At this stage, we found that ethene can generate the initial hydrocarbon pool species (MCP$^+$) through polymerization, cyclization, hydride transfer reactions. Importantly, the initial PMBs and their corresponding carbenium ions can be produced from MCP$^+$ via deprotonation, hydride transfer, ring expansion, and methylation reactions in the transition stage. Once the concentrations of the hydrocarbon pool species reach a certain extent, the

Scheme 1. Whole Mechanism of Methanol to Olefins[a]



[a](1)Tthe initial ethene is generated from methanol by direct mechanism; (2) MCP species are produced from initial ethene; (3) PMBs species are produced from the co-reaction of MCP species and methanol; and (4) the olefins are formed via indirect mechanism including of aromatics-based, alkenes-based, and cyclopentadienes-based cycles.

reaction enters the steady-state period with higher activity. Then, olefins can be effectively produced via indirect mechanism including alkenes-based, cyclopentadienes-based, and aromatics-based cycles.[30]

In conclusion, we have presented direct evidence on the formation and evolution of MCP^+ species via *in situ* ^{13}C MAS NMR, ^{13}C-isotope tracing, coreaction of MCP^+ and methanol experiments, and theoretical calculations. In the whole reaction process, MCP^+ species are initially formed as starting HCP species and tranformed to more active intermediates, PMBs, at the transition stage. MCP^+ species can not only mediate the light olefins formation directly via aromatics-based and cyclopentadienes-based cycle at the steady-state stage but also serve as a bridge to link the direct mechanism at the initial stage and the indirect mechanism at the steady-state stage. This work establishes the relationship of the MCP^+ and PMBs and highlights the importance of MCP^+ species in the whole reaction process.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c00799.

Experimental section, materials, and additional results (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the financial support from the National Natural Science Foundation of China (Nos. 21991092, 21972142, and 91745109), the Key Research Program of Frontier Sciences, Chinese Academy of Sciences (QYZDY-SSW-JSC024), the Youth Innovation Promotion Association of the Chinese Academy of Sciences (No. 2014165), the International Partnership Program of Chinese Academy of Sciences (121421KYSB20180007), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA21030200), and Liao Ning Revitalization Talents Program (XLYC1807227).

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