Reactive Intermediates

Direct Observation of Cyclic Carbenium Ions and Their Role in the Catalytic Cycle of the Methanol-to-Olefin Reaction over Chabazite Zeolites**

*Shutao Xu, Anmin Zheng, Yingxu Wei, Jingrun Chen, Jinzhe Li, Yueying Chu, Mozhi Zhang, Quanyi Wang, You Zhou, Jinbang Wang, Feng Deng, and Zhongmin Liu**

The diminishing reserve of crude oil and the rapidly increasing demands for the base chemicals, such as ethene and propene, provide strong driving force for exploring alternative chemical feedstocks and developing non-petrochemical processes. To date, the methanol-to-olefins (MTO) process has been one of the most successful non-petrochemical routes for the production of light olefins from abundant resources of natural gas or coal.[1–3] Considering the essential role of the products of the MTO reaction in the global energy chain and chemical industry,[4] investigations of the MTO reaction mechanism are crucial for both of the fundamental science and industrial application. Catalysts used in the MTO process are typically microporous solid acids, including zeolites and zeotype molecular sieves, among which the H-ZSM-5 zeolite with framework type MFI and SAPO-34 with framework type CHA deliver the best catalytic performance in the MTO reaction.[1–4] Despite the tremendous research efforts over the past 30 years,[4–8] the reaction mechanism of the first C−C bond in the MTO process remains elusive. In general, the hydrocarbon pool (HCP) mechanism,[9] that is, that cyclic organic species confined in the zeolite cage or intersection of channels act as co-catalysts, has been generally accepted as a rational explanation for the olefins production from the C_1 reactant, methanol.[2] Two reaction routes have been proposed to explain the MTO reaction pathway according to the HCP mechanism, namely the side-chain methylation route and the paring route. In both of the two routes, carbenium ions are involved and act as the important intermediates to

produce olefins.[10–15] Specifically, the paring mechanism involves the contraction of six-membered ring cations (poly-methylbenzenium cations) and the expansion of five-membered ring cations (polymethylcyclopentenyl cations). In contrast, the side-chain methylation route proceeds via the methanol methylation on polymethylbenzenium cations and subsequent elimination of side-chain groups to produce olefins.

Direct observation of these carbenium ions involved in the proposed mechanism under real conditions is of great significance to understand the reaction mechanism and the structure–performance correlation of the MTO reaction. Even though some carbenium ions in the MTO reaction, such as cations **1–4** (see Scheme 1) have been identified using in situ solid-state NMR, the formation of these carbenium
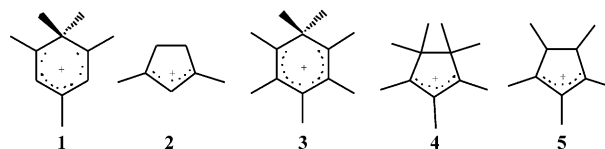
Scheme 1. The series of carbenium ions observed with in situ NMR spectroscopy in zeolites: **1**: 1,1,2,4,6-pentamethylbenzenium cation; **2**: 1,3-dimethylcyclopentenyl cation; **3**: heptamethylbenzenium cation (heptaMB$^+$); **4**: heptamethylcyclopentenyl cation (heptaMCP$^+$); **5**: pentamethylcyclopentenyl cation (pentaMCP$^+$).

[*] Dr. S. Xu,[+] Prof. Dr. Y. Wei, J. Chen, Dr. J. Li, M. Zhang, Q. Wang, Y. Zhou, J. Wang, Prof. Dr. Z. Liu
National Engineering Laboratory for Methanol to Olefins
Dalian National Laboratory for Clean Energy
Dalian Institute of Chemical Physics
Chinese Academy of Sciences, Dalian 116023 (P. R. China)
E-mail: liuzm@dicp.ac.cn

Prof. Dr. A. Zheng,[+] Y. Chu, Prof. Dr. F. Deng
State Key Laboratory of Magnetic Resonance and
Atomic Molecular Physics, Wuhan Center for Magnetic Resonance
Wuhan Institute of Physics and Mathematics
Chinese Academy of Sciences, Wuhan 430071 (P. R. China)

[+] These authors contributed equally to this work.

ions in the catalyst was verified mostly indirectly or by the aid of the reaction of co-feeding methanol and benzene or methylbenzene.[16–19] Owing to the difficulty in the direct observation of these HCP species, understanding of their formation and significance in methanol conversion over zeolites or SAPO catalysts under real working conditions is still a huge challenge. Until now, only cation **2** on H-ZSM-5 and cation **3** on DNL-6 with framework type RHO were observed directly under real working conditions using methanol as the only reactant.[17,20] H-SAPO-34 and H-SSZ-13 with framework type CHA are the very important catalysts for the MTO process owing to their great success or potential in the industrial applications.[2,10] However, still no experimental clue was reported towards the carbenium ions identifications over these two catalysts, in turn, the corresponding reaction pathways for the MTO reaction over them are remain unknown to date.

Herein, using the multiple techniques, we report the observations of six-membered (cation **3**) and five-membered (cation **5**) ring cations under the real working conditions of methanol conversion. Their simultaneous formation was identified for the first time in the H-SSZ-13 and H-SAPO-34 using methanol as the only reactant with ^{13}C MAS NMR. The cation **5** in particular is a new carbenium ion observed in the MTO reaction. The assignments of the two carbenium ions were unambiguously confirmed by the combined techniques of NMR, GC-MS, and theoretical calculation. Furthermore, on the basis of the experimental results, methanol conversion mechanisms (that is, side-chain methylation and paring mechanisms) with the two carbenium ions as the reaction intermediates were theoretically explored in more detail.

Structural characterizations of H-SSZ-13 and H-SAPO-34 are described in the Supporting Information, Figures S1–S3. The strategy to capture and observe the carbenium ions involves mild reaction conditions to lower their reactivity and appropriate catalytic environment for their accommodation and stabilization, such as the cage structure and acid environment of the catalysts. The catalytic performances of methanol conversion over H-SSZ-13 and H-SAPO-34 at a low temperature range of 275–400 °C are shown in the Supporting Information, Figure S4 and reported in our previous study.[21] Figure 1 shows representative ^{13}C MAS NMR spectra of H-

Figure 1. ^{13}C MAS NMR spectra of a) retained organic species in H-SAPO-34 after continuous-flow ^{13}CH$_3$OH reaction at 300 °C for 15 min and b) retained organic species in H-SSZ-13 after continuous-flow ^{13}CH$_3$OH reaction at 275 °C for 25 min. The asterisk denotes spinning side-bands. Insets: calculated ^{13}C chemical shifts of pentaMCP$^+$ and heptaMB$^+$ ions inside the H-SSZ-13 zeolite (the optimized structures of the two carbenium ions confined in H-SSZ-13 are shown in the Supporting Information, Figure S6).
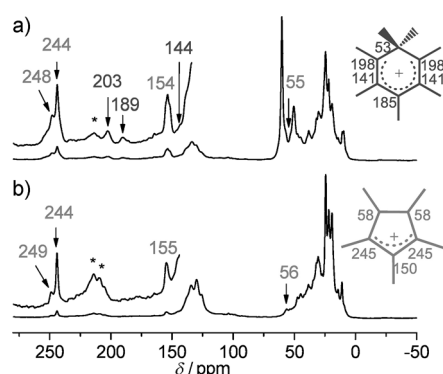
SAPO-34 and H-SSZ-13 catalysts during methanol conversion at 275 °C. Diamondoid hydrocarbons, such as methyladamantanes (10–50 ppm)[22] and alkylated aromatics, such as methylbenzenes (120–140 ppm),[23] are the most predominantly formed species among the retained organics. The adsorbed methanol at 50.5 ppm and dimethyl ether (DME) at 60.5 ppm can also be observed on H-SSZ-13 catalyst at 275 °C. Besides these stable organic species, even in low intensity, some signals appear in the downfield region (140–250 ppm) with the characteristic chemical shift at about 240–250 and

190–210 ppm. The appearance of the resonance peaks at 240–255, 155, and 56 ppm in the ^{13}C MAS NMR spectra implies the formation of five-membered ring cations (polymethylcyclopentenyl cations) over the two catalysts,[17,19] while for H-SSZ-13, apart from these signals from polymethylcyclopentenyl cations, the appearance of the peaks at 203, 190, and 144 ppm also confirms the formation of six-membered ring cations. According to the previous studies carried out over H-Beta[18] and DNL-6[20] catalysts, the benzenium cation observed here is ascribed to heptamethylbenzenium (heptaMB$^+$), which will be demonstrated later by theoretical calculations of the ^{13}C chemical shift (Supporting Information, Table S1). Therefore, for the first time, in the catalysts with chabazite topologies, the most important reaction intermediates, polymethylcyclopentenyl cations and polymethylbenzenium cations, were successfully captured and directly observed under real MTO reaction conditions.

For a precise structure determination, confined organic species in H-SSZ-13 after a parallel ^{12}CH$_3$OH reaction were analyzed by GC-MS[24] (Supporting Information, Figure S5). A peak at retention time of 10.4 min was ascribed to pentamethylcyclopentadiene (pentaMCP), indicating that the observed five-membered ring carbenium ions confined in CHA cages and observed with ^{13}C MAS NMR is pentamethylcyclopentenyl cation (pentaMCP$^+$). The deprotonation process from pentaMCP$^+$ to pentaMCP is shown in the Supporting Information, Scheme S1.

On the basis of accurate ^{13}C chemical shift calculations (Supporting Information, Figure S6, Table S1), the theoretical ^{13}C chemical shift of heptaMB$^+$ cation (at 198, 141, and 185 ppm) and pentaMCP$^+$ cation (at 245, 150, and 58 ppm) inside H-SSZ-13 are determined and in good agreement with NMR observations. Pure pentaMCP dissolved in 98% H$_2$SO4 (Supporting Information, Figure S7) and adsorbed in H-Beta zeolite (Supporting Information, Figure S8), methods to produce pure pentaMCP^{+},[25] show very close values in chemical shifts to the results in Figure 1. Therefore, the formations of heptaMB$^+$ and pentaMCP$^+$ were consolidated by combining the NMR and GC-MS techniques and theoretical prediction.

Notably, for H-SAPO-34, only pentaMCP$^+$ has been observed, while over H-SSZ-13, the generation of both heptaMB$^+$ and pentaMCP$^+$ was shown. Based on the extensive experimental attempts and the assistance of theoretical calculations, Nicholas et al. predicted that the carbenium ions can be persistent inside zeolites if their deprotonated neutral hydrocarbons have a proton affinity (PA) value more than 209 kcal mol^{-1}.[12] The theoretically predictions at MP2/6-311G(d,p) level indicate that the PA value of hexamethylmethylenecyclohexadiene (HMMC, the deprotonated form of heptaMB$^+$) and pentaMCP are 239.3 and 223.5–227.2 kcal mol^{-1}, respectively (Supporting Information, Figure S9). According to the assumption of Nicholas et al., the heptaMB$^+$ and pentaMCP$^+$ ions can exist inside both the H-SAPO-34 and H-SSZ-13 zeolites. And heptaMB$^+$ ion may be more stable than pentaMCP$^+$ owing to its larger PA value. This is in good agreement with the observation in H-SSZ-13 that these two carbenium ions have been determined by our ^{13}C NMR experiment. However, it is not the case for the H-

SAPO-34 over which only pentaMCP[+] is observed. This implies that PA value is not the only factor for estimating the stabilities of the carbenium ions in a confined environment. Considering their identical CHA cage for the carbenium ions accommodation, the difference in heptaMB[+] formation and observation is possibly associated with acid strength of the Brönsted acid sites that are responsible for the protonation and stabilization of the intermediates in the catalysts. Stronger Brönsted acidity of H-SSZ-13 than H-SAPO-34, confirmed by ^{1}H MAS NMR spectra, NH$_3$-TPD, and ^{13}C MAS NMR of [2-^{13}C]acetone adsorption (Supporting Information, Figures S3, S10, S11), was considered to be the reason of the stabilization of heptaMB[+] in H-SSZ-13. However, the PA value and acid strength cannot explain why heptaMB[+] ion is less stable than pentaMCP[+] ion in the CHA cage. Therefore, their reactivity during methanol conversion should also be considered as well as their generation and stabilization in acid catalysts. The methanol reaction performed at various temperatures over H-SSZ-13 and H-SAPO-34 catalysts (Supporting Information, Figures S12, S13) demonstrates that pentaMCP[+] could be observed in a wide temperature range, even at relatively high temperature of 350 °C, while heptaMB[+] was only observed at low temperature, such as 275 °C, implying its extremely high reactivity. More details about the activation energy barriers of heptaMB[+] and pentaMCP[+] conversions will be theoretically calculated and are discussed below.

To further investigate the roles of the observed carbenium ions in the MTO reaction, a series of tests of [13]CH$_3$OH conversion over H-SSZ-13 were performed at 275 °C and stopped at various times on-stream. The ^{13}C MAS NMR spectra presenting the variation of confined organics are shown in Figure 2 a, and the concentrations of heptaMB[+] and pentaMCP[+] were quantitatively calculated according to the integral area of the ring carbon atoms with the characteristic peaks at 189/190 ppm and 240–250 ppm, respectively. The concentration evolutions of heptaMB[+], pentaMCP[+] and both of the two carbenium ions with time on-stream (TOS) (Figure 2 b) are almost consistent with the methanol conversion variation, except for the 20 minute delay of highest concentration of heptaMB[+]. This confirmed the participation of the two cyclic carbenium ions in the MTO reaction as the important intermediates. The observations of heptaMB[+] and pentaMCP[+] and the correlation of their concentrations with methanol conversion mean that both paring and side-chain methylation mechanisms are possible for methanol conversion over H-SSZ-13 zeolite with framework type CHA. Even though the paring mechanism has not been proposed for methanol conversion over eight-ring catalysts, it cannot be ruled out on the base of the observation and confirmation of pentaMCP[+].

Previous studies have proved that heptaMB[+] is a very important intermediate during the MTO reaction over H-Beta and DNL-6 catalysts.[11,20] In the present work, the participation of pentaMCP[+] as a hydrocarbon pool species in MTO under real reaction condition were followed by [^{12}C]-methanol/[^{13}C]-methanol switch experiments (for the detailed procedure, see the Supporting Information). Feeding [^{13}C]-methanol upon the H-SSZ-13 catalyst with confined [^{12}C]-
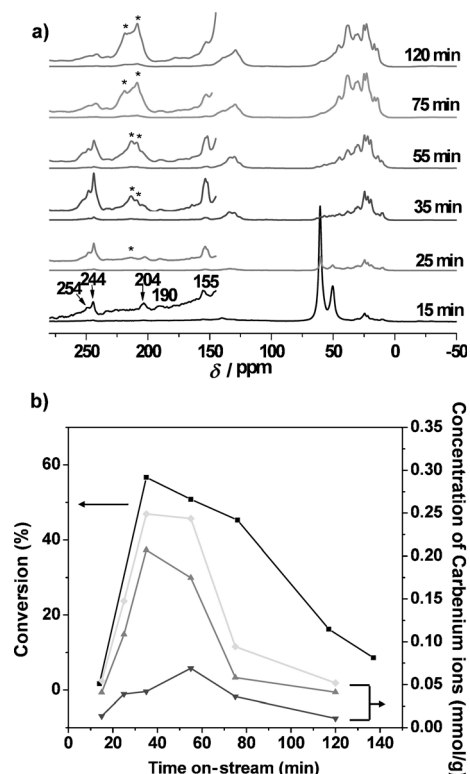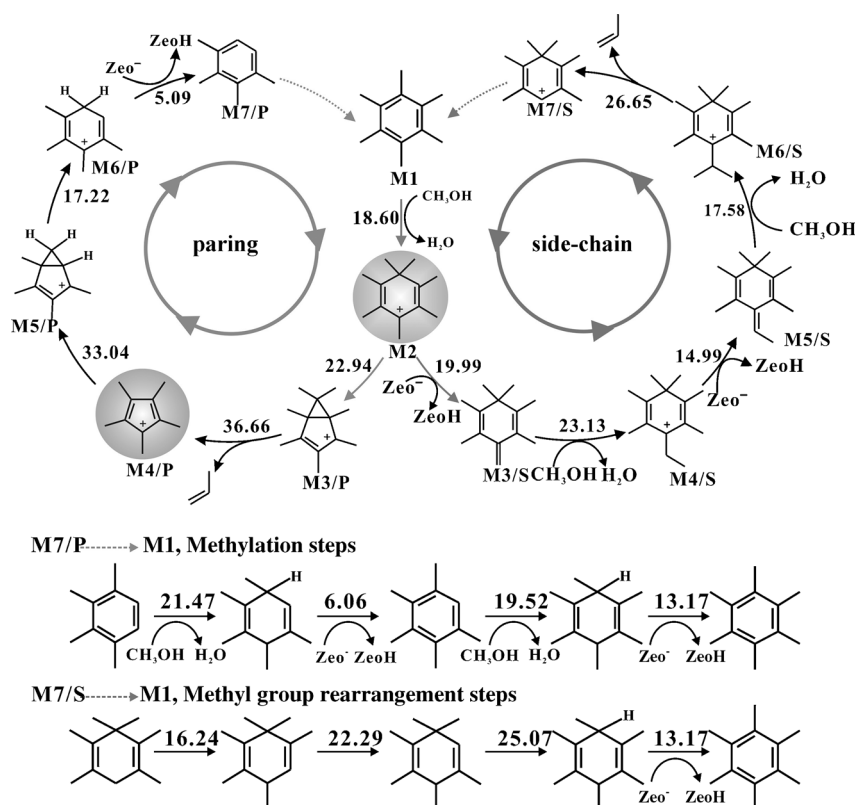

Figure 2. a) ^{13}C MAS NMR spectra of [13]CH$_3$OH reaction on H-SSZ-13 with time on-stream under continuous-flow condition at 275 °C. Asterisk denotes spinning side-bands. b) Relationship between the conversion of methanol and the concentrations of carbenium ions with time on-stream. ■ methanol conversion, ▲ pentaMCP[+], ▼ heptaMB[+], ◆ total concentration of the two ions.

pentaMCP[+] generated olefin products containing both ^{12}C and ^{13}C atoms (Figure 3; Supporting Information, S14), suggesting that olefins products were formed via the interaction of [^{13}C]-methanol and the confined [^{12}C]-carbenium ions. Moreover, the isotopic distribution of the confined pentaMCP, the deprotonated product of pentaMCP[+], indicates that ^{13}C atoms from labeled methanol are incorporated into pentaMCP[+] during the MTO reaction (Figure 3). This
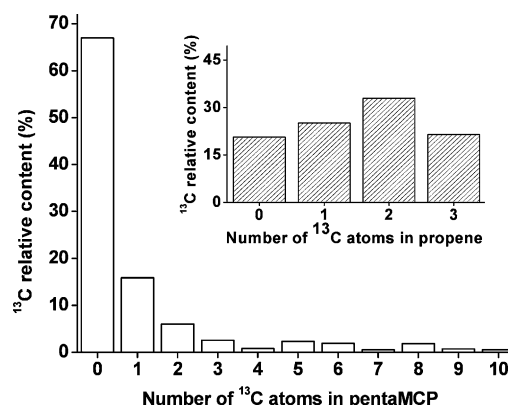
Figure 3. Isotopic distribution of pentaMCP formed in the [^{12}C/^{13}C]methanol switch experiments over H-SSZ-13 at 275 °C. Inset: the isotopic distribution of propene.

ZeoH
Zeo⁻
5.09
M7/P

M7/S
26.65

M6/S
H₂O
17.58
CH₃OH

M6/P
17.22

paring   M1   side-chain
18.60 CH₃OH
H₂O

M5/P
33.04

M6/S
M5/S
ZeoH

22.94
Zeo⁻
ZeoH
19.99
ZeoH
14.99
Zeo⁻
ZeoH

M4/P
36.66
M3/P
M2

M3/SCH₃OH H₂O
23.13
M4/S

M7/P ┄┄► M1, Methylation steps

21.47
CH₃OH H₂O
6.06
Zeo⁻ ZeoH
19.52
CH₃OH H₂O
13.17
Zeo⁻ ZeoH

M7/S ┄┄► M1, Methyl group rearrangement steps

16.24
22.29
25.07
13.17
Zeo⁻ ZeoH

Figure 4. Catalytic cycles of the paring and side-chain reaction mechanisms for the MTO conversion with the involvement of pentaMCP⁺ and heptaMB⁺ in H-SSZ-13 zeolite. The calculated energy barriers are given in kcal mol⁻¹.

further proved the participation of pentaMCP⁺ in the methanol conversion as the hydrocarbon pool species.

To clarify the prevailing reaction route of methanol conversion, theoretical calculations were carried out to evaluate the reaction pathway following the paring mechanism and side-chain methylation mechanism with the involvement of heptaMB⁺ and pentaMCP⁺ as the characteristic intermediates for these two mechanisms (Figure 4; Supporting Information, Figure S16). For the two catalytic cycles, the eliminations of propene from M3/P and M6/S (M3/P-M4/P and M6/S-M7/S steps in Figure 4), with activation energies of 36.66 and 26.65 kcal mol⁻¹, are the rate-determining steps for the paring and the side-chain methylation mechanisms. In the competitive reaction systems, the reaction usually follows the pathway with low activation energy, so the side-chain methylation mechanism may be more dominant in the MTO reaction over H-SSZ-13 zeolite. But noticeably, the difference in activation energy between the two mechanisms is not very large (ca. 10 kcal mol⁻¹), parallel occurrence of the two reaction cycles is also very possible in the MTO reaction. PentaMCP⁺ (M4/P, see Figure 4) formation and accommodation in the CHA cage of zeolite catalyst, and their participation in methanol conversion is the direct evidence of paring mechanism with the five-membered-ring carbenium involvement. Moreover, detailed isotopic distribution analysis of the main olefin product, propene (Figure 3) indicates that the contribution of paring mechanism for olefin generation is secondary, and side-chain methylation mechanism is

more important route for MTO reaction (for a detailed explanation, see the Supporting Information, Section S2.5 and Figure S15). This is in accordance with the theoretical calculation results.

Based on the proposed reaction cycles with carbenium ions as the important intermediates, the observability of the heptaMB⁺ and pentaMCP⁺ can be discussed. As their generation is energetically favorable, the capture of them is determined by their stability and lifetime, which are closely related with the reaction energy barriers of their further transformation to other intermediates. According to the catalytic cycle presented in Figure 4 (Supporting Information, Figure S17), the transformation of pentaMCP⁺ ions (M4/P) needs to overcome relative higher energy barriers (32.45 and 33.04 kcal mol⁻¹) than the heptaMB⁺ ions (17–23 kcal mol⁻¹). Therefore, the generated pentaMCP⁺ ion is more stable than heptaMB⁺ ion in H-SSZ-13, and can be more readily observed by the NMR method. This trend is also in good agreement with our experimental results that heptaMB⁺ ions only can be observed at low temperature.

In conclusion, for the first time two very important carbenium ions involved in MTO reaction, heptaMB⁺ and pentaMCP⁺ ions, have been directly observed in CHA-type catalysts under the real reaction conditions. The detection of the carbenium ions depends on the acid catalytic environment and the reactivity of these ions during the catalytic transformation. PentaMCP⁺ is more readily to be observed than heptaMB⁺ in the CHA nanocage owing to the higher activation energy required for its further transformation. ¹³C MAS NMR measurements and isotopic switch experiment provide substantial proofs that both pentaMCP⁺ and heptaMB⁺ are important intermediates for the MTO reaction. The evaluation of two catalytic cycles following paring and side-chain methylation mechanisms demonstrated that both are energetically feasible reaction routes, while the side-chain methylation mechanism is more predominant owing to the lower energy barrier.

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