

Reaction mechanisms

Experimental Evidence on the Formation of Ethene through Carbocations in Methanol Conversion over H-ZSM-5 Zeolite

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Abstract: The methanol to olefins conversion over zeolite catalysts is a commercialized process to produce light olefins like ethene and propene but its mechanism is not well understood. We herein investigated the formation of ethene in the methanol to olefins reaction over the H-ZSM-5 zeolite. Three types of ethylcyclopentenyl carbocations, that is, the 1-methyl-3-ethylcyclopentenyl, the 1,4-dimethyl-3-ethylcyclopentenyl, and the 1,5-dimethyl-3-ethylcyclopentenyl cation

were unambiguously identified under working conditions by both solid-state and liquid-state NMR spectroscopy as well as GC-MS analysis. These carbocations were found to be well correlated to ethene and lower methylbenzenes (xylene and trimethylbenzene). An aromatics-based paring route provides rationale for the transformation of lower methylbenzenes to ethene through ethylcyclopentenyl cations as the key hydrocarbon-pool intermediates.

Introduction

The methanol to olefins (MTO) process on acidic zeolite catalysts has attracted increasing attention because of its potential for providing an alternative for the production of light olefins (e.g., ethene and propene) against the backdrop of decreasing oil reserves. Although the MTO process has currently found a number of commercial applications,^[1] the mechanism underlying the reaction, which is crucial for the rational development of efficient catalysts and catalytic processes, still remains unclear.

Since the H-ZSM-5 zeolite was first reported for the catalytic MTO reaction in the 1970s, continuous effort has been devoted to the reaction mechanism studies.^[2] Focusing on the initial formation of light olefins, different routes have been proposed in the past decades but are still intensively debated.^[3] The “hydrocarbon pool”, trapped in the void of zeolites, that undergoes methylation and olefin elimination has been widely accepted as the reaction center for the formation of light olefins on H-ZSM-5 as well as other types of zeolites (such as SAPO-34, Beta, Mordenite, etc.).^[2a-c,4] Methylated benzenes and cyclic carbocations are mostly considered as the hydrocarbon-pool species, on the basis of which two different routes were proposed for the hydrocarbon-pool mechanism.^[5] One is the side-

chain methylation route, which describes the formation of light olefins by elimination of the alkyl chain that is generated by the repeated methylation of aromatics.^[2b,c,5b,6] The other, the paring route, proposes a ring contraction and expansion of a benzenium ion, resulting in the formation of an alkyl chain and its subsequent splitting to light olefins.^[7]

In the most recently developed “dual-cycle” model,^[8] ethene was rationally linked to lower methylbenzenes (i.e., xylene and trimethylbenzene) in the aromatics-based cycle, whereas the olefins-based cycle was considered to be responsible for the formation of C₃₊ olefins. Considering the ethene formation in the aromatic-based route, the side-chain methylation was believed to be important^[2b] though later theoretical calculations demonstrated that this route was highly unfavorable due to a prohibitive energy barrier involved.^[9] On the other hand, isotopic scrambling experiments indicated that tetramethylbenzene was the precursor to ethene and a paring pathway was claimed.^[10]

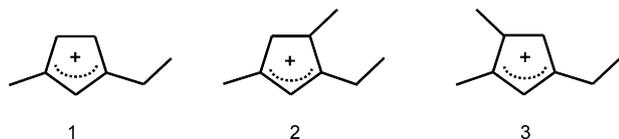
Carbocations are generally believed as critical intermediates in various acid-catalyzed reactions. In the MTO reaction, a variety of carbocation intermediates were observed on different zeolite and zeolite-type catalysts. Cyclopentenyl cations with different methyl group substitutions, for example, were identified on ZSM-5 zeolite,^[11] and the formation of benzenium ions has been reported on zeolites (ZSM-5 and Beta)^[12] and SAPO-type molecular sieves.^[13] These carbocations that were considered as the basis for the formation of C–C bonds were proposed to be involved in the key step to generate the light olefins. For example, it has been demonstrated that the 1,3,4-trimethylcyclopentenyl cation and the 1,3-dimethylcyclopentenyl cation were formed on the H-ZSM-5 zeolite as intermediates to produce propene^[11b] and isobutene,^[14] respectively, through a pentamethylbenzenium ion. With respect to the formation of ethene, the crucial role of cyclic carbocations has been theo-

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retically predicted.^[11a,15] The lack of experimental evidence on the ethene formation encouraged us to explore the carbocation chemistry of the MTO reaction over the H-ZSM-5 zeolite.

In this work, the experimental insight into the formation of ethene in the MTO reaction over the H-ZSM-5 zeolite was presented. We reported for the first time the observation and identification of three ethylcyclopentenyl cations (1, 2, and 3, see Scheme 1) under the MTO working conditions. Their reactivity was fully characterized and the mechanistic relationship between these carbocations and ethene as well as the lower methylbenzenes is established in the aromatic-based hydrocarbon-pool route.



Scheme 1. Three ethylcyclopentenyl cations observed in the MTO process by NMR spectroscopy.

Results and Discussion

Observation and identification of the ethylcyclopentenyl cations

The MTO reaction was performed under flow conditions over H-ZSM-5 zeolites at elevated temperatures. As shown in Figure 1, the effluent products contain a typical range of light olefins, like ethene, propene, and C₃₊ compounds. Due to the spatial constraint imposed by the zeolite channel, tetramethylbenzene (TetraMB) is the largest aromatic compound that can be found in the effluent even under higher reaction temperatures. These results are similar to previous reports.^[16] Because some species with large size trapped inside the zeolite channels are more likely related to the hydrocarbon pool,^[3b] the trapped species on the catalysts were also analyzed by GC-MS to provide more information on the hydrocarbon-pool species. The catalysts were dissolved in HF solution and the organic species were extracted with CH₂Cl₂ solution. As shown in Figure 2, polymethylbenzenes with the methyl groups in the range of approximately 2–6 dominates the GC-MS spectra of the extract. Although in low concentration, some cyclic C₅ species with different substitutes were observable along with the dominant aromatics. Among them, 1,3-dimethyl-1,3-cyclopentadiene (1,3-DiMCP), 1,2,3-trimethyl-1,3-cyclopentadiene (1,2,3-TriMCP), and 1,2,4-trimethyl-1,3-cyclopentadiene (1,2,4-TriMCP) were previously identified in the MTO reaction on H-ZSM-5.^[11b] Interestingly, three new types of ethylcyclopentadienes were also detectable. On the basis of GC-MS, we attentively assigned them to 1-methyl-3-ethyl-1,3-cyclopentadiene (1-M-3-ECP), 1,4-dimethyl-2-ethyl-1,3-cyclopentadiene (1,4-D-2-ECP), and 1,2-dimethyl-4-ethyl-1,3-cyclopentadiene (1,2-D-4-ECP). In order to confirm the assignments, these presumed compounds were deliberately synthesized separately and the corresponding GC-MS analysis (see Figures S1–S4 in the Supporting Information) on these synthesized compounds unambiguously supports our above-described assignments.

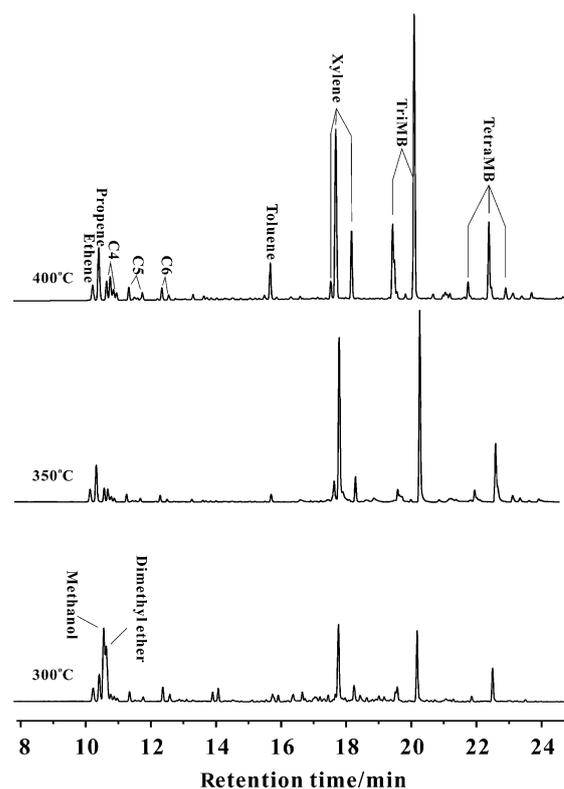


Figure 1. Gas chromatography analysis of the effluent products obtained from the reaction of methanol over H-ZSM-5 at various temperatures for 30 min.

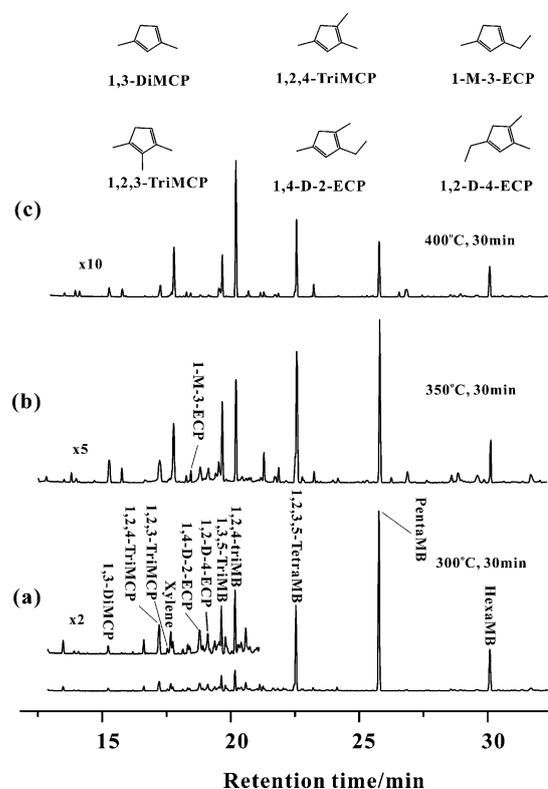


Figure 2. Gas chromatography analysis of the trapped products obtained from the reaction of methanol over H-ZSM-5 for 30 min at a) 300, b) 350, and c) 400 °C.

Although the cyclic C_5 and C_6 species are not unusual, this is the first time that the cyclic C_5 species with ethyl groups have been observed experimentally in the MTO reaction. The cyclopentadiene can be considered as a conjugated base of the corresponding cation confined in the zeolite channels. Indeed, the presence of the 1, 3-dimethylcyclopentenyl cation (1,3-DiMCP⁺), the 1,2,3-trimethylcyclopentenyl cation (1,2,3-TriMCP⁺), and the 1,3,4-trimethylcyclopentenyl cation (1,3,4-TriMCP⁺) on H-ZSM-5 has been confirmed by solid-state NMR spectroscopy.^[2d,11] As important intermediates in the MTO reaction, cyclopentenyl cations are believed to be key hydrocarbon-pool species.^[3b] To detect these carbocations on the zeolite catalyst, we performed the reaction with $^{13}C_3OH$ as reactant over H-ZSM-5 under flow conditions at 350 °C for 30 min, which was then quenched by liquid N_2 . The catalyst containing trapped species was analyzed by solid-state NMR spectroscopy. The presence of carbocations is evidenced by a series of low-field signals around $\delta = 250$ ppm (Figure 3a), which characterizes the formation of cyclic C_5 cations. In addition, the formation of the pentamethylbenzenium ion ($\delta = 207$ and 191 ppm) is also evident.^[12a]

The formation of cyclic C_5 cations was further verified by liquid-state NMR spectroscopy which could provide a much higher resolution for overlapped signals. The extract of the trapped species was used for analysis. Because the carbocations observed on the catalyst would convert into conjugated dienes during the extract process, a reverse transformation of these neutral species into carbocations can be readily performed by protonation of the dienes in a Brønsted acid system (such as concentrated sulfuric acid) prior to NMR measurement.^[17] Accordingly, the extracted product was mixed with 98% H_2SO_4 solution so that the cyclopentadienes were protonated to form stable carbocations, which could be readily observed by liquid-state NMR spectroscopy. As expected, a considerable high resolution is achieved on these species (Figure 3b). Inspired by this, we deliberately synthesized the six cyclopentadienes that were observed by GC-MS and applied the protonation approach to them for NMR analysis. As shown in Figure 4, the ^{13}C chemical shifts of the six individual cyclopentenyl cations, that is, 1, 3-DiMCP⁺, 1,2,3-TriMCP⁺, 1,3,4-TriMCP⁺, the 1-methyl-3-ethylcyclopentenyl cation, (1-M-3-ECP⁺, **1**), the 1,4-dimethyl-3-ethylcyclopentenyl cation (1,4-D-3-ECP⁺, **2**), and the 1,5-dimethyl-3-ethylcyclopentenyl cation (1,5-D-3-ECP⁺, **3**) were clearly identified in the liquid-state ^{13}C NMR spectra, and these signals give a good match to those of the extract products (see Table 1). On the basis of these experimental results, the ^{13}C magic angle spinning (MAS) solid-state NMR spectrum of the carbocations trapped in H-ZSM-5, was deconvoluted and the signals were accordingly assigned (Figure 3 top, also see Table 1). The experimental solid-state NMR results allow us to decisively confirm the presence of these cyclopentenyl cations in the MTO reaction. Although some alkyl-substituted carbocations were previously observed,^[3b,11a,13b,18] to the best of our knowledge, the ethylcyclopentenyl cations **1**, **2**, and **3** are identified for the first time as persistent cyclic C_5 carbocations, with a side chain longer than a methyl group, in the MTO chemistry over H-ZSM-5.

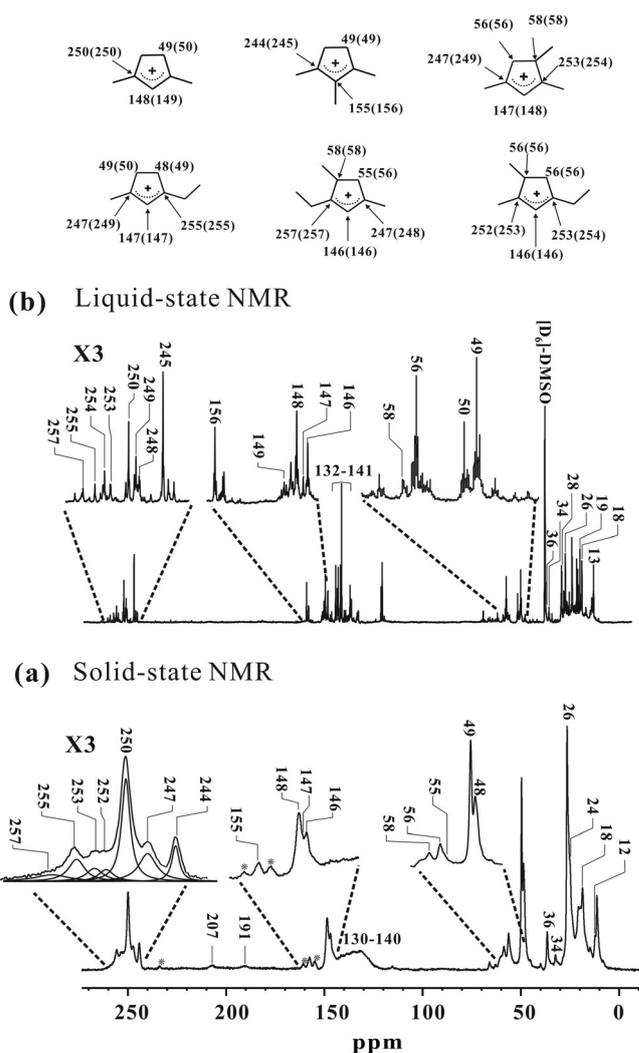


Figure 3. a) Solid-state ^{13}C MAS NMR and b) liquid-state ^{13}C NMR spectra (acquired at 18.8 T) of the trapped products obtained from the reaction of ^{13}C -labeled methanol over H-ZSM-5 at 350 °C for 30 min. The ^{13}C chemical shifts of both the solid-state and the liquid-state NMR spectra are indicated for the observed carbocations (those from the liquid-state NMR experiment are given in parentheses). Asterisks denote spinning sidebands.

Stability and reactivity of the ethylcyclopentenyl cations

The stability of the cations **1**, **2**, and **3** was further studied under the MTO working conditions. All the reactions were allowed to proceed for 30 min prior to solid-state MAS ^{13}C NMR analysis of the quenched catalysts (Figure 5). At 275 °C, the reaction occurred to a lesser extent, which is reflected by the large amount of unreacted reactants (methanol at $\delta = 50$ ppm and dimethyl ether at $\delta = 60$ ppm), but the pentamethylbenzenium ion (at $\delta = 207$ and 191 ppm) had been generated (Figure 5a). Because the cyclopentenyl cations have not been formed, the polymethylbenzenes ($\delta = 130$ –140 ppm) and the pentamethylbenzenium ions might serve as the precursor to them. At 300 °C, the concentration of both the polymethylbenzenes and the pentamethylbenzenium ions largely increased, and the formation of the cyclopentenyl cations was evidenced by the appearance of MAS ^{13}C NMR signals at $\delta = 240$ –

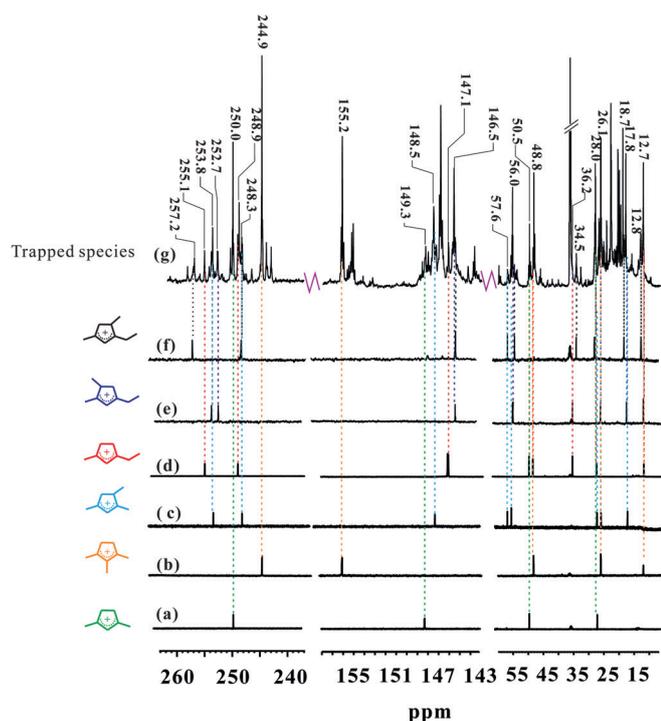


Figure 4. Liquid-state ^{13}C NMR spectra of a–f) the deliberately synthesized methyl or ethyl-substituted cyclopentadienes in natural abundance and g) the trapped species obtained from the reaction of ^{13}C -labeled methanol over H-ZSM-5 at 350°C for 30 min. The synthesized compounds are protonated by concentrated sulfuric acid to generate the corresponding cyclopentenyl cations. The ^{13}C NMR chemical shifts of the individual methyl- or ethyl-substituted cyclopentenyl cations are indicated. The solvent was $[\text{D}_6]\text{-DMSO}$.

260 ppm (Figure 5b). The simultaneously increased concentration of the olefins and the alkanes ($\delta = 10\text{--}60$ ppm) indicates that the pentamethylbenzenium ions and the cyclopentenyl cations may mediate the production of these hydrocarbons. It is interesting to note that the concentration of the pentamethylbenzenium ions, the methylbenzenes, and the ethylcyclopentenyl cations decreased to different extents at 350°C , whereas that of the 1,3-dimethylcyclopentenyl cation (1,3-diMCP $^+$, $\delta = 250$ and 148 ppm) considerably increased (Figure 5c). The transformations between these carbocations might link to the formation of light olefins, especially ethene. At 400°C , the carbocation species could hardly survive, in which cations 1, 2, and 3 were almost unobservable and only a small amount of 1,3-diMCP $^+$ remained (Figure 5d). The time evolution of the ethylcyclopentenyl carbocations was further correlated to the methanol conversion at 350°C . A similar variation trend of the carbocations to that of the methanol conversion (Figure S5 in the Supporting Information) indicates that these carbocations could play an intermediate role in the MTO reaction.

To gain more insight into the reactivity of these ethylcyclopentenyl cations under working condition, $^{12}\text{C}/^{13}\text{C}$ isotopic scrambling experiments were performed. The incorporation of ^{13}C atoms into the products was monitored after switching unlabeled methanol to ^{13}C -labeled methanol on stream. After the switching and the reaction being allowed to proceed for 0.5, 1,

Table 1. Experimental ^{13}C NMR chemical shifts of the carbocations observed by liquid-state and solid-state NMR spectroscopy. The numbers of the appropriate carbon atoms are given in parenthesis.

Carbocation	δ (liquid-state NMR) [ppm]	δ (solid-state NMR) [ppm]
 1,3-diMCP $^+$	250 (1, 3) 149 (2) 50 (4, 5) 28 (6, 7)	250 (1, 3) 148 (2) 49 (4, 5) 26 (6, 7)
 1,2,3-triMCP $^+$	245 (1, 3) 156 (2) 49 (4, 5) 26 (6, 8) 13 (7)	244 (1, 3) 155 (2) 49 (4, 5) 24 (6, 8) 12 (7)
 1,3,4-triMCP $^+$	249 (1) 148 (2) 254 (3) 58 (4) 56 (5) 26 (6) 28 (7) 18 (8)	247 (1) 147 (2) 253 (3) 58 (4) 56 (5) 24 (6) 26 (7) 18 (8)
 1-M-3-ECP $^+$	249 (1) 147 (2) 255 (3) 49 (4) 50 (5) 28 (6) 36 (7) 13 (8)	247 (1) 147 (2) 255 (3) 48 (4) 49 (5) 26 (6) 36 (7) 12 (8)
 1,4-diM-3-ECP $^+$	248 (1) 146 (2) 257 (3) 58 (4) 56 (5) 18 (6) 34 (7) 28 (8) 13 (9)	247 (1) 146 (2) 257 (3) 58 (4) 55 (5) 18 (6) 34 (7) 26 (8) 12 (9)
 1,5-diM-3-ECP $^+$	253 (1) 146 (2) 254 (3) 56 (4, 5) 18 (6) 26 (7) 36 (8) 13 (9)	252 (1) 146 (2) 253 (3) 56 (4, 5) 18 (6) 24 (7) 36 (8) 12 (9)

and 2 min, both the effluent products and the trapped species were analyzed on the ^{13}C content evolution (Figure 6). It can be seen that ethene exhibits a lower ^{13}C incorporation rate than the C_3^+ olefins but a similar trend to xylene and trimethylbenzene. In agreement with the previous work of Svelle et al.,^[8a,b] the lower methylbenzenes (xylene and trimethylbenzene) could serve as precursor to ethene, and thus they pos-

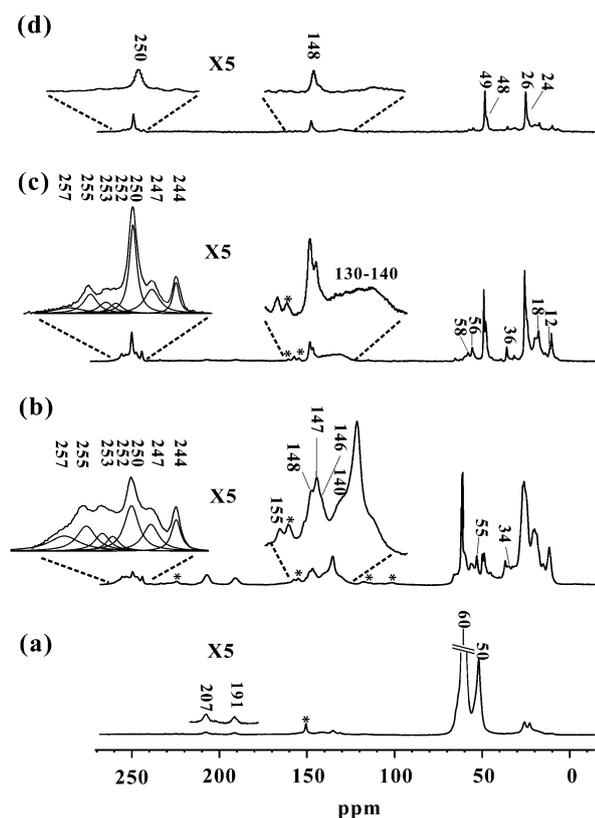


Figure 5. Solid-state ^{13}C MAS NMR spectra of the products obtained from the reaction of ^{13}C -labeled methanol over H-ZSM-5 at a) 275, b) 300, c) 350, and d) 400 °C for 30 min. Asterisks denote spinning sidebands.

sess similar reactivity. Interestingly, 1-M-3-ECP, 1,2-D-4-ECP, and 1,4-D-2-ECP as the conjugated bases of cations **1**, **2**, and **3**, respectively, that were trapped in H-ZSM-5 can also be well correlated with the certain olefins and aromatic products. They show a similar increasing trend of the ^{13}C content to ethene (and thus to xylene and trimethylbenzene). This result unambiguously demonstrates the comparable reactivity of the lower methylbenzenes, the ethylcyclopentenyl cations, and ethene, suggesting the presence of a catalytic route connecting these species in the MTO reaction.

On the basis of their similar reactivity, we sought to identify the relationship between the three ethylcyclopentenyl cations and ethene. The reversible transformation of the cations and the corresponding conjugated dienes allowed us to gain further insight into the reactivity of the cations. The conjugated dienes of the three cations were separately reacted over H-ZSM-5, which was carried out on a pulse-quench reactor. Analysis of the effluent products shows that light olefins like ethene and propene were readily formed from all these dienes at 350 °C within 8 s of reaction time (Figure 7a and Table 2). Compared with methanol as the reactant (see Table 2), the ethylcyclopentadienes exhibit higher selectivity to ethene and a lower propene-to-ethene ratio (P/E). This means that the formation of ethene is more favored by the ethylcyclopentadienes. According to the above-described NMR results, the cations **1**, **2**, and **3** should be readily formed from these dienes

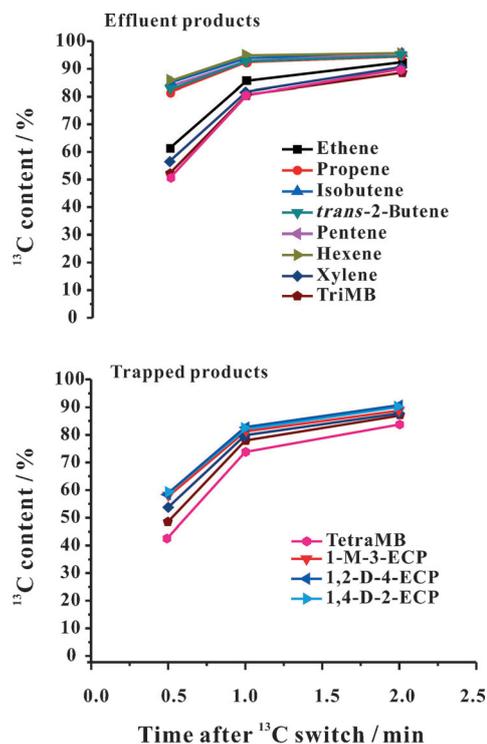


Figure 6. Time evolution of the ^{13}C content in the effluent and the trapped species obtained from the reaction of methanol for 30 min, followed by switching to ^{13}C -labeled methanol over H-ZSM-5 at 350 °C.

Table 2. Product selectivity (C [%]) in the effluent obtained from the conversion of ethylcyclopentadienes and methanol over H-ZSM-5.

Reactant	P/E	Ethene	Propene	Benzene	Toluene	Xylene	Others
1-M-3-ECP	2.1	7.1	15.0	8.9	32.0	18.3	18.7
1,2-D-4-ECP	2.0	13.3	26.7	4.0	30.7	–	25.3
1,4-D-2-ECP	2.5	12.2	30.5	1.8	28.0	–	27.4
methanol	3.6	4.2	15.1	4.2	14.0	17.6	44.8

under the reaction condition. We assume that the ethyl groups can readily split off the cations **2** and **3**, bringing about ethene and dimethylcyclopentenyl cations as the intermediate products. This is supported by the formation of 1,3-DiMCP as the conjugated base of the dimethylcyclopentenyl cation in the trapped products (Figure 7b). In agreement with the work by Haw et al.,^[11a] the dimethylcyclopentenyl cation can readily transform into toluene, which dominates the polymethylbenzenes in the effluent when 1,2-D-4-ECP and 1,4-D-2-ECP are used as reactants (Figure 7a). Thus, our experiments evidence the formation of ethene from the specific cyclic C_5 cations on H-ZSM-5. Analogously, when 1-M-3-ECP is used, splitting off ethene from cation **1** would lead to the formation of the 1-methylcyclopentenyl cation. The corresponding conjugated base 1-methylcyclopentadiene is invisible in the extract but found in the effluent (Figure 7a), confirming the formation of the 1-methylcyclopentenyl cation. Importantly, in this case, formation of a much higher amount of benzene validates the transformation of the cyclic C_5 cations into benzene. In addi-

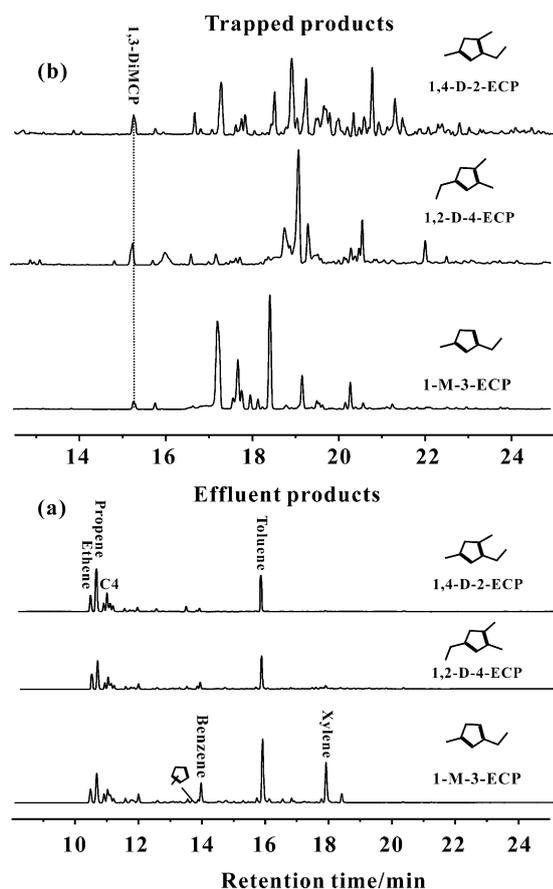


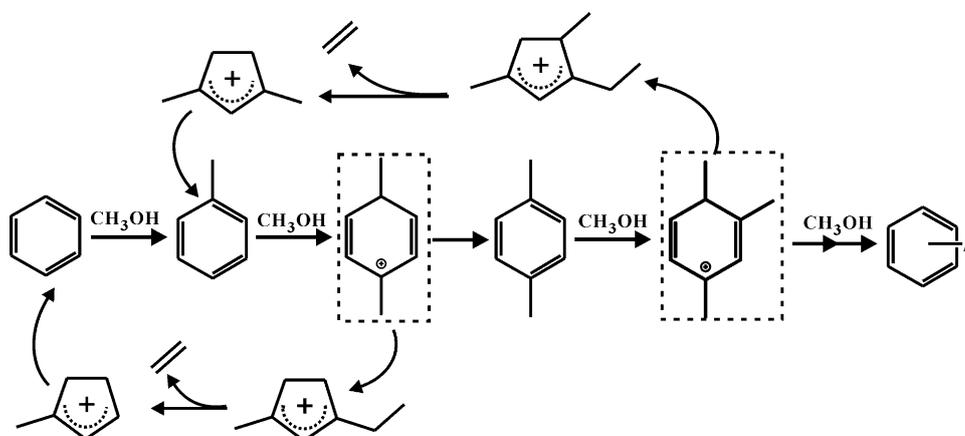
Figure 7. Gas chromatography analysis of a) the effluent products and b) the trapped products obtained from the reaction of ethylcyclopentadienes over H-ZSM-5 at 350 °C for 8 s.

tion to benzene, toluene and xylene are produced from 1-M-3-ECP as well. We deduce that 1-M-3-ECP loses one methyl group through a methyl shift, forming dimethylcyclopentadiene that can produce toluene through ring expansion. This is evidenced by the appearance of a small amount of 1,3-dimethylcyclopentadiene (1,3-DIMCP) in the trapped products (Figure 7b). Similarly, the direct transformation of 1-M-3-ECP through ring expansion could generate xylene. It is noteworthy that propene and other C_{3+} olefins are formed along with ethene for all these ethylcyclopentadienes. Polymerization/cracking of ethene could be responsible for the formation of these olefins.^[19] On the other hand, we cannot rule out the formation of long-chain alkyl groups due to the methyl shift on the ethylcyclopentadienes, which could subsequently split off propene and other C_{3+} olefins.^[11a]

Formation mechanism of ethene

As revealed by our ^{13}C -labeling experiments, the facile transformation of the ethylcyclopentyl cations into ethene accounts for their comparable reactivity. A considerable amount of work on the co-reaction of methanol and aromatic compounds on H-ZSM-5 indicated that part of the ethene products contained carbon atoms originated from the aromatic compounds.^[2c, 10, 20] The rearrangement of methylated aromatics by expansion ($6 \rightarrow 7$) or contraction ($6 \rightarrow 5$) of the benzene ring could result in the observed ^{13}C atom scrambling.^[10, 15] Our above-described experimental results allow us to propose that the formation of ethene can be linked to xylene and trimethylbenzene by the specific ethylcyclopentyl cation intermediates (Scheme 2). In the MTO reaction, the methylation and protonation of aromatics by methanol is prevalent along with the formation of light olefins.^[21] The benzene ring contraction ($6 \rightarrow 5$) occurs on the protonated methylbenzenes, forming ethylcyclopentyl cations, and the ethyl groups subsequently split off and generate ethene (cations **2** and **3** undergo a similar process). Along with the formation of ethene, the ring expansion of the methylcyclopentyl cations produces benzene or methylbenzene,^[14] from which the subsequent methylation induces a new catalytic cycle. The catalytic cycle constitutes a typical pairing route in which ethene and methylbenzenes are mechanistically linked through the ethylcyclopentyl cations. With respect to the transformation of the cyclopentyl cation intermediates, their high reactivity is also characterized by the facile skeleton rearrangements, which happen at elevated temperatures and lead to the formation of polymethylbenzenes (see Figure 5).

The delicate “dual-cycle” model proposed by Svelle et al. described the formation of propene and ethene through different but not completely separate routes on H-ZSM-5, in which ethene is closely related to lower methylbenzene.^[8a] We herein revealed the mechanistic link between xylene and trimethylbenzene and ethene through the ethylcyclopentyl cations. This could have implications on the mechanistic understanding of MTO reactions occurring over other catalysts such as zeolite ZSM-22^[22] and the zeo-type material SAPO-5^[23] where the prevalence of the “dual-cycle” model has been proved. Actually, the



Scheme 2. Proposed catalytic cycle for the formation of ethene from lower methylbenzenes over H-ZSM-5.

relationship between ethene and lower methylbenzene has been proposed on Beta zeolite^[8c] and the typical MTO catalyst SAPO-34^[24] as well, although the exact undertaking mechanism is not well known. There is no doubt that the carbocations play a crucial role in the MTO reaction over acidic zeolite catalysts. The observation and characterization of persistent carbocations has considerably deepened our understanding of the MTO chemistry. Recently, cyclic carbocations such as the 1,3,4-trimethylcyclopentenyl cation and the pentamethylbenzenium ion were simultaneously observed and identified in the MTO reaction as the key intermediates to produce propene on H-ZSM-5.^[11b] The formation and stabilization of special carbocations in the channels or cages of zeolites strictly depends on the spatial and chemical environment where the carbocations reside. Bulky carbocations such as both the heptamethylbenzenium cation and the pentamethylcyclopentenyl cation can be produced from repeat methylation of aromatics in zeolite SSZ-13, which has the same topology structure as SAPO-34 (having a three-dimensional cage of ca. $6.7 \times 12 \text{ \AA}^2$).^[13b] Theoretical calculations suggested a feasible side-chain route for the formation of propene and ethene through the heptamethylbenzenium ion.^[25] In comparison, the geometric constraints imposed by medium pore (sinusoidal channel: $5.5 \times 5.1 \text{ \AA}^2$, straight channel: $5.3 \times 5.6 \text{ \AA}^2$) of H-ZSM-5 only allows pentamethylbenzenium ions to be present as the persistent species. Moreover, as indicated by theoretical calculations,^[11b,14] the pentamethylbenzenium ions favor the formation of propene and isobutene on H-ZSM-5. Although bulky methylbenzenes (e.g., pentamethylbenzene) that cannot diffuse from the channel of H-ZSM-5 are formed in the MTO reaction, the higher reaction barriers involved make it difficult to form olefins like ethene through a side-chain route on the basis of methylbenzenes.^[9] On the contrary, the contraction of the C_6 ring of aromatics into smaller cyclic C_5 ethylcyclopentenyl cations provides an alternative to the aromatics-based hydrocarbon-pool route for the formation of ethene. Our experimental results unambiguously demonstrated that the aromatics-based paring route is viable for the formation of ethene through the ethylcyclopentenyl cation intermediates in the MTO reaction over zeolite H-ZSM-5.

Conclusion

In summary, by using NMR spectroscopy and GC-MS, we investigated the methanol to olefins conversion over the H-ZSM-5 zeolite. Strong evidence was found for ethyl-substituted cyclopentadienyl species being intermediates in the ethene formation on H-ZSM-5 during the MTO reaction. The stable ethylcyclopentenyl cations **1**, **2**, and **3** as key intermediates were for the first time experimentally observed and identified in the MTO reaction. The distinct reactivity of the ethylcyclopentenyl cations was linked to lower methylbenzenes (xylene and trimethylbenzene) and ethene. All these compounds can be integrated in a full catalytic cycle working through a paring mechanism in which the ethylcyclopentenyl cation acts as the critical hydrocarbon-pool species splitting off an ethyl group as ethene product. The results presented here shed new insight into the hydrocarbon-pool chemistry and provide a viable

route for the formation of ethene in the MTO reaction over zeolite H-ZSM-5.

Experimental Section

Material and catalytic reactions: Methanol (WHSV = 2 h^{-1}) was reacted over H-ZSM-5 (0.3 g, Si/Al = 15) in a fixed bed reactor at a temperature range of approximately 275–400 °C. In each case, the catalysts were compressed to wafers that were crushed and sieved to obtain 60–80 mesh particles, and then the particles were activated in place prior to the reaction by heating at 400 °C in flowing helium for 1 h. The methyl- or ethyl-substituted cyclopentadienes were synthesized according to previously reported procedures.^[26] For the reaction of the ethylcyclopentadienes, a pulse-quench reactor was used to quench the reaction by reducing the reaction temperature with liquid nitrogen within a very short period (< 1 s).^[2d] Typically, when the reaction proceeded in a pulse-quench reactor for a pre-set period, the reaction was thermally quenched by pulsing liquid nitrogen onto the catalyst bed, which was achieved by using high-speed valves controlled by a GC computer. In each case, an aliquot of the reactant (10 μL) was pulsed into the reactor (heated at 350 °C) containing H-ZSM-5 (0.3 g) and allowed to react for 8 s, before quenching by liquid nitrogen. The effluent and the trapped products were determined by GC-MS analysis.

In the $^{12}\text{C}/^{13}\text{C}$ methanol isotope transient experiments, ^{13}C natural abundance methanol was fed at 350 °C for 30 min before switching to ^{13}C -labeled methanol (99% ^{13}C) and was allowed to react for a variable period up to 2.5 min. The evolution of the ^{13}C components in the effluent was determined by GC-MS analysis after the ^{13}C methanol switch at 0.5, 1, and 2 min. The corresponding isotopic data for the trapped species in the zeolite channels during the reaction were obtained.

GC and GC-MS analysis: The effluent products were analyzed quantitatively by online GC (Shimadzu GC-2010 plus) equipped with a flame-ionization detector and a fused silica capillary column Supel-Q PLOT (30 m, 0.32 mm i.d., 15 μm film thickness). The temperature programming started at 35 °C (maintained for 1 min), followed by a rate of 5°C min^{-1} to a final temperature of 200 °C (maintained for 30 min).

The catalyst with the trapped products was dissolved in 20 wt% HF solution and then the solution was extracted with CH_2Cl_2 . The bottom layer containing the organic phase of the extracted solution was separated and analyzed by gas chromatograph.

The isotopic compositions of the retained compositions were analyzed by GC-MS (Shimadzu GCMS-2010 plus) equipped with a fused silica capillary column Petrocol DH 100 (100 m, 0.25 mm i.d., 0.5 μm film thickness). The following temperature programming was applied: maintained at an initial temperature of 50 °C for 1 min, followed by a rate of $10^\circ\text{C min}^{-1}$ to a final temperature of 250 °C (maintained for 20 min).

Solid-state and liquid-state NMR analysis: The MTO reaction was carried out by reacting ^{13}C -labeled methanol over H-ZSM-5 (0.3 g) for 30 min at 350 °C. After the reaction was quenched by liquid nitrogen, the reactor containing the catalyst sample was sealed. The sealed reactor was transferred to a glovebox filled with pure N_2 and the catalyst sample containing the trapped species was packed into to an NMR rotor for NMR measurements. All solid-state NMR experiments were acquired on a Bruker-Avance III-800 spectrometer at 18.8 T, equipped with a 3.2 mm probe, with resonance frequencies of 800.20 and 201.23 MHz for ^1H and ^{13}C , respectively. Single-pulse ^{13}C MAS experiments with ^1H decoupling were

performed by using a $\pi/2$ pulse width of 3.8 μs and a repetition time of 5 s. The magic angle spinning rate was set to 18 kHz. The ^{13}C chemical shifts were referenced to hexamethylbenzene (a second reference to TMS).

For liquid-state NMR analysis, the quenched catalyst was dissolved in 20 wt% HF solution (5 mL) and then the solution was extracted with CH_2Cl_2 (1 mL). The extract was transferred into a flask (10 mL) and concentrated sulfuric acid (1 mL) was added. The obtained mixture was gently shaken for 1 min, and then the deep reddish-brown concentrated sulfuric acid was separated from the CH_2Cl_2 phase, which was subsequently removed by vacuum. The remained deep reddish-brown solution was transferred into a 5 mm liquid-state NMR tube for measurements. The liquid-state NMR spectra were acquired on a Bruker-Avance III-800 spectrometer at 18.8 T, with resonance frequencies of 800.20 and 201.23 MHz for ^1H and ^{13}C , respectively. Single-pulse ^{13}C experiments with ^1H decoupling were performed by using a $\pi/6$ pulse width of 3.5 μs and a repetition time of 2 s. The ^{13}C chemical shifts were referenced to TMS. Two drops of $[\text{D}_6]\text{DMSO}$ were added and used as a field lock signal.

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Keywords: carbocations • olefins • reaction mechanisms • solid-state NMR spectroscopy • zeolites

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