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# Methylbenzene hydrocarbon pool in methanol-to-olefins conversion over zeolite H-ZSM-5



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# ABSTRACT

The formation and reactivity of a methylbenzenes (MBs) hydrocarbon pool in the induction period of the methanol-to-olefins (MTO) reaction over zeolite H-ZSM-5 was investigated and the mechanistic link of MBs to ethene and propene was revealed. Time evolution analysis of the formed MBs and  ${}^{12}C/{}^{13}C$ methanol-switching experiments indicate that in the induction period bulkier compounds such as tetraMB and pentaMB have higher reactivity than their lighter counterparts such as p/m-diMB and triMB. By correlating the distribution of MBs trapped on H-ZSM-5 with ethene and propene, we found that tetraMB and pentaMB favor the formation of propene, while p/m-diMB and triMB mainly contribute to the formation of ethene. On the basis of this relationship, the olefin (ethene and propene) selectivity can be controlled by regulating the distribution of trapped MBs by varying the silicon-to-aluminum ratio of ZSM-5, reaction temperature, and space velocity. The reactivity of MBs and the correlation of MBs with olefins were also verified under steady-state conditions. By observation of key cyclopentenyl and pentamethylbenzenium cation intermediates using in situ solid-state NMR spectroscopy, a paring mechanism was proposed to link MBs with ethene and propene. P/M-diMB and triMB produce ethylcyclopentenyl cations followed by splitting off of ethene, while tetraMB and pentaMB generate propyl-attached intermediates, which eventually produce propene. This work provides new insight into the MBs hydrocarbon pool in MTO chemistry.

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# 1. Introduction

Olefins such as ethylene and propene that are mainly produced from cracking of crude oil are building blocks for producing polyethylene and polypropylene. The methanol-to-olefins (MTO) process based on acidic zeolite catalysts is becoming a promising alternative to the oil route. The prominent advantage of MTO is that the feed methanol can be obtained from a wide range of sources, such as coal, natural gas, and biomass [1–4]. Mechanistic understanding of the MTO reaction is essential in achieving selectivity control of specific olefins, which, however, is a big challenge. Although intensive experimental and theoretical effort has been dedicated to this issue, the exact mechanism underlying methanol conversion has remained poorly understood over the past decades [4–9].

Direct formation of C–C bonds by C1 entities was initially considered, but is still debated, because a prohibitively high-energy

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reaction barrier is involved from the theoretical point of view [10–12]. An indirect mechanism, known as the hydrocarbon pool (HP), has been widely accepted for olefin formation [3,4,8–10]. The HP mechanism that was introduced by Dahl and Kolboe describes a catalytic reaction center (HP species) formed in zeolite, on which repeated C-C bond forming and breaking occurs to produce olefin products [13-15]. Polymethylbenzens (MBs) and cyclic carbenium ions were identified as active HP species on zeolites (ZSM-5, MOR, and Beta) and zeotype materials (SAPO-34 and SAPO-5) [2,3,16-23]. On the basis of HP species, two different routes have been proposed to explain the operation of the HP mechanism, namely, the side-chain methylation route [16,17,24–26] and the paring route [27,28]. A dual-cycle mechanism was recently claimed on H-ZSM-5 with ethene being related to light MBs and  $C_3^+$  olefins to propene [29], and thus both MBs and olefins could serve as HP species.

The co-reaction of methanol and/or dimethyl ether (DME) with aromatics on H-ZSM-5, H-MOR, and H-Beta has shown that ethene and propene can be related to MBs [23,30,31]. This is evidenced by isotopic scrambling experiments, which reveal that some carbons

of ethene and propene originate from co-fed aromatics. Ilias and Bhan further showed that MBs such as tetraMB could be precursors to ethene and propene under steady-state conditions [31]. Another important catalyst, SAPO-34, with small pore size and large cage structure, does not permit the entrance of aromatic reactants, which can be only formed in place in the MTO reaction. On the basis of <sup>13</sup>C isotopic analysis, Arstad and Kolboe demonstrated that pentaMB and hexaMB in SAPO-34 were active species responsible for the formation of ethene and propene [32].

Theoretical calculations and in situ NMR experiments provide more insight into the exact route to light olefins from MBs. The DFT calculations of McCann et al. showed that an aromaticsbased paring cycle operates on H-ZSM-5, where methylation of aromatics produces  $C_{5}\xspace$  and  $C_{6}\xspace$  cyclic carbocation intermediates and isobutene is generated by the ring contraction of the C<sub>6</sub> carbocation [33]. Using a combined in situ solid-state NMR, GC-MS, and DFT calculation approaches, we recently correlated olefins with the HP species on ZSM-5 [34] and revealed an aromatic-base paring route for the formation of propene, in which MBs are mechanistically linked to propene via pentamethylbenzenium and 1,3,4-trimethylcyclopentenyl cations. The formation of ethene on H-ZSM-5 from aromatics was theoretically studied by Lesthaeghe et al. [35]. A side-chain route was proposed, but the higher barrier of 200 kJ/mol for the ethene elimination step makes this route unfavorable. Most recently, we identified ethylcyclopentenyl carbocations as intermediates in the aromatics-based cycle on ZSM-5 and demonstrated that the elimination of ethyl groups from the ethylcyclopentenyl cations provides a viable route for ethene formation [36].

Among the produced hydrocarbons, a wide range of aromatics from benzene to hexamethylbenzenes are readily formed on H-ZSM-5 in the typical MTO reaction. Although previous results demonstrated the correlation between light olefins and MBs [16, 17,29–31,37–39], the mechanistic link of specific MBs to product selectivity is not established. It is also noted that the MTO reaction is well studied under steady-state conditions when olefins are steadily produced and complex secondary reactions consisting of methylation, alkylation, oligomerization, cracking, etc. are prevailing [5–7,40,41]. The secondary reactions bring about considerable difficulty in distinguishing the exact role of MBs from other compounds in the formation of light olefins. We previously found the formation of MBs and cyclic carbocations on H-ZSM-5 [34]. Importantly, at lower temperatures, these HP species were observed prior to the formation of olefins and the boom of secondary reactions. Since the induction period is of vital importance in MTO reactions that are associated with the formation of the first C-C bonds in olefin products, investigation of MBs in the induction period in addition to the steady-state period would allow us to gain more insight into the MTO chemistry.

In this work, the reactivity of MBs produced in the induction period of MTO reactions over H-ZSM-5 was studied in detail. We found that the initially formed MBs were intrinsically correlated with light olefins. The specific link of lighter MBs (p/m-diMB and triMB) with ethene and bulkier MBs (tetraMB and pentaMB) with propene were identified. Moreover, the mechanism underlying the relation between MBs and ethene and propene was discussed.

# 2. Experimental

### 2.1. Materials and catalysis experiments

Before the MTO reactions, the H-ZSM-5 (Si/Al = 15, 100, and 200) zeolites were calcined at 550  $^{\circ}$ C under flow air for 5 h to remove organic impurities that would affect the MTO reaction. GC analysis shows that no organic species are present after the

heating treatment in all samples (Fig. S1 in the Supplementary Material). The Brønsted acid sites concentrations are 860, 130, and 65 µmol/g on H-ZSM-5 (15), H-ZSM-5 (100), and H-ZSM-5 (200), respectively, as determined by <sup>1</sup>H solid state NMR. The H-ZSM-5 zeolites were pressed into pellets between 60 and 80 mesh and the pellets (0.2 g) were activated at 400 °C in flowing helium for 1 h prior to the reactions. The pulse-quench reactions were carried out in a pulse-quench reactor [42] for a preset period using a carrier gas (He) flow of 500 mL/min; then they were thermally quenched by pulsing liquid nitrogen onto the catalyst bed, using high-speed valves controlled by a GC computer (<1 s). Typically, 490 µmol (20 µL) methanol was pulsed into the reactor for each pulse reaction. For the continuous-flow reaction, methanol with a weight hourly space velocity (WHSV) of 2 h<sup>-1</sup> was reacted over the H-ZSM-5 (0.2 g) pellets in a fixed-bed reactor.

In  ${}^{12}C/{}^{13}C$  methanol isotope transient experiments, methanol in  ${}^{13}C$  natural abundance was reacted on H-ZSM-5 for a predetermined period, followed by switching to  ${}^{13}C$ -methanol (99%  ${}^{13}C$ ), and was allowed to react for a certain time. The evolution of the  ${}^{13}C$  components in the products was determined by GC–MS analysis.

# 2.2. Analysis of trapped species

The catalyst with trapped products was dissolved in 20 wt.% HF solution and then extracted with  $CH_2Cl_2$ . The bottom layer containing the organic phase of the extracted solution was separated and analyzed by gas chromatography (GC). In addition, the catalyst with trapped products was also directly analyzed by solid-state NMR spectroscopy (see the following).

### 2.3. Gas chromatography

The effluent was analyzed quantitatively by online GC (Shimadzu GC-2010 plus) equipped with a flame ionization detector and a Petrocol DH 100 fused silica capillary column (100 m, 0.25 mm i.d., 0.5  $\mu$ m film thickness). The temperature programming started at 50 °C (maintained for 15 min), followed by a rate of 15 °C min<sup>-1</sup> to a final temperature of 200 °C. The isotopic compositions of the trapped species were analyzed by GC–MS (Shimadzu GCMS-QP2010) with the same capillary column as used for GC analysis. The following temperature programming was applied: maintained at an initial temperature of 50 °C for 1 min, followed by a rate of 10 °C min<sup>-1</sup> to a final temperature of 200 °C, maintained for 10 min.

### 2.4. NMR experiments

After the reaction was quenched, the pulse-quench reactor containing the catalyst was sealed. The sealed reactor was then transferred to a glove box filled with pure  $N_2$  and the catalyst was packed into an NMR rotor for NMR measurements.

All solid-state NMR spectroscopy experiments were carried out at 11.7 T on a Bruker-Avance III-500 spectrometer, equipped with a 4 mm probe, with resonance frequencies of 500.57 and 125.87 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively. Single-pulse <sup>13</sup>C MAS experiments with <sup>1</sup>H decoupling were performed using a  $\pi/2$  <sup>13</sup>C pulse width of 3.9 µs and a repetition time of 5 s. The magic angle spinning rate was set to 10.6–12.5 kHz. For the <sup>1</sup>H  $\rightarrow$  <sup>13</sup>C CP/MAS NMR experiments, the Hartmann–Hahn condition was achieved using hexamethylbenzene (HMB), with a contact time of 4 ms and a repetition time of 2 s. The <sup>13</sup>C chemical shifts were referenced to HMB (a second reference to TMS).

# 3. Results and discussion

# 3.1. Formation of methylbenzenes on H-ZSM-5

To monitor the formation of MBs and primary olefins in the initial stage, the MTO reactions were carried out on H-ZSM-5 (15) at a relatively lower temperature (350 °C) and quenched by liquid nitrogen within a short period (<1 s). Moreover, a high feed rate (500 mL/min) of methanol was utilized to suppress the secondary reactions. Fig. 1 shows the GC chromatogram of the effluent products obtained from methanol reacting for 2-64 s at 350 °C. When the reaction time is very short (<4 s), the conversion is only ca. 5% and a considerable fraction of MBs (ca. 96%), mainly toluene and p/m-diMB, is produced, whereas the light olefins such as ethene and propene are negligible (Table 1). After 8 s, the formation of olefins including  $C_3^+$  olefins is prevailing while the content of MBs is decreasing, indicating that the consumption of MBs generates olefins. This provides evidence that the MBs serve as precursors to the light olefins [31,34]. The secondary reaction is prevailing at longer reaction times, reflected by the increase in MBs after 16 s. This is due to the preferential transformation of the formed  $C_3^+$  olefins and  $C_5-C_{10}$  hydrocarbons on the acid sites of H-ZSM-5. The lower temperature and short reaction time allows the observation of MBs evolution in relation to olefins. In comparison, the reaction at a higher temperature of 400 °C produces a considerable amount of light olefins at a conversion of 74% even within 2 s of reaction time (Fig. S2 and Table S1). The sum of ethene and propene is over 50%, but the MBs are very low (ca. 1%). At a similar conversion (ca. 76%), the selectivity to MBs (2.23%) at 350 °C is almost twice that (1.26%) at 400 °C. This is likely due to the enhanced reactivity of MBs at the higher temperature. In addition, the enhanced formation of light olefins could also be associated with the secondary reactions at higher temperature. The cracking of the formed longer alkenes such as C<sub>3</sub><sup>+</sup> compounds (Tables 1 and S1) into ethene and propene with high activation energy could be prevalent at higher temperatures. It should be noted that the remarkably reduced induction period at



**Fig. 1.** GC analysis of effluent products obtained from methanol pulse reaction over H-ZSM-5(15) at 350 °C for various times.

#### Table 1

Product	selectivity	(C%)	and	methan	nol	conversion	(%)	obtained	from	one	pulse
reaction	of methano	ol on	H-ZS	M-5 at	350	°C. The se	electiv	vity of MI	Bs is in	ndica	ted in
parenthe	eses.										

RT (s) <sup>a</sup>	Con.	P/E <sup>b</sup>	$C_2$	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6+</sub>
2	0	-	-	-	-	-	- (-)
4	4.72	0.72	2.44	1.77	-	-	95.79 (95.79)
8	37.55	11.01	2.80	30.84	8.04	14.74	43.57 (39.54)
16	76.32	12.95	3.49	45.18	18.93	13.43	18.97 (2.23)
32	89.54	6.52	5.42	35.33	15.30	11.81	32.15 (11.56)
64	97.31	5.43	5.55	30.15	4.40	2.61	57.29 (48.56)

<sup>a</sup> Reaction time after one methanol pulse.

<sup>b</sup> Propene-to-ethene ratio.

higher temperature leads to a rapid conversion of formed olefins and hydrocarbons back into MBs along with the reaction time being increased (MBs amount to ca. 67% at 64 s).

The reactive MBs in the very early period would have a great impact on olefin formation. As is well known in various zeolite and zeotype catalysts, the interaction of MBs with the zeolite framework would generate a catalytic center of HP in the MTO reaction [20,43–46]. Thus, the analysis of organic species trapped inside H-ZSM-5 will give more insight into the role of MBs in the formation of olefins.

# 3.2. Stability and reactivity of trapped methylbenzenes

The trapped organic compounds on H-ZSM-5(15) were obtained by thermally quenching the methanol pulse reactions rapidly at a preset reaction time. Since the MBs show higher reactivity at higher temperature, the analysis was performed on the trapped species obtained at 400 °C. Fig. 2a shows the GC-MS data of the extract of trapped species formed on H-ZSM-5(15). MBs ranging from p/m-diMB to pentaMB are found in the very early stage (2 s). Differently from what is observed in the effluent, bulkier species with more methyl substituents dominate the trapped products. particularly before 16 s. It is noteworthy that hexaMB is not present in our trapped products, whereas it was abundant under the steady-state conditions [29]. The previous work of Svelle and co-workers indicated that hexaMB formed on ZSM-5 was virtually unreactive in the MTO reaction [29]. Additionally, hydrocarbons larger than hexaMB, which were considered as coke species, are not formed on our catalysts. Therefore, our experimental results indicate that the formation of MBs is dynamically favored in the induction period and the large and unreactive molecules would be accumulated over a long reaction time.

The evolution of trapped MBs was further analyzed from 2 to 32 s of reaction time. As shown in Fig. 2b, the normalized pentaMB reaches a maximum at 4 s, followed by a rapid decrease. In comparison, 1,2,3,5-tetraMB exhibits a relatively slow increase and decline rate. The light MBs, such as p/m-diMB and 1,2,4-triMB, share a similar trend, increasing and decreasing at a much lower rate. This allows us to give a stability order for the observed MBs: pentaMB < 1,2,3,5-tetraMB < 1,2,4-triMB  $\approx$  p/m-diMB. The stability of MBs can reflect to some extent the reactivity, which is related to their formation, transformation, and diffusion in zeo-lite channels. For a qualitative analysis of the reactivity, the formation, transformation, and diffusion rates of MB with *i* methyl groups are defined by  $v_{for}^i$ ,  $v_{tra}^i$  and  $v_{diff}^i$ , respectively. Thus the change in concentration of trapped MBs with time can be described by the formula

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = v_{for}^i - v_{tra}^i - v_{diff}^i \tag{1}$$

where  $n_i$  denotes the amount of MB with *i* methyl groups. The MBs having higher reactivity can be more easily transformed into other



Fig. 2. GC-MS analysis of trapped products obtained from one pulse reaction of methanol over H-ZSM-5(15) at 400  $^\circ C$  (a) and the evolution of the normalized trapped MBs (b).

compounds, giving a higher  $v_{tra}^i$ . In a certain zeolite with a welldefined channel system and pore size, the diffusion rate is largely affected by the molecular size of the respective MB. The MB with a larger molecular size would have a lower diffusion rate due to the confinement effect imposed by the zeolite framework. PentaMB. 1.2.3.5-tetraMB, and 1.3.5-triMB were not found in the effluent products (Fig. S2), indicating that these MBs are too big to diffuse out of the zeolite channels. Therefore, their diffusion rates are defined to be zero. As for the lighter MBs such as diMBs, 1,2,4triMBs, and 1,2,4,5-tetraMBs detected in the effluent, they should have higher diffusion rates than the above-mentioned bulkier MBs. By comparing the molecular sizes, we deduce that their diffusion rate follows the order diMBs > 1,2,4-triMB > 1,2,4,5-tetraMB. Taken together, the diffusion rates of MBs in the zeolite channels would follow the order p/m-diMB > 1,2,4-triMB > 1,2,4,5tetraMB > 1,3,5-triMB = 1,2,3,5-tetraMB = pentaMB = hexaMB.

The rate of change in certain MB concentration decreases when the sum of transformation and diffusion rates  $(v_{tra}^i + v_{diff}^i)$  is greater than the formation rate  $(v_{for}^i)$ , and vice versa. In the reaction, the methanol reactant on H-ZSM-5 is decreasing after the pulse. At the moment when the formation rate of a certain MB is equal to

the sum of transformation and diffusion rates, the rate of change in MB concentration is zero, indicating that the concentration of trapped species reaches a maximum. For pentaMB, the diffusion rate is nearly zero; thus the concentration changing rate can be described by  $\frac{dn_5}{dt} = v_{for}^5 - v_{tra}^5$ . The negative growth of residual pentaMBs after 4 s indicates that the transformation rate is higher than the formation rate (Fig. 2b). This leads to the conclusion that pentaMB is an active species and could be transformed into other hydrocarbons, at least in the initial period. A similar trend is found for 1,2,3,5-tetraMB, but with relatively lower rates of increase and decrease. Since the diffusion rate of 1,2,3,5-tetraMB can be considered to be zero, it can be concluded that 1,2,3,5-tetraMB is an active species as well, but its reactivity is lower than that of pentaMB. P/m-diMB and 1,2,4-triMB exhibits almost the same trend. Although easy diffusion will contribute to the reduction of these two compounds in the zeolite channels, the decrease could be due to some extent to the transformation of these two compounds. Indeed, the reactivity of p/m-diMB and triMB has been noted in the MTO reaction over H-ZSM-5 and related to the formation of light olefins such as ethene under steady-state conditions [21,37].

It has been established in the MTO reaction that the reactivity of organic species trapped in the zeolite voids can be assessed by a transient <sup>12</sup>C/<sup>13</sup>C methanol-switching experiment [29,47]. To gain further insight into the reactivity of MBs formed in MTO reaction, a series of <sup>12</sup>C/<sup>13</sup>C methanol-switching experiments were conducted. Methanol in natural abundance was reacted on H-ZSM-5 (15) for 32 s at 400 °C. After the <sup>12</sup>C methanol was completely converted, the reaction was rapidly switched to <sup>13</sup>C methanol and allowed to proceed for another 4 s. Analysis of the incorporation of <sup>13</sup>C atoms into the MBs would reveal the reactivity: more incorporated <sup>13</sup>C atoms indicate a higher reactivity of MBs and vice versa. Fig. 3 shows the <sup>13</sup>C isotopic distribution of p/m-diMB, triMB, tetraMB, and pentaMB trapped in the H-ZSM-5(15) channels. All these <sup>13</sup>C-compounds were formed by gradually labeling the <sup>12</sup>C methanol-generated MBs rather than directly from <sup>13</sup>C methanol, because few fully labeled products were observed. Obviously, all the MBs show reactivity to methanol reactant. A large difference is demonstrated, however, in both <sup>13</sup>C distribution and total <sup>13</sup>C content among the MBs. The incorporation of <sup>13</sup>C increases with the increase in the number of methyl substituents. PentaMB displays much broader <sup>13</sup>C atoms distribution and contains about 42%<sup>13</sup>C atoms, tetraMB having slightly fewer <sup>13</sup>C atoms (36%), while much fewer <sup>13</sup>C atoms are incorporated into p/mdiMB and triMBs (ca. 20% <sup>13</sup>C atoms). This allows us to conclude that the reactivity of MBs follows the order pentaMB > 1,2,3,5tetraMB, >p/m-diMB  $\approx$  1,2,4-triMB. Thus, the rapid decrease of pentaMB and tetraMB observed in Fig. 2b can be explained by their high reactivity, which results in quick transformation. It is worth noting that light MBs could be formed as products in this process. In the proposed paring mechanism in the MTO reaction over H-ZSM-5, light MBs are produced along with splitting off olefins from bulkier MBs [6,33]. Additionally, the formed olefins could regenerate light MBs via polymerization and cyclization. Both contribute to the accumulation of p/m-diMB and triMBs. Fig. 2b shows that the formation rate of the light MBs seems to fit well with the transformation rate of the bulky MBs. The lower reactivity of the light MBs is seen in the lower rate of decrease of these compounds, as compared with the bulky MBs.

# 3.3. The relation of methylbenzenes to propene and ethene

The hydrocarbon pool of MBs has been previously identified on H-ZSM-5 under steady-state conditions [16,31,37,48]. The above observation of MBs prior to light olefins and their reactivity implies a distinctive role of MBs in the induction period. Valuable



Fig. 3. Isotopic analysis of trapped MBs in H-ZSM-5(15) channels. The catalyst was first exposed to <sup>12</sup>C methanol for 32 s, and thereafter to <sup>13</sup>C-methanol for 4 s.

information about MBs in the formation of light olefins can be obtained by linking MBs to propene and ethene in the induction period. We used the average number of methyl groups per benzene ring (Me<sub>ave</sub>) to describe the distribution of MBs trapped in H-ZSM-5 [32]:

$$Me_{ave} = \sum_{n=2}^{5} nf_n \tag{2}$$

 $f_n$  denotes the fraction of MB with *n* methyl groups. Accordingly, a higher concentration of bulkier MBs gives a larger Meave and vice versa. The selectivity to ethene and propene is assessed by the propene-to-ethene ratio (P/E). Fig. 4a shows the calculated P/E and Me<sub>ave</sub> of trapped MBs obtained from the reactions in Fig. 2, as a function of reaction time. It is interesting to note that the P/E shows a trend similar to that of Me<sub>ave</sub>, gradually decreasing before 16 s and leveling off after 16 s. This indicates that the formation of propene and ethene in the initial period is linked to the distribution of MBs. At a very short time (2 s), the Me<sub>ave</sub> is 4.3, implying that bulkier MBs like pentaMB and tetraMB dominates the trapped MBs (also see Fig. S3). At the same time, a high selectivity to propene is obtained with P/E = 6.0. In comparison, an increase in selectivity to ethene occurs with P/E dropping to 4.4 when the Meave decreases to 3.1 after 16 s. The lower Meave indicates that p/m-diMB and triMB are becoming dominant and responsible for ethene formation. A similar correlation between Me<sub>ave</sub> and P/E is confirmed at a lower temperature of 350 °C (Fig. S4). Therefore, our experimental observations clearly demonstrate that pentaMB and tetraMB favor propene formation, while p/m-diMB and triMB favor ethene formation in the induction period.

The previous work of Haw and co-workers indicated that trapped MBs in SAPO-34 catalyst were essential for it to be active in MTO reaction [49]. The HP center of MBs formed after the first pulse of the methanol reaction would have a profound effect on the subsequent reaction. Here, the H-ZSM-5(15) was subsequently treated with an identical second pulse of methanol after 32 s of the first pulse (Fig. S5 and Table S2). The conversion of methanol



**Fig. 4.** Evolution of Me<sub>ave</sub> and P/E in a single-methanol-pulse experiment (a) and a double-pulse experiment (b) at 400 °C. For a double-pulse experiment, the H-ZSM-5 (15) catalyst was first exposed to 20  $\mu$ L of methanol for 32 s, and thereafter to another 20  $\mu$ L of methanol for 4 s. Me<sub>ave</sub> refers to the average number of methyl groups per benzene ring. P/E refers to the propene-to-ethene ratio.

quickly reaches 8% after 2 s of reaction. Consistent with the work of Haw et al. [45], the pre-established HP shortens the induction time of the following MTO reaction. The relationship of the MB distribution to ethene and propene is further analyzed. As shown in Fig. 4b, the concentration of MBs with more methyl groups reflected by higher Me<sub>ave</sub> is increasing and reaches a maximum of 4.1 at 4 s, followed by a steady decrease. The increase of Me<sub>ave</sub> is associated with formation of bulkier MBs due to the methylation of light MBs by methanol from the second pulse. However, the high reactivity of bulkier MBs leads to their rapid transformation to light MBs and thus a decrease in Me<sub>ave</sub> again at longer reaction time. Analysis of ethene and propene shows that the evolution of calculated P/E has a trend similar to that of Me<sub>ave</sub>. This agrees well with the observation in Fig. 4a and provides direct evidence that the MBs in the range from p/m-diMB to pentaMB are formed as reactive catalytic centers in the initial reaction period. Importantly, the selectivity of light olefins such as ethene and propene can be correlated with the distribution of MBs.

# 3.4. The factors affecting methylbenzene distribution and olefin selectivity

### 3.4.1. Space velocity

The space velocity is a key factor in the production of olefins in MTO reactions [20,50]. Here, the pulse reaction was carried out with two space velocities by varying carrier gas (He) flow rate from 200 to 500 sccm (keeping the methanol content constant). The P/E was calculated and the distribution of MBs was analyzed by Me<sub>ave</sub> from the trapped MBs (Fig. S6 and Table 2). The experimental data indicate that a higher He flow rate of 500 sccm gives a slightly higher Me<sub>ave</sub> of 3.51 as compared with 3.19 at a lower He flow rate of 200 sccm. Preferred formation of propene is evident at higher He flow rates, with P/E being 4.92 at 500 sccm and 2.91 at 200 sccm. This is consistent with the above observation that the distribution of MBs affects the selectivity of propene and ethene. The different diffusion properties of MBs in zeolite channels at different space velocities should result in variation of MB distribution. The MBs with more methyl groups, such as tetraMB and pentaMBs, would experience much more diffusion hindrance in the H-ZSM-5 channels than the light MBs. A high space velocity promotes the diffusion of light MBs out of zeolite channels but has little effect on bulkier MBs. Accordingly, a relatively higher concentration of bulkier MBs would be trapped on H-ZSM-5 and higher Me<sub>ave</sub> can be expected. Thus the selectivity of ethene and propene could be controlled by the He flow rate, which influences the diffusion of formed MBs.

### 3.4.2. Si/Al ratio

The Brønsted acidity associated with the Si/Al ratio of zeolite is essential to the MTO reaction. Chang et al. demonstrated that reducing the Brønsted acidity of H-ZSM-5 could improve the selec-

### Table 2

 $Me_{ave}$  and P/E ratio obtained from methanol pulse reactions over H-ZSM-5 at two flow rates and temperatures. The Si/Al ratio of zeolite is given in parentheses.

Sample	Flow rate (sccm)	Temperature (°C)	Time (s) <sup>a</sup>	Me <sub>ave</sub> <sup>b</sup>	P/E <sup>c</sup>
ZSM-5(15) ZSM-5(15) ZSM-5(15) ZSM-5(15) ZSM-5(100)	200 500 500 500 500	400 400 350 400 400	8 8 2 8	3.19 3.51 4.30 4.31 4.32	2.91 4.92 11.01 6.0 9.25

<sup>a</sup> Reaction time after one methanol pulse.

<sup>b</sup> Average number of methyl groups per benzene ring.

<sup>c</sup> Propene-to-ethene ratio.

tivity to propylene in the MTO reaction, based on which the commercial MTP (methanol-to-propene) process has been developed on high-silica ZSM-5 [51]. A series of MTO reactions by pulsing methanol were conducted over H-ZSM-5 with two different Si/Al ratios (15 and 100) at 400 °C (Fig. S7). The distribution of MBs and P/E was analyzed and the data were listed in Table 2. For ZSM-5 with a high Si/Al ratio, bulkier MBs are preferentially formed compared with light MBs, as reflected by the higher Me<sub>ave</sub>. The P/E increases from 4.92 (Si/Al = 15) to 9.25 (Si/Al = 100), which can again be correlated with the distribution of MBs. Indeed, the distribution of MBs is associated with the Brønsted acid concentrations on different samples. On a low-silica H-ZSM-5, there are more Brønsted acid sites on which MBs might be tightly adsorbed, while on a high-silica sample, the lower concentration of Brønsted acid sites would result in weaker adsorption of MBs. Taking into account the larger confinement effect imposed by the channel of H-ZSM-5 on the bulkier MBs. on the high-silica H-ZSM-5, the formed light MBs could easily transport and diffuse out of zeolite channels, leading to a higher concentration of bulkier MBs (larger Meave). Thus, the predominant bulkier MBs formed on the highsilica H-ZSM-5 contribute to the higher selectivity to propene.

### 3.4.3. Reaction temperature

Reaction temperature also influences the distribution of MBs and the selectivity of olefins. At 350 °C, Me<sub>ave</sub> is 4.3 and P/E is 11 at 8 s of reaction time. In comparison, Me<sub>ave</sub> and P/E drop to 3.5 and 4.9, respectively, at 400 °C (Table 2), which is consistent with the correlation between MB distribution and selectivity to ethene and propene. The effect of the temperature on the reaction was further analyzed by comparing P/E at different reaction times when Me<sub>ave</sub> is similar. It is noted that at 400 °C and 2 s of reaction time, the Me<sub>ave</sub> increases to 4.31, similarly to that at 350 °C and 8 s of reaction time. The corresponding P/E increases to 6.0, but still is much lower than that (P/E = 11) at 350 °C. Thus, it can be concluded that higher temperature favors the formation of ethene on H-ZSM-5. Similarly. Svell et al. demonstrated that P/E was sensitive to temperature and a higher temperature contributed to ethene on both H-SAPO-34 and H-SSZ-13 catalysts [52]. It is clear that the distribution of MBs can be related to ethene and propene at different temperatures. However, the higher selectivity to ethene observed at 400 °C and 2 s of reaction time suggests that additional factors might affect olefin formation. This may be understood by considering the thermodynamics of the formation of ethene and propene at different temperature [20]. We assume that ethene is produced through light MBs with a higher energy barrier than that for propene from bulkier MBs. The formation rates of both ethene and propene will increase with reaction temperature. However, ethene is more favored than propene at higher temperatures due to the higher energy barrier, which leads to a decreased P/E.

### 3.5. The methanol-to-olefins reaction under steady-state conditions

After analyzing the reactivity of MBs in the induction period, we extended our study to the reaction under steady-state conditions. The reactions were preformed over H-ZSM-5 with Si/Al ratios of 15, 100, and 200. Under 100% conversion at 400 °C, the turnover frequencies (TOF) were measured as 0.018, 0.12, and 0.27 s<sup>-1</sup> for H-ZSM-5(15), H-ZSM-5(100), and H-ZSM-5(200), respectively. The TOF value for our low-silica H-ZSM-5(15) is comparable to that  $(0.016 \text{ s}^{-1})$  determined for H-ZSM-5(15) is comparable to that  $(0.016 \text{ s}^{-1})$  determined for H-ZSM-5 with a Si/Al ratio of 25 in a previous report [53]. Fig. 5 shows the GC-MS chromatogram of trapped MBs on H-ZSM-5 after 15 min of reaction at 400 °C. MBs up to hexaMBs are observable on the three samples. The p/m-diMB and triMB decrease as the Si/Al ratio increases, while tetraMBs and pentaMBs exhibit the reverse trend. This can be

[sotopic distribution/%



**Fig. 5.** GC–MS analysis of trapped products obtained from methanol reaction at 400  $^{\circ}$ C for 15 min over H-ZSM-5 with Si/Al = 15 (a), 100 (b), and 200 (c).

#### Table 3

 $Me_{ave}$  and P/E ratio obtained from methanol reaction over H-ZSM-5 under steady-state conditions at 400  $^\circ C$  for 15 min.

Me <sub>ave</sub> <sup>a</sup>	P/E <sup>b</sup>
3.49	2.68
3.64	5.95
3.84	11.32
	Me <sub>ave</sub> <sup>a</sup> 3.49 3.64 3.84

*Note:* The Si/Al ratio of zeolite is given in parentheses.

<sup>a</sup> Average number of methyl groups per benzene ring.

<sup>b</sup> Propene-to-ethene ratio.

explained by considering both Brønsted acid site and zeolite framework confinement effects on the transport and diffusion behavior of MBs with different molecular sizes. The analysis of Meave and P/E over H-ZSM-5 catalysts with different Si/Al ratios shows a correlation of the MB distribution with the selectivity to ethene and propene (Table 3), which demonstrates that propene is favored when bulkier MBs are predominant while light MBs mainly contributes to ethene under steady-state conditions, consistent with the results derived from the induction period. It should be noted that the competing interconversions are proceeding under steady-state conditions, in which the methylation/cracking of  $C_3^+$  olefins might also contribute to propene formation [21,37]. The dependence of olefins on the MBs trapped on zeolite catalysts in both the induction period and the steady-state period definitely implies the importance of MBs in controlling the formation of both ethene and propene.

Transient  ${}^{12}C/{}^{13}C$  isotopic switch experiments were conducted to analyze the reactivity of trapped MBs under steady-state conditions. Fig. 6 shows the isotopic data on MBs trapped on ZSM-5 with Si/Al = 15 and 100. Different  ${}^{13}C$  distributions and total  ${}^{13}C$  content are observable for the various MB compounds. On H-ZSM-5 with Si/Al = 15, 1,2,3,5-tetraMBs and pentaMBs display a broad distribution centered on the isotopomers highly enriched in  ${}^{13}C$  atoms. The



<sup>13</sup>C atoms in molecule

**Fig. 6.** Isotopic distribution and total <sup>13</sup>C content (%) in trapped organic species obtained from transient <sup>12</sup>C/<sup>13</sup>C isotopic switch experiments over H-ZSM-5 with Si/Al = 15 and 100. <sup>12</sup>C methanol was first reacted on a freshly activated catalyst (0.2 g) at 400 °C for 15 min at a WHSV of 2 h<sup>-1</sup>, and then the reaction was switched to <sup>13</sup>C methanol and allowed to proceed for 0.5 min.

<sup>13</sup>C-labeled diMB and 1,3,5-triMBs are also broadly distributed, but the incorporation of <sup>13</sup>C atoms is less. In addition, hexaMB is dominated by isotopomers containing fewer <sup>13</sup>C atoms and has the lowest <sup>13</sup>C content. Analysis of the <sup>13</sup>C content among the MBs suggests the difference in their reactivity toward the addition of methanol reactant. Thus, the reactivity of the various MBs has the order pentaMB > 1,2,3,5-tetraMB > p/m-diMB > 1,3,5-triMB > 1,2,4-triMB > hexaMB. This is consistent with that obtained from the induction period. The low reactivity of hexaMB is also in agreement with the previous report [29], confirming the smaller importance of such species in the MTO reaction on H-ZSM-5. It is noted



**Fig. 7.** <sup>13</sup>C CP/MAS NMR spectra of trapped products obtained from methanol pulse-quench reaction over H-ZSM-5(15) at 350 (a-c) and 400 °C (d-f). Each sample was prepared by injecting 20  $\mu$ L of <sup>13</sup>C methanol onto a freshly activated catalyst bed (0.2 g) while He was flowed at 500 ml min<sup>-1</sup>, and the reaction was allowed to occur for different time followed by a rapid thermal quench.

that there exists a difference in the reactivity of 1,3,5-triMBs and 1,2,4-triMBs, with the former being more reactive than the latter. This indicates that the reactivity of MBs is sensitive to the geometry of the trapped molecules, though both triMBs have the same number of methyl substitutions. The confinement effect imposed by the zeolite channels is assumed to result in such a difference for the two triMBs.

The <sup>13</sup>C incorporation was also analyzed on the high-silica H-ZSM-5(100). Interestingly, the content of <sup>13</sup>C atoms in light MBs such as diMB and triMBs is notably increased and higher than that in tetraMB and pentaMB. The enhanced selectivity to propene on the high-silica sample compared with the low-silica sample (see Table 3) suggests that the higher <sup>13</sup>C incorporation rate of light MBs does not necessarily reflect the increase of reactivity. Otherwise, the selectivity to ethene would increase according to the above-established relationship between MBs and olefins. At the



**Fig. 8.** Gas chromatography analysis of trapped products obtained from methanol pulse reaction over H-ZSM-5(15) at 350 (a) and 400 °C. Each sample was prepared by injecting 20  $\mu$ L of <sup>13</sup>C methanol onto a freshly activated catalyst bed (0.2 g) while He was flowed at 500 ml min<sup>-1</sup>, and the reaction was allowed to occur for 8 s followed by a rapid thermal quench.

moment, it is still unclear why the higher <sup>13</sup>C incorporation rate of the light MBs is observed.

# 3.6. Mechanistic understanding of the relationship between methylbenzenes and olefins

In the co-reaction of methanol/DME with benzene, toluene, or p/m-diMB, the transfer of carbon atoms from the MBs' phenyl ring to ethene and propene suggests a paring mechanism responsible for the formation of light olefins [23,31,39]. In our previous work, by the observation and identification of the key active intermediates such as cyclic carbenium ions with in situ solid-state NMR, a detailed aromatic-based paring route was depicted for the formation of propene and ethene [34,36]. Here, we are seeking to gain insight into the mechanistic link between MBs and ethene and propene in the initial stage of the MTO reaction. Fig. 7 shows the <sup>13</sup>C CP MAS NMR spectra of trapped products obtained from pulsequench experiments on H-ZSM-5(15) in which <sup>13</sup>C-methanol was injected at 350 and 400 °C and reacted for between 8 and 32 s before thermal quench. After 8 s of reaction at 350 °C (Fig. 7a), the conversion of methanol (50 ppm) and dimethyl ether (60 ppm) is evidently accompanied by the formation of unsaturated compounds such as MBs at 130-140 ppm and cyclic carbocations at 240–260 ppm [34,45,54]. According to our previous work [34,36], the characteristic signals at 244, 247, 250, 252, 255, and 257 ppm evidence the formation of 1,3-dimethylcyclopentenyl, 1,2,3-trimethylcyclopentenyl, 1,3,4-trimethylcyclopentenyl, 1methyl-3-ethylcyclopentenyl, 1,5-dimethyl-3-ethylcyclopentenyl, and 1,4-dimethyl-3-ethylcyclopentenyl carbocations. It is noted that the signal intensities of these species are much lower than





Scheme 1. Proposed paring routes for the formation of ethene and propene.

those under steady-state condition [34,36], indicating the low concentration of these carbocations formed in the induction period. Besides these C<sub>5</sub>-cyclic cations, the formation of C<sub>6</sub>-cyclic cations such as pentamethylbenzenium ions is unambiguously demonstrated by the signals at 205 and 189 ppm [55] (Fig. 7a and b). To further support the assignment of these species, the trapped compounds on the catalysts were isolated by dissolving the catalyst with HF and extracting with CH<sub>2</sub>Cl<sub>2</sub> and then were analyzed by GC-MS. The GC spectra of trapped products show the presence of methyl- and ethylcyclopentadienes, such as 1,3-dimethylcyclopentadiene (1,3-DiMCP), 1,2,3-trimethylcyclopentadiene (1,2, 3-TriMCP), 1,2,4-trimethylcyclopentadiene (1,2,4-TriMCP), 1methyl-3-ethylcyclopentadiene (1-M-3-ECP), 1,4-dimethyl-2-ethy lcyclopentadiene (1,4-DiM-2-ECP), and 1,2-dimethyl-4-ethylcyclo pentadiene (1,2-DiM-ECP) (Fig. 8). Indeed, we have previously identified all these species obtained under steady-state conditions on H-ZSM-5 as well [34]. Since the cyclopentadienes can be considered as the conjugated bases of the corresponding cyclopentenyl cations [34,43], the methyl- or ethylcyclopentenyl cations (1,3dimethylcyclopentenyl, 1,2,3-trimethylcyclopentenyl, 1,3,4trimethylcyclopentenyl, 1-methyl-3-ethylcyclopentenyl, 1,5-dime thyl-3-ethylcyclopentenyl, and 1,4-dimethyl-3-ethylcyclopentenyl cations) should be formed and presented on H-ZSM-5 in the initial stage of MTO reaction, giving the low-field NMR signals (240-260 ppm). The MBs and methyl- or ethyl-substituted cyclopentenyl cations grow up after 8 s of reaction time, reflected by the increase of signals at 130-140 ppm and at 240-260 ppm. At the same time, the formation of light olefins speeds up as observed in Fig. 1, suggesting the intermediate role of the cations in the formation of olefins. All these cyclopentenyl cations can be observed at higher reaction temperature (400 °C) but at lower intensity (Fig. 7d–f). Comparison of reactions at different temperatures (325–400 °C) shows that the lower temperature definitely favors the stabilization and observation of the active carbocations especially pentamethylbenzenium cation (Fig. S8). Under steady-state conditions, similar C<sub>5</sub>- and C<sub>6</sub>-cyclic cations have been identified as key intermediates involved in the aromatics-base cycle for the formation of light olefins via a paring mechanism that connects MBs with isobutene [33], propene [34,56], and ethene [36]. Typically, MBs initiates the paring cycle, in which the key step is the ring contraction of C<sub>6</sub> to C<sub>5</sub> species and splitting off of an alkyl group from the  $C_5$  compound to form olefin. Thus, it can be expected that a similar mechanism proceeds in the induction period. We have established above that lighter MBs with two or three methyl groups are related to ethene, while bulkier MBs favor propene. Therefore, ethene and propene could be formed via a different aromatic-based paring route. Scheme 1 shows the proposed routes from MBs to olefins via the observed carbocations. The methylation of light MBs such as toluene would result in benzenium cations [57], and its contraction gives rise to ethylcyclopentenyl cations, which can split off ethene products (Scheme 1a). The observation of different ethylcyclopentenyl cations (1-methyl-3-ethylcyclopentenyl, 1,5-dimethyl-3-ethylcy clopentenyl, and 1,4-dimethyl-3-ethylcyclopentenyl cations) suggests that the methylation of MBs could be different (Scheme 1a-d), but the following ring contraction produces ethene in a similar way. The methylated bulkier benzenium ions that generate propene could be generated by gem-methylation of triMB and tetraMB [33]. The ring contraction of tetramethylbenzenium and pentamethylbenzenium ions generates propyl-attached 1,3,5, 6,6-pentamethylbicyclo[3.1.0] and 1,3,6,6-tetramethylbicyclo[3.1. 0] hexenyl cation transient state species, which subsequently split off propene with simultaneous formation of methyl cyclopentenyl cations (Scheme 1e and f). Based on energy calculations, this kind of reaction route has been rationalized in the formation of propene under steady-state conditions [34].

All these paring routes for the formation of ethene and propene are working in the full catalytic cycles and are interconnected. Along with the formation of ethene and propene, the active methylcyclopentenyl cations are readily rearranged back into aromatics that will be involved in a new catalytic cycle [33]. For example, the 1,3,4-trimethylcyclopentenyl cation produced by route (f) could be expanded to p/m-diMB, from which trimethylbenzenium ions are formed by methylation, subsequently leading to ethene via route (b) in Scheme 1.

The bulkier benzenium cations can be formed by a sequence of methylation of light MBs from methanol [58]. Waroquier et al. delicately demonstrated the striking effluence of the zeolite framework in the methylation reaction in the confined space in terms of reaction barriers and reaction energy [59]. The calculated results showed that the increase of methyl groups leads to more reactive benzenium cations. Pentamethylbenzenium ion was predicted to be the most stabilized cation that could be formed by methylation of tetraMB or protonation of rearranged pentaMBs [60]. This is consistent with our observation that bulkier MBs such as tetraMB and pentaMB have higher reactivity than their light counterparts because of the facile formation of stable benzenium, such as pentamethylbenzenium ions. Although the further methylation of pentaMB may also occur to form hexamethylbenzenium ions, this transformation would be unfavorable due to the higher reaction energy of hexamethylbenzenium ions in the confined space of the zeolite channel [59]. Additionally, the much larger heptamethylbenzenium ion that was observed in zeolites such as Beta [18] and SAPO-34 [43] with large pores or cavities is not likely to be formed over ZSM-5 by methylation of hexaMB because of the strong geometric constraint of the zeolite framework on the bulky molecule. This also explains the low reactivity observed for hexaMB in the MTO reaction.

# 4. Conclusions

The hydrocarbon pool of MBs in the MTO reaction was investigated over zeolite H-ZSM-5. The reactivity of MBs in the induction period was revealed by <sup>12</sup>C/<sup>13</sup>C switching experiments. Bulkier MBs (tetraMB and pentaMB) exhibit higher reactivity than lighter counterparts (p/m-diMB and triMB). The formation of ethene and propene was found to be correlated with the MBs trapped on H-ZSM-5. Lighter MBs such as p/m-diMB and triMB favor ethene formation, while bulkier MBs like tetraMB and pentaMB favor propene formation, particularly at low reaction temperature (<400 °C). The MBs distribution in the induction period directly influences the selectivity to ethene and propene. Preferential formation of propene can be achieved by using high-silica H-ZSM-5, a moderate reaction temperature, and a high space velocity (carrier gas flow). The same correlation of MBs with ethene and propene was found to be present under steady-state conditions as well. Using solidstate NMR spectroscopy in combination with GC-MS, C5- and

C<sub>6</sub>-cyclic carbocations were identified, suggesting the presence of a paring mechanism in the induction period. The intimate correlation between MBs and ethene and propene can be rationalized by the proposed paring routes. The ethyl and propyl group-attached cation intermediates are generated by ring contraction of lighter and bulkier MBs, respectively, from which the elimination of alkyl groups accounts for the formation of ethene and propene. These results confirm the essential role of MBs in the MTO reaction and shed new light on the MTO chemistry, particularly in the induction period. The established mechanistic correlation between MBs and ethene and propene is helpful for the design of zeolite catalysts for achieving selective production of light olefins.

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# **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2015.10.001.

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