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# The mechanism of aromatic dealkylation in methanol-to-hydrocarbons conversion on H-ZSM-5: What are the aromatic precursors to light olefins?

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# ABSTRACT

Co-reactions of 7.5–9.3 kPa of DME with 4 kPa of toluene, p-xylene, and 4-ethyltoluene on H-ZSM-5 at 523–723 K at low conversions (<10 C%) with varying isotopic feed compositions of  $^{13}C|^{12}C$  show that carbons originating from the aromatic ring are incorporated into ethene and propene. A comparison of the predicted  $^{13}C$ -contents of ethene and propene postulated on the basis of the paring, side-chain, and ring-expansion aromatic dealkylation mechanisms based on the experimentally observed isotopologue distribution of 1,2,4-trimethylbenzene, 1,2,4,5-tetramethylbenzene, and 4-ethyltoluene reveal that the predicted  $^{13}C$ -content of ethene and propene from 1,2,4,5-tetramethylbenzene via the paring mechanism most closely match the experimentally observed  $^{13}C$ -contents of ethene mechanisms and aromatic precursors examined. This work quantitatively shows that aromatic dealkylation to form ethene and propene occurs through the paring mechanism and that 1,2,4,5-tetraMB is the predominant aromatic precursor for light olefin formation for MTO conversion on H-ZSM-5 for a 200 K range in temperature.

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# 1. Introduction

The conversion of methanol over acid zeolite catalysts to a wide variety of hydrocarbons, including gasoline-range hydrocarbons (methanol-to-gasoline, MTG) and light olefins (methanolto-olefins, MTO) has been extensively studied because methanol can be produced from any carbon-based feedstock via a syngas  $(CO + H_2)$  intermediate [1–3]. Methanol-to-hydrocarbons (MTH) proceeds through an indirect "hydrocarbon pool" mechanism in which hydrocarbon formation occurs through repeated methylation and cracking of olefins and aromatics entrained within the zeolite pores [4-8]. Isotopic switching experiments in which a <sup>12</sup>C-methanol feed is switched with a <sup>13</sup>C-methanol feed during steady-state reaction on H-ZSM-5 at 623 K have shown that after the switch the <sup>13</sup>C-incorporation of ethene closely matched that of polymethylbenzenes (polyMBs), while the <sup>13</sup>C-incorporation of  $C_3$  and higher olefins matched each other [9,10]. This result showed that two different catalytic cycles are at work on H-ZSM-5, one involving ethene and polyMBs and the other involving  $C_3$ and higher olefins. Similar work has also been done on other zeolite and zeotype frameworks, either showing the prevalence of both cycles or showing the dominance of one cycle over another

\* Corresponding author. E-mail addresses: ilias003@umn.edu (S. Ilias), abhan@umn.edu (A. Bhan). [11–15]. Isotopic experiments on H-ZSM-5, H-BEA, and H-MOR in which methanol/dimethyl ether (DME) is co-reacted with aromatics have also shown that ethene and propene contain carbon atoms originating from the aromatic co-feed [16–18]. While these results show that both ethene and propene are mechanistically linked to polyMBs, the immediate precursor to ethene and propene, and the mechanism of aromatic dealkylation to form light olefins is still debated.

Experimental and theoretical work has postulated that light olefin formation from polyMBs occurs through a paring, side-chain, or ring-expansion mechanism (Schemes 1 and 2). The paring mechanism, first proposed by Sullivan et al. [19] for the hydrocracking of hexaMB on a nickel sulfide catalyst, is initiated by gem-methylation of a MB which is followed by ring contraction to a 5-membered ring. As a result, an isopropyl or isobutyl group is formed on the 5-membered ring, which can subsequently crack to form propene or isobutene, containing one aromatic ring carbon. Arstad et al. [20] proposed a ring-expansion mechanism for ethene and propene formation from heptamethylbenzenium. Similar to the paring mechanism, the ring-expansion mechanism is also initiated by gem-methylation of a polyMB and the eliminated olefin contains one aromatic ring carbon. Experimental work form Bjørgen et al. [21] in which <sup>13</sup>C-methanol is co-reacted with <sup>12</sup>C-benzene on H-BEA reported that at 543 K at least 50% of propene and isobutane (coming from isobutene) molecules contained









**Scheme 1.** Several mechanisms have been proposed for ethene and propene formation from MBs. The paring mechanism for ethene (1e) and propene (1p) formation from 1,2,4,5-tetraMB is shown in path 1. The side-chain mechanism for ethene (2e) and propene (2p) formation from 1,2,4,5-tetraMB is shown in path 2. Path 3e shows an alternative paring-type mechanism for ethene formation from 1,2,4,5-tetraMB that only requires protonation, not methylation; (–) aromatic ring carbon, ( $\bigcirc$ ) aromatic methyl carbon, and ( $\bigcirc$ ) methyl carbon from DME/methanol.



**Scheme 2.** Ring-expansion mechanism for ethene (4e) and propene (4p) formation; (-) aromatic ring carbon, ( $\bigcirc$ ) aromatic methyl carbon, and ( $\bigcirc$ ) methyl carbon from DME/methanol.

one <sup>12</sup>C-atom, showing that an aromatic ring carbon is incorporated into light olefins. Similar experiments by Westgård Erichsen et al. [22] at 523 K on H-SAPO-5 showed that at least 60% of ethene and propene molecules also contained one <sup>13</sup>C-atom. Although the incorporation of an aromatic ring carbon into light olefins shows that on these large-pore catalysts at low temperatures, aromatic dealkylation occurs via either a paring or ring-expansion mechanism, the experimental results reported by Bjørgen et al. and Erichsen et al. did not distinguish between the two mechanisms and the mechanism of aromatic dealkylation was not discernible for similar isotopic experiments on H-BEA at 603 K [22,23].

The side-chain mechanism is also initiated by gem-methylation of a MB, however, in this mechanism gem-methylation is followed by deprotonation and results in the formation of an exo-cyclic double bond. The exo-cyclic double bond can then undergo side-chain methylation to form a side-chain that can crack to form ethene or propene. Work by Sassi et al. [24] at 723 K on H-BEA shows that pulse reactions of <sup>13</sup>C-methanol with various <sup>12</sup>C-MBs result in ethene and propene having similar <sup>13</sup>C-contents as the overall <sup>13</sup>C-content of the methanol and aromatic methyls in the feed, suggesting that olefin formation at these conditions occurs via a side-chain mechanism. Reactions of <sup>13</sup>C-methanol with <sup>12</sup>C- ethyl, propyl, and butylbenzenes on H-BEA at 623 K produced high fractions (>50%) of completely <sup>12</sup>C-labeled ethene, propene, and butenes, respectively [24,25]. While the high fraction of completely <sup>12</sup>C-labeled olefins shows that the side-chain mechanism does occur under conditions where aromatics with C<sub>2+</sub> alkyl groups are co-fed with methanol, it is unclear to what extent the sidechain mechanism contributes to olefin formation under typical MTH conditions where the majority of aromatics are methylbenzenes [13]. Work by Sassi et al. at temperatures above 623 K on H-BEA suggests that the side-chain mechanism is occurring while the results reported by Biorgen et al. at temperatures below 573 K suggest that either the paring or ring-expansion mechanism predominantly contributes to olefin formation. These results are reconcilable if a change in the dealkylation mechanism occurs with temperature.

Theoretical studies by McCann et al. [26] using ONIOM methods on 46T clusters of H-ZSM-5 show that the highest barriers for isobutene formation from toluene are aromatic methylation steps  $(E_a = 150 - 162 \text{ kJ mol}^{-1})$ . Lesthaeghe et al. [27] investigated the side-chain mechanism for ethene formation from o-xylene on 46T clusters of H-ZSM-5 using ONIOM methods and found that the ethene elimination step had the highest barrier  $(E_{\rm a} \sim 200 \text{ kJ mol}^{-1})$ . The high barrier to ethene elimination led Lesthaeghe et al. [27] to hypothesize that side-chains may grow longer to eliminate propene or may eventually cause deactivation of the catalyst. Additionally, Seiler et al. [28] used in situ <sup>13</sup>C NMR for the continuous flow reaction of <sup>13</sup>C-methanol followed by a switch to <sup>12</sup>C-methanol on H-ZSM-5 at 548-573 K and observed that the peak at 10-30 ppm decreased by 40% after the switch. This range in chemical shift was assigned to alkyl groups on aromatics, and therefore, this 40% reduction in peak area was attributed to olefin formation via the side-chain mechanism. Alternatively, the 10-30 ppm region can also be assigned to methyl groups on aromatics [29], implying that the paring, side-chain, and ring-expansion mechanism are all consistent with the peak reduction following a switch to <sup>12</sup>C-methanol. While theoretical work suggests that barriers to aromatic dealkylation are lower for the paring mechanism on H-ZSM-5, experimental evidence has not been able to distinguish between the different aromatic dealkylation mechanisms on this zeolite.

Understanding the mechanism of aromatic dealkylation to form light olefins in MTH is key to understanding how ethene and propene selectivity can be controlled. In this work, we use the effluent isotopologue distributions of 1,2,4-triMB, 1,2,4,5-tetraMB, and 4-ethyltoluene for the co-reactions of DME with toluene, p-xylene, and 4-ethyltoluene, where either DME or the aromatic co-feed is labeled with <sup>13</sup>C-atoms, on H-ZSM-5 at 523-723 K to predict the <sup>13</sup>C-contents of ethene and propene based on the paring, side-chain, and ring-expansion mechanisms. 1,2,4-TriMB, 1,2,4,5-tetraMB are examined as precursors to ethene and propene formation because isotopic switching experiments on H-ZSM-5 have shown that the <sup>13</sup>C-content of ethene matches that of 1,2,4triMB and 1,2,4,5-tetraMB, but not the <sup>13</sup>C-content of penta- or hexaMB [9,10]. Additional isotopic experiments involving methanol/DME with aromatic co-feeds on H-ZSM-5 where either the aromatic or the methylating agent is <sup>13</sup>C-labeled show that a significant fraction of these aromatics (<30%) are not direct products of methylation of the aromatic co-feed and contain both <sup>12</sup>C and <sup>13</sup>C-atoms, leading to the conclusion that 1,2,4-triMB and 1,2,4,5tetraMB are rebuilt from repeated methylations and dealkylations

on H-ZSM-5 [17,18]. 4-Ethyltoluene is examined as an aromatic precursor because protonation of 4-ethyltoluene results in the formation of an intermediate to aromatic dealkylation for the side-chain mechanism. By comparing the predicted <sup>13</sup>C-contents of ethene and propene from the effluent isotopologue distributions of three aromatic precursors for the different aromatic dealkylation mechanisms that have previously been postulated to the experimentally observed <sup>13</sup>C-content of ethene and propene, both the dominant aromatic precursor and dominant aromatic dealkylation mechanism for ethene and propene formation was determined. The predicted <sup>13</sup>C-content of ethene and propene from 1,2,4,5-tetraMB via the paring mechanism mostly closely matches the experimentally observed <sup>13</sup>C-content of ethene and propene, showing for the first time that aromatic dealkylation in MTH conversion on H-ZSM-5 occurs through the paring mechanism and that 1.2.4.5-tetraMB is the dominant precursor to ethene and propene formation at 523-723 K.

#### 2. Materials and methods

#### 2.1. Catalyst preparation

The catalyst, H-ZSM-5 (CBV8014), Si/Al = 42.6, was obtained in the ammonium form from Zeolyst International. Structural and chemical characterization of the commercial H-ZSM-5 sample used in this study is reported in Section S.1 of the Supplemental information. The silicon-to-aluminum ratio of the commercial H-ZSM-5 sample was determined by ICP-OES elemental analysis (performed by Galbraith Laboratories). The ammonium-form zeolite was sieved to obtain aggregate particle sizes between 180 and 425  $\mu$ m (40–80 mesh) and treated in 1.67 cm<sup>3</sup> s<sup>-1</sup> of dry air (20–21% O<sub>2</sub>, <10 ppm H<sub>2</sub>O, Minneapolis Oxygen) at 773 K for 4 h (heating rate of 0.0167 K s<sup>-1</sup>) to convert it to the proton-form zeolite. The catalyst was pre-treated *in situ* in 1.67 cm<sup>3</sup> s<sup>-1</sup> of helium flow (99.995% purity, Minneapolis Oxygen) at 773 K overnight using a heating rate of 0.0167 K s<sup>-1</sup> prior to reaction.

### 2.2. Catalytic reactions of DME with aromatic co-feeds over H-ZSM-5

A stainless steel packed-bed reactor (0.25 in o.d.; 0.215 in i.d.) equipped with a concentric thermal well (0.0625 in o.d.; 0.0485 in i.d.) aligned along the tube center was used for the conversion of DME. The catalyst bed was supported between guartz wool plugs and operated at isothermal conditions using an ARI heating coil regulated by a Watlow Temperature Controller (96 Series). Reactions were performed using 10 mg of catalyst mixed with approximately 150 mg of quartz sand at 523 K with either  ${}^{12}C_2$ - or  ${}^{13}C_2$ -DME at 7.5–9.3 kPa ( ${}^{12}C_2$ -DME from Matheson Tri-Gas, 99.5% purity; <sup>13</sup>C<sub>2</sub>-DME from Aldrich Chemistry, 99% <sup>13</sup>C-atom purity;  $0.024-0.030 \text{ cm}^3 \text{ s}^{-1}$ ) with 4 kPa of an aromatic co-feed and a balance of helium so that the total feed flow rate was 0.417 cm<sup>3</sup> s<sup>-1</sup>. The aromatic co-feeds used were  ${}^{12}C_8$ -p-xylene (Sigma Aldrich, >99% purity),  ${}^{13}C_2$ -p-xylene where the  ${}^{13}C$ -atoms were on the methyl groups (Isotec, 99% <sup>13</sup>C-atom purity), <sup>12</sup>C<sub>7</sub>-toluene (Sigma Aldrich, >99.9% purity), and <sup>12</sup>C<sub>9</sub>-4-ethyltoluene (Fluka Analytical, >95.0% purity). <sup>13</sup>C NMR was performed on the p-xylene sample from Isotec to confirm that the <sup>13</sup>C-atoms were located only on the methyl carbons (Section S.2 of the Supplemental information). The aromatic co-feeds were fed as a liquid using a Cole Parmer EW-74900-00 syringe pump at rates of 0.61, 0.67, and  $0.72 \ \mu L \ s^{-1}$  for toluene, p-xylene, and 4-ethyltoluene, respectively. Heat traced lines (423 K) were used to transfer the aromatic co-feed to the reactor and the reactor effluent to a gas chromatograph-mass spectrometer (Agilent 7890-5975C) equipped with a methyl-siloxane capillary column (HP-1, 50.0 m  $\times$  320  $\mu$ m  $\times$ 

 $0.52 \ \mu\text{m}$ ) connected to a flame ionization detector and a 5% diphenyl, 95% methyl-siloxane capillary column (HP-5, 50.0 m × 320  $\mu\text{m} \times 0.52 \ \mu\text{m}$ ) connected to a mass spectrometer. The total pressure of the reactor was 130 kPa. Similar reactions were also performed at 623 K and 723 K, using 0.5 mg and 0.1 mg of catalyst, respectively, diluted in approximately 150 mg of quartz sand. Isotopologue distributions were determined from mass fragmentation patterns using the method outlined by Price and Iglesia [30].

#### 2.3. Predicting <sup>13</sup>C-content of ethene and propene from aromatics

In Section 1, three different proposed mechanisms for aromatic dealkylation in MTH were discussed and these mechanisms are examined in this work. For both the side-chain mechanism and the ring-expansion mechanisms, routes for ethene and propene formation have been previously proposed [16,20,24]. For the paring mechanism, however, only routes for propene and isobutene formation have been proposed [19,21]. Arstad et al. also performed calculations involving free carbocations investigating if a paring mechanism depicted in 3e of Scheme 1 was possible, but determined that the secondary carbenium ion formed was not stable, and therefore, this mechanism will not form ethene [31]. Recent work from Westgård Erichsen et al. [22] on the co-reaction of <sup>13</sup>C-methanol with <sup>12</sup>C-benzene on H-SAPO-5 shows that 60% of the ethene produced contains one ring carbon, which is consistent with the ring-expansion mechanism or a paring-type mechanism. We propose mechanism 1e (Scheme 1) to account for the possibility of ethene coming from a paring-type mechanism. In mechanism 1e, a methyl from the isopropyl group on the 5-membered ring shifts to the ring accompanied by a simultaneous hydrogen shift from the ring to the isopropyl group. Note that in this mechanism, ethene should always contain one ring carbon, but the other carbon may come from either methyl carbon on the isopropyl group.

In this work, multiple dealkylation mechanisms for ethene and propene formation are compared to determine which mechanism best fits the experimentally observed <sup>13</sup>C-content of ethene and propene based on the effluent isotopic composition of 1,2,4-triMB, 1,2,4,5-tetraMB, and 4-ethyltoluene. The <sup>13</sup>C-content of aromatic ring carbons and methyl carbons must be known to correlate the <sup>13</sup>C-content of these aromatic precursors to that of ethene and propene. To determine the <sup>13</sup>C-content of the ring and methyl carbons, we assume that methyl carbons on aromatics are the first to incorporate DME carbons. The limitations of this assumption for the isotopic results presented in this work are discussed further in Section 3. For a particular MB with a total of t methyl groups,  $m_i$ is the number of <sup>13</sup>C methyl carbons, and  $r_i$  is the number of <sup>13</sup>C ring carbons in a particular isotopologue of the MB with i<sup>13</sup>C-atoms. For  $i \leq t$ ,  $m_i = t$  and  $r_i = 0$ ; for i > t,  $m_i = t$  and  $r_i = i - t$ . If the overall fraction of the aromatic species with  $i^{13}$ C-atoms is  $x_i$ , then the total <sup>13</sup>C-content of the methyl groups  $(^{13}M)$  in the MB is

$$^{13}M = \sum_{i=0}^{t+6} m_i x_i,$$

and the total <sup>13</sup>C-content of the ring carbons  $(^{13}R)$  in the MB is

$$^{13}R = \frac{\sum_{i=0}^{l+6} r_i x_i}{6}$$

4.0

This method is also used to calculate the <sup>13</sup>C-content of the ring carbons and the exocyclic carbons for 4-ethyltoluene. For the specific case of 4-ethyltoluene, <sup>13</sup>M is the total <sup>13</sup>C-content of methyl and ethyl carbons.

Based on the four mechanisms for ethene formation (1e, 2e, 3e, and 4e) and the three mechanisms for propene formation (1p, 2p, 4p) shown in Schemes 1 and 2 and the effluent isotopologue distributions for the three aromatic precursors, the <sup>13</sup>C-contents

for ethene and propene can be predicted. The predicted <sup>13</sup>C-content depends on both the mechanism and the aromatic precursor. For example, 4-ethyltoluene if protonated has the same structure as an intermediate of the side-chain mechanism and the ringexpansion mechanism. Therefore, in both these mechanisms, the predicted <sup>13</sup>C-content of ethene from 4-ethyltoluene would simply be <sup>13</sup>M, the overall <sup>13</sup>C-content of the exocyclic carbons in 4-ethyltoluene. In the ring-expansion mechanism, the <sup>13</sup>C-content of ethene will depend on which methyl in the gem-methyl group is inserted into the 7-membered ring as well as if there is a methyl group ortho to the gem-methyl group. The equations used for the predicted <sup>13</sup>C-contents of ethene and propene for each aromatic precursor and mechanism examined in this work are summarized in Table 1, where <sup>13</sup>D is the fraction of <sup>13</sup>C-atoms in the methylating agent (DME or methanol). The absolute error for the predicted <sup>13</sup>C-content of the olefin formed ( ${}^{13}C_{pred}$ ) compared to the experimentally observed <sup>13</sup>C-content of the olefin formed  $({}^{13}C_{obs})$  is

$$\left| {}^{13}C_{obs} - {}^{13}C_{pred} \right|,$$

and the relative error is

$$\frac{\left|{}^{13}C_{obs}-{}^{13}C_{pred}\right|}{{}^{13}C_{obs}}$$

#### 3. Results and discussion

Isotopic experiments with feed compositions comprising of 4 kPa of toluene, p-xylene, or 4-ethyltoluene with 7.5–9.3 kPa of <sup>13</sup>C-DME in which the number of <sup>12</sup>C-methyls on the aromatic feed was varied were conducted and are enumerated below:

- (1)  ${}^{13}C_2$ -p-xylene: 0  ${}^{12}C$ -aromatic methyls. (2)  ${}^{12}C_7$ -toluene: 1  ${}^{12}C$ -aromatic methyl. (3)  ${}^{12}C_8$ -p-xylene: 2  ${}^{12}C$ -aromatic methyls.
- (4)  ${}^{12}C_9$ -4-ethyltoluene: 1  ${}^{12}C$ -aromatic methyl and 1  ${}^{12}C$ -aromatic ethyl.

Reactions 3 and 4 were also performed at higher temperatures (623-723 K) to determine if the mechanism of aromatic dealkylation changes with temperature. Additionally, <sup>13</sup>C<sub>2</sub>-p-xylene was co-reacted with <sup>12</sup>C-DME at 523 K so that the only <sup>13</sup>C-methyls were the two methyls on p-xylene. The isotopic compositions of olefin and aromatic products of reactions (1) and (4) are discussed in depth in Sections 3.1 and 3.2 and the time-on-stream dependence for reaction (1) is shown in Section S.3 of the Supplemental information. For the other reactions, the product isotopologue distributions are shown in Section S.4 of the Supplemental information. The total carbon converted in these experiments was less than 10 C% for all reactions (Table 2). For all the reactions performed, at 1 min time-on stream, ethene, propene, and C<sub>8+</sub> hydrocarbons accounted for 90-96% of the products formed, indicating that olefin methylation and cracking were suppressed (Table 2). Unless otherwise specified, all results shown in this work were collected at 1 min time-on-stream. While results at 1 min time-on-stream may still be in the induction period for MTH, the isotopologue distributions for the aromatic precursors examined at this time-on-stream contain fewer DME carbons incorporated into the aromatic ring compared to later times-on-stream. It is important to minimize the incorporation of DME carbons into the aromatic rings because it is unlikely that the incorporation of DME and aromatic methyl carbons into the ring is random. The models used for predictions of the <sup>13</sup>C-contents of ethene and propene, however, assume that <sup>13</sup>C-atoms in the aromatic ring follow a statistical distribution, and therefore, unless otherwise specified, only isotopic results at 1 min time-on stream are used.

# 3.1. Co-reaction of ${}^{13}C_2$ -p-xylene and ${}^{13}C$ -DME on H-ZSM-5

A major observable difference distinguishing the side-chain mechanism from either the paring or ring-expansion mechanisms for aromatic dealkylation reactions is that the paring and ringexpansion mechanisms result in the incorporation of an aromatic ring carbon into the olefin formed, whereas the side-chain mechanism only incorporates aromatic methyl carbons and carbons from the methylating agent (DME or methanol) into the olefin formed. In the co-reaction of  ${}^{13}$ C-DME with  ${}^{13}$ C<sub>2</sub>-p-xylene, all methyl carbons in the feed are  ${}^{13}$ C-labeled and aromatic ring carbons in the feed are <sup>12</sup>C-atoms.

#### 3.1.1. Isotopic composition of aromatics

Fig. 1c-f shows the isotopologue distribution of p-xylene, 1,2,4triMB, 4-ethyltoluene, and 1,2,4,5-tetraMB for the co-reaction of <sup>13</sup>C-DME with <sup>13</sup>C<sub>2</sub>-p-xylene at 523 K on H-ZSM-5. Nearly all of the p-xylene in the effluent contains only two <sup>13</sup>C-atoms, showing that the p-xylene in the effluent is almost entirely unreacted feed (Fig. 1c). Both 1,2,4-triMB and 1,2,4,5-tetraMB are predominantly methylation products of <sup>13</sup>C<sub>2</sub>-p-xylene, with 85.6% of 1,2,4-triMB and 76.8% of 1,2,4,5-tetraMB containing only three and four <sup>13</sup>C-atoms, respectively (Fig. 1d and f), suggesting that for the majority of these polyMBs, the benzene ring is comprised of all <sup>12</sup>C-atoms. The most abundant isotopologue of 4-ethyltoluene also contains three <sup>13</sup>C-atoms, showing that 4-ethyltoluene may form from methylation of <sup>13</sup>C<sub>2</sub>-p-xylene. A significant fraction of

Table 1

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Models used to predict the <sup>13</sup>C-content of olefins formed from 1,2,4-triMB, 1,2,4,5-tetraMB, and 4-ethyltoluene via different aromatic dealkylation mechanisms.
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Mechanism	Aromatic precursor	Olefin formed	
		Ethene (e)	Propene (p)
Paring 1	All	$\frac{{}^{13}M+{}^{13}D+2{}^{13}R}{4}$	$\frac{{}^{13}M+{}^{13}D+{}^{13}R}{3}$
Side-chain 2	1,2,4-triMB and 1,2,4,5-tetraMB	$\frac{{}^{13}M + {}^{13}D}{2}$	$\frac{1^{3}M+2^{13}D}{3}$
	4-Ethyltoluene	<sup>13</sup> <i>M</i>	$\frac{2^{13}M + {}^{13}D}{3}$
Paring 3	All	$\frac{\frac{13M+13R}{2}}{2}$	_
Ring expansion 4	1,2,4-triMB	$\frac{7^{13}M + 5^{13}D + 12^{13}R}{24}$	$\frac{3^{13}M + {}^{13}D + 2^{13}R}{6}$
	1,2,4,5-tetraMB	$\frac{5^{13}M + 3^{13}D + 8^{13}R}{16}$	$\frac{3^{13}M + {}^{13}D + 2^{13}R}{6}$
	4-Ethyltoluene	<sup>13</sup> M	$\frac{2^{13}M + {}^{13}D}{3}$

Table 2

Aromatic feed DME feed label	<sup>13</sup> C <sub>2</sub> -p-xylene			<sup>12</sup> C <sub>7</sub> -toluene	<sup>12</sup> C <sub>8</sub> -p-xylene	<sup>12</sup> C <sub>9</sub> -4-ethyltoluene		
	<sup>13</sup> C	<sup>13</sup> C	<sup>13</sup> C	<sup>12</sup> C	<sup>13</sup> C	<sup>13</sup> C	<sup>13</sup> C	<sup>13</sup> C
Temperature (K)	523	623	723	523	523	523	523	723
Conv. (C%) <sup>a</sup>	2.7	2.1	4.4	2.9	10.0	3.6	4.1	8.4
Selectivity (C%)								
Ethene	11.9	25.2	29.7	10.1	2.1	8.2	45.7	44.9
Propene	14.8	24.7	24.5	11.8	2.3	9.0	9.7	15.9
$C_4-C_7$ aliphatics	4.8	6.4	7.6	3.4	2.3	4.4	3.4	9.7
C <sub>2</sub> , aromatics <sup>b</sup>	68.6	437	38.2	744	93.3	78.4	41.2	29.4

Conversion and	product coloctivity	, for co reactions	of 75 02 kpa	of DME with 4	kPa of aromatic	at 522 722 V
Conversion and	product selectivity	V IOI CO-TEACTIONS	5 01 7.3-9.5 KPa (	JI DIVIE WILLI 4	KPd OI dIOIIIdUC	dl 323-723 K

<sup>a</sup> Based on overall conversion of DME and the aromatic co-feed.

<sup>b</sup> The aromatic co-feed present in the reaction effluent was not included in the assessment of product selectivity.



Fig. 1. Isotopologue distributions for the co-reaction of <sup>13</sup>C-DME with of <sup>13</sup>C<sub>2</sub>-p-xylene at 523 K for (a) ethene, (b) propene, (c) p-xylene, (d) 1,2,4-triMB, (e) 4-ethyltoluene, and (f) 1,2,4,5-tetraMB.

4-ethyltoluene (65.8%), however, does not contain exactly three  $^{13}\mathrm{C}\textsc{-}atoms$ , which shows that there are multiple routes to 4-ethyltoluene formation.

# 3.1.2. Isotopic composition of ethene and propene

For the co-reaction of  ${}^{13}$ C-DME with  ${}^{13}$ C<sub>2</sub>-p-xylene at 523 K on H-ZSM-5, 65.3% of ethene contains only one  ${}^{13}$ C-atom (Fig. 1a)

and 65.9% of propene contains only two <sup>13</sup>C-atoms (Fig. 1b), therefore, nearly 2/3 of both ethene and propene contain only one aromatic ring carbon ( $^{12}$ C), which is consistent with paring mechanisms 1e, 3e, and with the ring-expansion mechanism 4e in Schemes 1 and 2. While the incorporation of ring carbons into ethene and propene shows that the side-chain mechanism is not the dominant aromatic dealkylation mechanism under these

conditions, the paring and ring-expansion mechanisms cannot be differentiated and the predominant aromatic precursor to ethene and propene cannot be determined based solely on these results. A quantitative assessment of both the dominant aromatic dealkylation mechanism and the predominant precursor to ethene and propene formation is discussed in Section 3.3.

#### 3.1.3. Effect of temperature

The co-reaction of <sup>13</sup>C-DME with <sup>13</sup>C<sub>2</sub>-p-xylene on H-ZSM-5 was also performed at 723 K, and the isotopologue distributions for light olefins and aromatics in the effluent of this reaction are shown in Fig. 2. At these conditions, 89.7% of p-xylene in the effluent contained two <sup>13</sup>C-atoms, showing that the majority of p-xylene in the effluent was unreacted feed (Fig. 2c). Similar to the results at 523 K, a significant fraction of 1,2,4-triMB (55.7%) and 1,2,4,5-tetraMB (43.5%) produced at these reaction conditions are methylation products of the p-xylene co-feed, containing three and four <sup>13</sup>C-atoms, respectively (Fig. 2d and f). At 723 K, however, there is a higher fraction of isotopologues of these polyMBs containing more <sup>13</sup>C-atoms than the number of methyl groups, showing that at these reaction conditions, more <sup>13</sup>C-atoms are being incorporated into the aromatic ring of 1,2,4-triMB and

1,2,4,5-tetraMB. Additionally, 92.2% of 4-ethyltoluene contained at least four <sup>13</sup>C-atoms (Fig. 2e), showing that at higher temperatures ( $\sim$ 723 K), p-xylene methylation is not a major route for 4-ethyltoluene formation.

The majority of ethene and propene produced by the co-reaction of  $^{13}$ C-DME with  $^{13}$ C<sub>2</sub>-p-xylene on H-ZSM-5 at 723 K contains only one  $^{12}$ C-atom, originating from the aromatic ring of the  $^{13}$ C<sub>2</sub>-p-xylene feed (Fig. 2a and b). Compared to the isotopologue distributions of ethene and propene and 523 K, there is a higher fraction of all  $^{13}$ C ethene and propene at 723 K, most likely as a result of higher  $^{13}$ C content of the aromatics at 723 K compared to 523 K. The high fraction of ethene and propene containing only one  $^{12}$ C-atom at both 523 K and 723 K shows that aromatic dealkylation on H-ZSM-5 when a methylbenzene is co-reacted with DME results in the incorporation of an aromatic ring carbon into the olefin formed.

# 3.2. Co-reaction of <sup>12</sup>C-4-ethyltoluene and <sup>13</sup>C-DME on H-ZSM-5

4-Ethyltoluene was used as a co-feed to understand if and to what extent the side-chain mechanism contributes to light olefin production in MTH. The isotopologue distributions for light olefins



Fig. 2. Isotopologue distributions for the co-reaction of <sup>13</sup>C-DME with of <sup>13</sup>C<sub>2</sub>-p-xylene at 723 K for (a) ethene, (b) propene, (c) p-xylene, (d) 1,2,4-triMB, (e) 4-ethyltoluene, and (f) 1,2,4,5-tetraMB.



**Fig. 3.** Isotopologue distributions for the co-reaction of  ${}^{13}$ C-DME with of  ${}^{12}$ C-4-ethyltoluene at 523 K for (a) ethene, (b) propene, (c) p-xylene, (d) 1,2,4-triMB, (e) 4-ethyltoluene, and (f) 1,2,4,5-tetraMB at ( $\blacksquare$ ) 1, ( $\blacksquare$ ) 5, and ( $\square$ ) 10 min time-on-stream.

and aromatics for the reaction of <sup>13</sup>C-DME and <sup>12</sup>C-4-ethyltoluene at 523 K are shown in Fig. 3 at 1, 5, and 10 min time-on-stream.

#### 3.2.1. Isotopic composition at 1 min time-on-stream

Based on the side-chain mechanism (2e in Scheme 1), <sup>12</sup>C-4ethyltoluene should dealkylate and form all <sup>12</sup>C-ethene or the side-chain may undergo methylation by <sup>13</sup>C-DME and subsequently eliminate propene with only one <sup>13</sup>C-atom. At 1 min time-on-stream, 81.8% of ethene does have only <sup>12</sup>C-atoms and 38.2% of propene contains only one <sup>13</sup>C-atom (Fig. 3), which is consistent with the side-chain mechanism. For propene, however, the most abundant isotopologue contains two <sup>13</sup>C-atoms, which would be consistent with the paring mechanism assuming that incorporation of the <sup>12</sup>C-atom in propene results from activation of the aromatic ring.

At 1 min time-on-stream, 4-ethyltoluene contains a natural abundance of 1.1% <sup>13</sup>C, showing that the 4-ethyltoluene in the effluent is primarily unreacted feed (Fig. 3e). In contrast, 75.1% of 1,2,4,5-tetraMB at 1 min time-on-stream has three <sup>13</sup>C-atoms, suggesting that 4-ethyltoluene eliminates ethene to form toluene, which subsequently is methylated three times by <sup>13</sup>C-DME to form <sup>13</sup>C<sub>3</sub>-1,2,4,5-tetraMB (Fig. 3f). However, p-xylene and 1,2,4-triMB

do not follow this same pattern and have a significant fraction of isotopologues with 1–4 and 2–5  $^{13}$ C-atoms, respectively (Fig. 3c and d). The isotopologue distribution of toluene is not shown in Fig. 3 because the concentration of toluene in the reaction effluent was too low to accurately quantify the isotopologue distribution. Based on the results shown in Fig. 3c and d, it is unclear what mechanistic pathways form p-xylene and 1,2,4-triMB here.

## 3.2.2. Isotopic compositions at 5 and 10 min time-on-stream

With increasing time-on-stream, the <sup>13</sup>C-content of ethene, propene, p-xylene, 1,2,4-triMB, and 1,2,4,5-tetraMB increases (Fig. 3). The <sup>13</sup>C-content of 4-ethyltoluene, however, remains unchanged with increasing time-on-stream. The changing isotopologue distributions with time-on-stream show that the methylbenzenes in the aromatic hydrocarbon pool as well as the light olefins evolve with time-on-stream and become more <sup>13</sup>C-rich. In contrast, 90% of isotopologues of a methylation product of 4-ethyltoluene contained only one <sup>13</sup>C-atom at all times-on-stream. This product was determined to be a methylation product of 4-ethyltoluene based on its isotopologue distribution and because its concentration increased significantly when 4-ethyltoluene was co-fed with DME, compared to the co-reaction of DME with other

methylbenzenes. The absence of <sup>13</sup>C-atoms in 4-ethyltoluene and its methylation product show that these aromatics are not reformed at a rate as fast as 1,2,4-triMB or 1,2,4,5-tetraMB, suggesting that these ethylated aromatics are not co-catalytic. While the side-chain mechanism can occur in the presence of a 4-ethyltoluene, ethylated aromatics do not participate as co-catalysts in the MTH hydrocarbon pool mechanism on H-ZSM-5.

In the co-reaction of 4-ethyltoluene with DME at 523 K, 4-ethyltoluene initiates the aromatic hydrocarbon pool and dealkylation of 4-ethyltoluene to form toluene, which is subsequently methylated, results in the formation of MBs. These MBs can continue to react, undergoing repeated methylations and dealkylations and thus increasing the <sup>13</sup>C-content with increasing time-on-stream. As a result, both ethene and propene, which are formed primarily from MBs and not 4-ethyltoluene at later times-on-stream (5 and 10 min) also incorporate more <sup>13</sup>C-atoms. The evolution of the hydrocarbon pool for the co-reaction of <sup>12</sup>C-4-ethyltoluene and <sup>13</sup>C-DME at 523 K is depicted in Scheme 3.

# 3.2.3. *Effect of temperature*

The co-reaction of <sup>13</sup>C-DME and <sup>12</sup>C-4-ethyltoluene on H-ZSM-5 was also performed at 723 K. Due to rapid deactivation of the catalyst at these conditions (within 3 min time-on-stream), the product isotopologue distributions are only shown at 1 min timeon-stream (Fig. 4). For ethene, the isotopologues with zero and one <sup>13</sup>C-atoms have a similar fraction (41.4% and 35.1%, respectively, Fig. 4a), which is consistent with both the side-chain and paring mechanism. For propene, the most abundant isotopologue has only one <sup>12</sup>C-atom, consistent with the paring or ring-expansion mechanism (Fig. 4b), showing that while the side-chain mechanism does occur when 4-ethyltoluene is co-reacted with DME to form ethene, the paring or ring-expansion mechanism is also occurring in parallel to form propene. The most abundant isotopologue of p-xylene, 1,2,4-triMB, and 1,2,4,5-tetraMB contains 1, 2, and 3 <sup>13</sup>C-atoms, respectively, indicating that these methylbenzenes may form from ethene elimination from 4-ethyltoluene to form toluene, followed by sequential methylations of toluene by <sup>13</sup>C-DME (Fig. 4c, d, and f). Due to the observed fast deactivation of the catalyst at 723 K when 4-ethyltoluene is co-reacted with DME, it is likely that 4-ethyltoluene is a precursor to coke on H-ZSM-5, which is in agreement with results from Schulz [32], showing that ethylated and propylated benzenes were the predominant aromatics retained inside the deactivated H-ZSM-5 catalvst after the reaction of methanol at 543 K based on GC-MS analysis of organics extracted from the zeolite by dissolution in HF after reaction. Results in our work for the co-reaction of



**Scheme 3.** Depiction of the evolution of the hydrocarbon pool with increasing time-on-stream for the co-reaction of <sup>12</sup>C-4-ethyltoluene with <sup>13</sup>C-DME at 523 K on H-ZSM-5; ( $\bigcirc$ ) <sup>13</sup>C-atoms.

<sup>13</sup>C-DME and <sup>12</sup>C-4-ethyltoluene at both 523 K and 723 K suggest that while the side-chain mechanism does occur in the presence of ethylated aromatics, evidenced by the fraction of all <sup>12</sup>C-labeled ethene, a paring mechanism is also occurring in parallel, supported by the high fraction of ethene and propene containing both <sup>13</sup>C and <sup>12</sup>C-atoms.

# 3.3. Comparison of aromatic dealkylation mechanisms

Co-reactions of <sup>13</sup>C-DME were also performed with <sup>12</sup>C-toluene at 523 K, <sup>12</sup>C-p-xylene at 523 and 623 K, and <sup>12</sup>C-DME with <sup>13</sup>C<sub>2</sub>-p-xylene at 523 K (isotopologue distributions are shown in Figs. S.5 and S.6 of the Supplemental information) in addition to the co-reaction of <sup>13</sup>C-DME with <sup>13</sup>C<sub>2</sub>-p-xylene and <sup>12</sup>C-4-ethyltoluene at 523 and 723 K on H-ZSM-5 discussed above. In this set of reactions, the <sup>13</sup>C/<sup>12</sup>C composition of methyls (coming from both DME and the aromatic) in the feed is varied to distinguish between the paring and ring-expansion mechanism.

Parity plots of the different dealkylation mechanisms comparing the experimentally observed <sup>13</sup>C-content of ethene to the predicted <sup>13</sup>C-content of ethene from 1,2,4-triMB, 1,2,4,5-tetraMB, and 4-ethyltoluene from the different aromatic dealkylation mechanisms are shown in Figs. 5 and S.12 of the Supplemental information. Due to the change in dealkylation mechanism for ethene formation when 4-ethyltoluene is used as a co-feed compared to p-xylene as a co-feed (Section 3.2), the parity plots for ethene formation only show reactions in which in toluene or p-xylene were used co-feeds at temperatures ranging from 523 K to 723 K. While the isotopic results for ethene presented in Section 3.1 showed that nearly 2/3 of the ethene produced from the co-reaction of <sup>13</sup>C-DME with <sup>13</sup>C<sub>2</sub>-p-xylene contained only one ring carbon (Fig. 1e), the paring and ring-expansion mechanisms could not be distinguished from each other based on those results. By varying the  ${}^{13}C/{}^{12}C$ compositions of methyls (coming from both DME and the aromatic) and predicting the <sup>13</sup>C-content of ethene based on the four dealkylation mechanisms shown in Schemes 1 and 2, the parity plot in Fig. 5 and the mean absolute and relative errors shown in Table 3 show that the predicted <sup>13</sup>C-content of ethene coming from 1,2,4,5-tetraMB via the paring 1e mechanism is consistent with the observed <sup>13</sup>C-content of ethene and results in the lowest mean absolute and relative errors (Table 3) compared to the other aromatic dealkylation mechanisms and other aromatic precursors examined in this work. Both the mean absolute and relative error for the predicted <sup>13</sup>C-content of ethene coming from 4-ethyltoluene via the paring 1e mechanism are lower compared to the predicted <sup>13</sup>C-content of ethene from 4-ethyltoluene via other aromatic dealkylation mechanisms, showing that at these reaction conditions, 4-ethyltoluene most likely dealkylates via the paring 1e mechanism (Scheme 1), and not the side-chain 2e mechanism (Scheme 2). Comparing the predicted <sup>13</sup>C-content of ethene from the paring 1e mechanism, the mean absolute and relative error for 1,2,4,5-tetraMB is lower than that predicted when considering 1,2,4-triMB and 4-ethyltoluene as the predominant precursors to ethene, showing that while other aromatics may contribute to ethene formation, 1,2,4,5-tetraMB is the predominant precursor to ethene in MTH conversion on H-ZSM-5.

Parity plots for the three different mechanisms for propene formation are shown in Figs. 5 and S.13 of the Supplemental information. These parity plots include experimentally observed <sup>13</sup>C-contents for propene for the co-reaction of DME with toluene, p-xylene, and 4-ethyltoluene between 523 and 723 K. For propene formation from 1,2,4,5-tetraMB, the model predictions for the paring 1p mechanism fit the best with the observed <sup>13</sup>C-content of propene (Fig. 5). Both the mean absolute and relative errors for propene formation from the paring 1p mechanism are lower compared to the side-chain 2p and ring-expansion 4p mechanisms



Fig. 4. Isotopologue distributions for the co-reaction of <sup>13</sup>C-DME with of <sup>12</sup>C-4-ethyltoluene at 723 K for (a) ethene, (b) propene, (c) p-xylene, (d) 1,2,4-triMB, (e) 4-ethyltoluene, and (f) 1,2,4,5-tetraMB.



**Fig. 5.** Parity plots for the predicted vs. experimentally observed <sup>13</sup>C-content for ethene (squares) and propene (circles) from 1,2,4,5-tetraMB via the paring 1e and 1p mechanisms, respectively, for the co-reactions of (**●**) <sup>12</sup>C-DME with <sup>13</sup>C<sub>2</sub>-p-xylene, (**●**) <sup>13</sup>C-DME with <sup>13</sup>C<sub>2</sub>-p-xylene, (**●**) <sup>13</sup>C-DME with <sup>12</sup>C-p-xylene at 523 K, (**●**) <sup>13</sup>C-DME with <sup>13</sup>C<sub>2</sub>-p-xylene at 623 K, (**●**) <sup>13</sup>C-DME with <sup>13</sup>C<sub>2</sub>-p-xylene at 723 K, (**●**) <sup>13</sup>C-DME with <sup>12</sup>C-4-ethyltoluene at 523 K, and (**●**) <sup>13</sup>C-DME with <sup>12</sup>C-4-ethyltoluene at 723 K.

(Table 4). This result is in agreement with ethene formation occurring through paring 1e mechanism, as both the paring 1e and 1p mechanisms share common intermediates. Similar to ethene, for the paring 1p mechanism, the mean absolute and relative error for 1,2,4,5-tetraMB is lower than that of 1,2,4-triMB and 4-ethyltoluene (Table 4), leading us to postulate that 1,2,4,5-tetraMB is the predominant aromatic precursor to propene formation.

The parity plots in Figs. 5 and S.12 and S.13 of the Supplemental information quantitatively show that aromatic dealkylation in MTH conversion on H-ZSM-5 occurs primarily through the paring mechanism (1e and 1p in Scheme 1) and the paring mechanism is the dominant mechanism for light olefin formation through aromatic dealkylation on H-ZSM-5 for a 200 K range in temperature. Although the isotopic results in this work are only presented for data collected at 1 min time-on-stream, we expect that there should not be any significant change in the mechanism of aromatic dealkylation with increasing time-on-stream because tetraMBs are still retained within the zeolite pores even after 14 days time-onstream for the reaction of methanol on H-ZSM-5 at 643 K [9]. The results in this work show that ethene is formed from one aromatic ring carbon and the other carbon has a 50% chance of coming from the methylating agent and a 50% chance of coming from an aromatic methyl carbon. Propene is formed from one aromatic ring carbon, one aromatic methyl carbon, and one carbon coming from the methylating agent. Aromatic dealkylation studies for MTO

#### Table 3

Absolute and relative error for the model predictions of the <sup>13</sup>C-content of ethene formed from various aromatic precursors via the different aromatic dealkylation mechanisms compared to the experimentally observed <sup>13</sup>C-content of ethene when varying isotopic compositions of DME are co-reacted with p-xylene or toluene at 523–723 K. Units of absolute and relative error are percentage points of <sup>13</sup>C and%, respectively.

	Mean absolute error			Mean relative error		
	124triMB	1245tetraMB	4ET	124triMB	1245tetraMB	4ET
Paring 1e	8.0	4.0	5.8	21.9	8.9	15.6
Side-chain 2e	30.1	33.3	27.8	87.6	82.1	110.9
Paring 3e	16.8	9.1	11.2	61.2	34.3	45.0
Ring exp. 4e	9.5	4.8	27.8	28.5	14.0	110.9

#### Table 4

Absolute and relative error for the model predictions of the <sup>13</sup>C-content of propene formed from various aromatic precursors via the different aromatic dealkylation mechanisms compared to the experimentally observed <sup>13</sup>C-content of propene when varying isotopic compositions of DME are co-reacted with p-xylene, toluene, or 4-ethyltoluene at 523–723 K. Units of absolute and relative error are percentage points of <sup>13</sup>C and%, respectively.

	Mean absolute error			Mean relative error		
	124triMB	1245tetraMB	4ET	124triMB	1245tetraMB	4ET
Paring 1e	6.9	3.8	10.3	15.5	6.6	19.2
Side-chain 2e	25.5	26.9	23.1	47.2	45.2	52.1
Ring exp. 4e	13.4	6.9	23.1	44.3	27.6	52.1

conversion on large-pore materials H-BEA and H-SAPO-5 have also shown that aromatic ring carbons are incorporated into light olefins. The methods used in this study can also be applied to these catalysts to examine if the aromatic dealkylation mechanism changes with zeolite structure – for example, does a larger catalyst pore-size allow for the space-demanding ring-expansion mechanism to operate?

To determine the mechanism of aromatic dealkylation, five  ${}^{12}C/{}^{13}C$  feed compositions were used so that incorporation of DME methyls, aromatic methyls, and aromatic ring carbons into ethene and propene could be differentiated. Mechanism discrimination through the methods reported in work is applicable to any reaction system in which a single product species maybe be formed through multiple mechanisms or pathways as long the isotopic composition of the reactants can be varied in such way to allow for mechanism differentiation. Using these methods, we identify the mechanism and the predominant precursors to light olefin synthesis in methanol-to-hydrocarbons conversion and postulate that experimental conditions or co-feeds that enhance the resulting concentration of tri- and tetra-methylbenzenes in H-ZSM-5 will result in a concomitant increase in the selectivity to ethylene and propylene.

#### 4. Conclusions

Co-reactions DME with toluene, p-xylene, and 4-ethyltoluene with varying <sup>13</sup>C/<sup>12</sup>C feed compositions were performed to determine the mechanism of aromatic dealkylation in MTH conversion on H-ZSM-5. The co-reaction of <sup>13</sup>C-DME and <sup>13</sup>C<sub>2</sub>-p-xylene at 523 K and 723 K resulted in a high fraction of ethene and propene containing only one <sup>12</sup>C-atom, originating from the aromatic ring carbon of the <sup>13</sup>C<sub>2</sub>-p-xylene feed, showing that the mechanism of aromatic dealkylation on H-ZSM-5 results in the incorporation of an aromatic ring carbon into light olefins, which is consistent with both the paring and ring-expansion mechanisms. For the co-reaction of <sup>13</sup>C-DME and <sup>13</sup>C-4-ethyltoluene at 523 K and 723 K, the high fraction of ethene with only <sup>12</sup>C-atoms suggests that ethene can be formed via the side-chain mechanism, however, both 4-ethyltoluene and its methylation product incorporated negligible amounts of <sup>13</sup>C-atoms, indicating that while these species can undergo side-chain dealkylation, they are not co-catalytic in that they are not reformed fast enough to participate in the aromatic hydrocarbon pool.

Effluent isotopologue distributions of 1,2,4-triMB, 1,2,4,5-tetraMB, and 4-ethyltoluene were used to predict the <sup>13</sup>C-content of ethene and propene for co-reactions of DME with toluene. p-xylene, and 4-ethyltoluene where either DME or the aromatic was <sup>13</sup>C-labeled. Through the use of quantitative models presented in Table 1 to predict the <sup>13</sup>C-content of ethene and propene from various aromatic precursors, the mechanism of aromatic dealkylation in MTO conversion on H-ZSM-5 was determined. The results shown in Tables 3 and 4 quantitatively show that the paring mechanism for light olefin formation is occurring and that 1,2,4,5-tetraMB is the predominant precursor to ethene and propene formation for MTO conversion on H-ZSM-5 over a 200 K temperature range. The paring 1e and 1p mechanisms (Scheme 1) for ethene and propene formation can predict the <sup>13</sup>C-content of ethene and propene from the effluent isotopic composition of 1,2,4,5-tetraMB with greater accuracy than either the side-chain or ring-expansion mechanisms for the reaction of DME with three different aromatic co-feeds, five different <sup>13</sup>C/<sup>12</sup>C feed compositions and a 200 K range in temperature, showing that the paring mechanism is the dominant mechanism of aromatic dealkylation for MTO conversion on H-ZSM-5.

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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.2013.11.003.

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