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# Observation of Heptamethylbenzenium Cation over SAPO-Type Molecular Sieve DNL-6 under Real MTO Conversion Conditions

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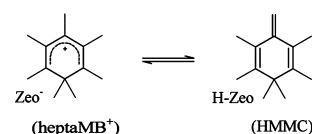
## S Supporting Information

**ABSTRACT:** The heptamethylbenzenium cation (heptaMB<sup>+</sup>) has been speculated to be one of the most important active intermediates involved in the “hydrocarbon pool” mechanism of methanol-to-olefin (MTO) conversion. By the use of DNL-6, a newly synthesized SAPO-type molecular sieve with large cavities, heptaMB<sup>+</sup> has for the first time been directly observed during methanol conversion under real working conditions. <sup>13</sup>C-labeling experiments suggested that olefin formation mediated by heptaMB<sup>+</sup> mainly follows the side-chain mechanism.

Methanol-to-olefin (MTO) conversion over acidic zeolites or zeotype molecular sieves has attracted much attention over the past few decades.<sup>1</sup> The mechanism governing the conversion of methanol molecules into olefins within zeolite cages or channels has drawn considerable interest because of the concern for C–C bond formation from C1 reactants.<sup>2</sup> Direct formation of a C–C bond by C1 species derived from methanol has been proved to be energetically unfavorable.<sup>3</sup> Alternatively, the “hydrocarbon pool” (HCP) mechanism,<sup>4</sup> an indirect pathway, avoids high energy barriers and consequently has garnered attention due to evidence from experimental observations and theoretical calculations.<sup>1,2,5</sup> The generally accepted HCP mechanism involves a series of steps, including methanol addition to the HCP species and the elimination of olefins from the pool. Polymethylbenzenes and the corresponding carbenium ions have been proposed as the active HCP species.<sup>2a,5</sup> With the aid of solid-state NMR spectroscopy (ssNMR), some carbenium ions have been identified as intermediates confined within zeolite catalysts, such as the cations 1,3-dimethylcyclopentadienyl, indanyl, and 1,1,2,4,6-pentamethylbenzenium within HZSM-5; heptamethylbenzenium (heptaMB<sup>+</sup>) within H-beta, and heptamethylcyclopentenyl (heptaCP<sup>+</sup>) within SAPO-34.<sup>6</sup> However, the formation of most of these carbenium ions during methanol conversion was proved via an indirect way; the direct observation of such HCP species and their roles in methanol conversion over zeolites or SAPO catalysts under real working conditions is still a huge challenge.

HeptaMB<sup>+</sup> (Scheme 1) is of particular importance as a reaction intermediate in the MTO reaction.<sup>1b,7</sup> Some advances in its synthesis have been made by the coreaction of benzene

Scheme 1. HeptaMB<sup>+</sup> and Its Deprotonated Form HMMC



and methanol over H-beta, H-MCM-22, and H-mordenite.<sup>6d,8</sup> However, there are still no reports that directly verify the existence of heptaMB<sup>+</sup> in MTO conversion. Furthermore, because of diffusion limitations, the coreaction of benzene and methanol, which was performed within H-beta, a 12-ring structure, is unfeasible for molecular sieves with small 8-ring pore openings, such as SAPO-34. The buildup of HCP species (especially heptaMB<sup>+</sup>) in catalysts with small pores is more mysterious. To understand MTO catalysis fully and elucidate the energetically favorable HCP mechanism, it is crucial to observe and identify this carbenium ion under real MTO reaction conditions. Difficulties in the direct observation of heptaMB<sup>+</sup> formed in the nanocage of SAPO-34 seem to be related to the very high reactivity of heptaMB<sup>+</sup> and the relatively weak acidity of SAPO catalysts relative to liquid-phase acids or zeolites. A catalyst with a particular structure and/or an acid environment might be needed to accommodate and stabilize this bulky carbenium cation.

It is also of great significance to know how olefins can be generated from HCP species such as heptaMB<sup>+</sup> during MTO conversion. Two types of mechanisms have been proposed, both based on the results obtained when cofeeding benzene or methylbenzenes and methanol. Haw and co-workers studied the reactions of ethylbenzene, cumene, 1,2,4-trimethylbenzene, durene, pentamethylbenzene, and hexamethylbenzene and also the coreactions of these aromatics with <sup>13</sup>C-methanol over H-beta. They concluded that the side-chain methylation mechanism is the predominant route to form olefins.<sup>9</sup> They also carried out theoretical calculations on the side-chain mechanism.<sup>10</sup> Kolboe and co-workers conducted the coreaction of benzene and <sup>13</sup>C-methanol over H-beta at a relatively low reaction temperature and concluded that the paring reaction mechanism is the major reaction route for olefin formation.<sup>8a,11</sup>

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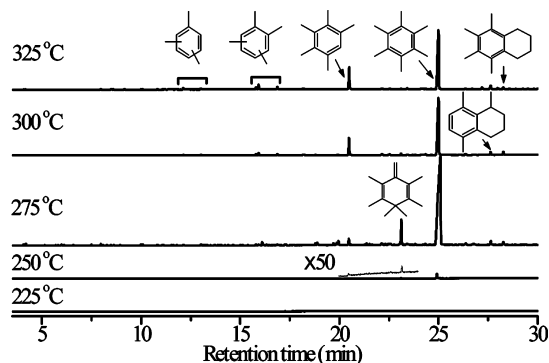


Very recently, Kolboe's group extended their research to H-MCM-22 and H-mordenite and drew similar conclusions.<sup>8b</sup>

DNL-6, an 8-ring SAPO molecular sieve with an RHO structure possessing large  $\alpha$  cages and relatively high acid concentration and strength, has recently been synthesized.<sup>12</sup> In this work, by the use of this novel SAPO molecular sieve as the catalyst, the heptaMB<sup>+</sup> ion has been directly observed as the HCP species confined in the catalyst during methanol conversion, and thus, its significance as the reaction intermediate during real MTO conversion conditions has been witnessed. These observations were consolidated by combining ssNMR and GC-MS. Furthermore, <sup>12</sup>C-methanol/<sup>13</sup>C-methanol switch experiments were used to investigate the olefin formation mechanism mediated by heptaMB<sup>+</sup>.

The DNL-6 synthesis procedure was reported in a previous study.<sup>12</sup> Characterization of the catalyst is described in Figures S1–S7 in the Supporting Information (SI). DNL-6 was shown to be an effective catalyst for MTO conversion (see Figures S8–S11). The induction period was both observed and sustained over a long period at a low reaction temperature, consistent with the results obtained from MTO conversions over the extensively studied SAPO-34 and ZSM-5.<sup>13</sup> The selectivity for light olefins (ethene, propene, and butenes) was 70–90% at low temperature with low methanol conversion. Reactions performed at higher temperatures gave rise to increased methanol conversion, but the light olefin selectivity decreased slightly because of the formation of light alkane byproducts.

The materials confined in the catalyst cages were analyzed by GC-MS following the method introduced by Guisnet.<sup>14</sup> As shown in Figure 1, the confined materials at 325 and 300 °C



**Figure 1.** GC-MS chromatograms of the organic materials retained in a DNL-6 catalyst after methanol conversion for 60 min. MeOH weight hourly space velocity (WHSV) = 2.0 h<sup>-1</sup>; He/MeOH molar ratio = 3.

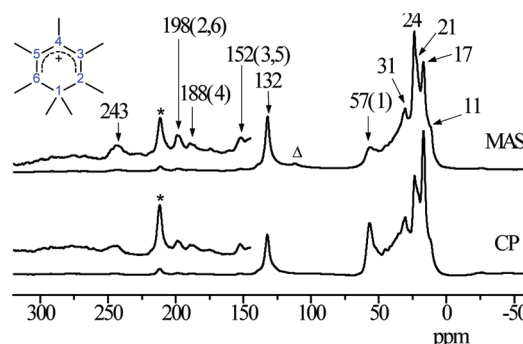
were mainly methylbenzenes. Among them, hexamethylbenzene (hexaMB) and pentamethylbenzene (pentaMB) were predominant, with trace amounts of trimethylbenzene (triMB) and tetramethylbenzene (tetraMB); toluene and xylene were almost undetectable. The peaks representing polycyclic aromatic hydrocarbons were very weak. Only parts of them could be clearly recognized, such as tri- and tetramethyl-substituted tetrahydronaphthalene. Some large molecules with molecular weights of 270–300 Da were also detected (Figure S12), but no reasonable matches in the NIST08 mass spectral library could be found.

At lower reaction temperatures (i.e., 275 °C), the intensity of the peak attributed to hexaMB increased while that of pentaMB decreased (Figure 1). Noticeably, a new peak appeared at a

retention time of 23 min, representing a new confined molecule. This substance presented exactly the same mass spectrum (Figure S13) as hexamethylmethylenecyclohexadiene (HMMC),<sup>8a</sup> the deprotonated form of heptaMB<sup>+</sup> (Scheme 1), implying the possible generation and confinement of this reaction intermediate in DNL-6. For the reactions performed at temperatures lower than 275 °C, only a small amount of HMMC was detected because of low methanol conversion and very slight coke deposition. Notably, even at very low intensity, HMMC could still be detected at 250 °C (Figure 1 inset).

To verify the above-mentioned heptaMB<sup>+</sup>/HMMC generation, a parallel experiment was also conducted to synthesize HMMC over H-beta using an indirect pathway (coreaction of benzene and methanol).<sup>7</sup> The generated HMMC species was analyzed and compared to the compound confined in DNL-6 after methanol conversion. The retention times and mass spectra were identical, confirming the formation of HMMC.

ssNMR measurements also proved heptaMB<sup>+</sup> formation during methanol conversion. <sup>13</sup>C magic-angle-spinning (MAS) and cross-polarization (CP)/MAS NMR spectra (Figure 2)



**Figure 2.** <sup>13</sup>C MAS and CP/MAS NMR spectra of the DNL-6 catalyst after <sup>13</sup>C-methanol conversion at 275 °C for ~50 min. \* indicates the spinning sideband and Δ the background.

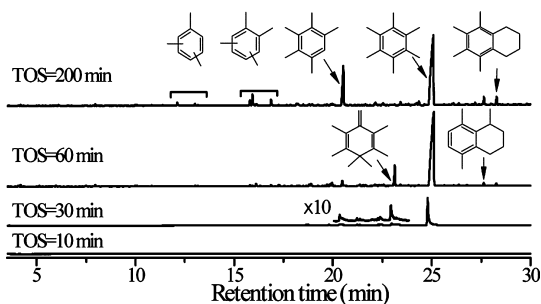
showed signals that could possibly stem from this carbenium ion. The resonance peaks with chemical shifts at 198, 188, and 152 ppm were assigned to C-2,6, C-4, and C-3,5 of the heptaMB<sup>+</sup> ion, respectively (Figure 2 inset).<sup>6d</sup> The chemical shift of C-1 was reported to be 58 ppm.<sup>6d</sup> However, the chemical shift of surface methoxy groups also covers the range 53–59 ppm.<sup>15</sup> As a result, a broad peak appeared near 57 ppm. All this evidence suggested the presence of heptaMB<sup>+</sup>, consistent with the GC-MS analysis of the retained organic materials. To our knowledge, this is the first time that heptaMB<sup>+</sup> and its deprotonated form, HMMC, have been detected during methanol conversion over SAPO-type molecular sieves. Both ssNMR and GC-MS yielded matching identifications of this intermediate. Interestingly, in the spectrum of the catalyst after <sup>13</sup>C-methanol conversion, signals also appeared at 243 and 152 ppm, representing another very important intermediate of methanol conversion, the polymethylcyclopentenyl ion. In previous work,<sup>6e</sup> this ion was formed by the reaction of acetone over SAPO-34, but with the use of DNL-6, it could also be detected under real MTO conversion conditions.

Theoretical calculations have shown that bulky carbenium ions can be well-accommodated within zeolite frameworks having large channels or cages.<sup>16</sup> The observation of carbenium cations in DNL-6 might be attributed to the presence of large cages and also to the acidity of this new SAPO molecular sieve.

Its body-centered cubic  $\alpha$  cage ( $\sim 10.4$  Å in diameter) is larger than the *cha* cage ( $6.7 \times 10$  Å) of SAPO-34, which avoids any possible steric constraint imposed by the zeolite framework on the formation of bulky carbenium ions such as heptaMB<sup>+</sup> and polymethylcyclopentenyl ion. Elemental analysis of DNL-6 by X-ray fluorescence (XRF) gave a molar composition of  $\text{Si}_{0.144}\text{Al}_{0.493}\text{P}_{0.362}\text{O}_2$ . The very high acidity of DNL-6 was predicted on the basis of the presence of three Si atoms per cage (24 T atoms) and all of the Si atoms in the coordination state of Si (4Al) (Figure S5 and ref 12), assuming that one Si corresponds to one acid site. By examination of the isotropic  $^{13}\text{C}$  chemical shift of the carbonyl carbon of acetone, a well-established method for measuring acidity,<sup>17</sup> the high acid strength of DNL-6 was also confirmed. Generally, the adsorption of acetone on Brønsted acid sites results in the formation of a hydrogen bond between the carbonyl oxygen and the acidic hydroxyl group. The corresponding downfield shift of the carbonyl carbon  $^{13}\text{C}$  signal has been employed to evaluate acid strength.<sup>17</sup> It has been reported that the chemical shift of the carbonyl carbon of the adsorbed acetone is 217 ppm for SAPO-34;<sup>6c</sup> this value for the SAPO catalyst used in this study was 223 ppm (Figure S7), which is higher than that of SAPO-34 and comparable with those of silicoaluminate zeolites such as ZSM-5 (224 ppm<sup>17a</sup>). This implies that the acidity of DNL-6 is stronger than that of SAPO-34 and close to or even stronger than that of silicoaluminate zeolites. The formation and stabilization of the heptaMB<sup>+</sup> possibly benefits from the ideal surroundings provided by DNL-6, namely, very high acidity and large cage space.

Notably, a shoulder peak at 232 ppm was also observed in the  $^{13}\text{C}$  MAS NMR spectra (Figure S7). A chemical shift in this range is typical for acetone interacting with Lewis acid sites.<sup>17c,d</sup> However, extraframework aluminum was not observed in DNL-6, as evidenced by the  $^{27}\text{Al}$  MAS NMR results (Figure S4). More detailed studies on the distribution and coordination states of Si, Al, and P atoms in DNL-6 are in progress and will be correlated with theoretical calculations.

A detailed study revealed the change in materials retained with reaction time during MTO conversion at 275 °C (Figure



**Figure 3.** GC–MS chromatograms of the organic materials retained in DNL-6 after methanol conversion at 275 °C. MeOH WHSV = 2.0 h<sup>−1</sup>; He/MeOH = 3.

3). The peak intensities for the retained materials increased with reaction time, except for HMMC, whose concentration (peak intensity) increased during the first hour, reached a maximum, and then began to decrease until the peak disappeared, at which point the concentration of HMMC was negligible. This precisely corresponds to the evolution of the catalytic activity, suggesting that heptaMB<sup>+</sup>/HMMC may act as the reaction intermediate during MTO conversion.

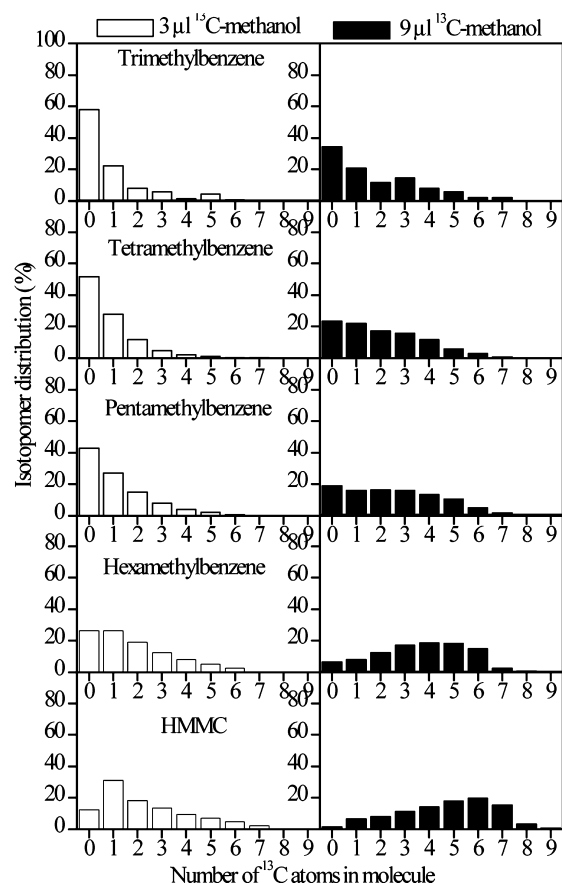
The one-step geminal methylation of hexaMB formed very active heptaMB<sup>+</sup>/HMMC species. These may go through further methylation and/or rearrangement to form larger reaction intermediates that could eliminate olefins or age to polycyclic coke species by hydrogen transfer and cyclization.<sup>8,18</sup> Although only small amounts of polycyclic aromatics were detected in DNL-6, its  $\alpha$  cage actually could accommodate up to five or six cyclic and graphene-like coke species, which would be difficult to be extracted with  $\text{CH}_2\text{Cl}_2$ . UV–vis spectroscopy of the deactivated catalyst supported this speculation. These coke species might block the diffusion path of methanol within the cages, reducing contact with the reaction center and ultimately causing the deactivation of DNL-6, as happens during MTO conversion over SAPO-34.<sup>1,19</sup> As a result, the methylation of polymethylbenzenes would not proceed. This is in line with the observations that large amounts of pentaMB and hexaMB were occluded in the cages but no heptaMB<sup>+</sup>/HMMC was formed when the catalyst was completely deactivated. The HMMC/hexaMB and hexaMB/pentaMB ratios were plotted against time on stream (TOS) (Figure S14), and the results were consistent with the above discussion.

The reactivity and role of heptaMB<sup>+</sup>/HMMC under real MTO conversion conditions were followed by  $^{12}\text{C}$ -methanol/ $^{13}\text{C}$ -methanol switch experiments (for the detailed procedure, see the SI). Injection of  $^{13}\text{C}$ -methanol generated olefin products containing large amounts of  $^{12}\text{C}$  atoms (Figure S15), suggesting that they were formed through the interaction of  $^{13}\text{C}$ -methanol with “hydrocarbon pool” species instead of direct coupling of  $^{13}\text{C}$ -methanol.<sup>20</sup> The isotopic distribution of the confined species (triMB, tetraMB, pentaMB, hexaMB, and HMMC; Figure 4) indicates that more  $^{13}\text{C}$  atoms from labeled methanol appeared in polymethylbenzene than in the less-substituted methylbenzenes, especially HMMC, which presented the highest  $^{13}\text{C}$  content among the polymethylbenzenes. This further proved the feasibility of methanol conversion following the hydrocarbon pool mechanism, which involves the key step of methylation of hexaMB to form heptaMB<sup>+</sup> for further elimination of olefin products.

One notable observation is that most of the  $^{13}\text{C}$  atoms incorporated into the confined polymethylbenzenes were located in the methyl group rather than in the benzene ring (see Figure S16 and the accompanying discussion). This implies that the contraction and expansion of the cyclic intermediate suggested in the paring mechanism is actually harder to realize in methanol conversion catalyzed by DNL-6. Thus, a side-chain methylation mechanism should be the predominant route for olefin formation from the polymethyl-substituted “hydrocarbon pool” species.<sup>9</sup> However, the paring mechanism during MTO conversion cannot be completely ruled out. Polymethylcyclopentenyl cations, the most important carbenium intermediates of the paring mechanism,<sup>8</sup> were also observed in the  $^{13}\text{C}$  MAS NMR spectra. A broader isotopic distribution of the aromatics with fewer methyl substitutions (e.g., isotopomers with five to seven  $^{13}\text{C}$  atoms in triMB) was also detected. It should be mentioned that only traces of triMB were detected in DNL-6 (Figure 1).

In conclusion, with the aid of ssNMR and GC–MS measurements, the formation of heptaMB<sup>+</sup>/HMMC under real MTO conversion conditions over a SAPO molecular sieve was directly observed and verified by employing as the catalyst the recently synthesized DNL-6 with large cavities. Very big supercages and extremely high acid concentrations were responsible for the stabilization of this bulky intermediate in





**Figure 4.** Isotopic distribution of materials retained in the DNL-6 catalyst upon which  $^{13}\text{C}$ -methanol was injected after continuous-flow  $^{12}\text{C}$ -methanol conversion for 60 min at 275 °C. MeOH WHSV = 2.0  $\text{h}^{-1}$ ; He/MeOH = 3.

the cage of an RHO-type SAPO molecular sieve. This finding supported the HCP mechanism of olefin generation with the involvement of heptaMB<sup>+</sup>/HMMC as the hydrocarbon pool species. Evidence from the  $^{12}\text{C}/^{13}\text{C}$ -methanol switch experiments suggested a side-chain methylation mechanism as the main reaction route for olefin production during MTO conversion over DNL-6.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental section, characterization data, and additional results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ ACKNOWLEDGMENTS

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