



# Heptamethylbenzenium cation formation and the correlated reaction pathway during methanol-to-olefins conversion over DNL-6



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## ABSTRACT

Methanol conversion over SAPO molecular sieve DNL-6 was investigated from the view point of the reaction mechanism. The organic materials confined in the cavities of DNL-6 were mostly polymethylbenzenes. By combination of in situ NMR study with ex situ GC–MS measurements, the structure of heptamethylbenzenium ion (heptaMB<sup>+</sup>) formed during MTO reaction was definitely confirmed. Further evidences from the mass spectra and <sup>13</sup>C solid-state NMR spectra in the isotopic switch experiments showed that the side chain methylation mechanism was the main reaction route for olefin formation from hydrocarbon pool species.

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## 1. Introduction

Methanol-to-olefins (MTO) reaction over acidic zeolites or zeotype molecular sieves has been a very important process for light olefins production from non-petrochemical resources, such as natural gas or coal [1–4]. Over the past decades, considerable efforts have been devoted to the understanding of MTO reaction mechanism concerning the C–C bond formation from C1 reactants [5,6]. The direct mechanism concerning the first C–C bond formation via various C1 species derived from methanol has been proposed to be energetically unfavorable [7]. Nowadays, the “hydrocarbon pool” (HCP) mechanism [8–10], an alternative pathway avoiding high energy barriers, has been widely accepted. Two reaction routes for olefins generation, paring mechanism and side-chain methylation mechanism, have been proposed, in which MTO reaction goes through a series of steps including methanol addition to the HCP species and the elimination of olefins from the HCP species [10]. Cyclic organic species, polymethylbenzenes, polymethylcyclopentadiene and their corresponding carbenium ions have been proposed to be the active HCP species [11–13]. However, the direct evidences of the roles that these HCP species play in methanol activation and product formation under real working conditions are still required for the deep understanding of detailed MTO reaction mechanism (Scheme 1).

Heptamethylbenzenium ion (heptaMB<sup>+</sup>) is of particular importance as a reaction intermediate in the MTO reaction [10]. The formation of heptaMB<sup>+</sup> in the cavities or channels of zeolites were evidenced earlier by co-reaction of benzene and methanol over H-beta, H-MCM-22 and H-mordenite [14–16]. Until very recently, the direct verification of the heptaMB<sup>+</sup> formation during methanol to olefin conversion was accomplished for the first time by employing DNL-6 (RHO topology) as the catalyst, a novel SAPO molecular sieve possessing large cavities connected with 8-ring window and high acid concentration and strength [17]. Based on this progress, it was possible to study the reactivity and the role of heptaMB<sup>+</sup> at different stages of MTO reaction. At the same time, it was also of great significance to know how olefins were generated during MTO conversion with the participation of heptaMB<sup>+</sup>. As a continuous work of our previous research [17], some further studies were conducted in the present contribution to confirm the structure and reactivity of this important carbenium cation, heptaMB<sup>+</sup>. New evidences from NMR and GC–MS investigations were obtained and used to correlate the generation of heptaMB<sup>+</sup> to the catalytic cycle of MTO reaction for olefin formation. Detailed reaction route was discriminated by the aid of the <sup>12</sup>C/<sup>13</sup>C switch experiments, solid-state NMR and mass spectrometry.

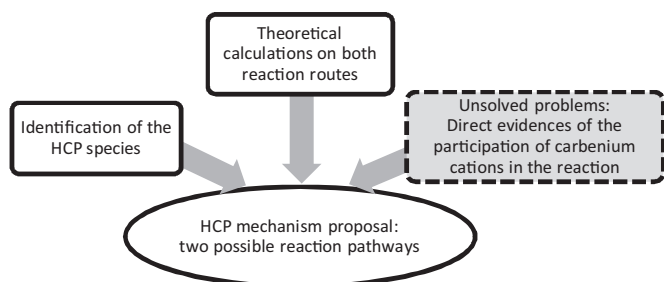
## 2. Experimental

### 2.1. Catalyst preparation and characterization

The synthesis procedure and characterization of DNL-6 have been reported previously [17,18]. H-beta with Si/Al of 12 was

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**Scheme 1.** Development of hydrocarbon pool mechanism of MTO over zeolites.

obtained commercially from Nankai University catalyst Co., Ltd. The chemical composition of the catalysts was determined with X-ray fluorescence (XRF) spectrometer (Philips Magix-601).

## 2.2. Methanol conversion and co-reaction of methanol and benzene

The as-synthesized DNL-6 was calcined at 550 °C for 4 h to remove the template, and then was extruded and sieved into small particles in 40–80 meshes. Methanol-to-olefins conversion was performed on a fixed-bed quartz tubular reactor under atmospheric pressure. The reactions were carried out at the temperature range of 225–325 °C. The methanol was fed by passing the carrier gas (He) through a methanol saturator maintained at 33 °C. The molar ratio of carrier gas to methanol was about 3. The WHSV of methanol was 2.0 h<sup>-1</sup>. The effluent products from reactor were kept warm and analyzed online by gas chromatography equipped with a PoraPLOT Q-HT capillary column and a FID detector.

The co-reaction of methanol and benzene over H-beta were carried out at 235 and 245 °C. The molar ratio of MeOH to benzene is about 7 and WHSV of MeOH is 0.9 h<sup>-1</sup>. The carrier gas (N<sub>2</sub>) to methanol ratio is about 30 (in mol). The co-reactions were conducted for 1.5 min to obtain the HMMC species by following the procedure reported in Ref. [15].

## 2.3. Confined organics determination with GC-MS and <sup>13</sup>C solid-state MAS NMR

The hydrocarbons retained in the catalyst were analyzed by GC-MS after dissolving the discharged catalyst in 20% HF solution and extracting the organics in CH<sub>2</sub>Cl<sub>2</sub>. This procedure followed the method introduced by Guisnet et al. [19].

<sup>13</sup>C solid-state NMR measurements were performed on a Varian Infinityplus-400 spectrometer equipped with a 5 mm MAS probe at a resonance frequency of 100.5 MHz with a spinning rate of 8 kHz. <sup>13</sup>C MAS NMR spectra were recorded using high-power proton decoupling. A 2700 scans were accumulated with a  $\pi/4$  pulse width of 1.8  $\mu$ s and a 4 s recycle delay. <sup>1</sup>H → <sup>13</sup>C CP/MAS NMR spectra were performed with a contact time of 2 ms, a recycle delay of 1 s, and 2100 scans. The chemical shifts of <sup>13</sup>C NMR spectra were referenced to adamantane with the upfield methine peak at 29.5 ppm.

The catalyst sample used in <sup>13</sup>C solid-state NMR experiments was prepared by employing <sup>13</sup>C-methanol as reactant. In order to eliminate the influence of methoxy groups on the structure confirmation of heptaMB<sup>+</sup> cation, the feed was switched to <sup>12</sup>C-methanol and allowed to react for further 3 min after <sup>13</sup>C-methanol reaction for a predetermined time. The reactor containing the catalyst sample was removed from the feeding line and the catalyst sample was immediately put into the liquid nitrogen. The transfer should be as quick as possible to prevent the active intermediates from further transformation. The typical time for the transfer was about 5–30 s. After the liquid nitrogen evaporated, the container was sealed and

moved to glove box for transferring the catalyst sample to an NMR probe without exposure to ambient air.

In the <sup>12</sup>C/<sup>13</sup>C switch experiments, the <sup>12</sup>C-methanol was fed into the reactor to build up <sup>12</sup>C-hydrocarbon pool species in the cavities of DNL-6, and then the feeding of <sup>12</sup>C-methanol was stopped and the reactor was purged with helium for one minute. Then a predetermined amount of <sup>13</sup>C-methanol was introduced into the reactor by a syringe and the catalyst was quickly cooled down. The isotopic distribution of the effluents and the confined organic species were analyzed by GC-MS.

## 3. Results and discussion

### 3.1. DNL-6 and its acidity

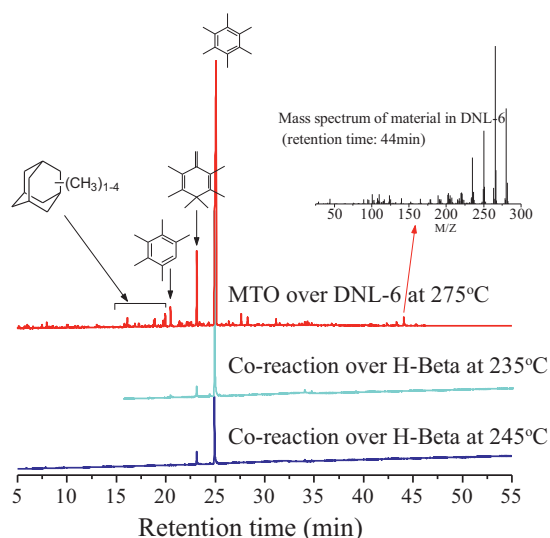
As an 8-membered ring SAPO molecular sieve, DNL-6 (RHO) has body-centered cubic  $\alpha$  cavity, ca. 10.4 Å in diameter [20], which is larger than the *cha* cavity (6.7 Å × 10 Å) of SAPO-34 (CHA) [20], the most important 8-membered ring SAPO catalyst for MTO process [1,2]. Elemental analysis by XRF showed that the Si/(Si + Al + P) of DNL-6 sample was 0.144, suggesting three Si atoms per cavity (24 T atoms) and the NMR measurements showed that all of the Si atoms were in the coordination state of Si (4Al) [17,18].

In our previous report [17], the acidity of DNL-6 has been determined by the isotropic <sup>13</sup>C chemical shift of the carbonyl carbon of probe molecular acetone in <sup>13</sup>C NMR spectrum [21,22]. The acid strength of DNL-6 was proved to be higher than that of SAPO-34 [23] and close to or even higher than that of silicoaluminate zeolites [24]. A shoulder peak at 232 ppm was also observed in the <sup>13</sup>C MAS NMR spectra [17]. The chemical shift at this range was reported to be typical for acetone interacting with Lewis acid sites [21,22]. However, extra framework aluminum was not observed in DNL-6, as evidenced by the <sup>27</sup>Al MAS NMR results [17,18]. The <sup>29</sup>Si MAS NMR spectrum of DNL-6 [17,18] also presented only one peak centered at -92 ppm which indicated no silicon islands were formed. The further study for revealing the high acid strength of DNL-6 is still ongoing.

### 3.2. Catalytic performances and confined organic materials identification

The catalytic performances of methanol conversion at different reaction temperatures have been reported in our previous study [17]. Even an induction period was observed when the reaction was performed at low temperature, DNL-6 was an effective catalyst for olefin production from methanol conversion at relatively higher temperature. The light olefins (ethene, propene and butenes) selectivity was about 70–90%. It should be noticed that the butenes selectivity was always comparable with propene selectivity and higher than ethene selectivity. High temperature reaction or the reaction during the catalyst deactivation stage generated more C<sub>1</sub>–C<sub>3</sub> alkanes, which was consistent with the high acid strength of DNL-6.

The organic materials formed and confined in the large  $\alpha$  cavities of DNL-6 during MTO conversion were compared with those in H-beta during co-reaction of methanol and benzene. As shown in Fig. 1, after co-reaction of benzene and methanol over H-beta according to Ref. [15], the peak of synthesized hexamethylmethylenecyclohexadiene (HMMC) appeared at the retention time of 23 min on the GC-MS chromatograms of the extracted organics. For the GC-MS chromatogram of organics confined in DNL-6, a peak also appeared at the retention time of 23 min and presented the same mass spectrum as the synthesized HMMC (the deprotonated form of heptaMB<sup>+</sup>). This confirmed the formation of HMMC in DNL-6 after methanol conversion under real reaction condition.

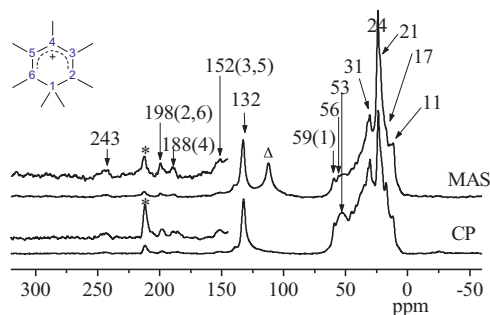


**Fig. 1.** GC–MS chromatograms of the organic materials retained in DNL-6 catalyst after methanol conversion for 60 min (WHSV of MeOH = 2.0 h<sup>-1</sup>, He/MeOH (in mol) = 3, insert shows the mass spectrum of the compound with its peak appearance at 44 min) and those retained in H-Beta after co-reaction of methanol and benzene for 1.5 min (MeOH/Benzene (in mol) = 7, WHSV of MeOH = 0.9 h<sup>-1</sup>, N<sub>2</sub>/MeOH (in mol) ≈ 30).

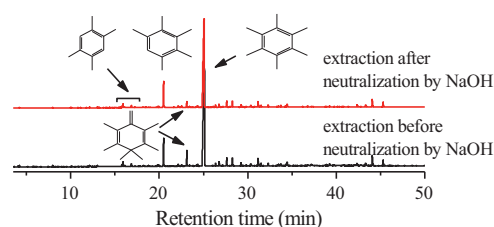
Furthermore, Fig. 1 shows that the materials confined in DNL-6 were predominantly hexamethylbenzene (hexaMB). Pentamethylbenzene (pentaMB) and alkyl-admantants were also detected. The intensities of other polymethylbenzenes were very low. Noticeably small amount of polycyclic aromatic hydrocarbons were also detected at the retention time of 25–45 min, but only a part of them could be clearly recognized and some of them with molecular weight higher than 250 (inset of Fig. 1) could not find reasonable matches in the NIST08 mass spectral library.

### 3.3. Confirmation of heptaMB<sup>+</sup> by solid state NMR

The carbenium ion, heptaMB<sup>+</sup>, is the protonated form of HMMC, which is believed to behave as an important reaction intermediate during MTO conversion [14–17]. In our previous report [17], the solid state NMR measurements have been carried out to determine the formation of heptaMB<sup>+</sup> over DNL-6 under real MTO reaction condition. It has been confirmed that in the <sup>13</sup>C MAS and CP NMR spectra of DNL-6 catalyst after methanol conversion at 275 °C, 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 (see inset of Fig. 2 for carbon atom number indication) [17]. The chemical shift of C-1 was reported to be 58 ppm [14]. However, the chemical shift of surface methoxy groups also covered the range of 53–59 ppm



**Fig. 2.** <sup>13</sup>C MAS and CP/MAS NMR spectra of the DNL-6 catalyst after methanol conversion at 275 °C, <sup>13</sup>C-methanol feeding for 28 min and then <sup>12</sup>C-methanol feeding for 3 min. \*Indicates the spinning sideband and Δ indicates the background.



**Fig. 3.** GC–MS chromatograms of the organic materials retained in DNL-6 obtained by employing different treatment method after methanol-to-olefins reaction at 300 °C.

[25]. As a result, a broad peak appeared near 57 ppm in the spectra of DNL-6 after <sup>13</sup>C-methanol conversion [17].

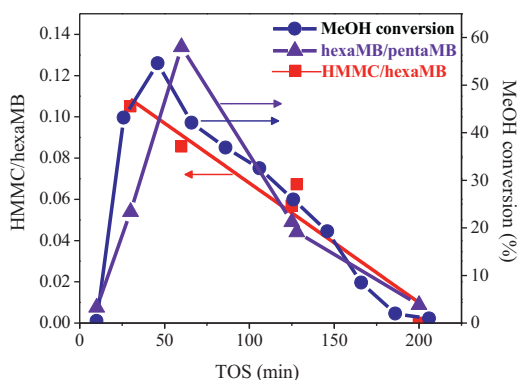
To eliminate the resonance signal of the methoxy groups, a switch experiment with <sup>13</sup>C-methanol feeding for 28 min and then <sup>12</sup>C-methanol feeding for 3 min was performed. From the spectra of Fig. 2, it was evidenced that the peak around 57 ppm was clearly separated and the intensity of the signal at 59 ppm did not increase in the CP MAS NMR spectrum compared to the <sup>13</sup>C MAS NMR spectrum, indicating this signal was from the C-1 of heptaMB<sup>+</sup> without neighboring H atoms. These evidences further confirmed the formation of heptaMB<sup>+</sup> during MTO conversion over DNL-6, corresponding to the observation in the retained organic materials analysis with GC–MS.

The signals with chemical shifts of 243 and 152 ppm also appeared in the <sup>13</sup>C MAS NMR and CP MAS NMR, which were assigned to the very important 5-membered ring carbenium ions in methanol conversion, polymethylcyclopentenyl ions [23].

### 3.4. Correlation of the reactivity of HMMC/heptaMB<sup>+</sup> with MTO performances

HMMC was reported to be an unstable intermediate [15]. In our present study, it was found that the peak of HMMC at retention time of 23 min presented in Fig. 1 became weak with time and disappeared after a few days at room temperature. Trapping HMMC/heptaMB<sup>+</sup> under the realistic methanol reaction conditions depended on the stabilization effects from the special surroundings provided by DNL-6 molecular sieve i.e. very strong acidity and large cavity space. To test the stability of HMMC/heptaMB<sup>+</sup> in different environments, two control experiments were carried out by employing reverse procedures of extraction with CH<sub>2</sub>Cl<sub>2</sub> and neutralization with NaOH solution (5%) to treat the same discharged DNL-6 catalyst sample acquired after MTO reaction and being dissolved in HF solution, and the obtained GC–MS chromatograms of extracted organic materials are shown in Fig. 3. Even both of the two chromatograms present the peak of HMMC, the peak intensity was reduced by 50% when neutralization was conducted before extraction. After the DNL-6 framework was destroyed by HF solution, HMMC and heptaMB<sup>+</sup> were liberated. By the addition of CH<sub>2</sub>Cl<sub>2</sub>, HMMC could be extracted into the organic phase and the following neutralization by NaOH would not influence the concentration of HMMC. However, if the reverse procedure was employed, that is the acidic solution was neutralized before extraction, the observed HMMC would be diminished and sometimes could not be detected in the organic phase. This implied that HMMC/heptaMB<sup>+</sup> was relatively stable in the acidic solution, but the neutralization before extraction might cause the decomposition of HMMC/heptaMB<sup>+</sup> to form hexaMB and methanol in the non-acidic solution. This also proved the significance of strong acidity of DNL-6 with high acid site concentration and high acid strength, in the stabilization of the carbenium ions.

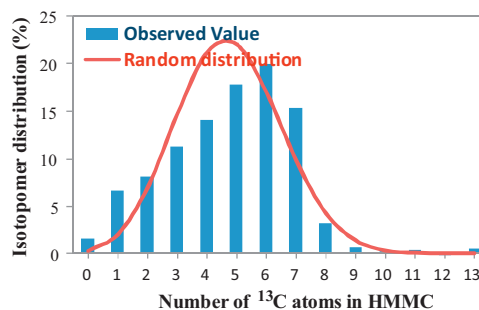
A further study tried to correlate the reactivity of HMMC/HeptaMB<sup>+</sup> to the conversion evolution of MTO reaction with time



**Fig. 4.** The weight ratio variation of retained hexaMB to pentaMB and HMMC to hexaMB with methanol conversion (275 °C) over DNL-6.

on stream carried out at 275 °C. In general, HMMC can be generated through the methylation of hexaMB, and hexaMB can be generated from the methylation of pentaMB. As shown in Fig. 4, the ratio of hexaMB to pentaMB was very high and its maximum attained to 60. However, HMMC/hexaMB ratio was very small (lower than 0.15). This could be explained from two aspects: one is that under these conditions hexaMB methylation was slower than pentaMB methylation; another one is that the further reaction or decomposition of HMMC was possible too fast. Theoretical calculation has shown that the barrier of hexaMB methylation is lower than pentaMB, which indicated the former reason is not reasonable and also proved the high reactivity of HMMC in DNL-6 once again. More importantly, the evolution of hexaMB/pentaMB and HMMC/hexaMB ratios corresponded precisely to the progress of catalytic activity (methanol conversion). This suggested that HMMC might act as the reaction intermediate during methanol to olefin conversion.

The role that heptaMB<sup>+</sup>/HMMC played in methanol conversion under real reaction conditions were further studied by <sup>12</sup>C-methanol/<sup>13</sup>C-methanol switching experiments. <sup>13</sup>C-methanol was conducted over DNL-6 after <sup>12</sup>C-methanol conversion for a predetermined period. Isotopic analysis showed that both <sup>12</sup>C and <sup>13</sup>C atoms appeared in the generated olefin products and confined species in the catalyst (Fig. 5), which suggested that they were formed through the interaction of <sup>13</sup>C-methanol with “hydrocarbon pool” species, instead of the direct coupling of <sup>13</sup>C-methanol [26]. The isotopic distribution of the methylbenzenes (triMB, tetraMB, pentaMB, hexaMB and HMMC) indicated that more <sup>13</sup>C atoms from labeled methanol appeared in polymethylbenzene than the lower-methyl substituted benzenes, especially HMMC presented the highest <sup>13</sup>C content. This further proved the feasibility of



**Fig. 6.** Observed isotopomer distribution of HMMC over DNL-6 compared with the random one calculated from the same <sup>13</sup>C content, the isotopic switch experiments: continuous flow <sup>12</sup>C-methanol conversion for 60 min at 275 °C followed by the injection of 9 μl <sup>13</sup>C-methanol, WHSV of MeOH = 2.0 h<sup>-1</sup>, He/MeOH (in mol) = 3.

methanol conversion following the hydrocarbon pool mechanism, which involved the key step of methylation of hexaMB to form heptaMB<sup>+</sup> as the most important HCP species, over which olefin products were eliminated in the further steps.

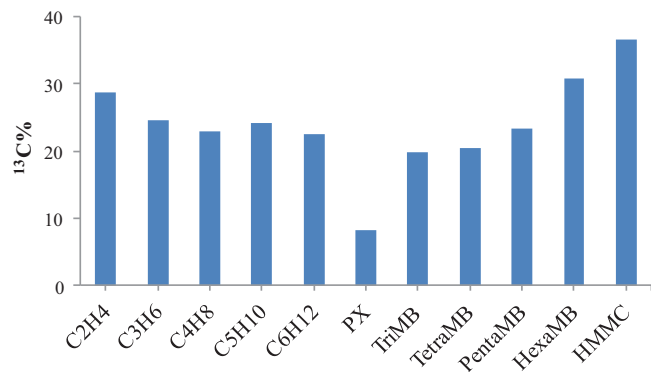
### 3.5. The reaction route of methanol to olefins conversion involving HMMC/heptaMB<sup>+</sup>

Haw and co-workers have studied the reactions of methylbenzenes and also the co-reactions of methylbenzenes with <sup>13</sup>C-methanol on H-beta, they concluded that the side-chain methylation mechanism was the predominant route to form olefins [27]. They also carried out the theoretical calculations on the side-chain methylation mechanism [28]. However, Kolboe and co-workers conducted the co-reaction of benzene and <sup>13</sup>C-methanol over H-beta at relatively lower reaction temperature and concluded that the paring reaction mechanism was the major reaction route for olefin formation [15,29]. Kolboe group extended their research to H-MCM-22 and H-mordenite and drew the similar conclusion as over H-beta [16].

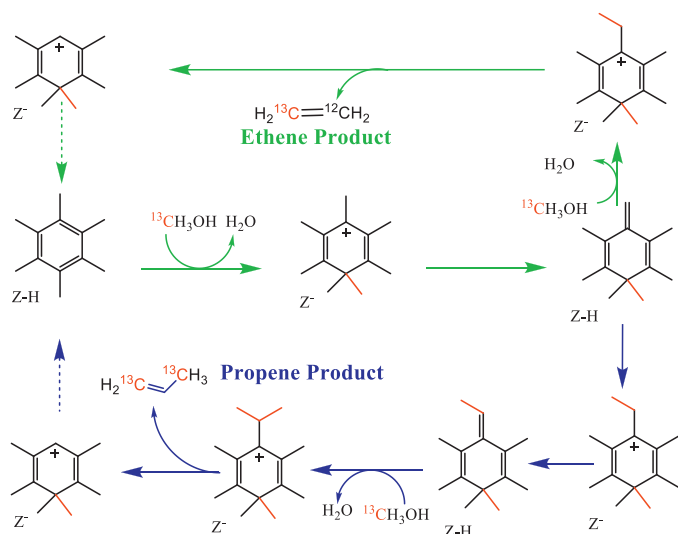
In the <sup>12</sup>C-methanol/<sup>13</sup>C-methanol switch experiments over DNL-6, it was found that the isotopomers of polymethylbenzenes confined in DNL-6 exhibited no random distribution. Fig. 6 shows the comparison of observed isotopomer distribution of HMMC confined in DNL-6 with the random distribution calculated from the same <sup>13</sup>C contents. The fraction of isotopomers containing 6 and 7 <sup>13</sup>C-atom exceeded random distribution, but the fraction of isotopomers containing more than 7 <sup>13</sup>C-atom were under random one. The difficulty of more than 7 <sup>13</sup>C-atom incorporation into HMMC indicated the highest number of incorporated <sup>13</sup>C atoms was exactly the total number of methyl groups on the benzene ring.

A detailed analysis of the ion mass distribution showed that the highest mass value of fragment ion (M-CH<sub>3</sub>) with prominent intensity was equal to the highest mass value of molecular ion with prominent intensity minus 16 not 15 (i.e. M-16 not M-15), which indicated that a methyl group with <sup>13</sup>C atom with *m/e* = 16 was split from the molecule (such as <sup>13</sup>C<sub>7</sub>-HMMC) [17]. Assuming that the fragmentation of methyl groups was identical on the electron bombardment, all of the methyl groups of HMMC with seven <sup>13</sup>C atoms would be <sup>13</sup>CH<sub>3</sub><sup>-</sup>, which derived from <sup>13</sup>C-methanol.

Furthermore, from the <sup>13</sup>C MAS NMR spectra in Fig. 2, one can find that after the feed was switched from <sup>13</sup>C-methanol to <sup>12</sup>C-methanol for some time, the peak intensity of methyl group at 17 ppm was greatly reduced while the resonance peaks at 132, 198 and 188 ppm representing the carbon atom from benzene ring maintained their intensity. This also proved that the incorporation of methyl groups from methanol into hydrocarbon pool species, such as polymethylbenzenes and the corresponding carbenium ions, by the substitution of the methyl group of side chain.



**Fig. 5.** <sup>13</sup>C content of the gas phase products (C<sub>2</sub>–C<sub>6</sub> olefins) and the methylbenzenes confined in DNL-6 after continuous flow <sup>12</sup>C-methanol conversion for 60 min at 275 °C followed by 9 μl <sup>13</sup>C-methanol injection, WHSV of MeOH = 2.0 h<sup>-1</sup>, He/MeOH (in mol) = 3.



**Scheme 2.** Illustration of the side-chain methylation mechanism for olefins generation from methanol conversion over DNL-6.

Based on the above evidences, it could be suggested that most of the incorporated  $^{13}\text{C}$  atoms appeared as the carbon atoms of methyl group rather than the carbon atoms of benzene ring. These observations implied that the reaction route of paring mechanism, with the contraction and expansion of the cyclic intermediate, was actually more difficult to realize in methanol conversion catalyzed by DNL-6. A side-chain methylation mechanism proposed in Scheme 2 was the predominant route for olefin formation with the polymethyl-substituted benzene as the “hydrocarbon pool” species.

#### 4. Conclusions

Methanol to olefins conversion was studied over a newly-synthesized SAPO molecular sieve, DNL-6. At low reaction temperature, very important intermediate HMMC/heptaMB<sup>+</sup> had been directly observed under real MTO reaction conditions. The reactivity of HMMC/heptaMB<sup>+</sup> was proved to be very high and catalytic environment provided by DNL-6 with strong acidity favored its formation and stabilization. The correlation of the reactivity of this intermediate with the variation of methanol conversion at different time on stream showed the involvement of this intermediate in the olefin generation. Based on the GC-MS and solid state NMR measurements after the isotopic labeling and switch experiments, side chain mechanism was suggested to be the main reaction route for methanol conversion over the large cavity molecular sieve, DNL-6.

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