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# 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 polymethylbenezenes. By combination of in situ NMR study with ex situ GC–MS measurements, the structure of heptamethylbenzenium ion (heptaMB$^+$) formed during MTO reaction was definitely confirmed. Further evidences from the mass spectra and $^{13}$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.

## 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, polymethylcyclopentediene 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$^+$) is of particular importance as a reaction intermediate in the MTO reaction [10]. The formation of heptaMB$^+$ 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$^+$ 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$^+$ 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$^+$. 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$^+$. New evidences from NMR and GC–MS investigations were obtained and used to correlate the generation of heptaMB$^+$ to the catalytic cycle of MTO reaction for olefin formation. Detailed reaction route was discriminated by the aid of the $^{12}$C/$^{13}$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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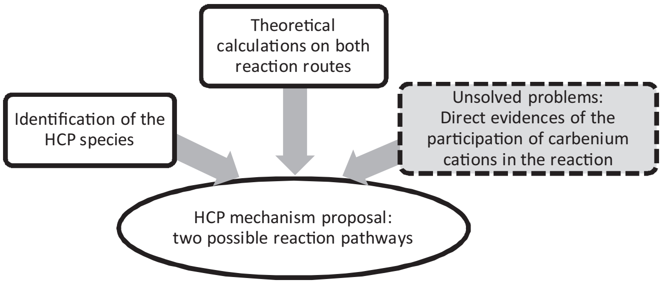

**Scheme 1.** Development of hydrocarbon pool mechanism of MTO over zeolites.

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 $h^{-1}$. 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 $h^{-1}$. The carrier gas ($N_2$) 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 $^{13}C$ 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 $CH_2Cl_2$. This procedure followed the method introduced by Guisnet et al. [19].

$^{13}C$ 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. $^{13}C$ MAS NMR spectra were recorded using high-power proton decoupling. A 2700 scans were accumulated with a $\pi/4$ pulse width of 1.8 μs and a 4 s recycle delay. $^{1}H \rightarrow {}^{13}C$ 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 $^{13}C$ NMR spectra were referenced to adamantane with the upfield methine peak at 29.5 ppm.

The catalyst sample used in $^{13}C$ solid-state NMR experiments was prepared by employing $^{13}C$-methanol as reactant. In order to eliminate the influence of methoxy groups on the structure confirmation of heptaMB$^{+}$ cation, the feed was switched to $^{12}C$-methanol and allowed to react for further 3 min after $^{13}C$-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 $^{12}C/^{13}C$ switch experiments, the $^{12}C$-methanol was fed into the reactor to build up $^{12}C$-hydrocarbon pool species in the cavities of DNL-6, and then the feeding of $^{12}C$-methanol was stopped and the reactor was purged with helium for one minute. Then a predetermined amount of $^{13}C$-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-memebered 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 $^{13}C$ chemical shift of the carbonyl carbon of probe molecular acetone in $^{13}C$ NMR spectrum [21,22]. The acid strength of DNL-6 was proved to 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 $^{13}C$ 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 $^{27}Al$ MAS NMR results [17,18]. The $^{29}Si$ 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 $C_1$–$C_3$ 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 hexamethylmethylene cyclohexadiene (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$^{+}$). This confirmed the formation of HMMC in DNL-6 after methanol conversion under real reaction condition.