

Zeolite Catalysts

Deutsche Ausgabe: DOI: 10.1002/ange.201510920
Internationale Ausgabe: DOI: 10.1002/anie.201510920**Direct Detection of Supramolecular Reaction Centers in the Methanol-to-Olefins Conversion over Zeolite H-ZSM-5 by ^{13}C - ^{27}Al Solid-State NMR Spectroscopy**Chao Wang⁺, Qiang Wang⁺, Jun Xu,^{*} Guodong Qi, Pan Gao, Weiyu Wang, Yunyun Zou, Ningdong Feng, Xiaolong Liu, and Feng Deng^{*}

Abstract: Hydrocarbon-pool chemistry is important in methanol to olefins (MTO) conversion on acidic zeolite catalysts. The hydrocarbon-pool (HP) species, such as methylbenzenes and cyclic carbocations, confined in zeolite channels during the reaction are essential in determining the reaction pathway. Herein, we experimentally demonstrate the formation of supramolecular reaction centers composed of organic hydrocarbon species and the inorganic zeolite framework in H-ZSM-5 zeolite by advanced ^{13}C - ^{27}Al double-resonance solid-state NMR spectroscopy. Methylbenzenes and cyclic carbocations located near Brønsted acid/base sites form the supramolecular reaction centers in the zeolite channel. The inter-nuclear spatial interaction/proximity between the ^{13}C nuclei (associated with HP species) and the ^{27}Al nuclei (associated with Brønsted acid/base sites) determines the reactivity of the HP species. The closer the HP species are to the zeolite framework Al, the higher their reactivity in the MTO reaction.

The methanol-to-olefins (MTO) conversion on acidic zeolite catalysts provides an alternative to produce lower olefins from crude oil and thus has attracted significant attention in both industry and academia.^[1] Owing to the complex network of steps involved in the MTO reaction, mechanistic understanding of the formation of olefins remains a great challenge in the field of heterogeneous catalysis.^[1c,d,2] The olefins are not produced immediately after the introduction of methanol onto zeolite catalysts, their formation follows a kinetic induction period,^[1c,d] indicating that conversion of methanol into olefins over Brønsted acid sites of zeolites is not straightforward.^[3] Alternatively, an indirect hydrocarbon-pool (HP) mechanism provides a viable route, in which methanol/dimethyl ether are added onto a reaction center (HP species) followed by splitting off of olefins, such as ethene or propene.^[1b,3a,4] More specifically, a “dual-cycle” HP

route, involving an aromatics-based cycle and an olefins-based cycle, runs in the MTO conversion on H-ZSM-5, in which olefins of different length are produced in the different catalytic cycles.^[5] The requirement of organic compounds on active catalysts to form reaction centers is not common in catalysis but distinctive in MTO chemistry on acidic zeolites. Haw and Marcus proposed a supramolecular entity to describe the reaction center comprising a zeolite channel or cage and a trapped organic component (HP species).^[6] Large organic molecules, such as methylbenzenes (MBs), are readily formed in the MTO reaction and are trapped in zeolite channels. Additionally, various C_5 and C_6 cyclic carbocations have been identified as trapped compounds on different zeolites and zeo-type catalysts.^[7] Over H-SAPO-34 zeolite, the trapped MBs and the cage were considered as a supramolecular entity which was a unique catalytic site for the MTO reaction.^[6,8] Thus, both organic and inorganic components are indispensable and work together to generate olefins. The trapped organic compounds of the supramolecular reaction centers could exert a pronounced influence on the MTO reaction. To date, although the HP species, such as MBs and cyclic carbocations, have been intensively investigated to understand the MTO mechanism, the existence of the supramolecular reaction center characterized by the interaction between organic and inorganic components, as well as its function in the MTO reaction, have never been experimentally demonstrated. Since the working of HP species requires the Brønsted acid site (SiOHAl) or its conjugate-base site (SiO^-Al) in place, the supramolecular center can thus be defined by the integration of trapped HP species and Brønsted acid/base sites in zeolite channels, which can be probed by advanced ^{13}C - ^{27}Al double-resonance solid-state NMR techniques^[9] in which the ^{13}C nucleus is associated with the organic component while the ^{27}Al nucleus with the inorganic component.

Our recent work has demonstrated the presence of an aromatic-based HP mechanism on H-ZSM-5 in which MBs are mechanistically linked to propene and ethene via cyclic carbocations.^[7c-e] Herein, we seek to identify the supramolecular reaction center on H-ZSM-5. For the first time, we provide direct experimental evidence on the formation of the supramolecular reaction center and its influence on the reactivity of the HP species in the MTO reaction.

The MTO reaction was performed at 300 °C and 350 °C for 15 min to produce HP species on H-ZSM-5 zeolites with $\text{Si}/\text{Al} = 15$. The effluent products contain a typical range of light olefins, mainly ethene and propene, and a small amount of

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lower MBs (Figure S1 in the Supporting Information). To analyze the trapped species, in situ solid-state NMR spectroscopy and GC were employed. In agreement with our previous work,^[7c-e] in situ ^{13}C MAS NMR analysis indicates the formation of C_5 and C_6 cyclic carbocations, including 1,3-dimethylcyclopentenyl, 1,2,3-trimethylcyclopentenyl, 1,3,4-trimethylcyclopentenyl, 1-methyl-3-ethylcyclopentenyl, 1,5-dimethyl-3-ethylcyclopentenyl, 1,4-dimethyl-3-ethylcyclopentenyl, and pentamethylbenzenium cations (Figure S2). Since a cyclopentadiene can be considered as a conjugate base of the corresponding carbocation confined in the zeolite channels,^[7c] the existence of the cyclopentenyl cations is also confirmed by detecting the corresponding cyclopentadienes using GC analysis (Figure S2).

The supramolecular centers are probed by detecting the dipolar interaction between the ^{13}C atom from the trapped organic species and the zeolite framework ^{27}Al atom from the Brønsted acid/base site via a recently developed ^{13}C - ^{27}Al symmetry-based rotational-echo saturation-pulse double-resonance (S-RESPDOR) method^[9b,c] (Figure S3). In this case, it is difficult to quantitatively measure the dipolar coupling constant or ^{13}C - ^{27}Al internuclear distance because of either the multispin systems or the fast decay of the NMR signals (see below). So a $\Delta S/S_0$ value expressed as $(S_0 - S)/S_0$ (S and S_0 represent the signal intensity with and without dipolar dephasing, respectively) was used to describe the degree of ^{13}C - ^{27}Al dipolar dephasing, characterizing the dipolar interaction and spatial proximity between trapped organic species and the zeolite framework Al atom. The recoupling time was set at 10 ms to ensure that the signals from ^{13}C sites adjacent to ^{27}Al sites were dephased sufficiently.^[9b] The S-RESPDOR experiments were carried out on the H-ZSM-5 samples after reaction at 300 °C and 350 °C. At 300 °C, as shown in Figure 1a, all the signals upfield from $\delta = 0$ to 60 ppm are subject to different degrees of ^{13}C - ^{27}Al dipolar dephasing

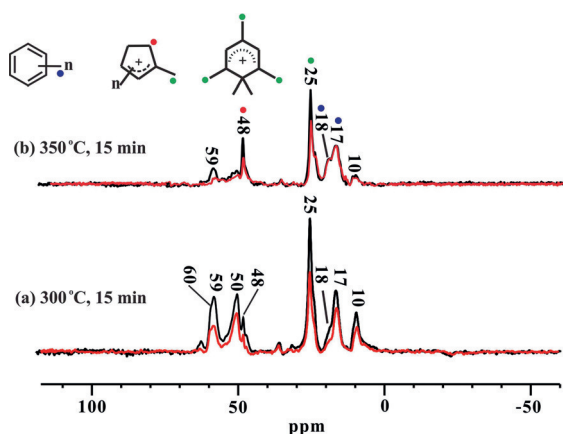


Figure 1. ^{13}C MAS NMR spectra of trapped products obtained from reactions of methanol over H-ZSM-5 at 300 °C and 350 °C for 15 min. The red spectrum is detected with (S) ^{13}C - ^{27}Al S-RESPDOR dipolar dephasing and the black spectrum without (S_0) ^{13}C - ^{27}Al S-RESPDOR dipolar dephasing. The $\Delta S/S_0$ value is expressed as $(S_0 - S)/S_0$. The signals from the methyl groups of methylbenzenes are marked with blue dots, from the methyl groups of cyclic carbocations by green dots. The signals of saturated carbon atoms in the rings of cyclopentenyl cations are indicated by red dots.

Table 1: $\Delta S/S_0$ (%) experimental ^{13}C - ^{27}Al S-RESPDOR fractions for the signals of trapped organic compounds obtained from the reactions of methanol over H-ZSM-5 at 300 °C and 350 °C for 15 min.

Parameter	Chemical shifts (ppm)				
	17	18	25	48	59
$\Delta S/S_0$ (300 °C) ^[a]	16.9	39.3	40.7	52.1	72.6
$\Delta S/S_0$ (350 °C) ^[b]	2.2	1.3	35.5	46.3	77.8

[a] The $\Delta S/S_0$ value for the reaction at 300 °C. [b] The $\Delta S/S_0$ value for the reaction at 350 °C.

(Table 1), demonstrating the spatial interaction/proximity between different ^{13}C species and framework ^{27}Al sites. The signals at $\delta = 50$ and 60 ppm can be assigned to methanol and dimethyl ether (DME) reactants, respectively, while the signals at $\delta = 59$ and 48 ppm are due to methoxy species typically formed in the MTO reaction and saturated carbon atoms in the rings of cyclopentenyl cations, respectively.^[7c,10] With the assistance of two-dimensional ^1H - ^{13}C HETCOR NMR experiment (Figure S4), the signals at $\delta = 17$ and 18 ppm are assigned to the methyl groups of aromatics (mainly pentaMBs and 1,2,3,5-tetraMBs, also see Figure S2), and the signal at $\delta = 25$ ppm to the methyl groups of cyclopentenyl cations and pentamethylbenzenium ion. Therefore, for the first time, these results provide the direct experimental evidence on the existence of spatial interaction/proximity between trapped HP species and zeolite framework (Brønsted acid/base site), indicative of the formation of a supramolecular reaction center. It can be expected that MBs interact with the Brønsted acid site (SiOHAl) by forming a π -complex, while cyclic carbocations interact with Brønsted base site ($\text{SiO}^- \text{Al}$) by forming an ion-pair complex. The ^{13}C - ^{27}Al dipolar dephasing also occurs on a weak signal at $\delta = 10$ ppm that probably arises from the substituents of ethylcyclopentenyl cation. Note that the downfield ^{13}C signals (from $\delta = 130$ to 257 ppm) corresponding to the rings of cyclic carbocations and aromatics completely disappear in the S-RESPDOR experiments (Figure S5, also see Figure S2). This change is because these signals have much shorter transverse relaxation time (T_2') compared with their highfield counterparts (Table S1). It should also be noted from Figure 1 and Figure S5 that the olefins formed are too mobile and unstable to be trapped in zeolite channels for detection by NMR spectroscopy.

Increasing the reaction temperature to 350 °C leads to a considerable consumption of the DME ($\delta = 60$ ppm) and methanol ($\delta = 50$ ppm) reactants (Figure 1b). A slight reduction of $\Delta S/S_0$ occurs on the signals at $\delta = 48$ and 25 ppm, whereas the $\Delta S/S_0$ values for the signals at $\delta = 18$ and 17 ppm are dramatically decreased (Table 1), implying that the C_5 and C_6 cyclic carbocations are still in close proximity to the framework Al sites but the MBs become more distant from the framework Al sites. This change is due to the facile transformation and diffusion of MBs at higher temperature, and much broader spatial distribution of MBs results in a large average ^{13}C - ^{27}Al distance to the framework Al sites.

The function of supramolecular centers in the MTO reaction is further explored by the ^{13}C - ^{27}Al S-RESPDOR experiments. The supramolecular centers are firstly built up

by allowing unlabeled methanol to react with the zeolite for 15 min, followed by switching to ^{13}C -labelled methanol for different times. This approach allows us to gain insight into how the HP species interact with methanol reactants in the MTO reaction. We focus on the organic species formed (Figure 1) not the methanol and DME reactants. As shown in Figure 2, the ^{13}C contents in MBs and carbocations gradually

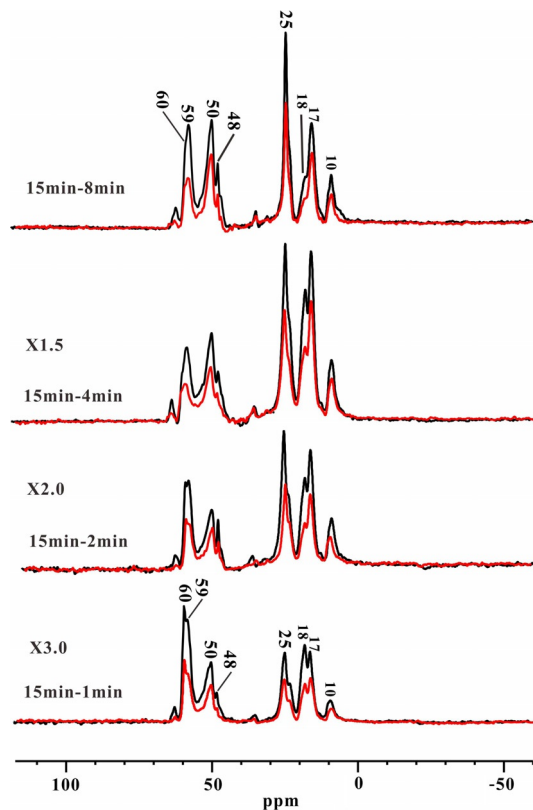


Figure 2. ^{13}C MAS NMR spectra of trapped products obtained from reaction of ^{12}C methanol for 15 min followed by switching to ^{13}C methanol and reacting for different time over H-ZSM-5 at 300°C . The red spectrum is detected with (S) ^{13}C - ^{27}Al S-RESPDOR dipolar dephasing and the black spectrum without (S₀) ^{13}C - ^{27}Al S-RESPDOR dipolar dephasing.

increase with reaction time. The ^{13}C labelling between the species concerned reaches equilibrium at 8 min after the ^{13}C methanol switch, and the ^{13}C NMR spectrum is similar to that recorded under steady-state conditions (i.e. Figure 1 a). The ^{13}C - ^{27}Al S-RESPDOR experiments performed on the catalysts show clear ^{13}C - ^{27}Al dipolar dephasing on these species. Interestingly, the $\Delta S/S_0$ values for the methyl groups in MBs ($\delta = 17$ and 18 ppm) are remarkably reduced along with the ^{13}C labelling while signal from surface methoxy species ($\delta = 59$ ppm) remains almost unchanged and those of carbocations ($\delta = 25$ and 48 ppm) experience a modest decrease (Table 2). The decrease of $\Delta S/S_0$ suggests the reduction of the apparent interactions between the labelled organic compounds and zeolite framework.

The decrease in the interactions can be attributed to an increase of the average distance between the labelled organic compounds and the zeolite framework Al atoms. At the

Table 2: $\Delta S/S_0$ [%] experimental ^{13}C - ^{27}Al S-RESPDOR fractions for the signals of ^{13}C -labelled species obtained from different evolution time (denoted in bracket) after switching from ^{12}C to ^{13}C methanol.

Parameter	Chemical shifts (ppm)				
	17	18	25	48	59
$\Delta S/S_0$ (1 min)	46.4	73.2	49.3	67.7	74.6
$\Delta S/S_0$ (2 min)	35.7	60.7	43.5	58.2	72.3
$\Delta S/S_0$ (4 min)	26.4	53.1	41.9	54.2	73.5
$\Delta S/S_0$ (8 min)	20.4	39.3	40.7	53.5	73.1

beginning, the ^{13}C -labelled methanol preferentially reacts with the HP species (both MBs and carbocations) located closely to Brønsted acid/base sites that shows stronger ^{13}C - ^{27}Al interactions which are reflected by relatively large $\Delta S/S_0$ (see Figure 2 and Table 2). At longer reaction times more HP species around the Brønsted acid/base sites are reacting with ^{13}C -labelled methanol, the facile diffusion and transportation of ^{13}C -labelled MBs away from the Brønsted acid sites leads to an increase in the average distance between these species and zeolite framework Al atoms. As a result, the dipolar interaction becomes weaker and $\Delta S/S_0$ considerably decreases. In contrast, the surface methoxy species ($\delta = 59$ ppm) and carbocations ($\delta = 25$ and 48 ppm) exhibit strong interactions with the zeolite framework and lower mobility during the $^{12}\text{C}/^{13}\text{C}$ methanol-switching reaction. This result can be understood in that methoxy species can only exist by directly bonding with the oxygen atom of the zeolite framework, showing an almost unchanged ^{13}C - ^{27}Al distance and constant $\Delta S/S_0$ regardless of the reaction time. Analogously, the stabilization of C_5 and C_6 cyclic carbocations requires charge-compensating centers (Brønsted base sites) in close proximity on the zeolite framework, which largely limits the mobility of the carbocations and produces a smaller change of $\Delta S/S_0$ during the reaction. Therefore, the ^{13}C - ^{27}Al S-RESPDOR experiments reveal the nature of the supra-molecular reaction center, that is, the HP species strongly interacting with the Al sites (Brønsted acid/base sites) possess higher reactivity toward methanol. Additionally, we can get further information on the distribution of HP species. The MBs are broadly distributed in space as reflected by the remarkable change of $\Delta S/S_0$ (Table 2). Considering their reactivity, only those MBs closely adsorbed on the zeolite framework as the organic component of the supramolecular center could serve as the real reactive HP species in the MTO reaction.

MBs were identified as the precursor to light olefins^[7c,11] and their chemical connectivity to olefins was previously established.^[7c-e] Their reactivity in the MTO reaction can be demonstrated from the supramolecular reaction center point of view. The $^{12}\text{C}/^{13}\text{C}$ isotope switch experiments were first performed to build up partially ^{13}C -labeled HP species on the catalysts, the system was then purged with carrier gas (He) at the working temperature. PentaMB as the main component of the trapped products was analyzed. The isotopic data shows that pentaMB is highly enriched by ^{13}C atoms with a broad distribution of isotopic molecules (Figure 3). A similar case was found for tetraMB (Figure S6).

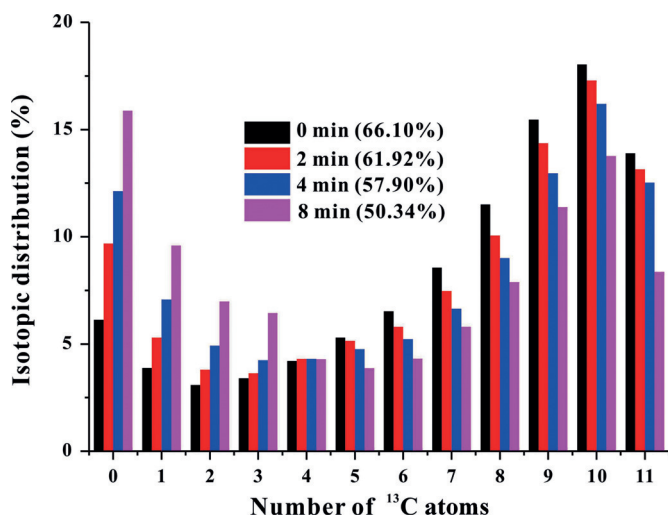


Figure 3. The ^{13}C content in the trapped pentaMB obtained from reaction of methanol over zeolite H-ZSM-5 at 300°C for 15 min, followed by switching to ^{13}C methanol for 2 min (black) and flushing with He for 2 min (red), 4 min (blue), and 8 min (violet) after cutting off methanol.

The presence of more ^{13}C labelled atoms points to higher reactivity. Since most of pentaMB and tetraMB are enriched by ^{13}C atoms (more than six ^{13}C atoms), they should have high reactivity on the H-ZSM-5 zeolite ($\text{Si}/\text{Al}=15$). In contrast, the amount of pentaMBs with high reactivity on a high-silica H-ZSM-5 ($\text{Si}/\text{Al}=200$) is much lower than that on the low-silica H-ZSM-5 ($\text{Si}/\text{Al}=15$), reflected by the lower content of pentaMBs enriched in ^{13}C atoms (Figure S7). We have shown above that HP species interacting with Brønsted acid/base sites form the supramolecular reaction center which exhibits high reactivity to the methanol reactant. The lower content of ^{13}C -enriched pentaMBs is likely due to the low concentration of Brønsted acid sites on the high-silica zeolite in which most of the pentaMBs in zeolite channels cannot form the supramolecular reaction centers.

The reactivity of MBs is further studied in their transformation. Increasing the purging time from 2 to 8 min after stopping ^{13}C methanol feeding leads to a decrease of highly ^{13}C -enriched pentaMBs with the number of ^{13}C atoms being 6–11, whereas the amount of less ^{13}C -enriched pentaMBs with between 0–3 ^{13}C atoms increases noticeably (Figure 3). This indicates that the highly ^{13}C -enriched pentaMBs decompose faster than those having less ^{13}C atoms. Thus, the formation of the supramolecular reaction center by close interaction of HP species with Brønsted acid/base sites should be responsible for the high reactivity of HP species in both their formation and transformation.

In summary, the interaction of hydrocarbon-pool (HP) species with the H-ZSM-5 zeolite framework in the MTO reaction has been revealed by ^{13}C – ^{27}Al solid-state NMR spectroscopy, which provides direct evidence of the formation of a supramolecular reaction center composed of HP species and the zeolite framework. Methylbenzenes (MBs) and carbocations form the supramolecular reaction center when they are located closely to Brønsted acid/base sites in the

zeolite channels. The results show the critical role of the spatial interaction/proximity of ^{13}C atoms (organic species) and ^{27}Al atoms (Brønsted acid/base site) in determining the reactivity of the HP species. Although the interactions of olefin HP species with Brønsted acid sites are undetectable owing to their high mobility and short lifetime in the zeolite channels, the olefin-based cycle might proceed via a route involving analogous supramolecular reaction centers. These results presented herein shed new insight into the hydrocarbon-pool chemistry in the MTO reaction over zeolite H-ZSM-5.

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