



Direct Mechanism of the First Carbon–Carbon Bond Formation in the Methanol-to-Hydrocarbons Process

Xinqiang Wu⁺, Shutao Xu⁺, Wenna Zhang, Jindou Huang, Jinzhe Li, Bowen Yu, Yingxu Wei,^{*} and Zhongmin Liu^{*}

Abstract: In the past two decades, the reaction mechanism of C–C bond formation from either methanol or dimethyl ether (DME) in the methanol-to-hydrocarbons (MTH) process has been a highly controversial issue. Described here is the first observation of a surface methyleneoxy analogue, originating from the surface-activated DME, by in situ solid-state NMR spectroscopy, a species crucial to the first C–C bond formation in the MTH process. New insights into the first C–C bond formation were provided, thus suggesting DME/methanol activation and direct C–C bond formation by an interesting synergetic mechanism, involving C–H bond breakage and C–C bond coupling during the initial methanol reaction within the chemical environment of the zeolite catalyst.

The methanol-to-hydrocarbons (MTH) reaction over either zeolite or SAPO catalysts has become the most successful method for olefin and synthetic fuel production from non-oil resources, such as natural gas or coal.^[1–3] Methanol/dimethyl ether (DME) conversion over solid acid catalysts realizes the carbon–carbon (C–C) bond assembly from C₁ reactants and the reaction presents a special autocatalysis character with low efficiency, thus proceeding through the initial stage followed by a highly accelerated conversion with the product generation.^[4–6] In the past 30 years, the reaction mechanism of MTH reaction has been debated. More than 20 direct mechanisms, including methyl-carbocation,^[5] oxonium-ylide,^[7,8] carbene,^[9,10] and methane-formaldehyde mechanisms,^[11,12] have been proposed to elucidate the formation of C–C bond in the MTH reaction. However, either the ultrahigh computed energy barriers or the difficulty in the capture of the intermediates reduce the potential for their acceptance. An indirect reaction pathway, the “hydrocarbon pool” (HCP) mechanism, has been verified as a thermodynamically beneficial route for C–C bond formation and

explained the efficient generation of olefins during the steady-state period of methanol conversion over zeolite catalysts.^[13,14] However, the formation of the initial C–C bond and the origin of the HCP species are still unsolved puzzles. Impurities in either the feedstocks or carrier gas, and the catalyst contaminations were once thought to be the source of the first C–C bond,^[15] whereas Hunger and co-workers indicated that trace amounts of organic impurities cannot support the formation of the HCP species and suggested that surface methoxy species (SMS) should be an essential intermediate for the first C–C bond formation.^[16–19] In an earlier methane-formaldehyde mechanism, proposed by Kubelkova et al.^[11] and Hirao et al.,^[12] methane and formaldehyde are generated by the interaction of SMS and methanol, and their further transformation results in the generation of the C–C bond. Based on experimental and theoretical studies of methanol conversion over SAPO-34, Fan et al.^[20] proposed the methoxymethyl carbocation (CH₃OCH₂⁺) as a crucial intermediate for the initial C–C bond formation and it can be formed by the interaction of SMS and DME. In the theoretical calculations from Hu et al.,^[21] the formation of CH₃OCH₂⁺ was predicted to be more energetically favorable from the interaction of SMS and formaldehyde. In 2016, Lercher and co-workers^[22] postulated that the surface-bonded acetyl group (Zeo-OCCH₃), from the reaction of SMS and carbon monoxide, was responsible for the first C–C bond during the early stage of the MTH reaction. Recently, Weckhuysen et al.^[23] provided spectroscopic evidence for the formation of surface acetate and methyl acetate and proposed the surface-species-assisted direct mechanism for the formation of the first C–C bond. The high reactivity of SMS makes it a possible intermediate in the early stage of the MTH reaction, but the exact mode of how it functions in the initial C–C bond formation is still under investigation. In this work, methanol conversion over the HZSM-5 zeolite catalyst was studied under real MTH reaction conditions. Accompanied by the detection of the very initial formation of ethene in the effluent, SMS and trimethyloxonium (TMO) were captured on the catalyst surface by solid-state nuclear magnetic resonance (ssNMR) spectroscopy. More importantly, some surface methyleneoxy analogue species, originating from activated DME, were observed directly for the first time by in situ ssNMR spectroscopy and recognized to be the most crucial intermediate for the formation of the initial C–C bond. Based on the experimental evidence and the theoretical calculations, new insights into the formation of the first C–C bond are provided, thus suggesting SMS/TMO-mediated DME/methanol activation over an acid zeolite catalyst and a direct

[*] Dr. X. Wu,^[†] Dr. S. Xu,^[†] Dr. W. Zhang, Dr. J. Huang, J. Li, Dr. B. Yu, Prof. Y. Wei, Prof. Z. Liu
National Engineering Laboratory for Methanol to Olefins
Dalian National Laboratory for Clean Energy, iChEM
State Key Laboratory of Catalysis
Dalian Institute of Chemical Physics
Chinese Academy of Sciences, Dalian 116023 (China)
E-mail: weiyx@dicp.ac.cn
liuzm@dicp.ac.cn

Dr. X. Wu,^[†] Dr. W. Zhang, Dr. B. Yu
University of Chinese Academy of Sciences
Beijing 100049 (China)

[†] These authors contributed equally to this work.

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mechanism for C–C bond formation from surface C_1 species during the initial stage of the MTH reaction.

Methanol conversion conducted over HZSM-5 (Si/Al = 20) at 300 °C was monitored by an online gas chromatography-mass spectrometer (GC-MS) and time-of-flight mass spectrometry (TOF-MS) to detect the compounds of the effluent from the initial stage of the reaction. During this stage, in which methanol was just fed onto the catalyst (Figure 1), the feeding of methanol for the first 20 seconds

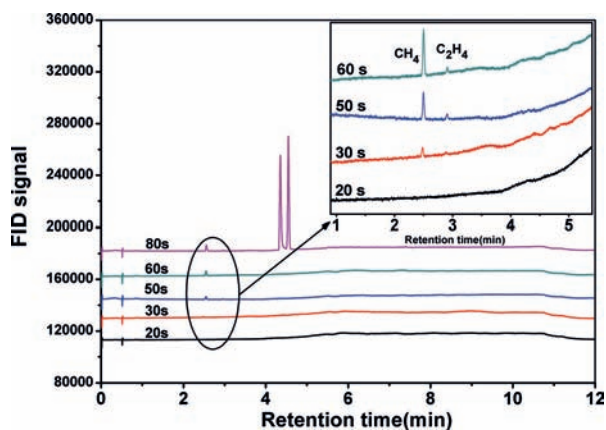


Figure 1. GC-MS chromatograms of effluent products from the MTH reaction run over the HZSM-5 catalyst at 300 °C with a methanol weight hourly space velocity (WHSV) of 2.0 h⁻¹. Details within the circle are enlarged in the inserted picture.

generated no signals on the gas chromatogram. From 30 to 60 seconds, a trace amount of methane, ethene, and formaldehyde appeared (formaldehyde captured by mass detector, see Figure S2 in the Supporting Information). Methanol and DME were absent during 0–60 seconds. Upon continued feeding of methanol, up to 80 seconds, methanol and DME were detected. The absence of methanol and DME for the first 60 seconds implied that the initially fed methanol and its dehydrated product DME stayed on the surface of the HZSM-5 as strongly adsorbed species until methanol was in excess. The initially formed hydrocarbons, especially ethene, which is the only compound with a C–C bond during this period, was speculated to derive from the conversion of the adsorbed species on the surface of HZSM-5. This proposal is supported by the ssNMR studies of [¹³C]methanol reacting with the HZSM-5 catalyst during the early stage of the reaction (see Figure S4). A time-resolved TOF-MS was used for the real-time monitoring of the effluent compounds (see Figure S3). The initially formed ethene was captured in about 40 seconds and the appearance of methanol was delayed, and was consistent with the result from GC-MS data. Ethene detection ahead of the release of the reactants indicated that the direct conversion of surface-adsorbed species, such as methanol, DME, SMS, and some other C_1 species, should be responsible for the formation of the initial hydrocarbons with C–C bond. The key to clarifying the first C–C bond formation during initial methanol conversion is focused on either the intermediates or the precursors from which C–C bonds can be directly generated using the C_1 materials.

To reveal ethene generation at the initial stage of the reaction, careful measurements of the surface organics on methanol-reacted HZSM-5, at different reaction times, were conducted by ¹³C CP/MAS NMR spectroscopy after the catalyst was quenched by liquid nitrogen. At the very beginning of the reaction, the introduction of methanol gives rise to two strong signals at δ = 60.0 and 50.0 ppm for adsorbed DME and methanol, respectively (Figure 2). The

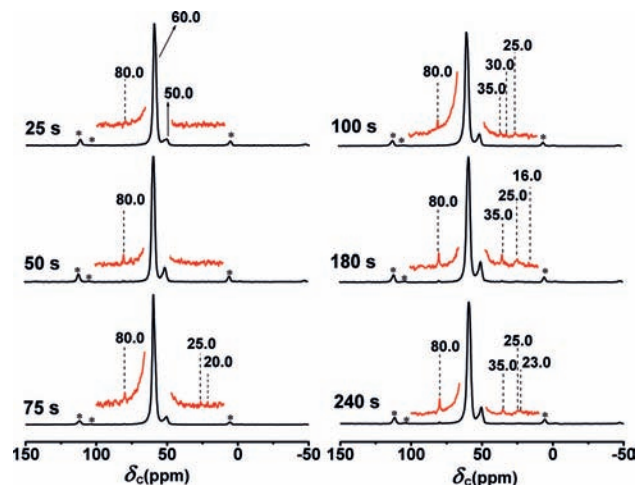


Figure 2. ¹³C CP/MAS NMR spectra of the HZSM-5 catalyst after [¹³C]methanol conversion at 300 °C for 25–240 s. * indicates the spinning sideband.

signal for SMS is at about δ = 59.0 ppm and overlaps with the other two signals (see Figure S4).^[24,25] Besides these signals, a peak at δ = 80.0 ppm, having a low intensity, is observed for the 25–240 second time period (Figure 2, the enlarged spectra) and is assigned to the TMO species.^[26,27] This evidence shows, for the first time, the capture of TMO in real methanol conversion over the HZSM-5 catalyst. During the initial methanol conversion time of 25–50 seconds, all the species on the catalyst surface are C_1 substances and TMO is the newly formed species from the reaction of adsorbed methanol, DME, and SMS. The direct mechanism of C–C bond generation by the oxonium ion-ylide pathway was firstly suggested by Olah and co-workers^[7,8] in the 1980s, but the significance of TMO was not acknowledged by Haw et al.^[28] The direct deprotonation of TMO to form dimethyl oxonium methylene (DOMY) and subsequent methylation to generate an ethyl dimethyl oxonium ion (EDMO), which could further give ethene and DME by way of β -hydride elimination, was theoretically predicted to be too difficult to be realized.^[29–31] Nevertheless, methylation of DME to form TMO caused a large decrease in the C–O stretching force constant (from 5.22 to 4.05 mdyne Å⁻¹) and this also made TMO a potential methylation agent just as SMS.^[32] The simultaneous detection of ethene among the effluents and the C_1 species on the HZSM-5 catalyst imply that the surface methylic species is of vital importance for the formation of the first C–C bond. In prolonging the reaction time to 75–240 seconds, the signals within the δ = 20–40 ppm range, representing either cycloalkanes or oligomerized olefins, indicated that the secondary

reactions, such as oligomerization and cyclization, of the initially formed ethene product were gradually proceeding and hence the formation of the HCP species (see Figure S5). The initially generated hydrocarbons trigger the autocatalytic reaction of methanol and correspondingly, the olefin generation was largely improved, and an abundance of olefins were detected after reaction for 15 minutes (see Figure S6). The most important HCP species, such as methylbenzenium and methylcyclopentyl cations, were also captured during this period (see Figure S7), and can facilitate the olefin generation by a more efficient pathway. Based on these observations, a complete picture of methanol conversion during the induction period and the efficient period is presented. Before the HCP species generation, the initial C–C bond, originating from the direct transformation of surface C_1 species (methanol, DME, SMS and TMO), is formed in a very inefficient way. Disclosing the specific role of the above-mentioned C_1 species in the very initial stage of the MTH reaction requires time-resolved techniques and in situ investigations.

In situ ssNMR measurements of the continuous-flow [^{13}C]methanol conversion over HZSM-5 were conducted in a rotor reactor, and provided a real-time and complete picture of the surface organics in the initial MTH process at the reaction temperature of 300 °C. As shown in Figure 3, three signals from the surface C_1 species occur at the very beginning of the reaction. TMO can be observed in low intensity with chemical shifts of $\delta = 80.0$ ppm. SMS gives rise to the signal with the chemical shift around $\delta = 59.5$ ppm. A surprising observation is that the signals at $\delta = 60.0$ and 50.0 ppm from surface adsorbed DME and methanol, respectively, which are apparently of high intensity in ex situ ^{13}C CP/MAS NMR spectra recorded at room temperature, are absent in the in situ spectra recorded online at 300 °C. A strong and broad band at about $\delta = 69.0$ ppm appears instead. Generally, the signal around $\delta = 70.0$ ppm is assigned to the methylene carbon atom of the framework-bonded ethoxy species, and was confirmed by the adsorption of either alcohol or $\text{CH}_3\text{CH}_2\text{I}$ on zeolites at relatively low temperatures.^[33,34] In addition, these studies indicated that no stable ethoxy species could be maintained on the zeolite surface at relatively high

temperature, and that heating at 300 °C would cause its immediate decomposition and elimination of ethene from the catalyst surface. In the present work, the failure to observe the carbon atom of $-\text{CH}_2-$ (about $\delta = 70.0$ ppm) and $-\text{CH}_3$ (about $\delta = 10.0$ ppm), simultaneously, excluded the capture of stable ethoxy group on H-ZSM-5 in the MTH reaction conducted at 300 °C (Figure 3). Therefore, the signal at $\delta = 69.0$ ppm was more likely from the surface-adsorbed DME, which was the dominant species on the catalyst surface detected by ex situ ^{13}C MAS NMR spectroscopy. More importantly, the appearance of the strong signals at $\delta = 69.0$ and 59.5 ppm was accompanied by the detection of the initial ethene product in the gas phase and also monitored by the detection of higher hydrocarbon products (the signals at $\delta = 20\text{--}40$ ppm; Figure 3). These observations implied a special activation of the adsorbed DME under the reaction conditions, and that it should be the key step for the subsequent generation of initial ethene.

The GIPAW periodic method was employed for the prediction of the ^{13}C chemical shift in ssNMR spectroscopy. Interestingly, the chemical shift of the carbon atom from DME is theoretically predicted to appear between $\delta = 59.5$ and 71.9 ppm when stretching the bond distance of one of the C–H bonds of DME from 1.108 to 1.309 Å. (see Figure S8 and Table S1). Similarly, the chemical shift of the carbon atom from methanol is theoretically predicted to lie between $\delta = 48.8$ and 60.5 ppm with the extension of one C–H bond from 1.105 to 1.263 Å (see Figure S9 and Table S2). In this way, the absence of the signal from adsorbed methanol possibly resulted from the overlap with the signal from SMS at $\delta = 59.5$ ppm upon the activation of methanol. In situ ssNMR measurement gave direct and real evidence of the activated state of the C_1 species at the very beginning of the reaction, and was crucial for the interpretation of the first C–C bond formation. The broadening of the signal at $\delta = 69.0$ ppm implied a strong interaction between the activated DME species and either the catalyst substrate or active surface groups (e.g. SMS, TMO) formed on Brønsted acid sites (BAS). The participation of active methylation agents, either SMS or TMO, and the nucleophilic attack from the negatively charged framework oxygen linked to the Al site would accelerate the breakage of the C–H bond of the C_1 reactant (DME or methanol) and the synchronistical formation of the initial C–C bond. For the first time, C_1 reactant activation was directly observed in the MTH reaction process using a zeolite catalyst. Undoubtedly, the activation of surface methylic species to generate a methyleneoxy analogue was critical for the first C–C bond generation. In an early DFT calculation study of the first C–C bond in the methanol to gasoline (MTG) process, when water was allowed to assist the reaction, SMS-mediated methanol or DME transformation to form adsorbed ethanol and methyl ethyl ether, respectively, was predicted with corresponding activation barriers of 251 kJ mol^{−1} and 211 kJ mol^{−1}, thus indicating the feasibility of the direct pathway for C–C bond formation in terms of the energy.^[35] Comparatively, TMO was

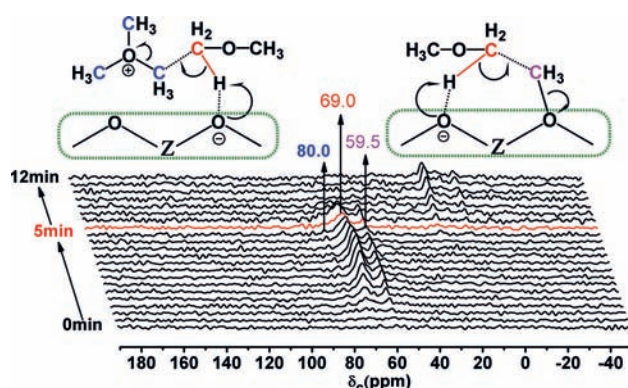
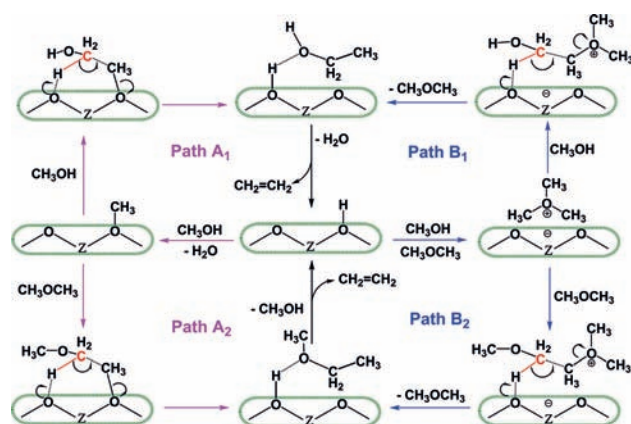


Figure 3. In situ solid-state ^{13}C MAS NMR spectra recorded during [^{13}C]methanol conversion over HZSM-5 at 300 °C. The spectra were recorded every 20 s from 0 to 5 min and then every 60 s from 5 to 12 min.

predicted to be less important in the formation of methyl ethyl ether because of the relatively high activation barrier. Actually, the direct mechanism of SMS/TMO-species-mediated conversion of either methanol or DME into hydrocarbons is operative only at the initial stage of the MTH reaction, because the signal at $\delta = 69.0$ ppm was only observed within the initial 6 minutes. Once ethene was formed, oligomerization and cyclization generated higher olefins (see Figure S10) and even active methylcyclopentyl carbenium ions (see Figure S11). On this occasion, methanol conversion propagates by efficient and indirect pathways with the regeneration of either olefins or active cyclic organic compounds.^[14,36]

Based on experimental evidence from in situ investigations, new insights into the formation of the first C–C bond in the initial stage of the MTH reaction are provided (Scheme 1). SMS is formed by methanol dehydration at



Scheme 1. Plausible routes for the first carbon–carbon bond formation during the early stages of the MTH reaction. The carbon atom in activated reactants is marked in red has been directly observed by in situ ssNMR spectroscopy in this work.

BAS, and TMO can be generated from the reaction of DME and SMS/methanol.^[8,30,31] At relatively high reaction temperatures, the C–H bond of either surface-adsorbed DME or methanol is stretched by the framework oxygen atom linked to Al site and weakened, to some extent, to generate the species containing the methyleneoxy analogue (R–O–CH₂–H–Zeo; R = H, CH₃). In an associative manner, as depicted in either path A₁/A₂ or path B₁/B₂, the activated DME/methanol will be methylated by either SMS or TMO to generate surface-adsorbed ethanol/methyl ethyl ether containing the first C–C bond, and will release the initial ethene. With the breakage of C–H bond from activated reactants and the ethene product generation, the H atom is donated back to the negatively charged framework oxygen atom and the surface BAS is recovered. Alternatively, when the H atom from either the activated methanol or DME does not donate back to the framework oxygen, but to SMS, methane and formaldehyde will be generated (see Scheme S1). This path is consistent with the detection of methane and formaldehyde in the effluent. Although the further transformation of methane and formaldehyde to ethene was theoretically predicted according

to the methane–formaldehyde mechanism,^[11,12] the failure in capturing the relevant intermediates on the catalyst surface implies that the path C₁/C₂ might be plausible routes to generate stable products of methane and formaldehyde rather than to further build a C–C bond.

In conclusion, the first C–C bond formed during the initial stage of the MTH process originates from the direct interaction of the surface adsorbed C₁ reactant (DME/methanol) and the intermediates (SMS/TMO) on HZSM-5 catalyst. For the first time, the activated DME was directly observed within a real catalytic environment of the acid zeolite catalyst by in situ ssNMR spectroscopy. The activation of the C–H bond of the adsorbed DME or methanol, by the aid of framework oxygen and surface organic species, either SMS or TMO, is the crucial step for the first C–C bond generation from C₁ reactants. The successful capture of activated DME with a methyleneoxy analogue group discloses an interesting synergetic mechanism involving C–H bond breakage and C–C bond coupling during the initial stage of the MTH reaction.

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Conflict of interest

The authors declare no conflict of interest.

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