Catalytic Mechanisms

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Formation Mechanism of the First Carbon–Carbon Bond and the First Olefin in the Methanol Conversion into Hydrocarbons

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***Abstract:** The elementary reactions leading to the formation of the first carbon–carbon bond during early stages of the zeolite-catalyzed methanol conversion into hydrocarbons were identified by combining kinetics, spectroscopy, and DFT calculations. The first intermediates containing a C−C bond are acetic acid and methyl acetate, which are formed through carbonylation of methanol or dimethyl ether even in presence of water. A series of acid-catalyzed reactions including acetylation, decarboxylation, aldol condensation, and cracking convert those intermediates into a mixture of surface bounded hydrocarbons, the hydrocarbon pool, as well as into the first olefin leaving the catalyst. This carbonylation based mechanism has an energy barrier of 80 kJ mol^{-1} for the formation of the first C−C bond, in line with a broad range of experiments, and significantly lower than the barriers associated with earlier proposed mechanisms.*

Catalytic conversion of methanol into hydrocarbons (MTH) on zeolites such as H-ZSM-5 and SAPO-34, has become an alternative pathway to crude-oil-derived hydrocarbons, as a basis for preparing gasoline (MTG) and light olefins (MTO).[1] Despite of the industrial success of this process, the full reaction mechanism is still under debate. It is accepted that the steady-state reaction network involves a mixture of hydrocarbons with long residence time in the zeolite pores, the so-called hydrocarbon pool, which remains in pseudo steady-state by a dynamic equilibrium between the carbon chain growth via alkylation with methanol and the product elimination by cracking and dealkylation. A dual cycle mechanism involving one catalytic cycle with long olefins as intermediates, and another cycle with aromatic intermediates has been well established and its role in controlling the product distribution is nowadays well understood.[2] However, the mechanism for the formation of a first carbon–carbon bond and the initiation of the hydrocarbon pool remains unclear.

The relatively low reactivity of methanol alone on Brønsted acid sites has raised doubts in the past about the existence of a direct reaction route from methanol and dimethyl ether (DME) to the hydrocarbon pool, and some studies suggested that the hydrocarbon pool originated from impurities in the reactant feed or in zeolite.[3] The approximately 20 different proposals for the direct formation of a first carbon–carbon bond from C$_1$ species documented in the literature were all eventually discarded by a comprehensive theoretical analysis using density functional theory.[4] From an industrial point of view, the early elementary steps forming the hydrocarbon pool seem irrelevant, because the usual industrial realization uses recycling of unwanted products. Then, the hydrocarbon pool is hypothesized to be readily generated via alkylation, bypassing the first C−C bond formation. However, our recent investigations on the nature of the active and deactivating carbon species formed inside the zeolite showed that strongly deactivating species are formed at the early stages of MTH making it very important to understand the elementary steps involved.[5] The fact that the composition of these deactivating species is different from the typical compounds of the hydrocarbon pool as well as from carbon deposits led us to revisit the methanol chemistry involved in the formation of first C−C bond.

The study aims, therefore, not only to reach a better understanding of the reaction mechanism during the initial stages of methanol conversion, but also to explore the possible link to a potentially strong and hitherto unidentified deactivation of the zeolite catalysts used for the process. The mechanistic exploration of the reactions during the early stage of MTH has been unsuccessful so far because of the low concentrations of intermediates containing a C−C bond and their fast transformation through the subsequent autocatalytic reactions with methanol. Using leads from products during the initial stages of methanol conversion, we were able to trace these reactions unequivocally. The feasibility of the reaction pathways is corroborated by density functional theory (DFT) calculations.

We show herein that the decomposition of methanol to formaldehyde and CO takes place readily under typical reaction conditions already on inert surfaces, such as silicalite, Na-ZSM-5, or γ-Al$_2$O$_3$ (Figure S1–S3 in the Supporting Information). Carbon monoxide is involved subsequently in several acid-catalyzed reactions, including carbonylation of methanol, leading to the formation of the first C−C bond. The initial methanol conversion was studied at 450 °C in a quartz tubular reactor. To investigate the chemistry of methanol during the initial stages, the feed was passed over silicalite. Methane, formaldehyde, and CO were detected, together

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with H_2, indicating that dehydrogenation and disproportionation of methanol took place in the absence of Brønsted acid site (Figure S1–S3). This observation is in line with the commonly observed high selectivity to CH_4 at very short contact times of methanol in zeolites.[5,6]

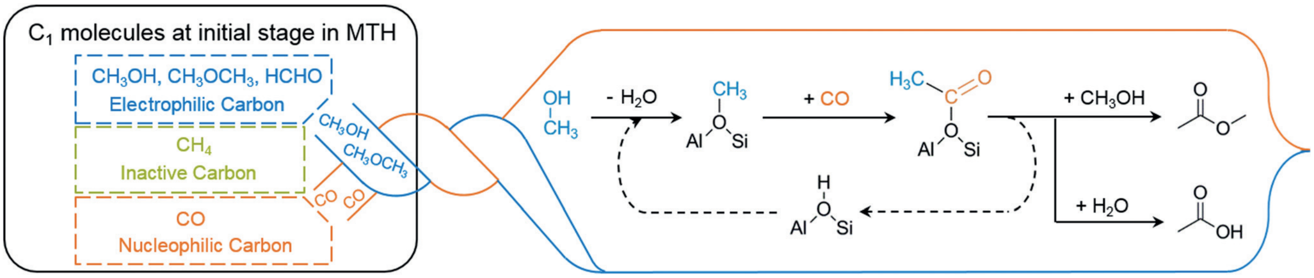
It is interesting to note that the formation of HCHO and CO in the MTH reaction has been widely reported, but often disregarded as an undesired byproduct arising from the presence of metal impurities in the zeolite, catalyzing methanol dehydrogenation.[3,7] The formation of methane, formaldehyde, and CO in an all quartz reactor system in the absence of catalyst indicates that these C_1 molecules are present in the reactant stream when passing through the catalyst bed, making them potential reactants in the catalytic pathway to the first C–C bond (Scheme 1).

The C atom in MeOH, DME, and HCHO is electrophilic, while the carbon atom in CO is nucleophilic (Scheme 1). This leads readily to the formation of a C–C bond between electrophilic and nucleophilic carbon. Acidic zeolites are able to catalyze such a C–C bond formation, that is, carbonylation of olefins,[8] alcohols,[9] methanol, and dimethyl ether.[10] In the present case, acetyl species were formed as intermediates at very low conversions, as described in detail below. Thus, we hypothesize that the first C–C bond is generated through carbonylation of methoxy groups on zeolite acid sites, leading to a surface acetyl group, which subsequently dissociates into methyl acetate (MeOAc) or acetic acid (HOAc; Scheme 1).

Theoretical calculations stringently supported the thermodynamic feasibility of the proposed initial reactions. For carbonylation, postulated as the crucial step of the first C–C bond formation, an energy barrier of 80 $kJ\,mol^{-1}$ (Figure S4) was calculated, in line with literature reports (54 $kJ\,mol^{-1}$ and 81 $kJ\,mol^{-1}$ [10c]). This energy barrier is over 60% lower than those calculated for alternative mechanisms proposed for the formation of the first C–C bond in MTH, namely the ylide type mechanism (320 $kJ\,mol^{-1}$,[11a] 330 $kJ\,mol^{-1}$ [11b]), the carbenium ion alkylation mechanism (210 $kJ\,mol^{-1}$,[11b] 300 $kJ\,mol^{-1}$ [11c]), the trimethyloxonium mechanism (340 $kJ\,mol^{-1}$[11c]), or the carbene mechanism (360 $kJ\,mol^{-1}$,[11a] 240 $kJ\,mol^{-1}$ [4]). The low energy barrier of the carbonylation route is attributed to the nucleophilicity of CO, which allows the circumventing of an energetically difficult transformation of MeOH into a nucleophile, such as a carbene or an oxonium ylide.

This hypothesis has its basis in experiments detecting methyl acetate and acetic acid as reaction intermediates (Figure 1) and the fact that the reaction rate increased with CO cofeeding during methanol conversion (Figure 2). For these experiments, methylal ($CH_3OCH_2OCH_3$) was used as feed, because it reacts on zeolites[12] to form DME, HCHO, and CO, simulating the partial decomposition of methanol during the MTH reaction, but with a higher ratio of HCHO and CO to DME. The reaction of methylal was conducted on H-ZSM-5 at 400 °C (Figure 1 A). Initially, full conversion was obtained, with olefins as the main product. Other products included paraffins, aromatics, CO, and water (not shown). With time on stream, the olefin yield decreased, and increasing concentrations of MeOH and DME were detected in the product stream. These are the stable C_1 products from the decomposition of methylal, and their appearance indicates the deactivation of the catalyst. Methyl acetate and acetic acid were detected shortly before methanol/DME breakthrough and they reached a maximum yield of less than 1%. Methyl acetate and acetic acid were primary products, while olefins appeared as secondary products (Figure 1 B). This is independent of the concentration of C_1 reactants and of the zeolite type, that is, methyl acetate and acetic acid were also observed during methanol or methyl formate conversion on H-MOR and H-BEA (Figure S5). The hypothesis that the first C–C bond is formed via carbonylation of MeOH or DME was further evidenced by converting MeOH on H-MOR with linearly increasing temperature (Figure 1 C). DME appeared at about 180 °C and approached equilibrium with MeOH above 300 °C, while olefin and aromatic production started only from approximately 320 °C and 340 °C (Figure S6). Methyl acetate and acetic acid were observed transiently in very low concentrations from 200 °C to 300 °C.

Olefin formation was promoted by exposing methanol adsorbed on H-ZSM-5 to CO at increasing temperatures (Figure 2). When heated under He flow, MeOH desorbed at 120 °C and 200 °C, DME at 250 °C and 400 °C, while olefins were not detected below 500 °C (Figure 2 A). In contrast, under CO flow olefins formed from 360 °C on (Figure 2 B). The desorption rates of MeOH and DME were almost unaffected, except for the decrease of DME around 370 °C owing to the onset of olefin formation. This difference in reactivity in presence of CO was also shown by abruptly replacing He with CO at 400 °C (Figure 2 C), which caused the



Scheme 1. First C–C bond formation in MTH through coupling between nucleophilic and electrophilic carbon atoms. Adsorption of MeOH (or DME) on a zeolite Brønsted acid site forms a surface methoxy group. The methoxy group undergoes nucleophilic attack by CO, forming a surface acetyl group which contains the first C–C bond. The acetyl group dissociates into methyl acetate and acetic acid in the gas phase. Energy barrier of the carbonylation step is 80 $kJ\,mol^{-1}$.

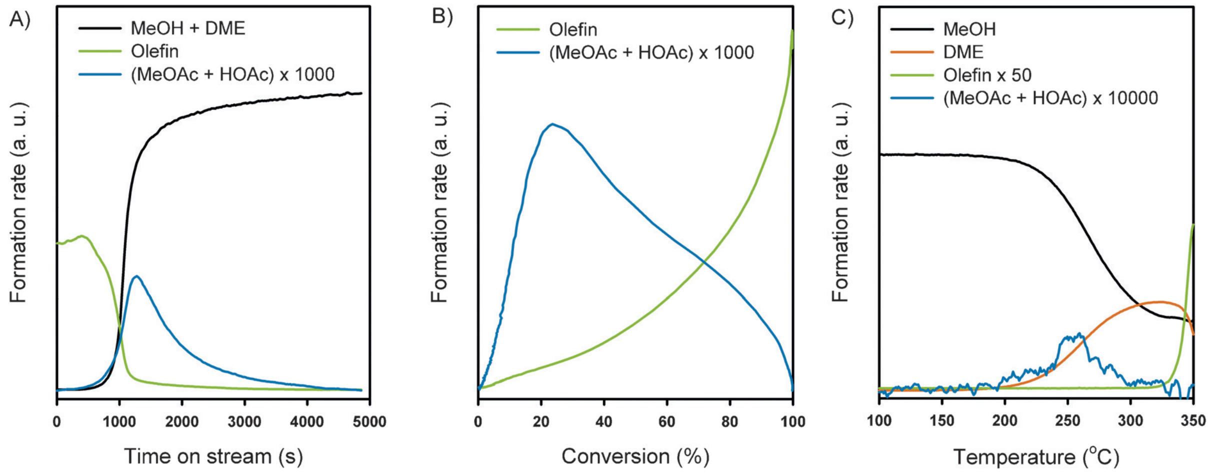


Figure 1. HOAc and MeOAc as intermediates in MTH reactions. A) and B) Product formation rate in the reaction of methylal on H-ZSM-5 as a function of A) time on stream and B) conversion. (Conditions: methylal 150 mbar, He 25 mL min^{-1}, 50 mg H-ZSM-5, reaction temperature 400 °C). C) Reaction of MeOH on H-MOR with linearly increasing temperature. (Conditions: MeOH 150 mbar, He 25 mL min^{-1}, 10 mg H-MOR, temperature ramping rate 10 °C min^{-1}).

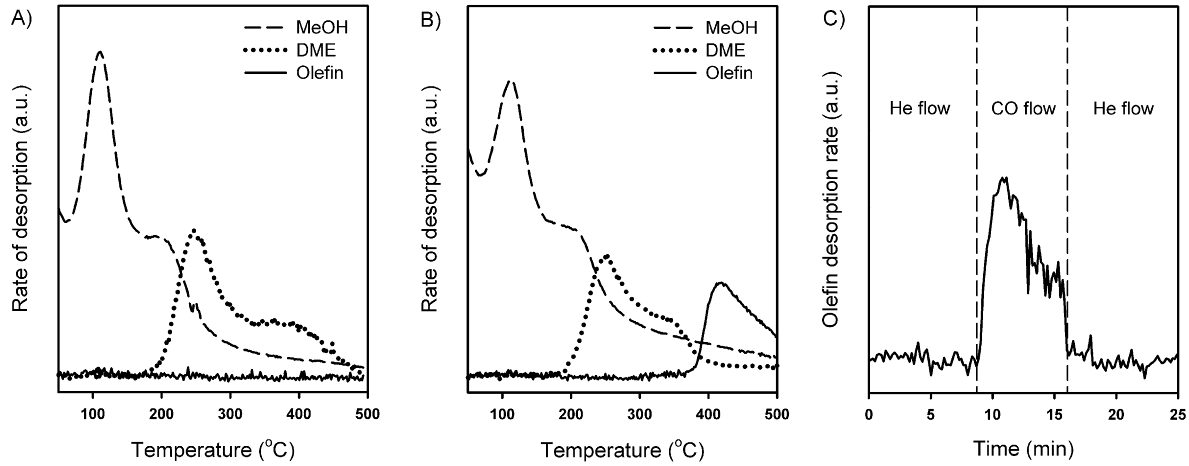


Figure 2. A),B) Temperature-programmed surface reaction of MeOH on H-ZSM-5 under A) He flow and B) CO flow. C) Olefin desorption rate in the surface reaction of MeOH on H-ZSM-5 under alternate He and CO flow at 400 °C. (Conditions: He or CO 25 mL min^{-1}, 25 mg H-ZSM-5, temperature ramping rate 10 °C min^{-1}).

nearly immediate formation of olefins as long as CO was present. IR spectra of H-ZSM-5 surface species taken in situ showed the existence of acetyl surface groups in the presence of CO and their transformation into unsaturated carbonyl groups concurrently with the first detection of olefins in the gas phase (Figure S7), indicating the formation route of olefins from carbonyl species. Conversely, under He flow, no such surface carbonyl species were formed and olefins were not formed under the chosen reaction conditions.

In contrast to the present results, such promotional effects of CO in MTH reaction were not observed in previous studies.[13] Therefore, the participation of CO was discarded and excluded from the dominant proposals for MTH reaction mechanism. The lack of this promotion in those experiments is attributed to the presence of the much higher partial pressure of water, a byproduct from the methanol dehydration to DME, inhibiting such reaction.[10a,b] In the carbonylation of DME on H-MOR (reported to be the most active zeolite for such reaction[10a,b]), the presence of only 6 mbar of water decreased the carbonylation rate to 20 % of the initial value, and it further reduced to below 2 % when 42 mbar water was present (Figure S8A). The inhibition was proposed to be due to competitive adsorption of water with CO[10a] or methanol,[10d] and blockage of 8MR pockets in H-MOR by water clusters.[10c] Similar inhibiting effects were also observed, when converting DME into olefins on H-ZSM-5 (Figure S8B). At low conversion (< 1 %), cofeeding 6 mbar water largely decreased the olefin yield, but it was recovered after removing the cofed water. Despite the low carbonylation rates to be expected in the zeolite under MTH conditions (S9, Supporting Information), the traces of methyl acetate and acetic acid formed via this pathway suffice to start conversions of the intermediates, triggering the formation of the hydrocarbon pool and subsequently the fast methanol conversion into hydrocarbons via alternative methylation and cracking pathways. Thus, the existence of the induction period in methanol conversion at short contact times[1b,c] is concluded to be the consequence of the very low rate of the first step of

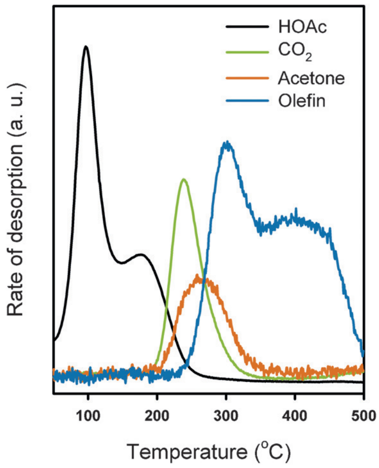


Figure 3. Product desorption rate in the surface reaction of HOAc adsorbed on H-ZSM-5 with increasing temperature. (Conditions: He 25 mL min^{-1}, 25 mg H-ZSM-5, temperature ramping rate 10 °C min^{-1}).

the mechanism, that is, the carbonylation of methanol or DME in the presence of water.

Having established how the first C–C bond can be formed via carbonylation, we only briefly address the subsequent transformation of MeOAc and HOAc intermediates into olefins and other hydrocarbon species. Surface reaction of HOAc adsorbed on H-ZSM-5 with increasing temperature (Figure 3) showed the formation of C_{2-4} olefins from 230 °C and reached a maximum at 300 °C. This result indicates the transformation of acetyl species to olefins even in the absence of MeOH. Before olefins were formed, acetone and CO_2 were detected, which indicates that HOAc undergoes acetylation followed by decarboxylation (ketonic decarboxylation).[14] And acetone has been reported to be converted into olefins via aldol self-condensation followed by cracking.[15] The very low concentrations of acetate formed in the reaction of methanol (Figure 2) explains that secondary intermediates, such as acetone, can hardly be detected with the analytics employed herein. Under MTH reaction conditions, methanol may also react with HOAc leading to a complex reaction network including reactions such as methylation and hydride transfer, which initiate and build up the hydrocarbon pool. The detailed reaction path analysis is currently explored, but is beyond the scope of the present contribution.

In conclusion, the identification of first intermediates containing a C–C bond in the MTH reaction and the analysis of reactivity of C_1 species on zeolite catalyst has revealed that formation of the first C–C bond involves carbonylation of methanol or dimethyl ether to form acetic acid and methyl acetates. Both direct evidences from experimental results and the energy barrier from theoretical calculations demonstrated the feasibility of this reaction pathway as being responsible for the initiation of the conversion of methanol into hydrocarbons.

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