

Recent Trends and Fundamental Insights in the Methanol-to-Hydrocarbons Process

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Abstract

The production of high-demand chemical commodities, such as ethylene and propylene (methanol-to-olefins), hydrocarbons (methanol-to-hydrocarbons), gasoline (methanol-to-gasoline) and aromatics (methanol-to-aromatics) from methanol—obtainable from alternative feedstocks, such as carbon dioxide, biomass, waste or natural gas through the intermediate formation of synthesis gas—has been central to research in both academia and industry. Although discovered in the late 1970s, this catalytic technology has only been industrially implemented over the last decade, with a number of large commercial plants already operating in Asia. However, as it is the case for other technologies, industrial maturity is not a synonym of full understanding. For this reason, research is still intense and a number of important discoveries have been reported over the last few years. In this review, we summarize the most recent advances in mechanistic understanding—including direct C-C bond formation during the induction period and the promotional effect of zeolite topology and acidity on the alkene cycle—and correlate these insights to practical aspects in terms of catalyst design and engineering.

In 1977, scientists at Mobile published the first patent on the methanol-to-hydrocarbons process (MTH)¹ claiming “A lower alcohol and/or ether feed is selectively converted to a mixture of light olefins, including ethylene and propylene, by catalytic contact of the feed, for example methanol or dimethyl ether, at sub-atmospheric partial pressure, with certain crystalline aluminosilicate zeolite catalysts exemplified by ZSM-5” (Fig. 1a). The possibility to obtain olefins (methanol-to-olefins, MTO), aromatics (methanol-to-aromatics, MTA) and/or gasoline (methanol-to-gasoline, MTG) without relying on oil (methanol can be produced from a wide range of carbon-containing sources, like biomass, waste, coal, natural gas or even CO₂) makes this family of processes a convenient alternative to the classical production routes of high-demand chemicals and intermediates.

As it is the case for other grand old ladies of the petrochemical industry, such as Fluid Catalytic Cracking (FCC),² the MTH process, despite being already commercialized, still attracts a great deal of attention from both industry and academia. Apart from the obvious economic driving force in improving the process, from a scientific point of view, understanding (and eventually controlling) the complex reaction mechanism behind such a complex overall stoichiometry remains a challenge. As we will elaborate below, the process is dictated by a large set of elementary reactions and the full picture of the MTH reaction mechanism is still elusive (Fig. 1b). On one hand, the chosen reaction conditions are important, as not all reactions have the same kinetic order and energies of activation. On the other hand, the zeolite microenvironment plays an even bigger role in defining product distribution and catalyst lifetime.³ MTH serves therefore as an outstanding example of complexity in zeolite chemistry and heterogeneous catalysis, as pinpointed in a number of classical⁴ and more recent reviews.^{5, 6, 7, 8, 9}

In this review article, we highlight current challenges of MTH chemistry by critically analyzing the existing literature to give an updated picture on the mechanism of reaction and to provide guidelines for catalyst design. We believe that, despite a number of excellent reviews in this field, knowledge on mechanistic aspects and structure-property relations in MTH has advanced tremendously over the last few years and we expect this article to bridge the gap between those earlier reviews dedicated to mechanism rationalization and catalyst engineering. To do so, we first summarize the recent efforts to unravel the mechanism that leads to the formation of the first C-C bond (*i.e.* coupling of two methanol or dimethyl ether molecules), a topic of intense debate over the last few decades. Formation of the direct C-C bond continues with the formation of longer hydrocarbons inside the zeolite pores, this mechanism along with the most recent spectroscopic evidences of its different steps are discussed in the second section. Finally, with this mechanistic information in hand, we define a number of catalyst design rules that should help the reader understand the effect of catalyst topology, acidity and reaction conditions on product distribution and catalyst deactivation. The review is completed with our personal view on future challenges both from the process and fundamental point of view.

The direct C-C bond.

The MTH process involves a very complex reaction mechanism.^{5, 6, 7, 8, 10} As of now, more than 20 different proposals have been postulated in the literature.⁴ Surprisingly, the exact route for the formation of the first carbon-carbon (C-C) bond during MTH was only very recently unveiled.^{11, 12, 13, 14, 15, 16, 17, 18} For a long time, the scientific community assumed that the presence of traces of impurities (e.g. in the methanol, catalyst, and/or carrier gas) was responsible for the formation of the direct C-C bond over any direct mechanism (i.e. the coupling of two methanol molecules). This assumption was primarily attributed to the lack of concrete experimental evidence in support of the direct mechanism.^{19, 20} Moreover, the feasibility of such direct coupling was anticipated to be low by theoreticians because of the high activation energies and unstable reaction intermediates.^{21, 22} In 2006, Hunger and co-workers systematically demonstrated that traces of organic impurities neither have any significant influence on product distribution, nor do they control the formation of hydrocarbon pool (HCP, *vide infra*) species during MTH reaction (Fig 1a).²³ That means a direct mechanism may be operative, at least in the early stages of the MTH reaction.¹⁶ Since then, other research groups (e.g. Kondo, Fan, Copéret, Lercher, Weckhuysen, and Liu) have delivered both experimental and theoretical evidence in support of the existence of a direct mechanism during the initial stages of MTH.^{11, 12, 13, 14, 15, 16, 17, 18, 23, 24, 25, 26, 27, 28, 29, 30} In essence, this reaction can be sub-divided in two parts: direct mechanism and conventional HCP/Dual cycle mechanism, during induction and autocatalytic period, respectively.

There are several excellent reviews available in the literature on this topic, which adequately describe history and developments of direct mechanisms.^{4, 6} Although a consensus has currently been reached regarding the existence of the direct mechanism, its actual nature/course of action is yet to be fully established. In all direct mechanistic proposals, a surface methoxy species (SMS), formed upon adsorption of methanol onto a Brønsted acid site is non-arguably the most experimentally verified intermediate (Fig. 2).^{13, 14, 18, 26} The ability of SMS to form a C-C bond at higher reaction temperature is a well-established phenomenon during any zeolite-catalyzed hydrocarbon conversion process.¹⁸ The idea of a carbene-insertion mechanism by SMS was first introduced by the group of Hunger, mostly based on NMR spectroscopy and carbene-trapping experiments.^{18, 26, 27} The carbene character of SMS was proposed to form through the polarization of the C-H bond of SMS by a neighboring adjacent oxygen (as depicted in Fig. 2a-c).^{31, 32} The carbene/ylide nature of SMS was confirmed by a carbene trapping experiment with cyclohexane as a probe molecule at $\geq 493\text{K}$, where methylcyclohexane was formed through an insertion reaction of carbene/ylide into the sp^3 C-H bond of cyclohexane (Fig. 2a).¹⁸ Later, Kondo et al. also arrived to the same conclusion with the help of IR spectroscopy: the C-C bond containing hydrocarbon species originated from the coupling between carbene-like SMS and methanol/dimethyl ether (DME) (Fig. 2b).^{11, 12} Another convincing evidence in support of the existence of a carbene-type mechanism was provided recently by Weckhuysen et al., by employing 2D magic angle spinning (MAS) solid-state NMR (both ^1H - ^{13}C and ^{13}C - ^{13}C) spectroscopy (Fig. 2c).¹³ The strong signals at 52.2 (^{13}C) and 3.59 (^1H) ppm were assigned to surface adsorbed methanol, while the signals at 57.7 (^{13}C) and 3.54 (^1H) ppm were attributed to SMS (red strip in Fig. 3a). Interestingly, a strong cross-peak between these ^{13}C signals was also

observed, which was due to the close proximity of surface adsorbed methanol and SMS (blue strip in Fig. 3a and schematic illustrated in Fig. 2c). Such close proximity does not only reveal the ongoing reaction between SMS and methanol (through the polarization of the C-H bond of SMS by a neighboring adjacent oxygen atom), but also showcases the carbene/ylide-character of SMS.

Apart from the carbene mechanism, multiple analogues of oxonium and methane-formaldehyde-type direct mechanistic proposals have also been shown in the recent literature. The conventional methane-formaldehyde mechanism of the MTH reaction was originally postulated by Hutchings et al. in 1987.³³ The direct C-C bond coupling reaction between methane and formaldehyde, as a result of disproportionation of methanol (through its hydride abstraction by SMS, as illustrated in Fig. 2d), was hypothesized to pose an unrealistically high energy barrier.²² However, several recently postulated proposals are conceptually similar to this mechanism. The methoxymethyl cation mechanism proposed by Fan et al. was developed from the original proposal of Hutchings et al., in order to make it energetically feasible.^{28, 29} Their experimentally and theoretically verified proposal involves the formation of direct C-C bond *via* (i) a methoxymethyl cation ($\text{CH}_3\text{OCH}_2^+$ from SMS and DME, *i.e.* instead of direct formation of formaldehyde), and (ii) its subsequent direct C-C coupling with another DME/methanol molecule to form $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OR}$ ($\text{R}=\text{H}, \text{CH}_3$) (a precursor for olefins, as shown in Fig. 2e).^{28, 29} Similarly, the methyleneoxy mechanism was recently reported by Liu et al. based on *in-situ* solid-state NMR spectroscopy by measuring ^{13}C -methanol conversion over H-ZSM-5 using a rotor reactor (Fig. 2f,g & Fig. 3b).¹⁴ Three major bands at 59.5, 69.0 and 80.0 ppm were generated almost instantaneously and were assigned to SMS, surface adsorbed DME and trimethyl oxonium (TMO), respectively. The appearance of these three bands was accompanied by formation of ethylene (detected by GC-MS) as well as higher hydrocarbons (chemical shifts of $\delta=20\text{-}40\text{ppm}$). Therefore, the direct C-C bond was proposed to be formed as a result of direct interaction between the reactant (methanol/DME) and zeolite bound surface intermediates, SMS and TMO (Fig. 2f,g). The important C-H bond activation step could be assisted by framework oxygen to form active methyleneoxy species ($\text{R-O-CH}_2\text{-H}\cdots\text{zeolite}$), which eventually led to the simultaneous formation of both olefin (Fig. 2h) and methane/formaldehyde (Fig. 2i). The unprecedented downfield response and relatively broader nature of SMS at 69.0 ppm under *in-situ* reaction conditions (compared to $\delta=59.0$ ppm under *ex-situ* reaction conditions) was attributed to the strong interaction between the activated DME species and active surface-zeolite catalyst (Fig. 2f, g). Although both methane and formaldehyde are proposed to be involved in the catalytic cycle (*via* assisting the regeneration of SMS), their role towards the formation of the direct C-C bond was not clarified.¹⁴

While numerous mechanistic reports have identified formaldehyde as a side-product, its fate/role during the MTH reaction is still a subject of debate. Formation of formaldehyde on solid acid catalysts from methanol is quite predictable, particularly at high temperatures. Interestingly, it could be easily associated to the Koch-carbonylation mechanism of the MTH reaction (Fig. 2j), another direct mechanistic route proposed independently by the groups of Lercher and Weckhuysen at the same time.^{13, 16} Lercher and co-workers first proposed methyl acetate ($\text{CH}_3\text{CO}_2\text{CH}_3$, derived via carbonylation of methanol/DME) as the

very first C-C bond-containing intermediate during the MTH reaction over H-ZSM-5.¹⁶ Spectroscopic evidence for this proposal came from the Weckhuysen group by employing a combination of solid-state NMR spectroscopy coupled with *operando* UV-visible diffuse reflectance spectroscopy (DRS) and on-line mass spectrometry and it was shown that the Koch-carbonylation route occurred during MTH over H-SAPO-34.¹⁶ In this case, the direct C-C bond containing zeolite-bound acetate species (Fig. 2j) is a Koch-carbonylation product of SMS. Here, either methanol or formaldehyde, in principle, could act as a carbonylating agent under MTH reaction conditions. Next, methyl acetate was formed after methoxylation of surface-bound acetate species, which independently could initiate the formation of HCP species and thus, olefins. In the carbonyl region of the NMR spectrum, clear cross-peaks to methyl carbon atoms were observed at both long and short mixing times (Fig. 3c). The signal at 180.5 ppm shows only one cross-peak, corresponding to zeolite-acetate species, at 22.5 ppm (Fig. 3c). Moreover, the signal at 178.5 ppm has a clear cross-peak with a ¹³C signal at 55.1 ppm at longer mixing times only (*i.e.* methoxy-carbon is not directly attached to the carbonyl-carbon). This ¹³C-methoxy signal correlates with a H signal at 3.82 ppm and has an additional very weak correlation signal with a methyl at 22.3 ppm (¹³C) at longer C-C mixing times (Fig. 3c). This cross-peak pattern is a signature response from a methyl acetate molecule. Thus, all three responsible intermediates of this mechanism (SMS, zeolite-acetate and methyl acetate) were spectroscopically identified by solid-state NMR spectroscopy. This Koch-carbonylation mechanism of the MTH reaction has recently been theoretically verified by Pleassow and Studt.³⁰ Interestingly, the simultaneous existence of (at least) two different direct C-C bond-forming routes (*i.e.* carbene and Koch-carbonylation) were spectroscopically identified (Fig. 2c, j & Fig. 3a, c).

Another interesting recent report by Copéret et al. should be mentioned: the formation of the direct C-C bond from DME alternatively proposed to be catalyzed by extra-framework aluminum atoms (Al) in acidic zeolites (Fig. 2k).¹⁷ Herein, the C-C bond forming step initially involves generation of a transient Al-oxonium species (*i.e.* formaldehydic oxygen coordinated to a Lewis acidic Al) through hydrogen abstraction from an Al-methoxy species. Next, Al-oxonium species react with a methane molecule to yield the direct C-C bond containing surface-ethanolic species (*i.e.* a precursor for ethylene). This contribution inevitably sparks the controversy about the actual involvement of the zeolitic Lewis acid sites during the direct mechanism of the MTH reaction.^{15, 17} However, such discussion is beyond the scope of the current review and demands further research to understand the phenomenon at the molecular level.

Dual-cycle concept.

After a rather short induction period assigned to the formation of the direct C-C bond, the MTH process continues with the steady-state formation of hydrocarbons in the so-called autocatalytic dual-cycle concept.³⁴ This notation is the result of merging the two mechanistic schemes developed in parallel for ZSM-5 and SAPO-34.⁵ For cage-like zeolites (SAPO-34), able to accommodate large aromatics, light olefins are believed to form *via* an indirect way through hydrocarbon pool species (Fig. 4). They can be visualised as typical ship-in-a-bottle molecules, which can be formed in zeolites but cannot desorb. These

species are methylated yielding light olefins like ethylene and propylene by elimination reactions, thus restoring the initial hydrocarbon pool species. For ZSM-5 and its analogues, formation of hydrocarbons was rationalized as a result of consecutive methylation and cracking reactions already in the 1980s by Dessau.³⁵ The dual-cycle represents a compromise between both mechanisms (olefinic and aromatic cycles) running in parallel (Fig. 4). Both cycles can be subcategorized further to elementary steps described by six types of reactions: methylation and cracking of olefins, methylation and dealkylation of aromatics, hydrogen transfer and cyclization, the latter two acting as the bridging step between the two cycles.⁸ Using transient switching experiments ¹²C/¹³C Svelle et al.³⁶ showed that, for ZSM-5, all olefins except ethylene are produced from the olefinic cycle. Ethylene evolution was linked to the presence of lower methylbenzenes, suggesting that ethylene is mostly a product of the aromatic cycle.³⁷ Sun et al.³⁸ further contributed to this topic by performing seminal kinetic investigations at different conversion levels in the presence of aromatic and olefinic co-feeds. They concluded that both cycles are active for ethylene and propylene production, with the aromatic cycle giving similar selectivity for both olefins. The olefinic cycle, on the other hand, was far more selective to propylene than ethylene, which implies that, if the two cycles equally contribute to the product distribution, most ethylene will be formed in the aromatic cycle.³⁹ The co-existence of the two cycles naturally renders them as competing.⁴⁰ In this spirit, one can speculate that a desired hydrocarbon range can be obtained by either stimulating or suppressing one over the other. Such co-catalytic features of HCP species during the MTH reaction were later theoretically verified by van Speybroeck et al.,⁴¹ indirectly reinforcing the concept of hybrid organic-inorganic nature of a working MTH catalyst, as originally proposed by Svelle et al.³⁶

UV-visible DRS is possibly the most utilized spectroscopic technique for the characterization and identification of zeolite trapped organics. The biggest advantage of UV-visible DRS is its ability to differentiate between carbocationic HCP species and their neutral counterparts. For instance, the absorption band of any arenium HCP cation is lower in energy than any electronic transition of its neutral counterpart. Moreover, UV-visible DRS provides insightful information regarding the zeolite framework dependent formation of deactivating species during the course of reaction. In general, multiple bands at around ≤ 295 , 340-360, 385-410, 460-500 and ≥ 600 nm, are observed during a MTH reaction and were typically attributed to neutral benzene/cyclopentadienyl species, dienyl carbocationic/methylbenzeniums (up to three methyl groups), highly methylated areniums (specifically hexamethylbenzenium ions, HMB⁺), trienylic and methylated polyarenium ions, respectively (Fig. 3d,e).^{25, 26, 42, 43, 44, 45, 46, 47} The formation and characteristics of these bands are quite unique depending on the zeolite framework topology and acidity. For instance, the specific role of alkyl cyclopentadienium ions over MFI zeolite (e.g. H-ZSM-5) was identified by Jentoft and Wulfers using *in-situ* UV-visible DRS (Fig. 3d).⁴⁶ Similarly, the Weckhuysen group identified the nature of governing active and deactivating methylated aromatic species during the MTH process over CHA zeolites (e.g. H-SAPO-34 and H-SSZ-13) employing a combination of *operando* UV-visible DRS and online gas chromatography/mass spectrometry.^{13, 42, 47} Using a similar strategy involving *operando* UV-visible DRS, the same group very recently monitored the formation of active HCP species

and the accumulation of coke molecules during both H-ZSM-5 and Mg-ZSM-5 catalysed MTH.⁴⁸ Such spatiotemporal UV-visible spectroscopic approach reveals the formation of a coke front at the beginning of reactor bed, which travels towards the end until full deactivation. Mg modification resulted in slower progression of the coke front and higher olefin selectivity. However, identification/assignment of zeolite-trapped any organic reaction intermediates by UV-visible DRS in combination with theoretical calculations is not always straightforward and, to some extent, confusing. For example, HMB⁺ and the 1-methylnaphthyl cation display a similar absorption band at ~390 nm.^{41, 44} Unfortunately, both are probable intermediates of the MTH reaction, while HMB⁺ is an active HCP species and the other is formed during the deactivation period.⁴¹ This is the reason behind the enormous rise of utilization of solid-state NMR spectroscopy in recent years for the accurate structural elucidation of trapped organics within zeolites (*vide supra*).^{13, 14, 17} The combination of solid-state NMR with UV-visible DRS has made significant advancement by the groups of Hunger^{18, 25, 43} and Haw.^{49, 50, 51}

Due to its capability to provide information at the molecular level, the utilization of solid-state NMR spectroscopy is increasing gradually in the field of heterogeneous catalysis.¹³ Using ¹³C-enriched methanol not only significantly increases NMR sensitivity, but also allows multi-dimensional solid-state NMR correlation experiments to be performed in order to construct the accurate molecular structures along with structural information of dominant carbenium ions involved in the HCP of the MTH-mechanism.^{6, 18, 49} For instance, the alkylated cyclopentadienium ion was detected as the primary HCP species over HMB⁺ within H-ZSM-5 and H-SSZ-13 zeolites during MTH reaction, whereas hexa-/hepta-methylbenzenium cation is widely acknowledged as the governing HCP species within SAPO-type molecular sieves (like SAPO-34, DNL-6) and H-Beta (Fig. 3f).^{6, 13, 24, 51, 52, 53, 54} This observation was quite consistent with the UV-visible DRS reports by the groups of Jentoft and Weckhuysen.^{13, 42, 47} These results demonstrate that the formation of dominant carbenium HCP species is entirely dependent on the zeolite's framework and acidity.

In a nutshell, the scientific community now accepts that the direct mechanism exists during the early stages of MTO reaction and that hydrocarbon pool species vary depending on zeolite framework, acidity and reaction conditions. Numerous recent mechanistic reports provide solid experimental and spectroscopic evidence and the simultaneous existence of multiple direct C-C bond forming routes during the MTO reaction is quite likely.⁶

Based on this mechanistic knowledge, several strategies can be put forward to drive selectivity of the process in different directions depending on the desired product. The first approach is related to the manipulation of the organic counterpart, *i.e.* changing the concentration of olefin and/or aromatic species. Obviously, the second approach deals with the inorganic element and can be achieved by making use of catalyst engineering. Taking propylene and ethylene (and/or aromatics) yields as the measure of cycle dominance, we will now analyse how certain factors selectively propagate one cycle over the other.

Towards improved selectivity in MTH.

When talking about catalyst and process design, the induction period was disregarded as a possible tool to manipulate both selectivity and lifetime because for a long time it was considered as a negligible part of the entire MTH mechanistic picture. Recent investigations indicated that formaldehyde – formed through disproportionation of methanol during direct C-C bond formation – causes catalyst deactivation *via* interaction with aromatic molecules resulting in the formation of polycondensed aromatics.⁵⁵ Besides, formaldehyde formation is accompanied with the production of CH₄.⁵⁶ It thus becomes clear that in order to achieve better catalyst stability and selectivity, the induction period should be re-engineered to avoid formaldehyde formation. This issue can be addressed at both the catalyst and reactor level. At the reactor level, utilization of a continuous stirred tank reactor (CSTR) instead of a plug flow reactor (PFR) leads to lower local methanol concentrations and lower oxygen containing species, thus mitigating catalyst deactivation.⁵⁷ Moreover, utilization of DME instead of methanol avoids the potential formation of formaldehyde and results in higher methylation rates in comparison to methanol, substantially prolonging catalyst lifetime.⁵⁶ At the catalyst level, it was proposed that addition of rare-earth oxides, such as Y₂O₃, should selectively decompose formaldehyde thus preventing its further interaction with aromatic species.⁵⁸ Utilization of DME (DME/water) instead of methanol seems to be the best solution, since apart from mitigating catalyst deactivation it decreases the overall heat release (the reaction enthalpy of DME dehydration is lower than that of methanol) making it more attractive from an industrial perspective.⁵⁹

Taking advantage of autocatalysis.

Both olefins and aromatics are recognized as competitive co-catalysts, the excessive presence of a certain product promotes the cycle from which it originates.^{38, 40} So the most straightforward strategy to enhance the yield of olefins (propylene and butenes) or aromatics is to increase their concentration by co-processing them with methanol. Several works report the effect of co-feeding a wide range of olefins and/or aromatics with methanol on the product distribution, however, with the main aim to shed light on mechanism details.^{60, 61}

In a wide range of temperatures and at different methanol conversion levels, co-feeding of toluene results in an increase of ethylene and methylbenzene concentration at the expense of propylene and higher olefins as a result of the aromatic cycle propagation.^{40, 62, 63, 64} This strategy can be used to respond to the constantly fluctuating market demands to produce a mixture of olefins with preassigned C₂₌/C₃₌ ratio. Olefins co-feeding turns out to be less straightforward and the propagation of the corresponding cycle depends on other parameters. The JGC corporation reported significantly enhanced propylene yield (up to 60-70%) when C₄-C₅ products were recycled with methanol feed at temperatures higher than 843K.⁶⁵ ⁶⁶ Co-feeding a small amount of propylene at low conversion levels at 548-623 K results in a higher contribution of the olefin cycle, confirmed by higher selectivity towards C₃₊ products,⁶³ while at 723 K and higher conversion levels there is no notable effect of olefins co-feed.⁴⁰ In the first scenario, methylation reactions are promoted over cracking, therefore any inclusion of short chain olefins like propylene results in a dramatic increase of C₃₊ products. At high methanol conversion levels (>70%), the olefinic cycle

becomes more important,³⁸ while further addition of olefins promotes both formation of higher olefins, which with equal success are either cracked or aromatized, thus contributing to both cycles. This brings another important conclusion – process parameters such as temperature and methanol space-time also contribute to the promotion of one cycle over the other when bed effects come into play. Temperature is another decisive parameter in determining the type of prevailing reactions. Higher temperatures promote cracking of higher olefins rather than their cyclization, which can be perceived as promotion of the olefinic cycle. Therefore, to maximize propylene production, the MTP process is carried out at temperatures higher than 723 K.

Influence of zeolite topology on product selectivity.

The zeolite skeleton dictates its shape-selective properties, allowing the participation in the chemical reaction of only those molecules able to fit inside the zeolite pores.⁶⁷ This broad definition can be further subcategorized into reactant-, product- and transition-state selectivity. Thus, being an inherent attribute of zeolitic materials, shape selectivity can be effectively utilized to propagate one cycle over another *via* product- and transition-state selectivity.^{68, 69}

Small pore 8MR zeolites are composed of large cavities interconnected by narrow window openings (Fig. 5a,b).^{70, 71} Window openings are limited by 8 atoms, big enough to let short-chain olefins pass through but sufficiently small as to retain bigger molecules inside their cages, thus creating an ideal playground to incubate the aromatic-based hydrocarbon pool.⁷ In such an architecture, cavity dimensions can influence the nature of the aromatic intermediates (transition-state selectivity),⁷² while window dimensions impose restrictions for the molecules formed inside (product selectivity). Thus, slight differences in both dimensions can affect product distribution and propylene/ethylene ratio, however guaranteeing high selectivity to short-chain olefins (up to 90%).⁷³ Note that the hydrocarbon pool trapped inside also serves as a scaffold for the formation of polycondensed species, eventually leading to catalyst deactivation. The challenge for this type of zeolites is to achieve steady-state performance of the aromatic cycle by slowing down coke formation, accomplished by utilization of silicoaluminophosphates with milder acidity.⁷⁴ On the other hand, steady-state performance with a constant coke content can be achieved by utilizing fluidized bed reactors, which additionally provide the advantage of a better heat dissipation.⁷ Such a reactor design, however, requires application of fluidizable catalysts, i.e. with specific particle size and density. CHA - the most studied topology – is composed from cylinder-like cavities with big dimensions able to host aromatic molecules up to pyrene (Fig. 5a,b).⁷⁵ Such big dimensions ensure long lifetime in comparison to other 8MR zeolites. Linked to the product distribution, the following conclusion can be drawn on the effect of cage dimensions: the more spacious is the cage the higher is selectivity to propylene.^{72, 76, 77} Compared at the same temperature (350 and 400°C), LEV with the smallest dimensions (7.5 x 6.5 Å) yields higher amount of ethylene, while more spacious CHA (10.9 x 6.7 Å) and AEI (12.7 x 11.6 Å) – propylene.⁷⁶ The product distribution can be further linked to the confined aromatics, that is, steric limitations imposed by LEV favour formation of methylbenzenes with limited amount of methyl groups which are responsible for ethylene

formation. The pear-shape of AEI is able to hold bulky aromatics, resulting in an unusually high selectivity to butenes (propylene/ethylene/butane = 2.8 / 1 / 1.1) at 400°C.⁷⁸ Large cage dimensions do not guarantee high selectivity to propylene/butenes if combined with very narrow pores hindering diffusion of the latter.⁷⁹ An example is AFX (13.0 x 8.3 Å) with very small window-openings (3.4 x 3.6 Å) promoting rapid growth of polycondensed species and therefore fast deactivation.⁷⁷ Similarly, the more spacious cage of ERI delivers higher selectivity to ethylene in comparison to CHA, which might be due to narrower window openings of ERI (3.6 x 5.1 Å) in comparison to CHA (3.8 x 3.8 Å).⁸⁰

Medium pore 10-ring zeolites, on the other hand, are composed of straight and/or curved channels (Fig. 5c-f). In such structures, the aromatic cycle is only able to operate in the more spacious channel intersections.^{81, 82} Choosing zeolites with absence of those ensures discarding the aromatic cycle. One-dimensional ZSM-22 with TON topology was the first zeolite for which suppression of the aromatic cycle was postulated,⁸³ the same observations latter being made for other 1D 10-ring zeolites (Fig. 5c,d).^{84, 85} The prevalence of the olefinic cycle combined with product shape selectivity results in the predominant formation of C₅₊ products ranging from 50 up to 75 % depending on the conversion levels. The obtained product mixture rather meets the requirements for gasoline (after hydrogenation step), with the formation of propylene being fairly low. Selectivity to propylene can be further improved by optimizing acidic properties of zeolites leading to up to 53 % of propylene selectivity at 450°C,⁸⁶ while optimization of textural properties dramatically prolongs catalyst lifetime.⁸⁷ For zeolites with intersections, two cycles work in parallel, and propagation of one cycle over the other can be achieved by other means (Fig. 5 e,f).⁸⁸

Logically, further increase of the number of T-atoms in window openings corresponding to 12-ring zeolites allows the aromatic cycle to proceed inside the zeolite channels. Therefore, 1D SSZ-24 with tubular channels comparable to the size of CHA cavities is almost exclusively selective to aromatics at low conversion levels (≈90%) and >26 % at high conversion levels (Fig. 5 g,h).⁸⁹ Besides, wider window dimensions result in the formation of much more alkylated aromatics for zeolite beta and MOR (mainly penta- and hexamethylbenzene) in comparison to 10-ring ZSM-5 (mainly BTX).⁹⁰ Thus, in 8- and 12-ring zeolites composed of large cavities and channels respectively, the aromatic cycle is preferred. Nevertheless, being imprisoned by narrow 8-ring windows it selectively produces short chain olefins in one case, and heavy aromatics with no such restrictions.

Impact of acidity on stability and product selectivity.

Concentration, location and strength of acid sites are the three most important parameters in defining the overall acidity in zeolites. Concentration of Brønsted acid sites is primarily linked to the amount of Al in the zeolite. A literature survey reveals a linear correlation between propylene selectivity and Si/Al ratio, while a notable reduction in aromatics selectivity corresponds to the decrease of Al content in the zeolite (established for MFI but also holding for other topologies).^{91, 92, 93, 94, 95, 96} Opposite trends strongly evidence the competing nature of the two cycles and that higher acid site density propagates the aromatic cycle (Fig. 6a-d). An increase of Al content enhances the chance of reactant molecules to interact with each

other, thus increasing the chance to form aromatics and ethylene – the product of the aromatic cycle.⁹⁷ The observed trends also account for the improved selectivity to propylene for post-synthetically modified catalysts with different elements as well demetalated zeolites. It has been extensively shown that phosphatation and incorporation of alkaline-earth metals lead to a significant reduction of Brønsted acidity and its effect can be regarded as an increase in the Si/Al ratio.^{98, 99} Yarulina et al. have shown that Ca incorporation results in an almost 10-fold reduction of Brønsted acidity. As a consequence, hydride transfer and cyclization reactions were suppressed, resulting in very low amounts of paraffins and aromatics and maximizing propylene yield up to 53%.⁹⁸ Apart from the development of the second type of porosity improving diffusional properties of zeolites, desilication and dealumination of zeolites can be also viewed as an instrument to dilute acid site density and inhibit secondary reactions.⁹⁴

Zeolites with similar bulk properties can still exhibit substantially different catalytic behaviour, which is a side effect of a heterogeneous distribution of Al within the crystal, also called Al zoning. For example, an Al-rich rim is characteristic for ZSM-5 crystals synthesized using TPA⁺ as structure-directing agent.¹⁰⁰ Al-zoning obviously can be considered as a local enhancement of acid density, which, as explained above, promotes the aromatic cycle. Hydrothermal synthesis conditions and the precursor composition mixture can also promote different locations of Al within the crystal lattice. Here it should be pointed out that the definition of Al zoning used in the following describes a gradient in the number of Al atoms per unit volume, not a distribution gradient of Al over the available T sites per unit cell. Al zoning in zeolites has been observed since the 1970s.¹⁰¹ Around that time and in the following years different distributions and effects were observed and in 1993 Althoff and co-workers published a systematic study of the parameters influencing Al zoning.¹⁰²

Besides influencing desilication and dealumination, because strength and number of catalytically active sites in zeolites affect the effective diffusion path of reactants, the presence and distribution of Al in the zeolite framework also directly affects catalytic performance (Fig. 6). It was shown that several acid-catalyzed reactions preferentially occur at the edges of large ZSM-5 crystals: in 2007, Roeffaers et al. applied *in-situ* fluorescence microscopy to monitor catalytic, condensed-phase reactions in individual zeolite crystals.¹⁰³ Specifically, they utilized the (acid-catalyzed) formation of chromophores during self-condensation of furfuryl alcohol to visualize the time dependent distribution of the fluorescent reaction products. With their study they showed that the presence of sub-units in large, coffin-shaped ZSM-5 crystals is relevant to catalysis, and proposed that the interfaces between the components act as diffusion barriers. The authors also observed unusual behavior of certain crystals, showing intense fluorescence emission confined to the outer surface of specific facets of the ZSM-5 crystals and linked this unusually intense emission to Al zoning. In the same year Kox et al. used *in-situ* UV-Vis micro-spectroscopy to study the oligomerization of styrene occurring in the micropores of ZSM-5 zeolite crystals,¹⁰⁴ linking reaction kinetics to the diffusion and catalytic properties of straight and zigzag channels in large ZSM-5 zeolite crystals. One year later Tzoulaki et al. studied the diffusion properties of large (aluminum-free) Silicalite-1 crystals using interference microscopy for monitoring time-dependent concentration profiles during

molecular uptake and release and found no evidence for a significant effect of internal transport resistances (at the interface of sub-units) or surface barriers on mass transport in these crystals.¹⁰⁵ They therefore concluded that an inhomogeneous Al distribution that is preferentially located close to the surface and at the interfaces of the crystal segments enhances catalytic activity and coke formation and is responsible for the observed diffusion barriers. In line with this hypothesis, later in 2008 Mores et al. confirmed the heterogeneous distribution of coke as a function of reaction time and temperature in large H-ZSM-5 and H-SAPO-34 crystals during the MTO reaction by a combination of *in situ* UV-visible and confocal fluorescence microscopy.¹⁰⁶ Three years later Weckhuysen et al.¹⁰⁷ showed that with decreasing Al concentration in large MFI crystals, coke formation decreases as well. Furthermore, a higher Brønsted acid site density did not influence the type of coke species generated, but instead increased the rate of formation of methyl-substituted aromatic species and the subsequent growth towards larger coke species. One year later, in 2012, Chen et al. reviewed the effect of acid site density, acid site strength and the role of coke formation on deactivation of SAPO zeolites⁷⁴ and in 2015 Olsbye et al. reviewed the MTH process *inter alia* discussing catalyst deactivation by coke formation.⁶

Catalyst deactivation by (hydro-) carbon residues is an important deactivation pathway in MTH. However, as discussed, after the formation of the first C-C bond species hydrocarbons are formed according to the autocatalytic dual-cycle concept, which implies that hydrocarbon species can be both activating and deactivating species.⁶ Therefore it is interesting to obtain insights about the nature and location of the first seeds of coke in zeolites. Intuitively one would expect the first coke species to form in regions with a) highest accessibility and b) of highest activity – both of which can be influenced by Al gradients in the catalyst. However, resolving the location of the first coke species formed at the length scale of nanometers and relating it to (local) Al gradients remains extremely challenging. Recently, the first use of atom probe tomography (APT) to investigate the 3-D distribution of elements in zeolites at the sub-nm scale has been reported.^{108, 109} In 2016 Schmidt et al. used APT to study coke formation and its relation to inhomogeneous Al distribution in large ZSM-5 crystals after MTH (using ¹³C-labelled methanol to distinguish the formed coke species from contaminations).¹⁰⁹ APT samples were taken from the (Al rich) surface and the (Al poor) core of the ZSM-5 crystal showing a clear correlation of coke formation and Brønsted acid site density. The authors reported the presence of carbon clusters (using the term cluster as synonym for a group of closely positioned atoms), which revealed insights into the coke formation mechanism, showing that the coke clusters form preferentially around areas with elevated Al content, even in the Al-poor core of the crystal. The median size of the observed ¹³C clusters was around 36-69 carbon atoms, which suggests that these clusters could contain several occluded aromatic species. Independently of the location of the APT (i.e. taken from the surface or core of the large ZSM crystal), ¹³C clusters were found in each sample, suggesting that in the beginning of the reaction methanol is present throughout the crystal (Fig. 6). As the MTH reaction and catalyst deactivation progress these large clusters merge into the coke rich regions observed e.g. in the surface of large ZSM crystals, *i.e.* in regions of elevated Al

concentrations. These observations were found to be in line with the previously suggested mechanism of coke formation in ZSM-5 during MTH (references 6, 93-96, among others).

Variation in silicon sources was taken as a strategy by Wang et al.⁸¹ to obtain ZSM-5 zeolites with acid sites located either in intersections or in straight and sinusoidal channels. Having the same Si/Al ratio, zeolites with acid sites located in channels exhibited significantly higher selectivity to propylene and longer lifetime. Such a location of Al inhibited the aromatic cycle which is operative in the more spacious intersections and resulted in the similar effect as if utilization of 1D 10-ring zeolites.

Finally, the effect of acid strength was extensively compared over aluminosilicates and their SAPO versions. The general observation is that $C_{3=}/C_{2=}$ ratio and methanol conversion capacity over SAPOs is higher suggesting lower formation rates of poly-condensed species.¹¹⁰ However any speculation on the dominating cycle is rather dubious as it was studied over 8-ring zeolites where the aromatic cycle is prevailing due to topology features. A similar comparison performed for 12-ring zeolites, reveals that while for H-SSZ-24 (AFI) the product distribution is dominated by aromatics, H-SAPO-5 (AFI) displays high selectivity to butenes and shows almost no aromatics. A combination of co-reaction experiments and theoretical calculations reveals that the acid strength has a profound effect on the reactivity of co-catalytic hydrocarbon pool species.⁸⁹ For H-SSZ-24, benzene methylation is significantly higher than that for propylene bringing the aromatic cycle into the dominating role - in sharp contrast to H-SAPO-5 exhibiting similar rates for olefins and aromatics methylation.¹¹¹

Host-guest interactions.

Throughout this review article, zeolite's framework topology and acidity dependent formation of products (both olefins and HCP species) during the MTH reaction have been highlighted. This feature could easily be linked to the host-guest chemistry between inorganic zeolite and organic HCP species during the reaction. More importantly, it also provides the necessary evidence in support of the hybrid organic-inorganic nature of working MTH catalyst (*vide supra*).^{36, 41} During evaluation of HCP species during the MTH process over three small-pore and eight-ring windows zeolites (CHA, DDR, LEV) by Goetze et al., generation of non-identical organics was noticed due to very small differences in cage size, shape, and pore structure of the zeolite frameworks.¹¹² By encompassing a combination of multivariate analysis of *operando* UV-visible spectroscopy and online gas chromatography along with bulk chemical analysis of the hydrocarbon deposits by GC/MS of extracted coke species and thermogravimetric analysis, it was observed that CHA, DDR and LEV were preferentially formed alkylated aromatics and pyrene, 1-methylnaphthalene, and methylated benzene and naphthalene, respectively. The molecular dimension of these retained organic species (*i.e.* the guest molecule) is comparable to the dimensions of the respective zeolite cages (*i.e.* the host molecule). As a result, lattice of all three zeolites were expanded during the MTH process, as revealed by *operando* X-ray Diffraction (XRD).¹¹³ The expansion of the c-axis of the CHA and LEV lattices (*i.e.* longitudinal direction of their cages) is about 0.9 % and 0.5 % during the MTH process, which is more than in the direction of a- and b-axes (*i.e.* in the direction of the width of the cage).

Contrary, relatively more expansion in the direction of a- and b-axes of DDR lattice (*i.e.* 0.5 % compared to 0.3 % along the c-axis) means it becomes wider during the MTH process due to coke deposition, whereas both CHA and LEV lattices become longer. This observation provides further evidence for distinctive host-guest chemistry between zeolite and retained organics during catalysis. To further elucidate the concept of host-guest interactions during catalysis, the report from Liu et al. should be mentioned. With the help of isotopic tracing and theoretical calculations, they showed that the cavity size of different SAPO molecular bearing identical 8MR pore openings (*i.e.* SAPO-35, SAPO-34, and DNL-6) control the molecular size as well as reactivity of the confined HCP-species, which eventually influences the conversion and selectivity of olefins during the MTH reaction.⁷² Although such confined/retained/trapped organics within the zeolite framework are believed to be rigid in nature, this is not completely true. While elucidating the reaction mechanisms of zeolite catalyzed MTH (Fig. 3a,c) and alkylation of aromatics, the same group adapted different solid-state NMR magnetization transfer techniques, which were previously developed for spectral separation of biomolecules on the basis of their mobility, in order to distinguish between mobile (*i.e.* molecule or group with fast tumbling or rotation) and rigid (*i.e.* molecule physisorbed in/on zeolite) species (*cf.* both were trapped within zeolite).^{13,114} However, this host-guest feature of zeolite catalysis has recently been developed and demands further research activities to confirm its implications in the actual process. Nevertheless, it contributes to the fundamental understandings of the zeolite-catalysed hydrocarbon conversion chemistry.

Summary and Outlook.

After more than 40 years, the methanol-to-hydrocarbons process remains as one of the most popular topics of research within the zeolite catalysis community. The recent industrial implementation, with several new commercial plants already running, has triggered even more attention from the academic and industrial communities. In this line, the interest towards the formation of the direct C-C bond, which until very recently was believed to be due to impurities, has risen over the last few years. The combined effort by several research groups helped identify several feasible low-barrier direct coupling pathways for this key mechanistic step, although feedstock impurities (in principle) could still shorten the induction period.¹¹⁵ Among them, formaldehyde formed through disproportionation of methanol was identified as a deactivating species due to its high reactivity with aromatics and the undesired formation of poly-aromatic species. This important discovery calls for new reactor concepts where reactant feeding should be performed carefully to avoid high concentrations of methanol and the consequences thereof, including heat effects.

The next mechanistic step, the dual-cycle, is now better understood and can be viewed as the main machine for controlling lifetime and selectivity to the desired products. The combination of NMR and UV-visible DRS helped pinpoint not only active intermediates, but also deactivating ones, although there is a fine line between them. It has been extensively shown that deactivating species can become reaction intermediates if, for example, higher reaction temperatures are used. Moreover, their reactivity depends on zeolite topology: channel/cage dimensions can cause spatial restrictions preventing certain

intermediates to participate in the mechanistic cycle. In 2012, Olsbye et al. posed the question whether the two cycles – olefinic and aromatic – can be promoted one over another and whether one of them can independently exist. The challenge has been partially addressed: recent catalytic results demonstrate that it is possible to extend catalyst lifetime up to circa $1\text{kg}_{\text{CH}_3\text{OH}}/\text{g}$ zeolite while maintaining high propylene selectivities (>50%). However, it should be further clarified if deactivating species in these cases are also of aromatic nature.

Considering that for both cycles the active intermediates act as co-catalysts, reaction conditions (temperature and methanol partial pressure), feed composition (*i.e.* the presence of olefinic or aromatic co-feed), zeolite topology and acidity can be tuned to further enhance performance. Having this said, most of the efforts over the last few years have been directed towards the selective formation of propylene (the main product from the olefinic cycle). In a potential scenario of lack of ethylene, it would be desirable to apply similar concepts towards the selective formation of this highly important chemical. How to achieve this objective without compromising catalyst lifetime is however still an open question, as ethylene is the main product of the aromatic cycle, its formation would in principle always be accompanied by a high rate of formation of aromatics. Along the same line, considering potential fluctuations in the olefin market, in an ideal scenario there should be a catalyst whose selectivity can easily be tuned by changing the reaction conditions. Here the best solutions seem to go in the direction of co-feeding the required products to promote the cycle of interest. This aspect again calls for additional efforts at the reactor level.

In summary, in our opinion, MTH is still a fascinating research topic with a number of scientific and engineering challenges to be addressed in the near future. Surprisingly, the latter (engineering) challenges have hardly been touched upon in the open literature, while these have been key in the success of the currently most applied MTH technology, which relies on the fast deactivating SAPO-34 and on fluidized bed technology. On a more fundamental note, we are looking forward to seeing the implications that the recent discoveries in MTH chemistry may have on other high temperature hydrocarbon chemistries, such as catalytic cracking and even direct methane activation, as well as bifunctional catalysis concepts, in which MTH chemistry may play an instrumental role. Indeed, the combination of zeolites with other functionalities opens new avenues for the direct conversion of CO_2 or syngas to olefins, hydrocarbons and aromatics.^{116, 117} In such a bifunctional systems, CO_2 or CO are first hydrogenated to methanol which is subsequently converted to hydrocarbons, the zeolite of choice being responsible for the second step. This is a rather promising concept, yet there are a number of obstacles to overcome, such as overhydrogenation of olefins to paraffins, high selectivity to CO and methane associated with metal functionality and how to find a proper catalyst matching in terms of deactivation.

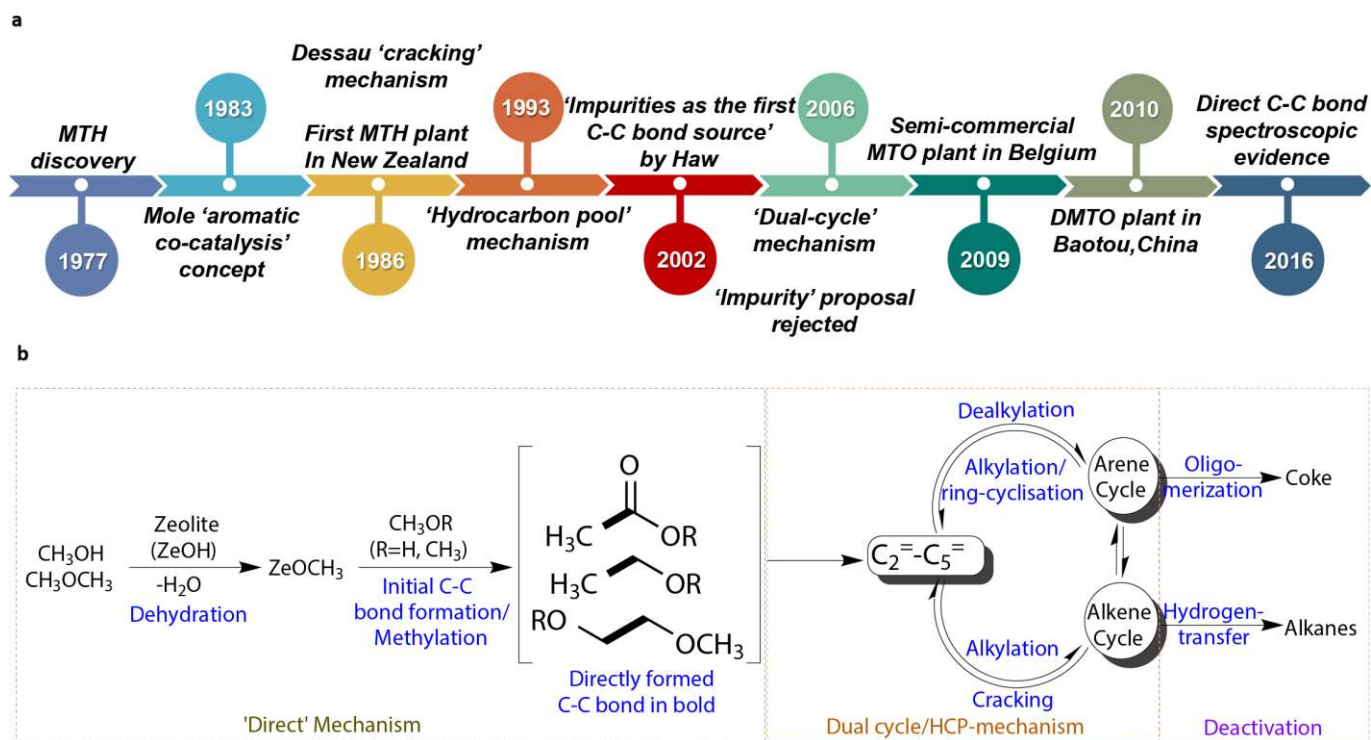


Figure 1. Milestones and mechanism development of the methanol-to-hydrocarbon (MTH) process. (a) MTH chronology shows that forty years of combined efforts produced several mechanistic concepts for both initial induction period and steady state period. The current simplified mechanistic picture is shown in **(b)**. The simplified scheme of the MTH mechanism reveals that though the aromatic cycle leads to the formation of light olefins, it also acts as a scaffold for coke formation; therefore olefins formation is preferred over the olefins cycle.

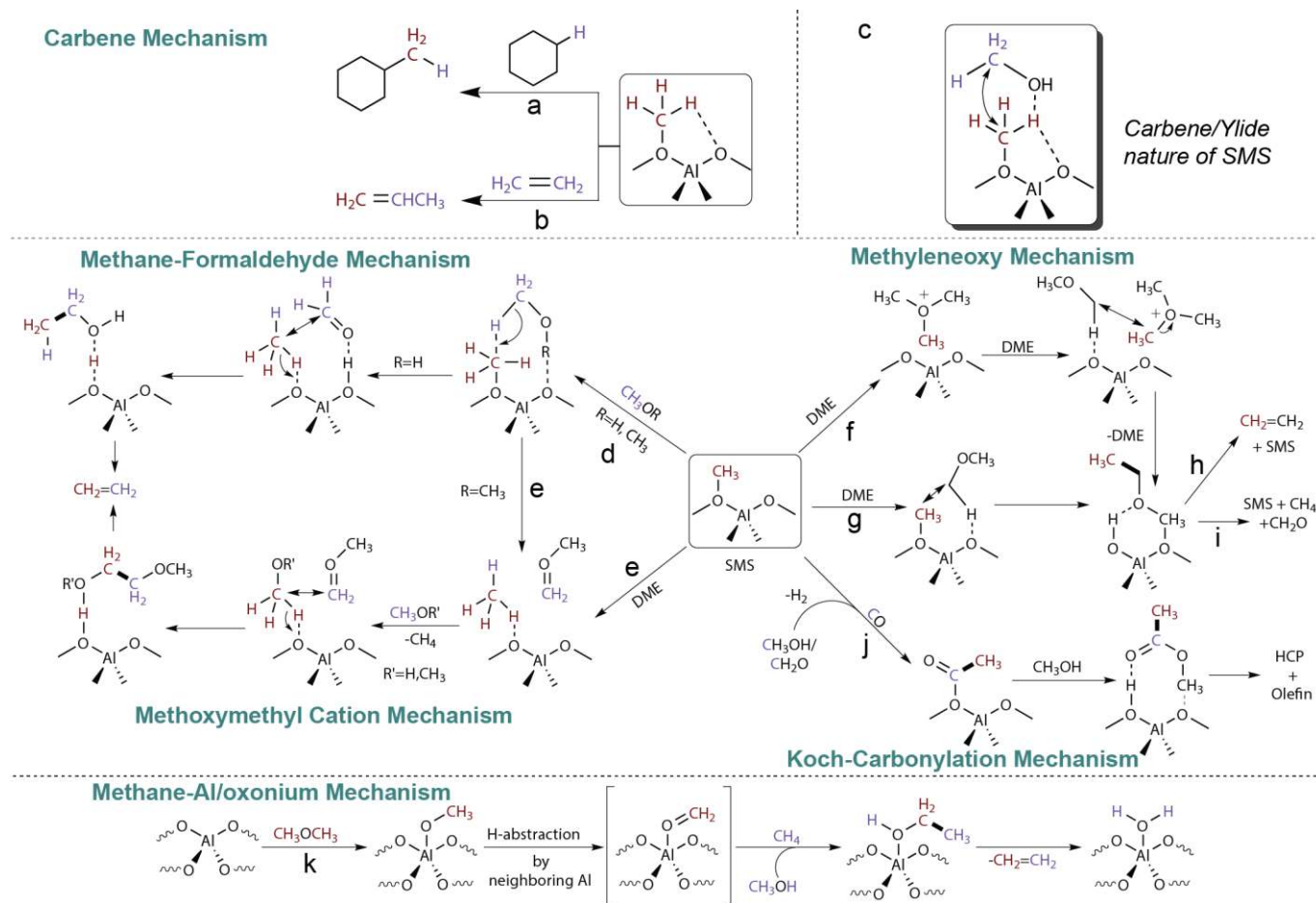


Figure 2. Several proposed direct mechanistic routes during the early stages of the zeolite catalyzed methanol-to-hydrocarbon (MTH) process. The proposed mechanism of the methanol conversion reaction between surface-methoxy species (SMS) and (a) cyclohexane and (b) ethylene via the carbene-type intermediate. (c) The spectroscopically verified intermediate consists of SMS and methanol, suggesting a possibility of C-H insertion of methanol by carbene-like SMS species. Schematic illustration of (d) the conventional methane-formaldehyde mechanism, and its modified analogue (e) the methoxymethyl cation mechanism. (f-i) The methyleneoxy mechanism of the MTH reaction, involving either (f) the trimethyloxonium or (g) the SMS intermediate. The SMS involving route initiates the formation of both (h) ethylene and (i) methane/formaldehyde simultaneously. Plausible routes for the direct formation of the carbon-carbon bond during early stages of the MTH reaction through (j) Koch-type carbonylation of SMS. (k) The methane-Al/oxonium mechanism for the conversion of methanol over alumina.

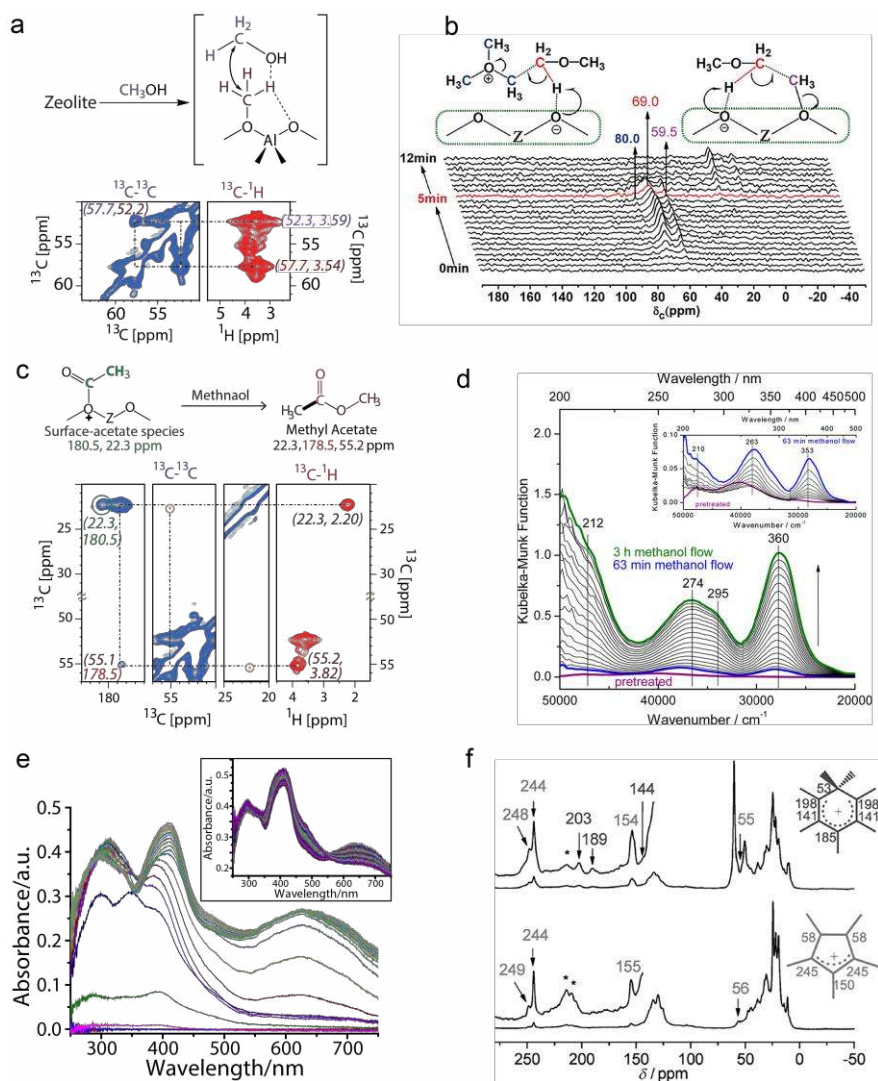


Figure 3. The spectroscopic signatures of crucial intermediates during the zeolite catalyzed methanol-to-hydrocarbon (MTH) process. (a) Solid-state NMR spectra of methoxy in H-SAPO-34 after the MTH reaction for 30 minutes at 673 K. Zooms from 2D ^{13}C - ^{13}C (blue strip) and ^{13}C - ^1H (red strip) magic angle spinning (MAS) solid-state NMR spectra with long mixing (150 ms) and cross-polarization (CP) contact time (500 ms), respectively, identifying surface adduct between SMS and methanol (arrow in molecular structure indicates ^{13}C - ^{13}C correlation). (b) In-situ ^{13}C MAS solid-state NMR spectra measured during MTH reaction over H-ZSM-5 at 573K for 12 min. (c) Solid-state NMR spectra of acetate species in H-SAPO-34 after the MTH reaction for 30 minutes at 673 K. Zooms from 2D ^{13}C - ^{13}C (blue strip) and ^{13}C - ^1H (red strip) MAS solid-state NMR spectra with long mixing (150 ms) or CP contact time (500 ms), respectively, indicating surface acetate and methyl acetate resonances. UV-visible diffuse reflectance spectra of (d) H-ZSM-5 and (e) H-SAPO-34 being exposed to the MTH reaction under *in-situ* (573K) and *operando* (673K) reaction condition, respectively. An absorption band at (d) 295 nm on H-ZSM-5 and (e) 387 nm on H-SAPO-34 were assigned to a methylated cyclopentadienium and hexamethylbenzenium ions, respectively. ((f) ^{13}C MAS solid-state NMR spectra of retained organic species in H-SAPO-34 (upper spectrum, 573K, 15 min) and H-SSZ-13 (lower spectrum, 548K, 25 min) after continuous-flow of $^{13}\text{CH}_3\text{OH}$ for 15 min (*=spinning side bands, chemical shifts on the molecular structures were theoretically calculated values).

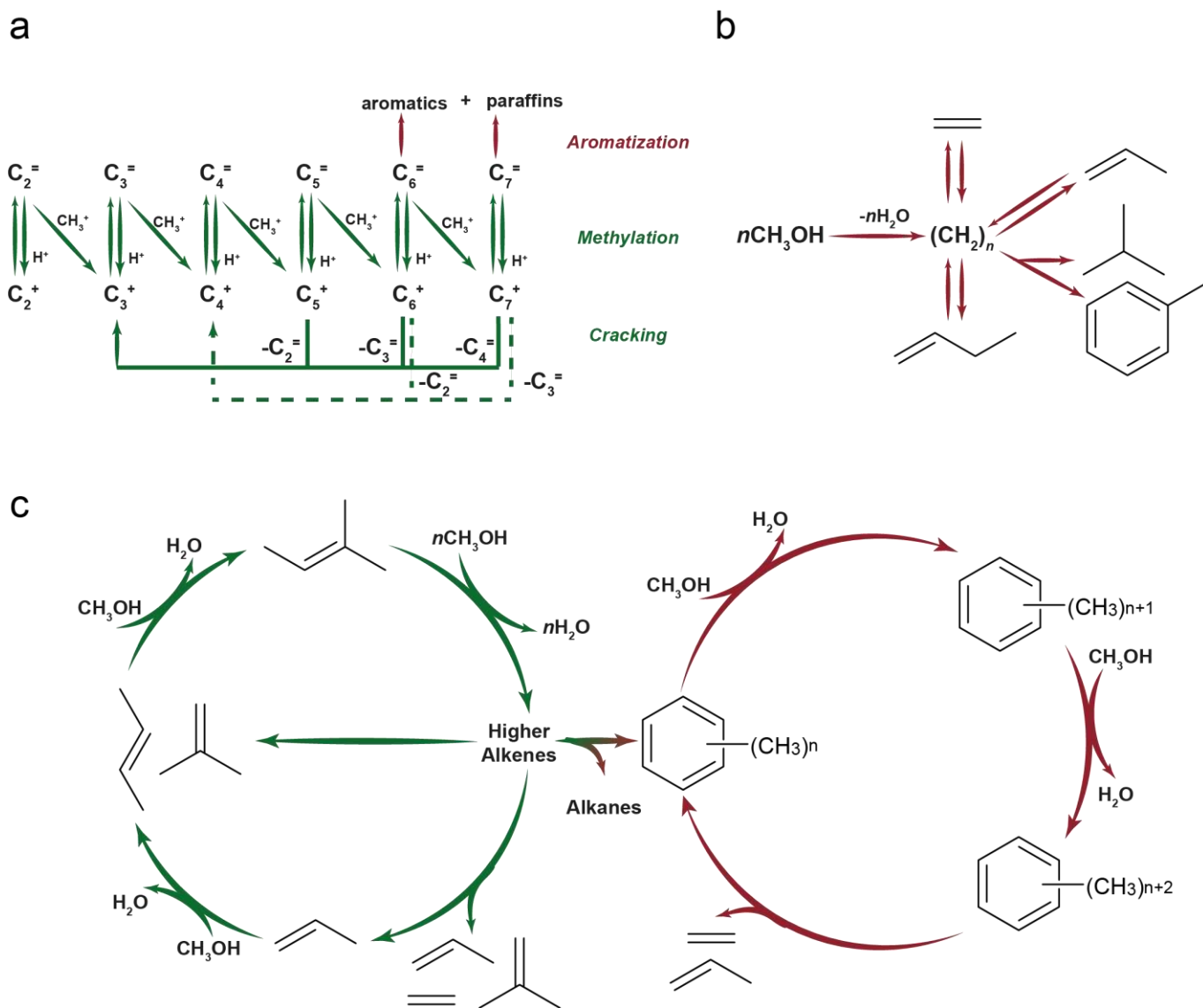


Figure 4. Steady-state mechanism development of the methanol-to-hydrocarbon (MTH) process. (a) Dessau and LaPierre described steady state kinetics of MTH reaction over ZSM-5 by a sequence of olefins methylation followed by their cracking or aromatization to give either olefins or aromatics. **(b)** In contrast, Dahl and Kolboe investigating MTH over SAPO-34 introduced the hydrocarbon pool concept – an active intermediate of aromatic nature – through which light olefins are formed by dealkylation. **(c)** The dual-cycle postulates that there are two competing cycles running in the zeolite channels governed by olefins and aromatics, both acting as co-catalysts for MTH and being active hydrocarbon pool species.

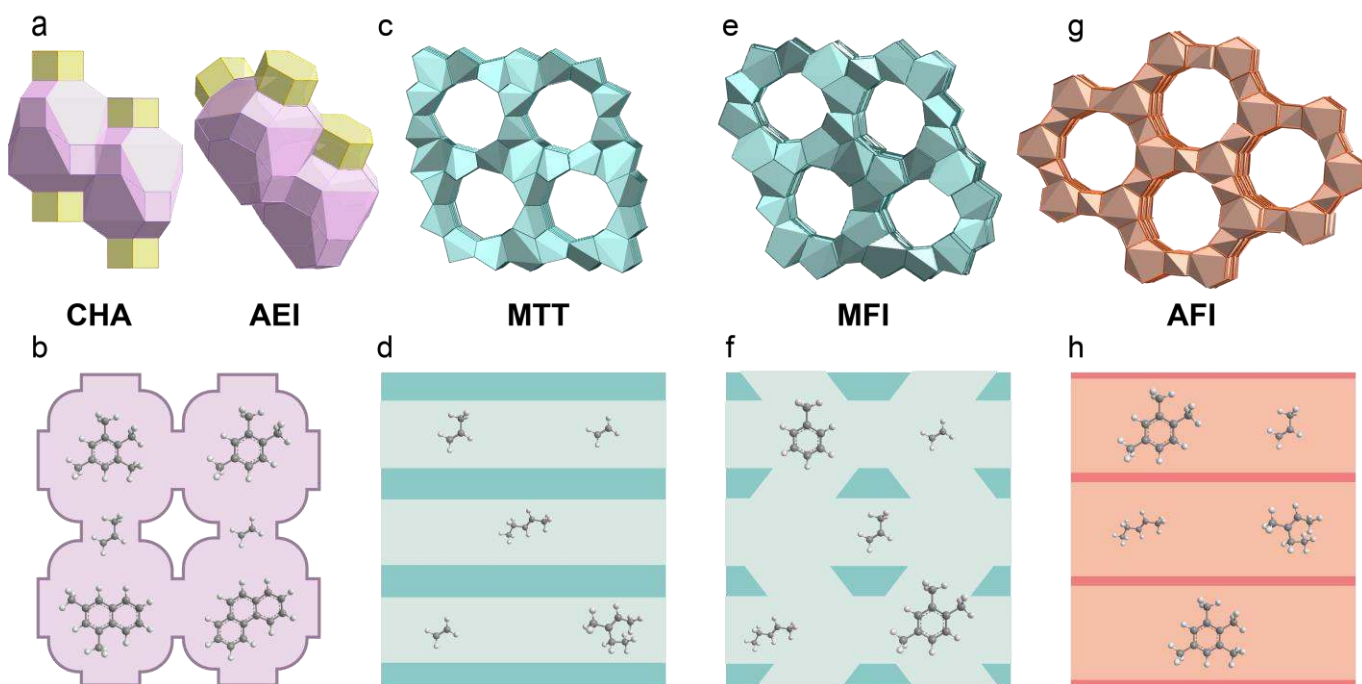


Figure 5. Impact of topology on cycles propagation. (a) 8-ring zeolites are composed of large cavities with small window openings; in such structures aromatics can be formed but cannot escape the cage (b). The aromatic cycle is prevailing and such topologies are characterized by high selectivity to short-chain olefins. (c) 1D 10-ring zeolites cannot accommodate aromatic molecules, therefore the aromatic cycle is suppressed in such type of topology. The product distribution is characterized by a gasoline range of hydrocarbons. (e) The 3D 10-ring MFI structure is described by two types of channels, straight and sinusoidal, forming relatively spacious intersections, which can host the aromatic cycle. (f) Both the aromatic and olefinic cycles are running in zeolite channels and the product is characterised by the presence of a wide range of hydrocarbons. (g,h) The channels of 12-ring zeolites are rather big and can host aromatic hydrocarbons, therefore the aromatic cycle can run inside the channels of 1D AFI zeolite.

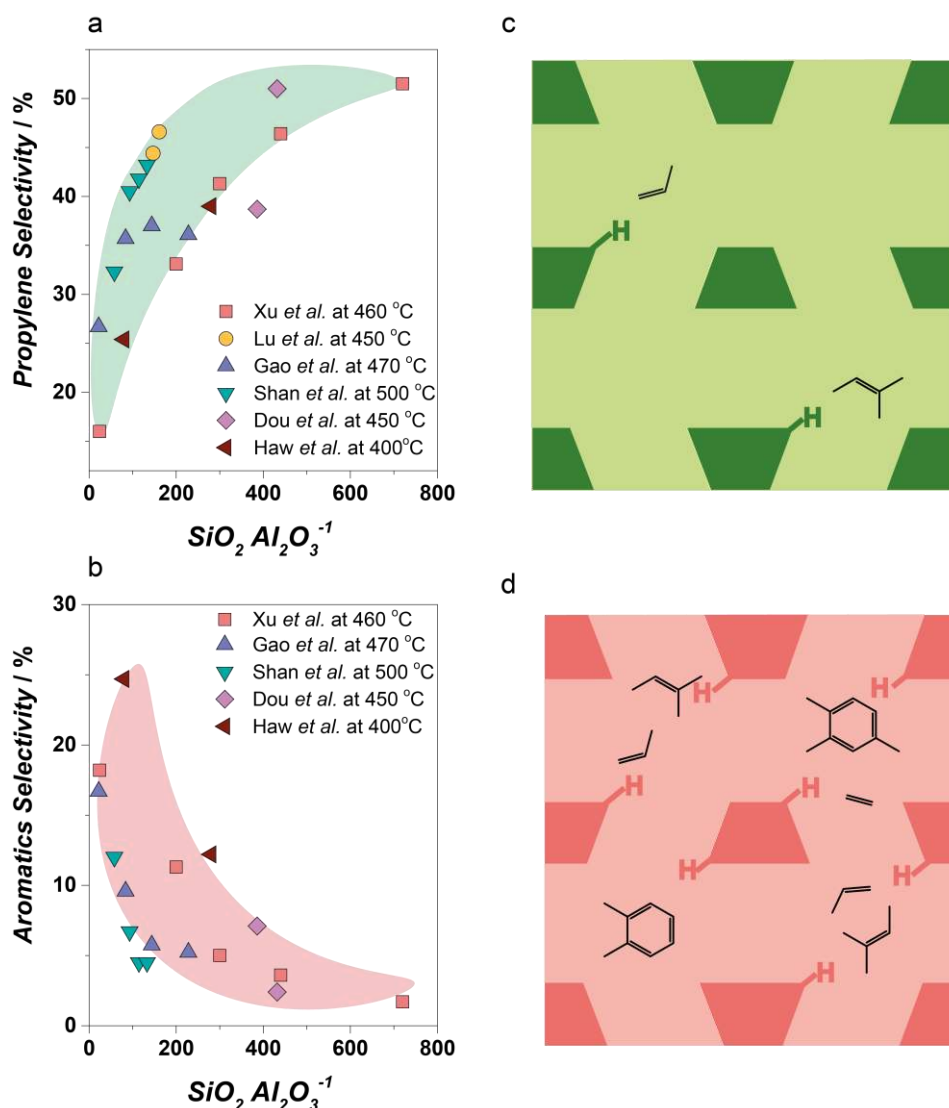


Figure 6. Impact of acidity on cycles propagation. (a, b) A literature survey (ref. 91-96) reveals (a) a noticeable increase of propylene and (b) a reduction of aromatics formed along with an increase of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for microporous ZSM-5 zeolites tested in the methanol-to-hydrocarbons reaction at 673 – 773 K and in the wide range of WHSV. Opposite trends highlight the competing nature of aromatics and olefins. (c) A significant reduction of Al in the zeolite framework leads to a decrease of BAS density, consequently propagating the olefinic cycle as a result of a decreased amount of secondary reactions leading to olefins cyclization and aromatic formation. (d) An increase of acid site density results in a higher probability for olefins to interact forming aromatic molecules. A reduction of Brønsted acidity can be achieved by post-synthetic modification with alkaline-earth metals or demetalation procedures (c, d) leading to similar trends.

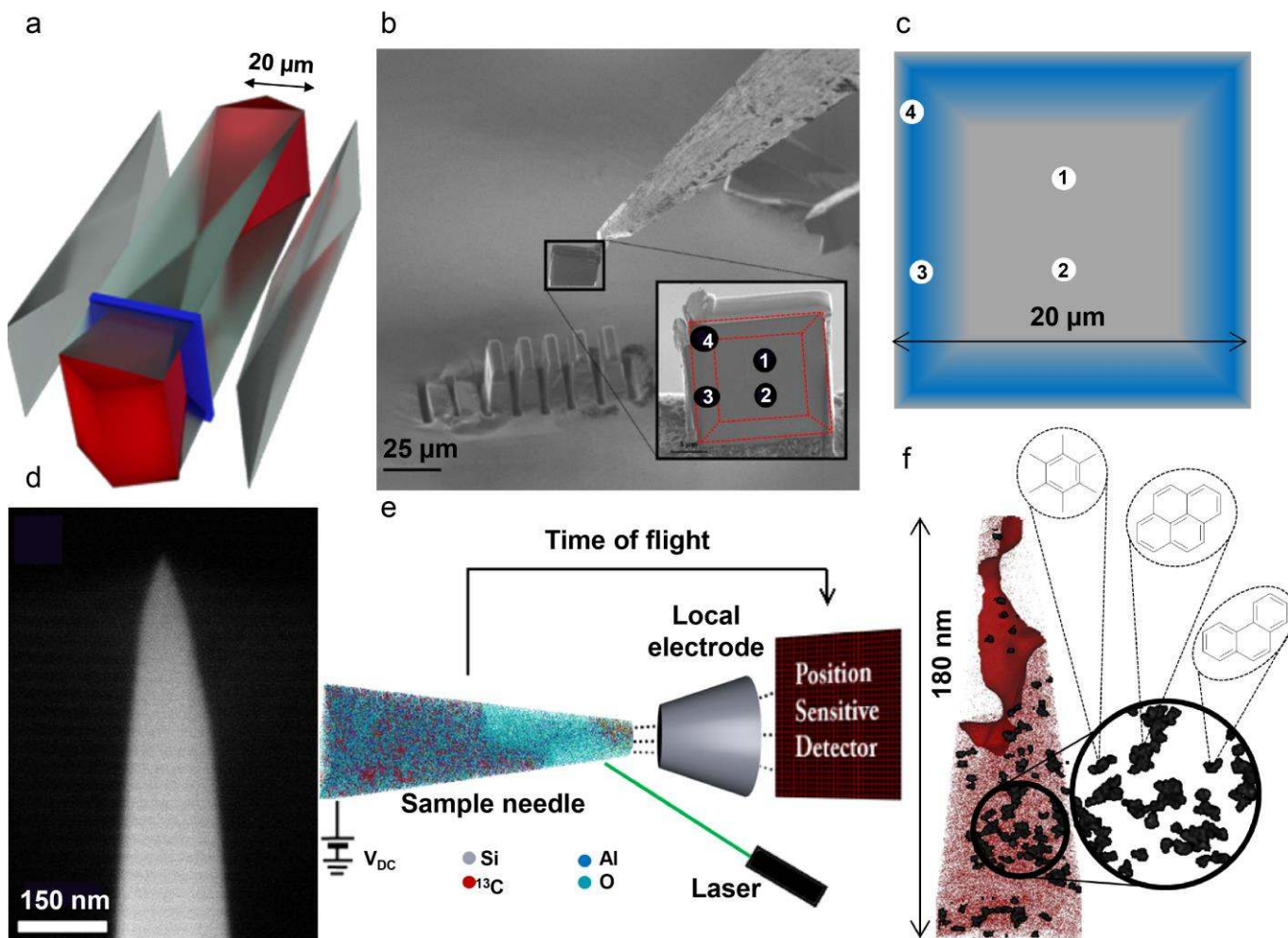


Figure 7. Resolving the location of the first coke species formed during the methanol-to-hydrocarbon (MTH) process using atom probe tomography (APT). APT was used to study coke formation and its relation to the inhomogeneous Al distribution in large ZSM-5 crystals after MTH reaction.¹⁰⁹ A cross section was prepared from a large ZSM-5 crystal after MTH reaction using ¹³C-labelled methanol by focused ion beam (FIB) cutting (panels **a** and **b**). For APT four samples (needles) were taken using FIB cutting from different regions of the crystal cross-section considering Al zoning: high Al concentrations are indicated in blue in panel **c** also showing the position of the samples investigated by APT. A typical needle is shown in panel **d**. APT then allowed mapping of the 3D distribution of Si, Al, O, and ¹³C atoms within each needle (panel **e**). Statistical analysis of the distribution of the ¹³C atoms revealed the presence of carbon clusters indicating the regions of first coke formation in the catalyst (panel **f**).

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