

Dynamic Catalytic Mechanism of the Methanol-to-Hydrocarbons Reaction over Zeolites

Xinqiang Wu, Yingxu Wei,* and Zhongmin Liu*



Cite This: *Acc. Chem. Res.* 2023, 56, 2001–2014



Read Online

ACCESS |

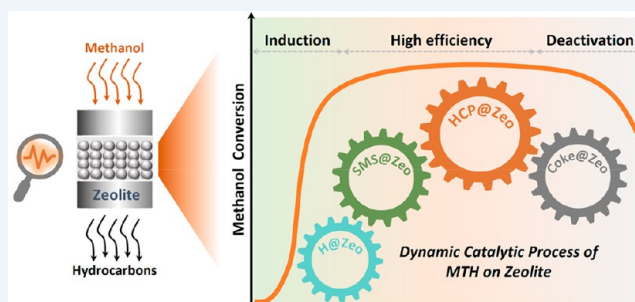
Metrics & More

Article Recommendations

CONSPPECTUS: The methanol-to-hydrocarbons (MTH) process has provided a new route to obtaining basic chemicals without relying on an oil resource. Acidity and shape selectivity endow the zeolite with a decisive role in MTH catalysis. However, the inherent reaction characteristics of the MTH reaction over zeolites, such as the complexity of catalytic reaction kinetics, the diversity of catalytic reaction modes, and even the limitations of catalytic and diffusive decoupling, have all confused people with respect to obtaining a comprehensive mechanistic understanding. By examining the zeolite-catalyzed MTH reaction from the perspective of chemical bonding, one would realize that this reaction reflects the dynamic assembly process of C–C bonds from C1 components to multicarbon products. The key to understanding the MTH reaction lies in the mechanism by which C–C bonds are formed and rearranged in the confined microenvironment of the channel or cage structures of zeolite catalysts to achieve shape-selective production.

The applications of advanced in situ spectroscopy as well as computational chemistry provide tremendous opportunities for capturing and identifying the details of the structure and properties of reactants, intermediates, and products in the confined reaction space of zeolite channels or cages, observing the real-time dynamic evolution of the catalytic surface, and modeling the elementary reaction steps at the molecular and atomic levels.

In this Account, the dynamic catalytic mechanism of the zeolite-catalyzed MTH reaction will be outlined based on decades of continuous research and in-depth understanding. The combination of advanced in situ spectroscopy and theoretical methods allowed us to observe and simulate the formation, growth, and aging process on the working catalyst surface and thus map the dynamical evolution of active sites from a Brønsted acid site (BAS) to an organic–inorganic hybrid supramolecule (OIHS) in the MTH reaction. Moreover, the ever-evolving dynamic succession of the OIHS from surface methoxy species (SMS) to active ion-pair complexes (AIPC) to inert complexes (IC) guided the dynamic autocatalytic process from initiation to sustaining and then to termination, resulting in a complex interlaced hypercycle reaction network. The concept of dynamic catalysis will provide deep insight into the complex catalytic mechanisms as well as the structure–activity relationships in MTH chemistry. More importantly, we are now getting closer to the nature of zeolite catalysis beyond the traditional view of BAS catalysis.



The key to understanding the MTH reaction lies in the mechanism by which C–C bonds are formed and rearranged in the confined microenvironment of the channel or cage structures of zeolite catalysts to achieve shape-selective production. The applications of advanced in situ spectroscopy as well as computational chemistry provide tremendous opportunities for capturing and identifying the details of the structure and properties of reactants, intermediates, and products in the confined reaction space of zeolite channels or cages, observing the real-time dynamic evolution of the catalytic surface, and modeling the elementary reaction steps at the molecular and atomic levels. In this Account, the dynamic catalytic mechanism of the zeolite-catalyzed MTH reaction will be outlined based on decades of continuous research and in-depth understanding. The combination of advanced in situ spectroscopy and theoretical methods allowed us to observe and simulate the formation, growth, and aging process on the working catalyst surface and thus map the dynamical evolution of active sites from a Brønsted acid site (BAS) to an organic–inorganic hybrid supramolecule (OIHS) in the MTH reaction. Moreover, the ever-evolving dynamic succession of the OIHS from surface methoxy species (SMS) to active ion-pair complexes (AIPC) to inert complexes (IC) guided the dynamic autocatalytic process from initiation to sustaining and then to termination, resulting in a complex interlaced hypercycle reaction network. The concept of dynamic catalysis will provide deep insight into the complex catalytic mechanisms as well as the structure–activity relationships in MTH chemistry. More importantly, we are now getting closer to the nature of zeolite catalysis beyond the traditional view of BAS catalysis.

KEY REFERENCES

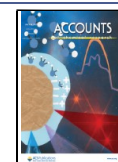
- Wu, X.; Xu, S.; Zhang, W.; Huang, J.; Li, J.; Yu, B.; Wei, Y.; Liu, Z. Direct Mechanism of the First Carbon–Carbon Bond Formation in the Methanol-to-Hydrocarbons Process. *Angew. Chem., Int. Ed.* **2017**, *56*, 9039–9043.¹ The first observation of methyleneoxy intermediates by in situ ¹³C MAS NMR and an SMS-mediated methanol/DME activation and transformation direct mechanism was proposed for the first carbon–carbon bond formation in the MTH process.
- Sun, T.; Chen, W.; Xu, S.; Zheng, A.; Wu, X.; Zeng, S.; Wang, N.; Meng, X.; Wei, Y.; Liu, Z. The first carbon–carbon bond formation mechanism in methanol-to-hydrocarbons process over chabazite zeolite. *Chem* **2021**, *7*, 2415–2428.² The complete and reasonable

C–C bond formation processes were established on the basis of in situ spectroscopic evidence, and the dynamic C–C bond coupling processes were visualized by the advanced ab initio molecular dynamics (AIMD) simulations.

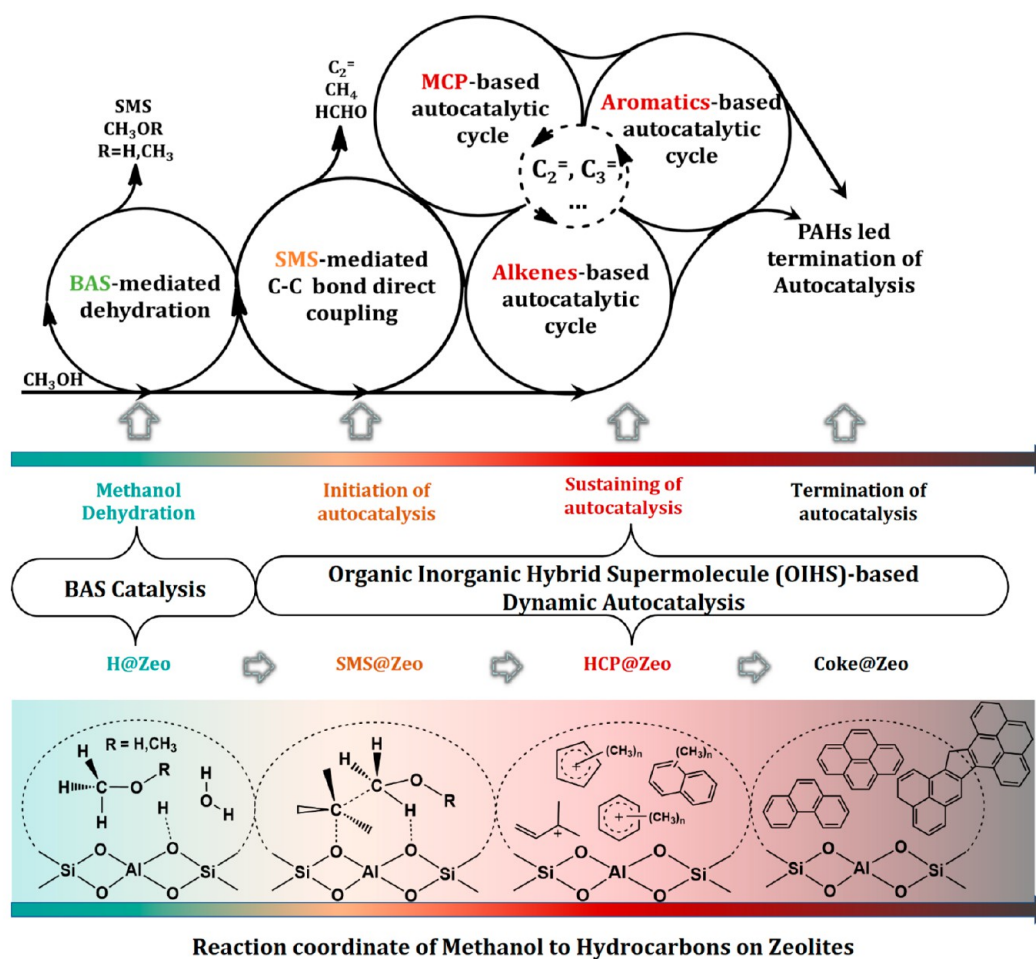
- Lin, S.; Zhi, Y.; Chen, W.; Li, H.; Zhang, W.; Lou, C.; Wu, X.; Zeng, S.; Xu, S.; Xiao, J.; Zheng, A.; Wei, Y.; Liu, Z. Molecular Routes of Dynamic Autocatalysis for

Received: April 6, 2023

Published: July 4, 2023



Scheme 1. Dynamic Catalytic Process of MTH on Zeolites



Methanol-to-Hydrocarbons Reaction. *J. Am. Chem. Soc.* **2021**, *143*, 12038–12052.³ Entire dynamic molecular routes and the chemical nature of the domino cascade of the autocatalytic reaction process of MTH reaction over HZSM-5 were revealed by a multitechnique approach.

- Wang, N.; Zhi, Y.; Wei, Y.; Zhang, W.; Liu, Z.; Huang, J.; Sun, T.; Xu, S.; Lin, S.; He, Y.; Zheng, A.; Liu, Z. Molecular elucidating of an unusual growth mechanism for polycyclic aromatic hydrocarbons in confined space. *Nat. Commun.* **2020**, *11*, 1079.⁴ Cage-passing growth forming cross-linked multicore polycyclic aromatic hydrocarbons (PAHs) with graphene-like structure was deciphered through integrating high-resolution MALDI FT-ICR mass spectrometry with an isotope labeling technique.

INTRODUCTION

Zeolites are natural crystalline or synthetic inorganic crystalline materials that are widely used as solid catalysts in the modern chemical industry for regulating product selectivity, accelerating the reaction rate, and reducing reaction energy consumption.^{5,6} Zeolites (e.g., ZSM-5) and SPAO molecular sieves (e.g., SAPO-34) exhibit unique catalytic performance in the methanol-to-hydrocarbons (MTH) reaction because of their highly efficient acid catalysis with shape selectivity.^{7,8} Kinetic studies have shown that methanol conversion over zeolites presents S-type kinetic characteristics,⁹ which are

typically interpreted as the dynamic behavior of autocatalysis, so that a complete MTH reaction process is usually divided into three stages, including the initial stage, the steady-state stage, and the deactivation stage. However, the diversity of the chemical composition, both in effluent products and in the zeolite interface, implies the occurrence of many reactions, including the alkylation and isomerization of aromatics, the homologation and oligomerization of olefins, and the cyclization and hydride transfer reactions inherent in olefins' disproportionation to aromatics and alkanes in the MTH reaction.^{10,11} The dynamically evolving catalytic conversion and the diversity of catalytic reaction types pose great challenges for the mechanistic study of MTH catalysis. One of the key scientific questions, namely, how methanol is activated in the initial reaction stage and further converted to generate the first C–C bond, has puzzled people for many years.^{12–14} At present, the direct coupling reaction of surface methoxy species (SMS) with C1 reactants possibly existing in the initial reaction stage (such as methanol, dimethyl ether, formaldehyde, methane, and carbon monoxide) has been experimentally confirmed and accepted.¹⁵ However, there are still different views on the formation of the first C–C bond, from the surface intermediates to the olefin precursor, especially the controversy over the specific functional mode of SMS. In addition, impurities rather than SMS have been suggested as the source of the first C–C bond.¹⁶ In fact, obtaining reliable and intuitive experimental evidence by in situ

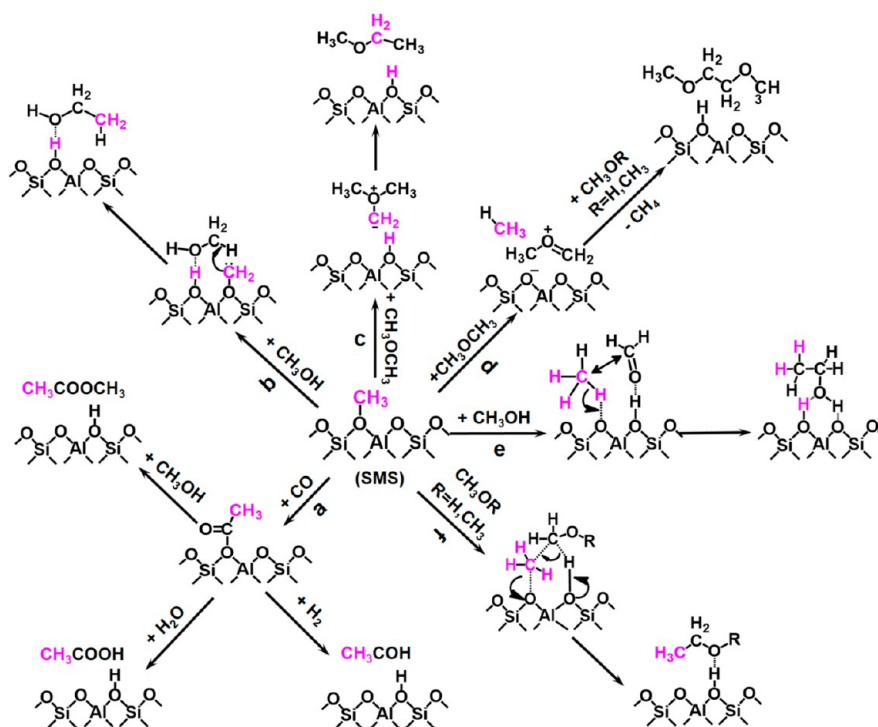


Figure 1. Schematic illustration of several direct mechanisms proposed for MTH conversion over acidic zeolite catalysts during the initial reaction stage. (a) Koch carbonylation mechanism; (b) surface carbene/ylide mechanism (c); oxonium–ylide mechanism; (d) methoxymethyl cation mechanism; (e) methane–formaldehyde mechanism; and (f) SMS-mediated methanol/DME activation mechanism.

spectroscopy with high time resolution and detection sensitivity and verifying the feasibility of the suggested mechanism with appropriate models and reasonable parameters by advanced theoretical calculations and simulations should be a more convincing scientific way to unravel this mystery. After the formation of the first C–C bond, autocatalysis, referring to a process by which a reaction product acts as a catalyst to accelerate the reaction by producing more of itself, has been widely recognized as the primary pattern, explaining the significant improvements in methanol conversion and hydrocarbon production. It should be noted that, unlike classical autocatalytic reactions that occur in the open space of organic solvents,¹⁷ autocatalysis in the MTH reaction proceeds in the confined zeolite channels or cages. The application of advanced in situ spectroscopy (e.g., NMR, DRIFTS, GC-MS, and MALDL-TOFMS) and theoretical methods (e.g., DFT, VASP, and AIMD) in the field of zeolite catalysis has greatly facilitated our study of the details of the structure and properties of the confined species and the catalytic events occurring in zeolite channels and cages. With the accumulation of research and progressive understanding over decades,^{1–4,18–23} the dynamic catalytic process of MTH chemistry is revealed in this Account. As shown in Scheme 1, MTH catalysis is no longer one-way BAS catalysis, and the involved active center starts from bridging hydroxyl groups and is then replaced by the supramolecular assemblage by the hybridization of an inorganic zeolite framework and organic species confined in zeolite channels or cages. The transition from BASs to an organic–inorganic hybrid supramolecule (OIHS) guides the conversion of methanol from a BAS-mediated dehydration reaction to an OIHS-mediated C–C bond assembly reaction. As the organic fragments dynamically evolve as the reaction proceeds, the OIHS is upgraded from a

surface methoxy species (SMS) in the initial reaction period to an active ion-pair complex (AIPC) in the efficient reaction period, in which polymethylcyclopentadienium (polyMCP⁺) and polymethylbenzenium (polyMB⁺) are the most reactive intermediate species that can significantly improve the methanol conversion efficiency and the targeted synthesis of olefin products. The in situ dynamic adjustment of the zeolite catalytic microenvironment triggers the orderly and synergistic operation of multiple catalytic reaction cycles through the continuous structural transformation and evolution of OIHS, leading to a significant increase in the methanol conversion efficiency and thus constructing an alternating and intertwined hypercyclic reaction network of autocatalysis. The thermodynamically driven growth of organic fragments of OIHS through condensation and cross-linking will lead to the deposition of polycyclic aromatic hydrocarbons (PAH), and the formed inert complexes (IC) will undoubtedly cause the zeolite to exhibit low activity or even complete deactivation in the MTH reaction. Accordingly, in this Account, the dynamic catalytic mechanism of MTH chemistry will be presented sequentially along the course of the reaction: (1) during the induction stage, C1 reactant molecules undergo dynamic activation and achieve SMS-mediated C–C coupling; (2) during the autocatalytic stage, the dynamic evolution of OIHS induces the orderly and synergistic operation of the three main involved catalytic cycles and constructs an efficient hypercyclic reaction network; and (3) during the deactivation stage, the duality of bulky HCP species and the growth and cross-linking of PAHs lead to the termination of autocatalysis.

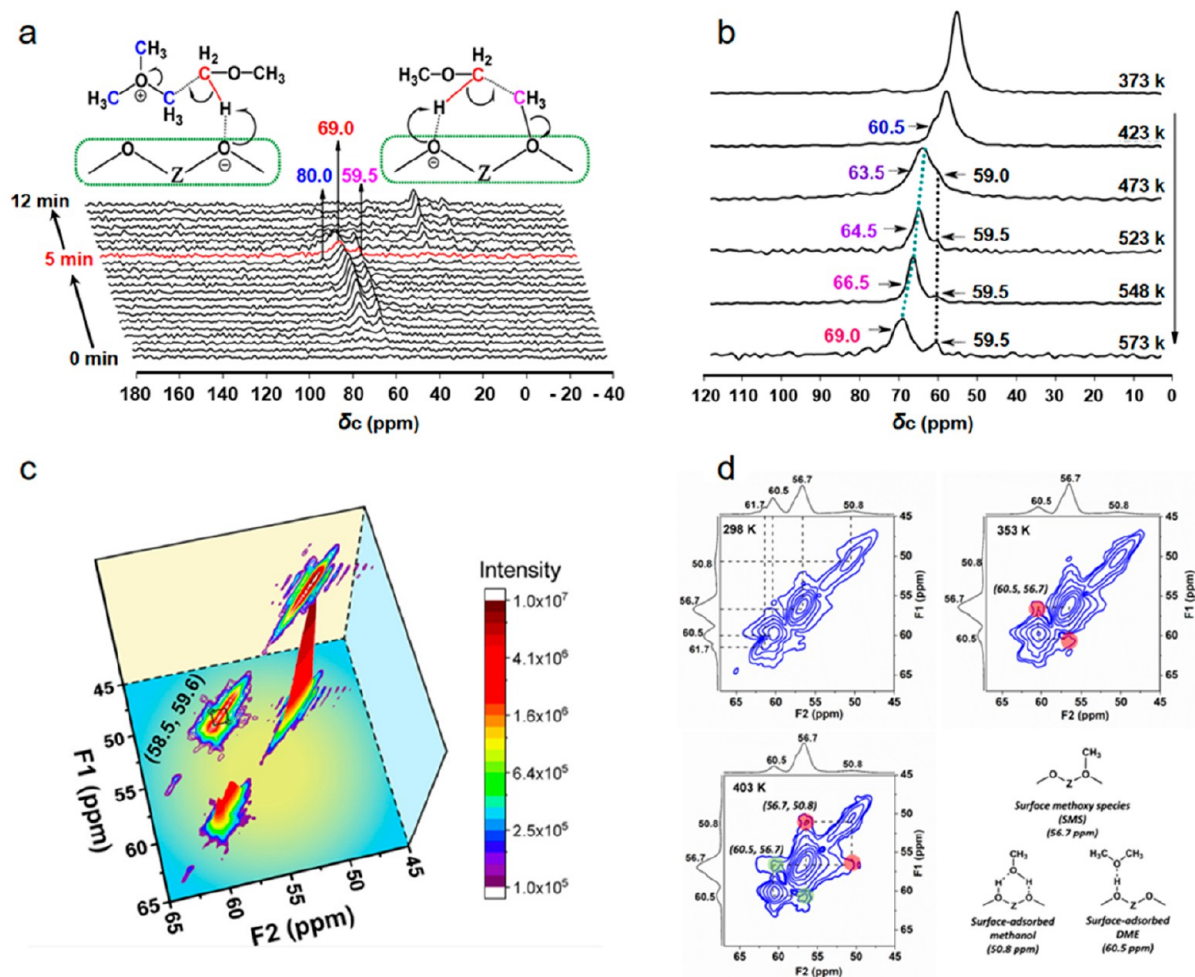


Figure 2. (a) In situ solid-state ¹³C MAS NMR spectra recorded during ¹³C-methanol conversion over HZSM-5 at 573 K, adapted with permission from ref 1. Copyright 2017 John Wiley and Sons. (b) In situ ¹³C MAS NMR spectra during the ¹³C methanol continuous-flow conversion over HZSM-5 in the NMR rotor reactor under the condition of a linear temperature increase from 373 to 573 K, adapted with permission from ref 18. Copyright 2021 American Chemical Society. (c) 2D ¹³C–¹³C CORD (combined R₂^v-driven) spin diffusion MAS NMR correlation spectra for C1 species on HZSM-5 after MTH reaction for 20 s at 573 K, adapted with permission from ref 3. Copyright 2021 American Chemical Society. (d) 2D ¹³C–¹³C MAS NMR spectra with a mixing time of 150 ms are recorded at 298, 353, and 403 K after the MTO reaction over SAPO-34 for 60 s at 573 K, adapted with permission from ref 19. Copyright 2018 American Chemical Society.

■ DYNAMIC ACTIVATION OF C1 REACTANT MOLECULES AND SMS-MEDIATED C–C COUPLING

How methanol is activated and further converted to generate the first C–C bond is the long-standing and most challenging scientific mystery of the acid zeolite-catalyzed MTH reaction. In early mechanistic studies in the last century, it was imagined that methanol might be activated on acidic zeolites and form highly reactive intermediates such as a methyl cation, a radical, carbene, oxonium ylides, and even a methane-formaldehyde complex.²⁴ All of these species or groups are highly reactive for the generation of C–C bonds via direct coupling, whereby more than 20 direct mechanisms for the conversion of methanol on zeolites have been proposed. However, these proposed mechanisms lack reliable experimental evidence, leading to the disagreement on the activation of methanol on zeolite catalysts and bringing the experimental study of the direct mechanism to a long halt.¹³ With the application of more and more in situ spectroscopic techniques and theoretical calculations in zeolite catalysis, the study of the first C–C bond in the zeolite-catalyzed MTH reaction has

been revived and developed.¹⁵ Most of the recently proposed direct mechanisms are based on SMS, which is the most experimentally verified C1 intermediate formed upon methanol adsorption, with detailed differences in the natural properties and function under real MTH reaction conditions. As shown in Figure 1, SMS, formed on the typical Brønsted acid sites (BAS), appears as an activator of the surface-adsorbed C1 reactant molecules in all mechanistic proposals. Although the initial ethylene product was thought to be generated through these reaction pathways, the process of forming the first carbon–carbon bond is markedly different. In route a in Figure 1, the SMS-mediated Koch carbonylation was proposed as the first C–C bond formation based on spectroscopic studies and theoretic calculations.^{25–29} In routes b–f in Figure 1, the activation of the C–H bond of SMS or methanol/DME is the landmark reaction step for the formation of the first C–C bond in the MTH reaction, which is quite different from the first step in the Koch carbonylation reaction in route a.^{14,26,30–33} In addition to these studies on the formation of SMS on BASs and the induction of C–C bond formation mentioned above, some researchers have

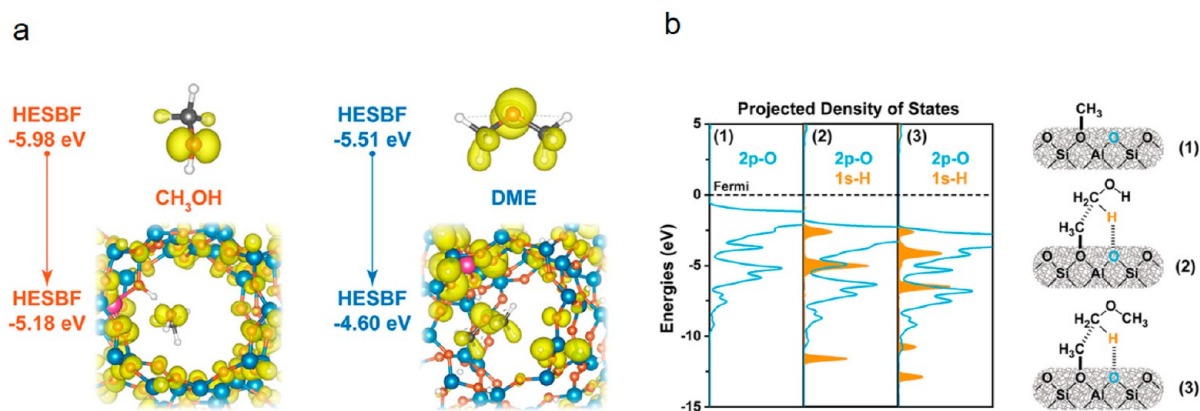


Figure 3. (a) Energies of HESBF for methanol and DME in the gas phase and in zeolite confined space. (b) Projected density of state analysis for interactions of methanol and DME with the SMS. Adapted with permission from ref 3. Copyright 2021 American Chemical Society.

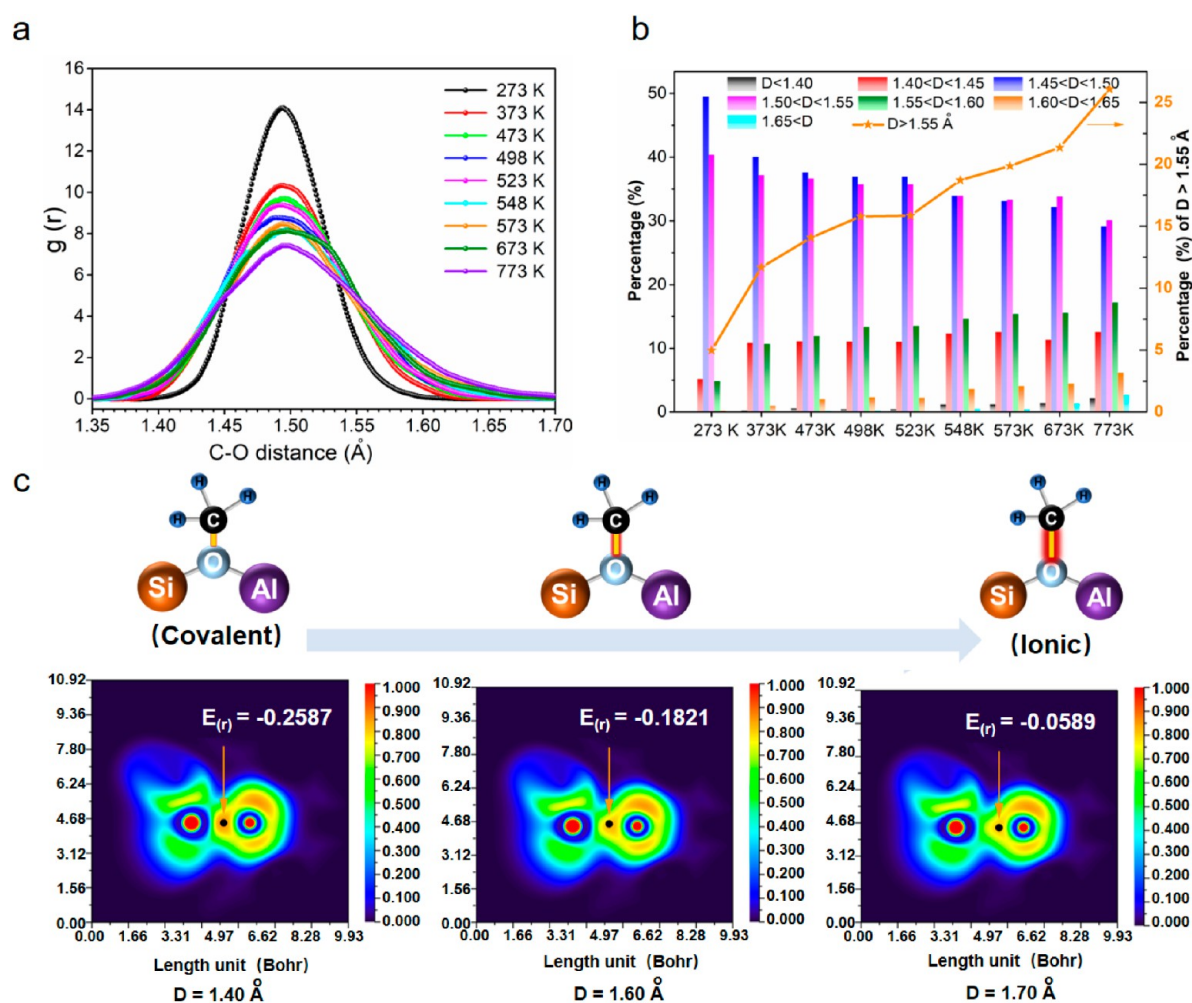


Figure 4. (a) Radial distribution ($g(r)$) as a function of the C-O bond distance of SMS and (b) percentage at the different D (D represents the C-O distance) values, based on 50 ps NVT AIMD simulations. (c) Electron localization function (ELF) of the C-O bond from SMS theoretically predicted at 1.40, 1.60, and 1.70 Å and the relevant energy density ($E(r)$) at the bond critical point. Adapted with permission from ref 18. Copyright 2021 American Chemical Society.

proposed mechanisms for the formation of the first C-C bond through the conversion of methanol at the extra-framework aluminum (EFAL) sites.^{34–36} However, it is worth emphasizing that the mechanistic studies require one to deal carefully with the details and to try to obtain relevant evidence under

real/quasi-reaction conditions. To study the methanol activation and transformation in the initial stage of the MTH reaction, we have monitored the catalytic events using in situ spectroscopy (e.g., NMR, DRIFTS, and GC-MS) under continuous methanol flow conditions and tracked and

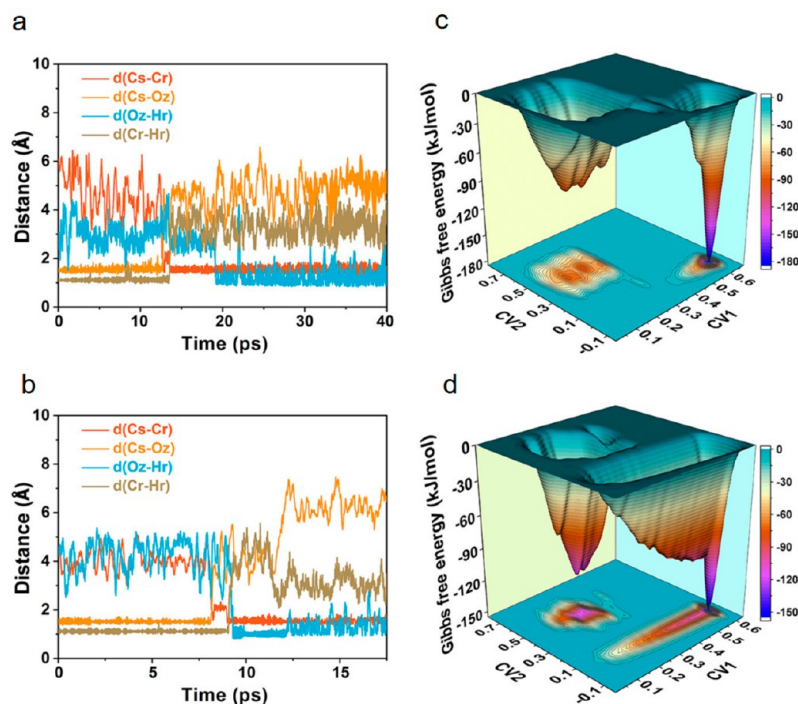


Figure 5. Operando AIMD simulation for (a, c) SMS-mediated methanol and (b, d) DME activation. (a, b) Evolution trajectories of bond distances $d(\text{Cs}-\text{Oz})$, $d(\text{Cr}-\text{Hr})$, $d(\text{Cs}-\text{Cr})$, and $d(\text{Oz}-\text{Hr})$, on the picosecond time scale, at 673 K over HZSM-5. (c, d) 2D-FES and its projection. Adapted with permission from ref 3. Copyright 2021 American Chemical Society.

visualized the elementary reaction steps using advanced computational tools (e.g., AIMD). Based on the spectroscopic evidence under the real/quasi-MTH reaction conditions and theoretical calculations, we proposed that C1 reactant molecules methanol/DME can be activated by the synergy of SMS and zeolite framework oxygen, and the further coupling of the activated C1 molecule and SMS will give the first C–C bond (route f).^{1,2,18,19,37} As shown in Figure 2a, the first-time capture of a methyleneoxy analogue ($\delta_{13\text{C}} = 69.0$ ppm) species during the in situ ^{13}C ssNMR detection on HZSM-5 under a continuous flow of methanol at 573 K suggests that the surface-adsorbed C1 reactant molecules, methanol/DME, have been activated under the real MTH reaction conditions, which is presumably associated with the simultaneous observation of the C1 surface intermediates, SMS ($^{13}\text{C} = 59.5$ ppm) and TMO ($^{13}\text{C} = 80.0$ ppm).¹ This demonstration is greatly supported by the series of ssNMR spectra of the continuous flow of methanol on HZSM-5 at the programmed temperature.¹⁸ A sequence of progressive activation states of DME (63.5 ppm at 473 K, 64.5 ppm at 523 K, 66.5 ppm at 548 K, and 69.0 ppm at 573 K) evoked by SMS has been directly observed (Figure 2b).¹⁸ To the best of our knowledge, this is the first time that the dynamic activation of C1 molecules in zeolite catalysis has been captured. The reaction between SMS and surface-adsorbed C1 reactant molecules is further supported by 2D MAS NMR correlation spectra, indicating the spatial proximity and strong interactions of surface C1 species formed during the methanol conversion on HZSM-5. In Figure 2C,³ 2D $^{13}\text{C}-^{13}\text{C}$ CORD spin diffusion MAS NMR correlation spectra detection on HZSM-5 showed that a pair of cross peaks between DME (59.6 ppm) and the SMS (58.5 ppm) were successfully captured in addition to two sets of self-cross peaks of methanol (50.2 ppm) and DME (59.6 ppm), indicating a strong interaction between SMS and DME with

spatial proximity. Also, on SAPO-34 shown in Figure 2d,¹⁹ a pair of cross peaks between SMS (56.7 ppm) and methanol (50.8 ppm) were observed in addition to the 2D $^{13}\text{C}-^{13}\text{C}$ correlation spectra of SMS (56.7 ppm) and DME (60.5 ppm) when the temperature was increased to 403 K, providing direct evidence for the spatial proximity and interaction of C1 surface species. The 2D MAS NMR correlation spectra obtained on HZSM-5 or SAPO-34 suggest that the chemical reaction between SMS and C1 reactant molecules is ongoing, and the C–C bond may be constructed between the associated carbon atoms. In addition, this deduction was later theoretically supported by energy analyses of the highest electronic states below the Fermi level (HESBF) and PDOS analysis of the electronic interactions between methanol or DME and the SMS. The energies of the HESBF increased by 0.8 and 0.91 eV for methanol and DME, respectively, in the HZSM-5 channel relative to in the gas phase (Figure 3a),³ suggesting a marked preactivation of DME compared with methanol in zeolite confined space. The theoretic analysis of PDOS is shown in Figure 3b,⁵ in which the 1s-H orbital (methyl H of methanol or DME) overlaps with the 2p-O orbital (framework O of the ZSM-5 zeolite), which implies the existence of an electronic interaction between methyl H and framework O. This PDOS electronic analysis indicates a significant preactivation of C1 reactant molecules, especially DME, in the restricted catalytic microenvironment of zeolites. Considering the influence of temperature, the radial distribution $g(r)$ as a function of the C–O bond distance of SMS was plotted over the temperature range from 273 to 773 K while the variation of the electron localization function (ELF) and the expanded value of the energy density at the bond critical point ($E_{(r)}$) were measured at 1.40, 1.60, and 1.70 Å, as shown in Figure 4a–c.¹⁸ The results showed that the CH_3 -Zeo hybrid system acquires more electrophilic/nucleophilic properties (enhanced electrophilic-

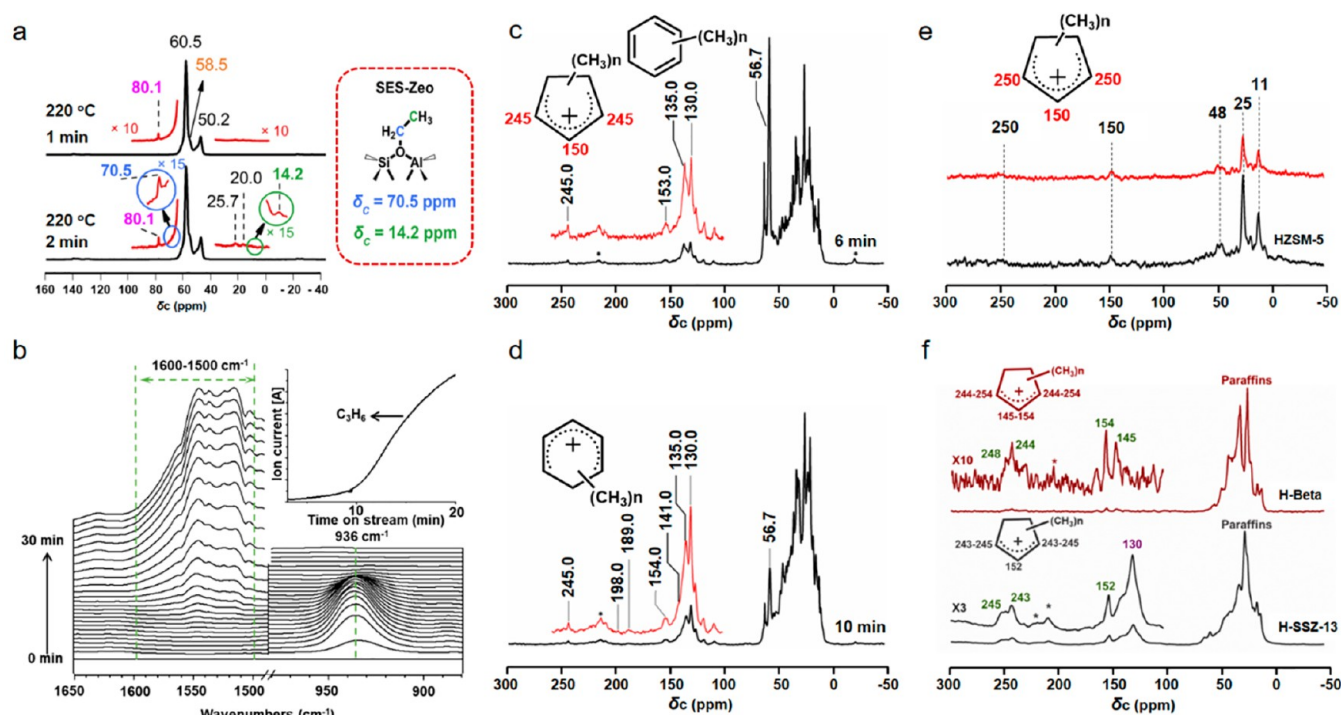


Figure 6. (a) ¹³C CP/MAS NMR spectra of the HSSZ-13 catalyst after ¹³C-methanol conversion for 1 to 2 min. (b) In situ DRIFT spectra recorded during methanol conversion over HSAPO-34 at 573 K from 0 to 30 min. (c, d) ¹³C CP/MAS NMR spectrum of reacted HSAPO-34 after ¹³C-methanol conversion at 573 K for 6 and 10 min. (e) In situ ¹³C MAS NMR spectra of reacted HZSM-5 after ¹³C-ethene conversion at 573 K. (f) ¹³C MAS NMR spectra of H-SSZ-13 and H-beta zeolites in the reaction of adsorbed ¹³C-ethene at 548 K for 60 and 30 s, respectively. An asterisk denotes a spinning side band. (a) Adapted with permission from ref 2. Copyright 2021 Elsevier. (b–e) Adapted with permission from ref 19. Copyright 2021 American Chemical Society. (f) Adapted with permission from ref 22. Copyright 2020 American Chemical Society.

ity of CH₃^{δ+} and nucleophilicity of Zeo^{δ-}, which improves the ionicity, flexibility, and mobility to activate the approaching C1 reactant molecules. To obtain more mechanistic details of methanol activation and the transformation on HZSM-5, the dynamic activation and transformation of C1 molecules in the CH₃-Zeo hybrid system were tracked and visualized by AIMD simulations. Compared to static DFT calculations, AIMD simulations visually reproduce the scenario of the reaction process on the picosecond time scale. In Figure 5a,b,^{3,37} the chemical bond evolving trajectory shows the transition of the Cs–Oz bond from covalent to the ionic property with the elongation of the Cr–Hr bond with the assistance of framework oxygen, as implicated by PDOS analysis of 2p-O1 and 1s-H orbitals in Figure 2e. In just a few picoseconds, the Cs–Cr bond formed synchronously under nucleophilic attack, and then proton H returns from the broken Cr–Hr to framework O, restoring the acidity of the zeolite. In Figure 5c,d,³ the two-dimensional free-energy surface (2D-FES) exhibits two separate low-energy regions corresponding to the reactant and product states, and the minimum-energy pathway shows free-energy barriers of 154 kJ/mol for the SMS-mediated DME pathway and 184 kJ/mol for the SMS-mediated methanol pathway. In another work on the activation and conversion of methanol on the HSSZ-13 zeolite, corresponding to the direct capture of surface ethoxy species (SES) by ssNMR spectroscopy under the real MTH reaction, AIMD simulated the energetically feasible reaction pathways and presented realistic scenarios of dynamic C–C bond coupling in video form.² Through these experimental observations and theoretical calculations and simulations, we know the initial reaction of MTH from the molecular

activation of the C1 reactant to the formation of a C–C bond. Consequently, the dynamic activation of C1 reactant molecules and the direct coupling routes mediated by SMS have been constructed by in situ spectroscopy combined with quantum calculations and molecular dynamic simulations, providing molecular- and atomic-level insight into the first C–C bond formation in the MTH reaction. In short, the existence of a direct mechanism for the formation of the C–C bond via the SMS-mediated direct coupling of C1 components is gradually recognized and proposed, but many mechanistic studies with solid experimental and spectroscopic evidence imply that multiple C–C direct mechanisms may exist in the early stages of the MTH reaction.

■ DYNAMIC CATALYTIC RESPONSE TO THE EVOLUTION OF OIHS: DYNAMIC AUTOCATALYTIC MECHANISM AND HYPERCYCLE REACTION NETWORK

The MTH reaction is ignited by BAS catalysis in the zeolite channels or cages, and the performance is largely determined by the zeolite acidity (acid strength, acid density, and acid site location) and the shape selectivity (including the control of reactant and product transport and the confinement effects on intermediates and transition states). Although the active center of the bridge hydroxyl group still belongs to the category of BAS catalysis, MTH catalysis cannot be mechanically equated with a proton-mediated methanol dehydration reaction. Since the dynamic activation of methanol and the first C–C bond formation mediated by SMS have been exhaustively analyzed in the first part, we will focus in this part on the occurrence and

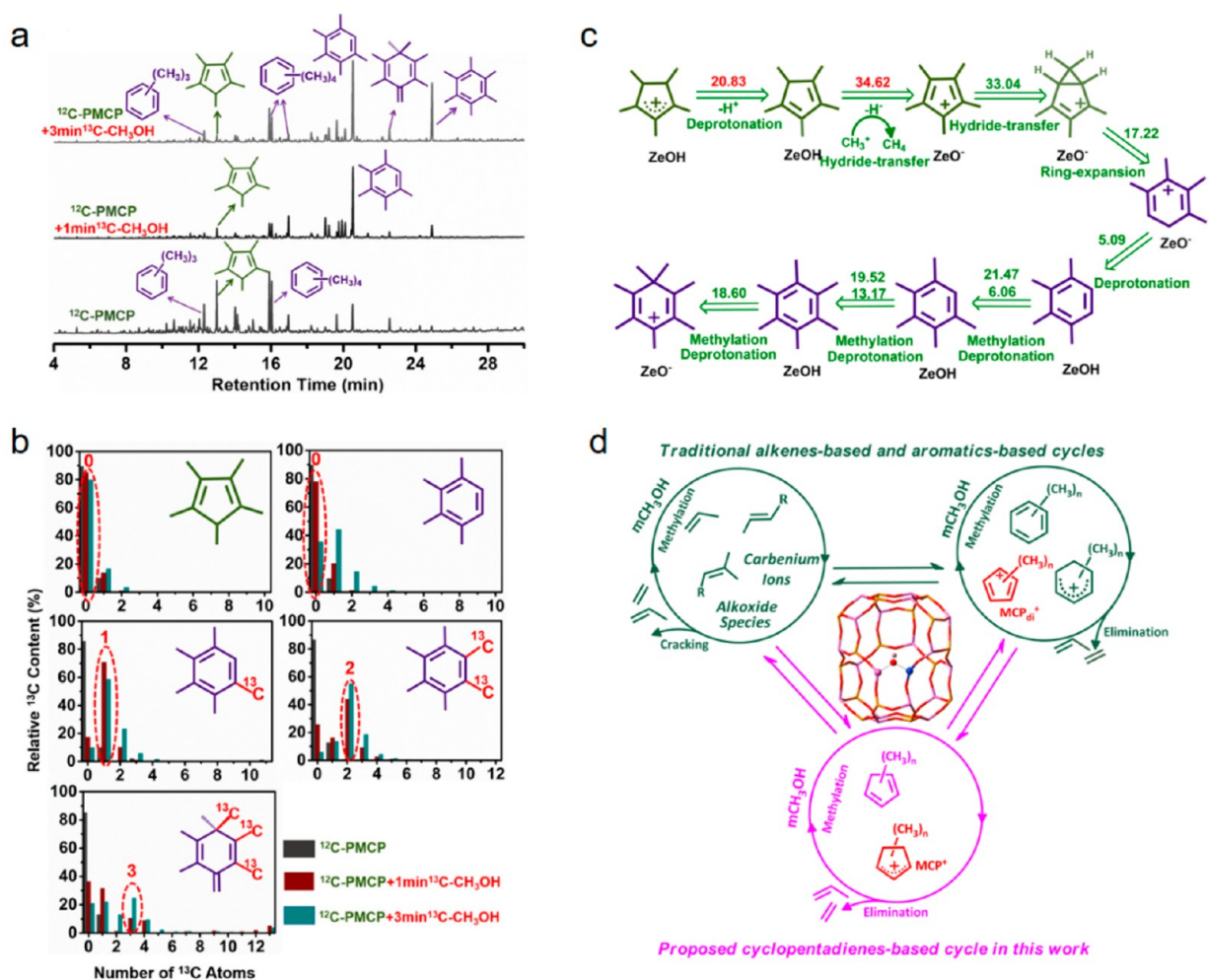


Figure 7. (a) GC-MS chromatograms and (b) isotopic distribution of the organic species retained in the H-beta catalyst after the co-reaction of ^{12}C -pentaMCP and ^{13}C -methanol at 548 K. (c) Proposed reaction route for the formation of initial PMBs from MCP⁺ on H-SSZ-13. Calculated energy barriers are given in kcal/mol. (d) Traditional dual cycles (alkene-based and aromatic-based cycles) and the proposed cyclopentadiene-based cycle. (a–c) Adapted with permission from ref 22. Copyright 2020 American Chemical Society. (d) Adapted with permission from ref 21. Copyright 2019 American Chemical Society.

development of the catalytic events after the formation of the first C–C bond.

Most of the proposed C–C coupling direct mechanisms strongly favor ethene as the primary product, but this cannot explain the diversity of products in the MTH reaction, either in the gas effluent or in the retained species in the zeolite. The special S-type conversion in the MTH reaction is often interpreted as a kinetic behavior of autocatalysis, which prompts the belief that some other indirect mechanisms in the autocatalytic mode have higher efficiency in controlling methanol conversion. Among them, the consecutive methylation and cracking mechanism proposed by Dessau et al.³⁸ and the aromatic cocatalysis mechanism proposed by Mole et al.³⁹ were insightful indirect mechanisms in the early studies of the MTH reaction. Later, the schematic “hydrocarbon pool” (HCP) concept proposed by Kolboe and Dahl attracted more attention and influenced subsequent studies.⁴⁰ So far, both polyMCP⁺ and polyMB⁺ have been experimentally confirmed as the most crucial HCP intermediates for the methanol conversion over zeolites with different topologies.^{41–44} Considering the possible coexistence of this aromatic-based HCP mechanism and the olefin-based

consecutive methylation and cracking mechanism, the newly developed “dual-cycle” mechanism proposed by Olsbye et al. thereafter represents a compromise between the two mechanisms running in parallel.^{45,46} However, a complete understanding of MTH catalysis still requires us to revisit how such diverse intermediates evolve and the corresponding dynamic response of MTH catalysis, including the catalysis transition from inefficient direct mechanisms to efficient autocatalytic indirect mechanisms and the hypercycle reaction network constructed by the dynamic alternation/interweaving of the autocatalytic cycles. In our recent study (Figure 6a),² SMS was confirmed as the initial surface C1 intermediate, and the highly reactive ethene precursor, SES, was directly captured by *ex situ* ssNMR under the real MTH reaction on the CHA zeolite (HSSZ-13). The dynamic process from SMS to SES and then to ethene is theoretically visualized by advanced AIMD simulations, which link the C1 species to the initially generated ethene. The continuous flow conversion of methanol on the CHA zeolite (HSAPO-34) was explored at 573 K (Figure 6b)¹⁹ by *operando* DRIFTS and online mass spectroscopy, which provided time-resolved information on the dynamic evolution of the organic groups on the catalyst

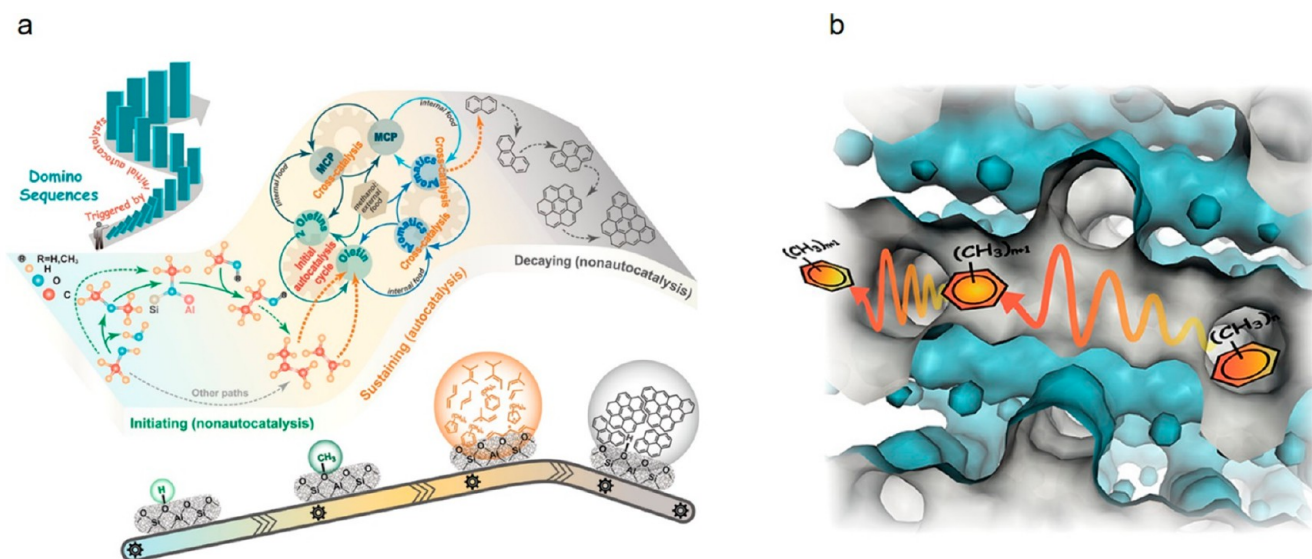


Figure 8. (a) Full molecular picture of the MTH reaction with diverse and cooperative autocatalytic events associated with the dynamic restructuring of active sites along the evolutionary trajectory. The autocatalytic sets, operating by a hypercyclic network embedded in the large interlinked network, interlinked by three autocatalytic entities (olefin, MCP, and aromatic species), driving the autocatalytic turnover. (b) Illustration of the “hydrocarbon pool” concept. (a, b) Adapted with permission from ref 3. Copyright 2021 American Chemical Society.

surface as well as among the gas components. For structural elucidation, GC-MS analysis and *ex situ* ^{13}C CP/MAS NMR were performed by quenching the methanol conversion on the HSAPO-34 catalyst bed, and it was found that the observed conjugated carbon groups originated from polyMCP⁺ and polyMB⁺ species trapped in CHA cages (Figure 6c,d).¹⁹ Moreover, the observation of polyMCP⁺ during the introduction of ^{13}C -ethene into zeolites (HZSM-5 at 573K, H-beta, and HSSZ-13 at 548 K)^{1,21,22} provided direct spectroscopic evidence for the more reactive HCP species generated from initially formed olefins (Figure 6e,f).^{21,22} Through ^{13}C -isotope tracing (Figure 7a,b)²² and the theoretical prediction (Figure 7c),²¹ it was confirmed that polyMB could be formed by the co-reaction of polyMCP and methanol through deprotonation, hydride-transfer reactions, ring expansion, and methylation reaction steps. As more and more cages are gradually occupied by these bulky HCP species, the indirect mechanism of HCP dominates the methanol conversion, leading to the catalysis transition from direct C–C coupling to indirect autocatalysis. Not only mediating the light olefin formation as active HCP species, polyMCP⁺ also serves as a bridge between the initial intermediates (e.g., SMS and SES) and the higher active HCP species (e.g., polyMB⁺). The combination of *in situ* spectroscopy and DFT calculations on HSAPO-34 also verified the crucial role of polyMCP that not only operates independently to produce olefins (a new cyclopentadiene-based autocatalytic cycle) but also links the conventional alkene-based cycle to the aromatic-based cycle (Figure 7d).²¹ A similar dynamic process was also found on HZSM-5 in our recent studies.³ Based on these studies, the real-time tracking of the zeolite surface allows us to draw a panoramic view of the dynamic evolution of surface intermediates and the corresponding MTH catalytic reaction, as shown in Figure 8a.³ Along the reaction coordinates, SMS is the crucial initial intermediate that activates the C1 reactant molecule and mediates the formation of the first C–C bond. SES is the initial ethene precursor from which ethene elimination triggers autocatalysis. Then reactive HCP species,

such as polyMCP, are generated through the alkene-based cycle, and thereafter the more reactive HCP species, such as polyMB, are generated through the cyclopentadiene-based cycle and transmit the autocatalysis from the cyclopentadiene-based cycle to the aromatic-based cycle. Although the three catalytic cycles (alkene-based cycle, cyclopentadiene-based cycle, and aromatic-based cycle) show a rough order from the initiation to the maintenance of autocatalysis, they usually operate in concert to form a hypercycle reaction network that governs the generation of olefins and drives the autocatalytic turnover of the MTH reaction. Notably, the dynamic evolution process of surface species/intermediates is similar on HZSM-5 and HSAPO-34, but the “walk-in-channel” behavior of HCP species is found only on the former in Figure 8b.³ HCP species, such as polyMB, are spatially delocalized and can “randomly walk through” the channels of HZSM-5, manifesting as the mobile “hydrocarbon pool”. This cannot occur on the cavity-type zeolites, such as HSAPO-34, because bulky HCP species would be “imprisoned” in the cages due to the constrained diffusion. Thus, the aromatic-based HCP cycles dominate the methanol conversion on HSAPO-34, while the dual-cycle indirect mechanism is run in parallel on HZSM-5. Taking advantage of the privilege of imprisoning aromatics, HSAPO-34 has become the most popular catalyst for the MTO industry by selectively producing light olefins (enriched with ethene and propene) through aromatic-based HCP autocatalytic cycles. Moreover, the refinement of the chemical modifications resulting from this dynamic evolution of confined molecules is reflected in a comparative study of HSAPO-34, HSAPO-35, HSAPO-18, and H-RUB-50, which possess the same 8MR with different cavity sizes.^{20,47} Based on experimental evidence and theoretical calculations, the cavity-controlled shape selectivity of the confined molecules has been revealed. The cavity size controls the structure and reactivity of key intermediates and the transition state of the elementary steps for performing the aromatic-based HCP reaction, leading to different MTH activity and product selectivity. In particular, the steric constraints imposed by the smaller cavities limit the

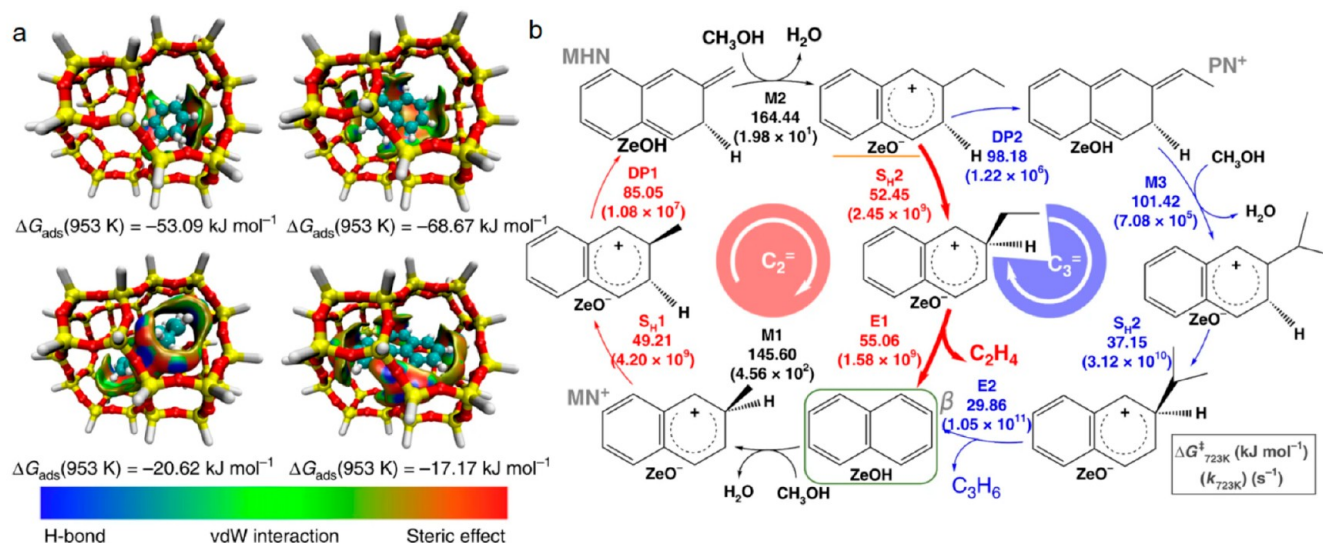


Figure 9. (a) Isosurface plots of the reduced density gradient and Gibbs free energy of adsorption at 953 K for the benzenic, naphthalenic, phenanthrenic, and pyrenic carbenium ions confined in the neutral pure silica model of the CHA cavity. (b) Proposed side-chain mechanism in the SAPO-34 zeolite for ethylene ($\text{C}_2=$) and propylene ($\text{C}_3=$) formation starting from sterically stabilized naphthalene. (a, b) Adapted with permission from ref 23. Copyright 2021 the authors. Published by Springer Nature under a Creative Commons Attribution 4.0 International License.

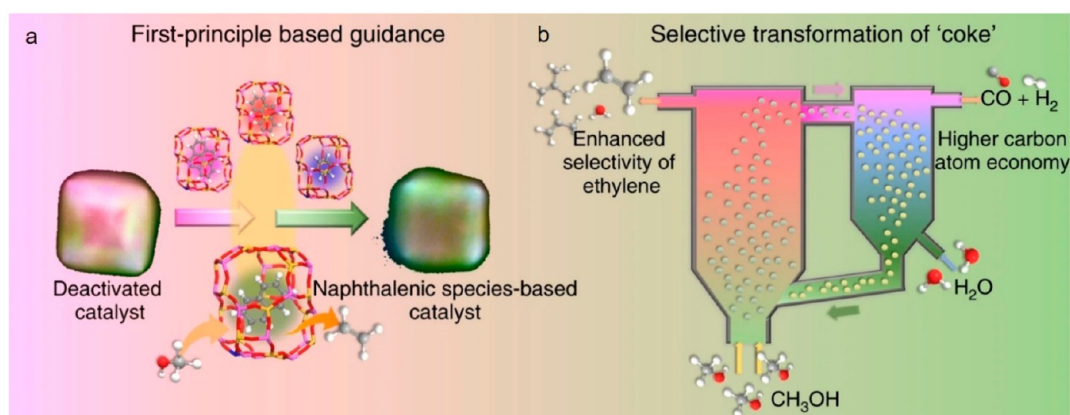


Figure 10. (a) First-principles-based simulations provide the criteria of stability and the functionality of organic intermediates confined in the nanocavity. (b) Selective transformation of coke into a specific naphthalenic species-rich catalyst and the improvement of MTO performance and atom economy implemented in the circulating fluidized bed reactor–regenerator configuration. (a, b) Adapted with permission from ref 23. Copyright 2021 the authors. Published by Springer Nature under a Creative Commons Attribution 4.0 International License.

formation and reactivity of bulky intermediates, resulting in a higher ethene selectivity.

Revisiting the autocatalysis in the MTH reaction, the ever-evolving dynamic inherency of the active site in zeolites will lead to the dynamic response of catalytic mechanisms, resulting in a complex interlaced hypercycle reaction network as a special dynamic autocatalytic mechanism.

■ DUALITY OF BULKY HCP SPECIES AND TERMINATION OF AUTOCATALYSIS BY THE GROWTH AND CROSS-LINKING OF PAHS

The catalytic stability and product selectivity of MTH are closely related to the speciation and evolution of the organic species enclosed in the zeolite pores or cages. As mentioned above, the autocatalytic efficiency increases significantly when the surface species evolve from C1 species to multicarbon HCP species. However, this does not mean that larger or more condensed aromatic species are always helpful for the MTH

process to generate target hydrocarbon products. Excessive growth of the confined species into bulky hydrocarbons, such as PAHs, may cause a diffusion limitation or deactivate the zeolite catalyst, either by blocking the pores or covering the acid sites. Thermodynamically, the polycyclic aromatic hydrocarbon formation is more strongly driven than competing reactions (i.e., polycyclic aromatic hydrocarbon dealkylation to form olefins and less methylated benzene analogs).¹³ This thermodynamic prediction is consistent with the experimental observation in the MTH reaction that the quantity and size of aromatic hydrocarbons occluded in zeolites increase with reaction time, from monocyclic compounds to multicore PAHs. In this section, we will focus on the duality of bulky HCP species and the termination of autocatalysis by the excessive growth of PAHs in the deactivation stage. Heptamethylbenzenium (heptaMB⁺) is confirmed to be an active HCP intermediate for the formation of light olefins during the methanol conversion over zeolites, while Bjørgen et

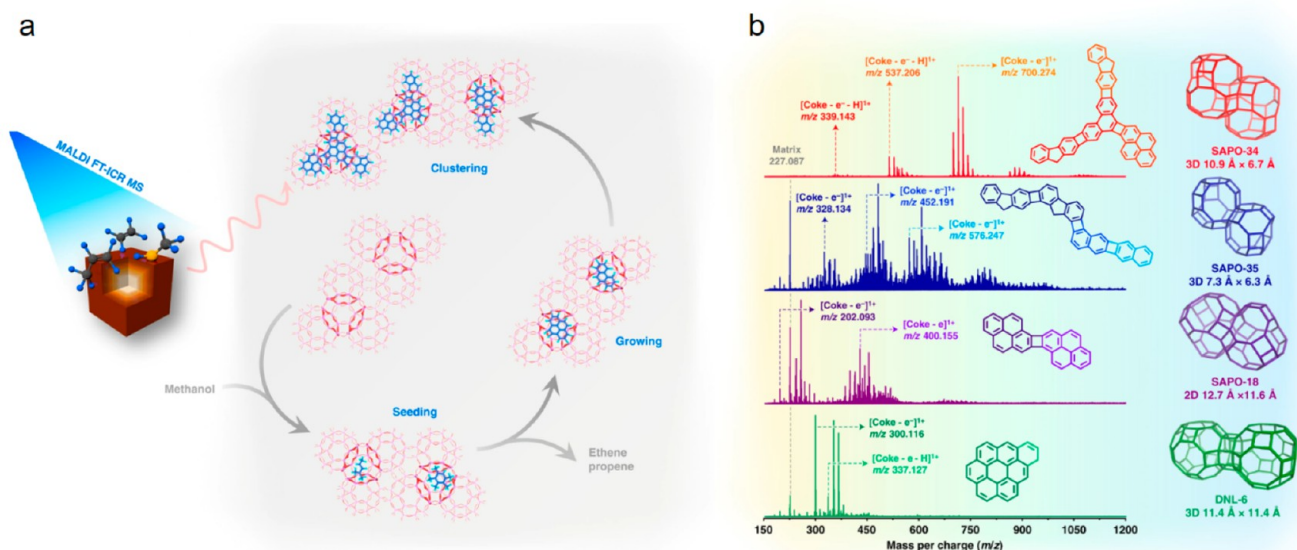


Figure 11. (a) Dynamic process of PAHs evolving from occluded long-chain olefins and light polyMB (coined “seeding”) to three- to four-ring PAHs behaving as building units for aromatic cluster formation (“growing”) and eventually to cage-passing aromatic clusters (“clustering”). (b) MALDI FT-ICR mass spectra for extracts obtained from other cage-structured molecular sieves and the deduced possible molecular structure of PAHs. (a, b) Adapted with permission from ref 4. Copyright 2020 the authors. Published by Springer Nature under a Creative Commons Attribution 4.0 International License.

al. also found that the rearrangement of heptaMB⁺ formed by *gem*-methylation of hexaMB may be the major pathway for the formation of bicyclic compounds, such as naphthalene, based on a cofeeding study of ¹³C-methanol and ¹²C-naphthalene over three 12-ring topologies (H-beta, H-MCM-22, and H-MOR).⁴⁸ In our previous work, two possible routes for the evolution of polyMB to naphthalenic species were proposed based on the capture of three possible naphthalenic derivative precursors.⁴⁹ In general, naphthalenic and more condensed PAHs are usually considered to be deactivating species in the MTH reaction, where they may induce diffusion limitations and/or deactivate the zeolite catalyst, either by blocking the pores or covering the acid sites. However, in our recent work, naphthalenic cations are theoretically predicted to be spatially stable within the CHA cavity (Figure 9a)²³ and are active HCP species that enhance ethene production at high temperatures (Figure 9b).²³ This prediction was experimentally verified in a fluidized bed reactor–regenerator pilot plant, where coke species enclosed in SAPO-34 were converted to naphthalenic species by steam cracking. An unexpectedly high light olefin selectivity of 85%, 88% valuable CO and H₂, and negligible CO₂ as regenerated byproducts were achieved under continuous operation such as industrial operation, as schematically shown in Figure 10a,b.²³ Combined with these studies, we can see that the evolution of the bulky active HCP species continues as MTH proceeds on zeolite. Considering the concentration-dependent reaction kinetics, diffusion constraints in zeolites, and differences in thermodynamic driving forces, the involvement of the bulky active HCP species depends not only on the acidity (acid strength and acid density) and topology (e.g., confinement effect and diffusion constraints) of the zeolite catalyst but also on the reaction conditions, especially the temperature and reactant partial pressure. To gain insight into the coking and deactivation of the MTH reaction, a complete molecule-resolved route for PAH speciation and evolution was unveiled in our recent study

by integrating high-resolution MALDI FT-ICR mass spectrometry and an isotope labeling technique.⁴ Figure 11a shows the dynamic process of PAHs from seeding to growth and then to aggregation. The elucidation of a previously unrecognized mechanistic step is noteworthy: cage-passing growth forming cross-linked multinuclear PAHs with a graphene-like structure. The analysis of organic extracts obtained from cage-structured molecular sieves, SAPO-34, SAPO-18, and SAPO-5, based on MALDI FT-ICR mass spectrometry demonstrates the generality of this mechanistic concept (Figure 11b).⁴ The cross-linked, multinuclear hydrocarbon clusters (with fluorene, phenanthrene, and pyrene as building units) are prone to residing in the shell layer of crystals. Such near-surface-enriched, cross-linked, and bulky coke clusters can impede the diffusion of reactants, thus frustrating the structural extension of the lighter aromatic species within the near-core portion of the crystal and ultimately leaving some of the internal acid sites unused. On ZSM-5, another important zeolite catalyst applied in the MTH reaction consisting of a clear molecularly resolved speciation and mechanistic picture of the evolution of PAHs remains a promising addition to future studies, despite numerous mass spectrometric, spectroscopic, and theoretical studies identifying PAHs and graphite-like molecules as the major components of the internal and external coke, respectively.

Accordingly, the bulky HCP species and their evolution contribute to the MTH reaction in two possible ways: either as the active intermediates to promote the autocatalysis by completing the HCP-based cycles or as coke precursors to hinder the autocatalysis by extending and aggregating into more condensed PAHs.

CONCLUSIONS AND PERSPECTIVES

Acidity and shape selectivity endow zeolites with a decisive role in MTH catalysis. The active center for MTH catalysis is no longer a one-way BAS but starts with a bridging hydroxyl

group and is then transformed into an OIHS by hybridization of the confined organic molecules and inorganic zeolite frameworks. The dynamic activation and transformation of C1 molecules is realized by the first generation of an OIHS, known as SMS, which breeds the first C–C bond in the MTH reaction. Autocatalysis is then initiated by the nascent olefins and develops dynamically with the growth of the second generation of the OIHS, called AIPC, which turns zeolites into the working catalyst during the highly efficient autocatalysis reaction period. According to the orderly and synergistic operation of the three catalytic cycles involved (an alkene-based cycle, a cyclopentadiene-based cycle, and an aromatic-based cycle), a hypercyclic reaction network is constructed and displays the dynamic autocatalytic motifs in the zeolite-catalyzed MTH reaction. Driven by thermodynamics, the excessive growth of confined organics inevitably aging into PHAs with the proceeding of the MTH reaction and their further extension and cross-linking will deactivate the zeolite by exacerbating the diffusion limitation or covering the acid sites.

The combination of modern advanced in situ spectroscopic techniques and computational chemistry (e.g., quantum calculations and molecular dynamic simulations) provides important mechanistic information, such as the observation of intermediate species on the working catalyst and the *operando* simulation of elementary reaction steps at the molecular level, which are undoubtedly essential for understanding the catalytic mechanism under real reaction conditions. In recent years, we have carried out this strategy and achieved surprising results in zeolite chemistry and catalysis research. Among these findings, the discovery of dynamic reversible T–O–T bond breaking and healing is upending the conventional wisdom of zeolite crystallography and hydrothermal properties, while the dynamic MTH process reveals an extraordinarily complicated autocatalytic reaction course and network. The concept of dynamic catalysis in the zeolite-catalyzed MTH reaction will draw attention to the nature of zeolite catalysis under real working conditions. Furthermore, all of these understandings and efforts will support industrial applications for efficient and controllable catalytic conversion.

AUTHOR INFORMATION

Corresponding Authors

Yingxu Wei – National Engineering Research Center of Lower-Carbon Catalysis Technology, Dalian National Laboratory for Clean Energy, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 Liaoning, China; orcid.org/0000-0002-0412-1980; Email: weiyx@dicp.ac.cn

Zhongmin Liu – National Engineering Research Center of Lower-Carbon Catalysis Technology, Dalian National Laboratory for Clean Energy, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 Liaoning, China; State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 Liaoning, China; University of Chinese Academy of Sciences, Beijing 100049, China; orcid.org/0000-0002-7999-2940; Email: liuzm@dicp.ac.cn

Author

Xinqiang Wu – National Engineering Research Center of Lower-Carbon Catalysis Technology, Dalian National Laboratory for Clean Energy, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 Liaoning, China

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.accounts.3c00187>

Notes

The authors declare no competing financial interest.

Biographies

Xinqiang Wu is an associate professor at the Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences (CAS). He received his Ph.D. from DICP CAS in 2019. His research focuses on the mechanism of the zeolite-catalyzed methanol conversion process.

Yingxu Wei is a professor at DICP CAS. She received her Ph.D. from DICP in 2001 and has been the group leader of catalysis and new catalytic reactions since 2009. She has worked with the research on heterogeneous catalysis and MTO catalysis and has gained the national support plan for high level talents.

Zhongmin Liu is an academician of CAS and the director of DICP CAS. He received his Ph.D. in chemical physics from DICP CAS in 1990. He has long been working with catalysis research, process development, and technology transfer in energy conversion and utilization and has made significant achievements. He is the leading scientist of DMTO technology and DMTE technology.

ACKNOWLEDGMENTS

We thank the following funding agencies for supporting this work: the National Natural Science Foundation of China (21991092, 21991090, 21902153, and 22288101), the National Key R&D Program of China (no. 2021YFA1502600), and the Youth Innovation Promotion Association, CAS (2022182).

REFERENCES

- (1) Wu, X.; Xu, S.; Zhang, W.; Huang, J.; Li, J.; Yu, B.; Wei, Y.; Liu, Z. Direct Mechanism of the First Carbon-Carbon Bond Formation in the Methanol-to-Hydrocarbons Process. *Angew. Chem., Int. Ed.* **2017**, *56*, 9039–9043.
- (2) Sun, T.; Chen, W.; Xu, S.; Zheng, A.; Wu, X.; Zeng, S.; Wang, N.; Meng, X.; Wei, Y.; Liu, Z. The first carbon-carbon bond formation mechanism in methanol-to-hydrocarbons process over chabazite zeolite. *Chem* **2021**, *7*, 2415–2428.
- (3) Lin, S.; Zhi, Y.; Chen, W.; Li, H.; Zhang, W.; Lou, C.; Wu, X.; Zeng, S.; Xu, S.; Xiao, J.; Zheng, A.; Wei, Y.; Liu, Z. Molecular Routes of Dynamic Autocatalysis for Methanol-to-Hydrocarbons Reaction. *J. Am. Chem. Soc.* **2021**, *143*, 12038–12052.
- (4) Wang, N.; Zhi, Y.; Wei, Y.; Zhang, W.; Liu, Z.; Huang, J.; Sun, T.; Xu, S.; Lin, S.; He, Y.; Zheng, A.; Liu, Z. Molecular elucidating of an unusual growth mechanism for polycyclic aromatic hydrocarbons in confined space. *Nat. Commun.* **2020**, *11*, 1079.
- (5) Dusselier, M.; Davis, M. E. Small-Pore Zeolites: Synthesis and Catalysis. *Chem. Rev.* **2018**, *118*, 5265–5329.
- (6) Van Speybroeck, V.; Hemelsoet, K.; Joos, L.; Waroquier, M.; Bell, R. G.; Catlow, C. R. Advances in theory and their application within the field of zeolite chemistry. *Chem. Soc. Rev.* **2015**, *44*, 7044–7111.

- (7) Tian, P.; Wei, Y.; Ye, M.; Liu, Z. Methanol to Olefins (MTO): From Fundamentals to Commercialization. *ACS Catal.* **2015**, *5*, 1922–1938.
- (8) Olsbye, U.; Svelle, S.; Bjorgen, M.; Beato, P.; Janssens, T. V.; Joensen, F.; Bordiga, S.; Lillerud, K. P. Conversion of methanol to hydrocarbons: how zeolite cavity and pore size controls product selectivity. *Angew. Chem., Int. Ed.* **2012**, *51*, 5810–5831.
- (9) Ono, Y.; Mori, T. Mechanism of Methanol Conversion into Hydrocarbons over Zsm-5 Zeolite. *J. Chem. Soc., Faraday Trans. 1 F* **1981**, *77*, 2209–2221.
- (10) Gong, X.; Caglayan, M.; Ye, Y.; Liu, K.; Gascon, J.; Dutta Chowdhury, A. First-Generation Organic Reaction Intermediates in Zeolite Chemistry and Catalysis. *Chem. Rev.* **2022**, *122*, 14275–14345.
- (11) Hwang, A.; Bhan, A. Deactivation of Zeolites and Zeotypes in Methanol-to-Hydrocarbons Catalysis: Mechanisms and Circumvention. *Acc. Chem. Res.* **2019**, *52*, 2647–2656.
- (12) Haw, J. F.; Song, W.; Marcus, D. M.; Nicholas, J. B. The mechanism of methanol to hydrocarbon catalysis. *Acc. Chem. Res.* **2003**, *36*, 317–326.
- (13) Olsbye, U.; Svelle, S.; Lillerud, K. P.; Wei, Z. H.; Chen, Y. Y.; Li, J. F.; Wang, J. G.; Fan, W. B. The formation and degradation of active species during methanol conversion over protonated zeotype catalysts. *Chem. Soc. Rev.* **2015**, *44*, 7155–7176.
- (14) Wang, W.; Hunger, M. Reactivity of surface alkoxy species on acidic zeolite catalysts. *Acc. Chem. Res.* **2008**, *41*, 895–904.
- (15) Yarulina, I.; Chowdhury, A. D.; Meirer, F.; Weckhuysen, B. M.; Gascon, J. Recent trends and fundamental insights in the methanol-to-hydrocarbons process. *Nat. Catal.* **2018**, *1*, 398–411.
- (16) Song, W.; Marcus, D. M.; Fu, H.; Ehresmann, J. O.; Haw, J. F. An oft-studied reaction that may never have been: direct catalytic conversion of methanol or dimethyl ether to hydrocarbons on the solid acids HZSM-5 or HSAPO-34. *J. Am. Chem. Soc.* **2002**, *124*, 3844–3845.
- (17) Jogunola, O.; Salmi, T.; Eranen, K.; Warna, J.; Mikkola, J. P. Rates and equilibria of ester hydrolysis: Combination of slow and rapid reactions. *Chem. Eng. Process.* **2011**, *50*, 665–674.
- (18) Wu, X.; Chen, W.; Xu, S.; Lin, S.; Sun, T.; Zheng, A.; Wei, Y.; Liu, Z. Dynamic Activation of C1 Molecules Evoked by Zeolite Catalysis. *ACS Cent. Sci.* **2021**, *7*, 681–687.
- (19) Wu, X.; Xu, S.; Wei, Y.; Zhang, W.; Huang, J.; Xu, S.; He, Y.; Lin, S.; Sun, T.; Liu, Z. Evolution of C–C Bond Formation in the Methanol-to-Olefins Process: From Direct Coupling to Autocatalysis. *ACS Catal.* **2018**, *8*, 7356–7361.
- (20) Zhang, W.; Chen, J.; Xu, S.; Chu, Y.; Wei, Y.; Zhi, Y.; Huang, J.; Zheng, A.; Wu, X.; Meng, X.; Xiao, F.; Deng, F.; Liu, Z. Methanol to Olefins Reaction over Cavity-type Zeolite: Cavity Controls the Critical Intermediates and Product Selectivity. *ACS Catal.* **2018**, *8*, 10950–10963.
- (21) Zhang, W.; Zhi, Y.; Huang, J.; Wu, X.; Zeng, S.; Xu, S.; Zheng, A.; Wei, Y.; Liu, Z. Methanol to Olefins Reaction Route Based on Methylcyclopentadienes as Critical Intermediates. *ACS Catal.* **2019**, *9*, 7373–7379.
- (22) Zhang, W.; Zhang, M.; Xu, S.; Gao, S.; Wei, Y.; Liu, Z. Methylcyclopentenyl Cations Linking Initial Stage and Highly Efficient Stage in Methanol-to-Hydrocarbon Process. *ACS Catal.* **2020**, *10*, 4510–4516.
- (23) Zhou, J.; Gao, M.; Zhang, J.; Liu, W.; Zhang, T.; Li, H.; Xu, Z.; Ye, M.; Liu, Z. Directed transforming of coke to active intermediates in methanol-to-olefins catalyst to boost light olefins selectivity. *Nat. Commun.* **2021**, *12*, 17.
- (24) Stöcker, M. Methanol-to-hydrocarbons: catalytic materials and their behavior. *Microporous Mesoporous Mater.* **1999**, *29*, 3–48.
- (25) Liu, Y.; Muller, S.; Berger, D.; Jelic, J.; Reuter, K.; Tonigold, M.; Sanchez-Sanchez, M.; Lercher, J. A. Formation Mechanism of the First Carbon-Carbon Bond and the First Olefin in the Methanol Conversion into Hydrocarbons. *Angew. Chem., Int. Ed.* **2016**, *55*, 5723–5726.
- (26) Chowdhury, A. D.; Houben, K.; Whiting, G. T.; Mokhtar, M.; Asiri, A. M.; Al-Thabaiti, S. A.; Basahel, S. N.; Baldus, M.; Weckhuysen, B. M. Initial Carbon-Carbon Bond Formation during the Early Stages of the Methanol-to-Olefin Process Proven by Zeolite-Trapped Acetate and Methyl Acetate. *Angew. Chem., Int. Ed.* **2016**, *55*, 15840–15845.
- (27) Plessow, P. N.; Studt, F. Unraveling the Mechanism of the Initiation Reaction of the Methanol to Olefins Process Using ab Initio and DFT Calculations. *ACS Catal.* **2017**, *7*, 7987–7994.
- (28) Yang, L.; Yan, T.; Wang, C.; Dai, W.; Wu, G.; Hunger, M.; Fan, W.; Xie, Z.; Guan, N.; Li, L. Role of Acetaldehyde in the Roadmap from Initial Carbon–Carbon Bonds to Hydrocarbons during Methanol Conversion. *ACS Catal.* **2019**, *9*, 6491–6501.
- (29) Chen, W.; Li, G.; Yi, X.; Day, S. J.; Tarach, K. A.; Liu, Z.; Liu, S. B.; Edman Tsang, S. C.; Gora-Marek, K.; Zheng, A. Molecular Understanding of the Catalytic Consequence of Ketene Intermediates under Confinement. *J. Am. Chem. Soc.* **2021**, *143*, 15440–15452.
- (30) Hutchings, G. J.; Gottschalk, F.; Hall, M. V. M.; Hunter, R. Hydrocarbon formation from methylating agents over the zeolite catalyst ZSM-5. Comments on the mechanism of carbon–carbon bond and methane formation. *J. Chem. Soc., Faraday Trans. 1 F* **1987**, *83*, 571.
- (31) Li, J.; Wei, Z.; Chen, Y.; Jing, B.; He, Y.; Dong, M.; Jiao, H.; Li, X.; Qin, Z.; Wang, J.; Fan, W. A route to form initial hydrocarbon pool species in methanol conversion to olefins over zeolites. *J. Catal.* **2014**, *317*, 277–283.
- (32) Olah, G. A.; Doggweiler, H.; Felberg, J. D.; Frohlich, S.; Grdina, M. J.; Karpeles, R.; Keumi, T.; Inaba, S.-i.; Ip, W. M.; Lammertsma, K. Onium Ylide chemistry. 1. Bifunctional acid-base-catalyzed conversion of heterosubstituted methanes into ethylene and derived hydrocarbons. The onium ylide mechanism of the C1. fwdarw. C2 conversion. *J. Am. Chem. Soc.* **1984**, *106*, 2143–2149.
- (33) Yamazaki, H.; Shima, H.; Imai, H.; Yokoi, T.; Tatsumi, T.; Kondo, J. N. Evidence for a “carbene-like” intermediate during the reaction of methoxy species with light alkenes on H-ZSM-5. *Angew. Chem., Int. Ed.* **2011**, *50*, 1853–1856.
- (34) Chu, Y.; Yi, X.; Li, C.; Sun, X.; Zheng, A. Bronsted/Lewis acid sites synergistically promote the initial C–C bond formation in the MTO reaction. *Chem Sci* **2018**, *9*, 6470–6479.
- (35) Comas-Vives, A.; Valla, M.; Coperet, C.; Sautet, P. Cooperativity between Al Sites Promotes Hydrogen Transfer and Carbon-Carbon Bond Formation upon Dimethyl Ether Activation on Alumina. *ACS Cent Sci* **2015**, *1*, 313–319.
- (36) Wang, C.; Chu, Y.; Xu, J.; Wang, Q.; Qi, G.; Gao, P.; Zhou, X.; Deng, F. Extra-Framework Aluminum-Assisted Initial C–C Bond Formation in Methanol-to-Olefins Conversion on Zeolite H-ZSM-5. *Angew. Chem., Int. Ed.* **2018**, *57*, 10197–10201.
- (37) Lin, S.; Zhi, Y.; Liu, Z.; Yuan, J.; Liu, W.; Zhang, W.; Xu, Z.; Zheng, A.; Wei, Y.; Liu, Z. Multiscale dynamical cross-talk in zeolite-catalyzed methanol and dimethyl ether conversions. *Natl. Sci. Rev.* **2022**, *9*, nwac151.
- (38) Dessau, R. M.; Lapierre, R. B. On the Mechanism of Methanol Conversion to Hydrocarbons over HZSM-5. *J. Catal.* **1982**, *78*, 136–141.
- (39) Mole, T.; Whiteside, J. A.; Seddon, D. Aromatic Co-Catalysis of Methanol Conversion over Zeolite Catalysts. *J. Catal.* **1983**, *82*, 261–266.
- (40) Dahl, I. M.; Kolboe, S. On the Reaction-Mechanism for Propene Formation in the Mto Reaction over Sapo-34. *Catal. Lett.* **1993**, *20*, 329–336.
- (41) Xu, T.; Barich, D. H.; Goguen, P. W.; Song, W. G.; Wang, Z. K.; Nicholas, J. B.; Haw, J. F. Synthesis of a benzenium ion in a zeolite with use of a catalytic flow reactor. *J. Am. Chem. Soc.* **1998**, *120*, 4025–4026.
- (42) Bjorgen, M.; Bonino, F.; Kolboe, S.; Lillerud, K. P.; Zecchina, A.; Bordiga, S. Spectroscopic evidence for a persistent benzenium cation in zeolite H-beta. *J. Am. Chem. Soc.* **2003**, *125*, 15863–15868.
- (43) Li, J.; Wei, Y.; Chen, J.; Tian, P.; Su, X.; Xu, S.; Qi, Y.; Wang, Q.; Zhou, Y.; He, Y.; Liu, Z. Observation of heptamethylbenzenium

cation over SAPO-type molecular sieve DNL-6 under real MTO conversion conditions. *J. Am. Chem. Soc.* **2012**, *134*, 836–839.

(44) Xu, S.; Zheng, A.; Wei, Y.; Chen, J.; Li, J.; Chu, Y.; Zhang, M.; Wang, Q.; Zhou, Y.; Wang, J.; Deng, F.; Liu, Z. Direct observation of cyclic carbenium ions and their role in the catalytic cycle of the methanol-to-olefin reaction over chabazite zeolites. *Angew. Chem., Int. Ed.* **2013**, *52*, 11564–11568.

(45) Svelle, S.; Joensen, F.; Nerlov, J.; Olsbye, U.; Lillerud, K. P.; Kolboe, S.; Bjorgen, M. Conversion of methanol into hydrocarbons over zeolite H-ZSM-5: ethene formation is mechanistically separated from the formation of higher alkenes. *J. Am. Chem. Soc.* **2006**, *128*, 14770–14771.

(46) Bjorgen, M.; Svelle, S.; Joensen, F.; Nerlov, J.; Kolboe, S.; Bonino, F.; Palumbo, L.; Bordiga, S.; Olsbye, U. Conversion of methanol to hydrocarbons over zeolite H-ZSM-5: On the origin of the olefinic species. *J. Catal.* **2007**, *249*, 195–207.

(47) Li, J.; Wei, Y.; Chen, J.; Xu, S.; Tian, P.; Yang, X.; Li, B.; Wang, J.; Liu, Z. Cavity Controls the Selectivity: Insights of Confinement Effects on MTO Reaction. *ACS Catal.* **2015**, *5*, 661–665.

(48) Bjørgen, M.; Akyalcin, S.; Olsbye, U.; Benard, S.; Kolboe, S.; Svelle, S. Methanol to hydrocarbons over large cavity zeolites: Toward a unified description of catalyst deactivation and the reaction mechanism. *J. Catal.* **2010**, *275*, 170–180.

(49) Yu, B.; Zhang, W.; Wei, Y.; Wu, X.; Sun, T.; Fan, B.; Xu, S.; Liu, Z. Capture and identification of coke precursors to elucidate the deactivation route of the methanol-to-olefin process over H-SAPO-34. *Chem. Commun.* **2020**, *56*, 8063–8066.