

Dynamic Activation of C1 Molecules Evoked by Zeolite Catalysis

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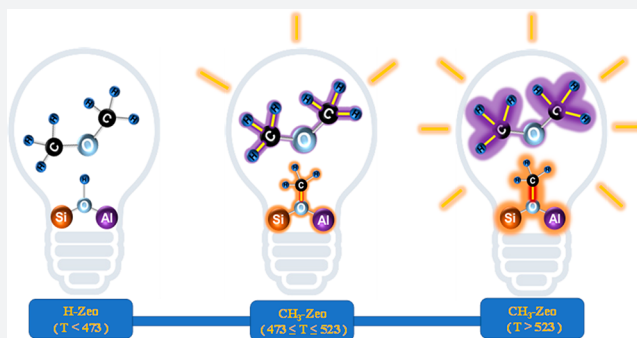


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ABSTRACT: Direct observation of the activation and transformation of reactant molecules is extremely attractive but very challenging in the study of most chemical processes. Here is reported the first case of dynamic activation of C1 molecules in zeolite-catalyzed chemistry. During the methanol conversion over the HZSM-5 zeolite, a sequence of progressive activation states of dimethyl ether (DME) evoked by the special catalysis from CH₃-Zeo, a hybrid supramolecular catalytic system formed by the organic methylic species growing on the inorganic silico-aluminate zeolite framework, has been directly observed by *in situ* ssNMR spectroscopy at programmed temperatures. *Operando* simulations visually display the variability of this hybrid supramolecular system of which the C–O bond property goes through a dynamic transition from covalent to ionic with the temperature increase, and thus the gradually enhanced electrophilicity of CH₃^{δ+} and nucleophilicity of Zeo^{δ-} lead to the dynamic activation of DME. This dynamic transition is generally reflected in the alkyl-Zeo system with other alkoxy groups, which linked the alkoxy species and carbocations in zeolite catalysis. Consequently, this work not only sheds light on the key issue of the first carbon–carbon (C–C) bond formation in the methanol to hydrocarbons (MTH) process but also brings a new awareness on the essence of acid catalysis in zeolite mediated chemical processes.



INTRODUCTION

The zeolite-catalyzed chemical processes have played a crucial role in the modern chemical industry, especially in the petrochemical industry and the emerging coal-based chemical industry.^{1–3} As the critical step in the coal-based chemical industrial process, the methanol to hydrocarbons (MTH) reaction catalyzed by zeolites or SAPO molecular sieves has gained great achievements both in industry and academia.^{4–7} For the fundamental research, the so-called hydrocarbon pool (HCP) reaction pathways are widely acknowledged and alkenyl- or/and phenyl-based HCP species have been identified as efficient intermediates, via which methanol can be transformed into a range of hydrocarbons.^{8,9} Nevertheless, the HCP mechanism cannot account for the origin of the initial HCP species or the formation of the first C–C bond in the induction reaction period.¹⁰ Recently, many excellent works reported that initial hydrocarbons or surface complex containing the first C–C bond could be generated via the direct coupling reaction of C1 species.^{11–20} Moreover, surface methoxy species (SMS) as the critical intermediate have attracted much attention in this research area. Especially in the very initial reaction period, SMS are formed by the dehydration of methanol over the traditionally Brønsted acidic site (BAS) and succeed to work as a methylation reagent for the carbon chain growth reaction.^{15,21–25} However, due to the complicity and instantaneity of the methanol conversion

reaction over zeolites, available data on the activation and conversion of C1 reactant molecules is quite limited. As a consequence, understanding the catalytic behaviors under the realistic MTH reaction condition is critical in uncovering the nature of special acid catalysis evoked by zeolites.

In this work, by the advanced *in situ* solid-state nuclear magnetic resonance (ssNMR) technique, a sequence of progressive activation states of DME evoked by CH₃-Zeo catalysis has been directly observed during the methanol conversion over the HZSM-5 zeolite. Moreover, the critical role of CH₃-Zeo, a hybrid supramolecular catalytic system formed by the organic methylic species growing on the inorganic silico-aluminate frameworks, has been visually revealed by *operando* simulations via *ab initio* molecular dynamics (AIMD). It is found that the C–O bond situated at the organic–inorganic boundary can be regulated with temperature variation. The temperature increase leads to the C–O bond ionization and thus induces the activation and transformation of the approaching C1 reactant molecules. In

Received: January 3, 2021

Published: March 24, 2021



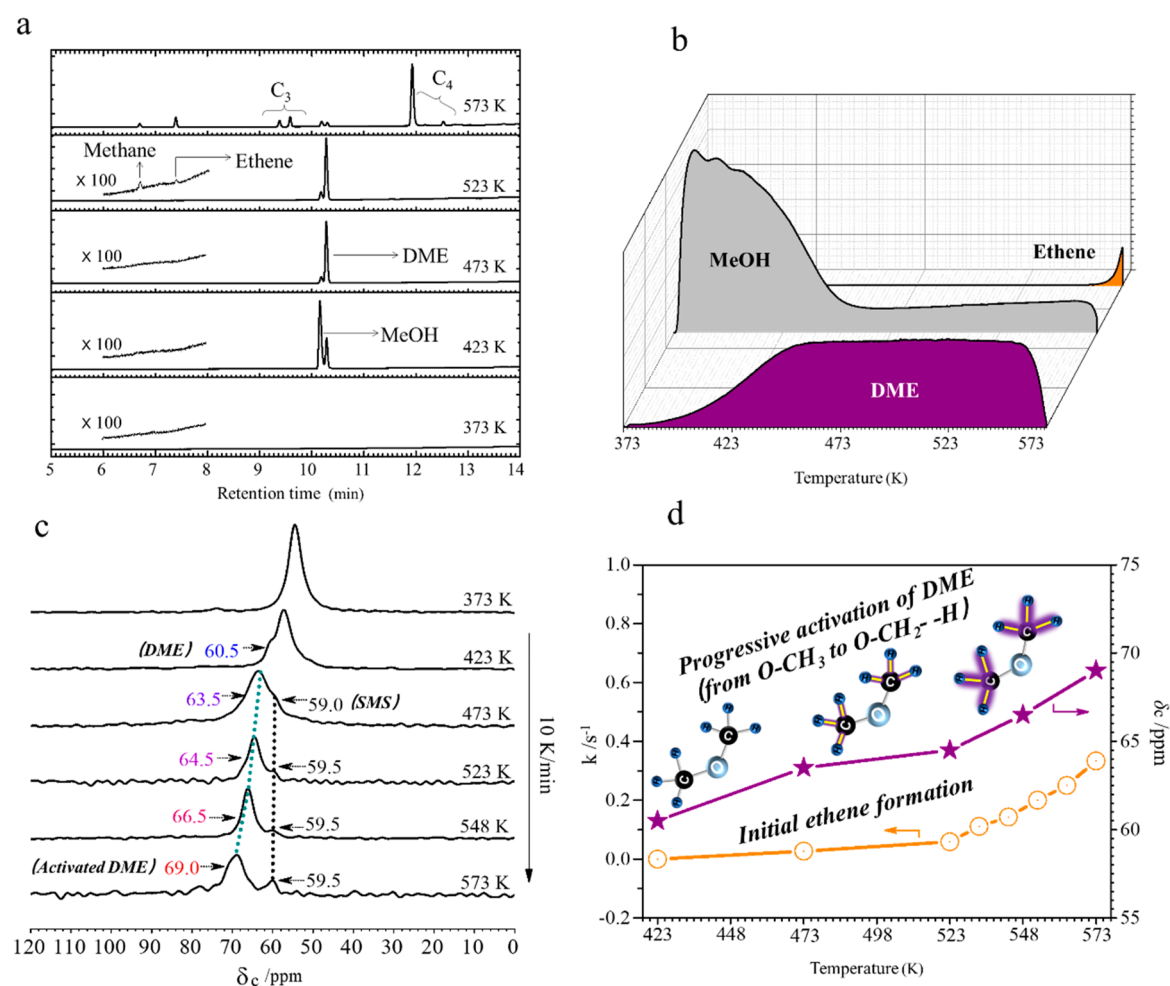


Figure 1. (a) GC-MS chromatograms of the continuous-flow methanol conversion over HZSM-5 in a fix-bed reactor under the linear temperature increase from 373 to 573 K and (b) real-time tracking of the effluents by Online Mass Spectroscopy (methanol weight hourly space velocity (WHSV): 2.0 h⁻¹, temperature ramping rate: 2 K/min). (c) *In situ* ¹³C MAS NMR spectra during the ¹³C methanol continuous-flow conversion over HZSM-5 in an NMR rotor reactor under the condition of the linear temperature increase from 373 to 573 K (WHSV = 1 h⁻¹, temperature ramping rate = 10 K/min, ¹³C MAS NMR spectra were recorded using one pulse sequence with a spinning rate of 3 kHz). (d) The apparent reaction rate of C1 reactants and the chemical shift value of DME as the function of the reaction temperature from 423 to 573 K.

addition, *in situ* observations of the methanol conversion on weakly acidic NaZSM-5 and nonacidic silicate-1 by ssNMR and FTIR also consolidate the crucial role of CH₃-Zeo for the activation of C1 reactants and the initiation of the MTH reaction.

RESULTS AND DISCUSSION

The methanol conversion over HZSM-5 (Figure S1–S5) was proceeded in a fixed-bed quartz reactor under the condition of the linear temperature increase from 373 to 573 K at a rate of 2 K/min. The effluents were analyzed with Gas Chromatography Mass Spectrometry (GC-MS) and continuously monitored by online Mass Spectroscopy (MS). As shown in Figure 1a, the methanol dehydration is present as the main reaction and is promoted with the temperature increase from 373 to 473 K, as indicated by the enlarged ratio of DME to methanol. At this temperature range, one can only observe methanol and DME, and no hydrocarbons or special intermediates are detected among the effluents. It means that the methanol dehydration to DME is readily realized at this temperature range, but their further transformation to those C–C bond containing products may need a higher reaction temperature condition.

As the temperature increases to 523 K, a trace amount of ethene appeared and is the only detected C–C bond containing product. In the real-time tracking of online MS shown in Figure 1b, the signals of ethene are almost absent below 473 K but grow very fast with the temperature increase, especially from 523 to 573 K. Obviously, the direct conversion of methanol, DME, SMS, or/and even some other surface C1 species to generate C–C bond containing products can be responsible for the initial ethene formation.

To survey the catalyst surface under the same reaction conditions, HZSM-5 is loaded into an NMR rotor reactor, and the real-time evolution has been *in situ* recorded by ¹³C ssNMR spectroscopy. As shown in Figure 1c, during the ¹³C-methanol continuous introduction, only methanol can be observed on the catalyst surface below 373 K. The shoulder peak at 60.5 ppm attributed to DME^{26,27} adsorbed on BAS in forms of end-on type is observed at 423 K, while the other confirmation (side-on type) at 63.5 ppm becomes detectable at 473 K. More importantly, the signal simultaneously appearing at 59.0 ppm attributed to SMS signifies that an organic–inorganic hybrid catalytic system, CH₃-Zeo, is established on this zeolite catalyst at this moment. Subsequently, with the

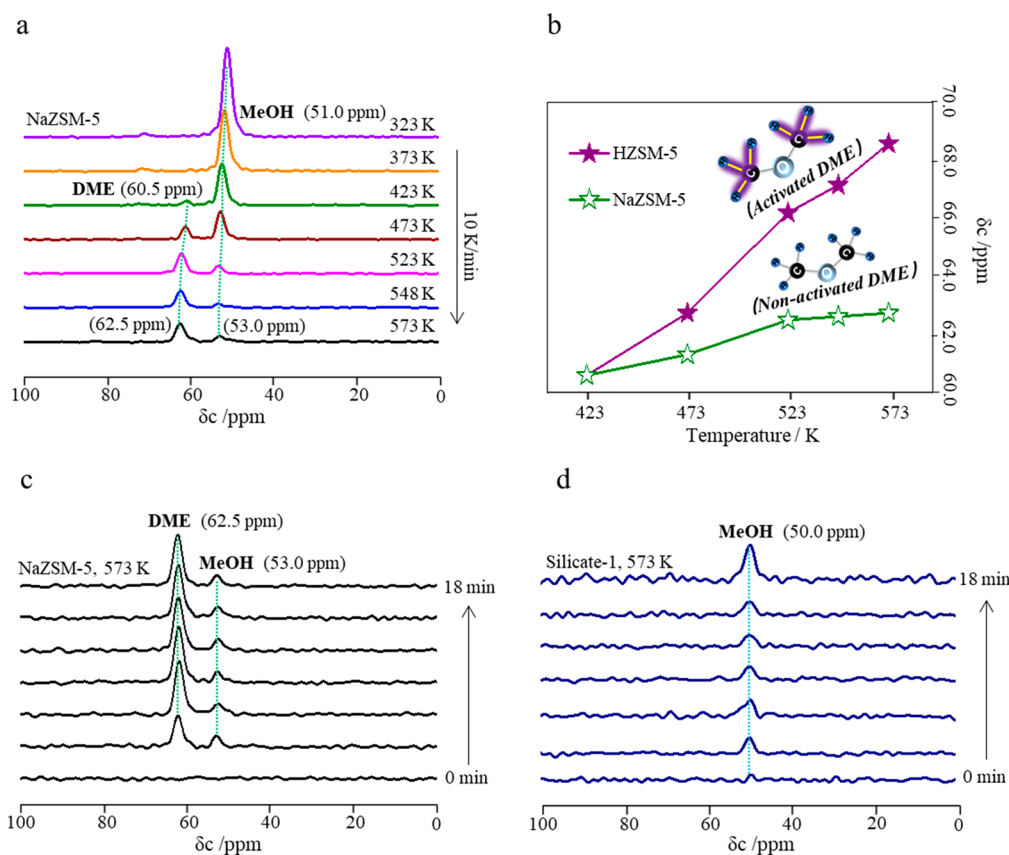


Figure 2. (a) *In situ* ¹³C MAS NMR spectra recorded during the continuous-flow methanol conversion over NaZSM-5 proceeded in an NMR rotor reactor under heating conditions with the linear temperature increase from 323 to 573 K. (b) On NaZSM-5 and HZSM-5, the chemical shift variation of DME as the function of the reaction temperature from 423 to 573 K. (c) *In situ* ¹³C MAS NMR spectra during the continuous-flow methanol conversion over NaZSM-5, and (d) over silicate-1 (methanol weight hourly space velocity (WHSV) of 2.0 h⁻¹, temperature ramping rate 10 K/min, ¹³C MAS NMR spectra were recorded using one pulse sequence with a spinning rate of 3 kHz).

linear temperature increase from 473 to 573 K, a most striking observation is that the chemical shift of DME is gradually migrated from 63.5 to 69.0 ppm (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). At 573 K, the signal at 69.0 ppm indicates that the highly activated DME presents the characteristics of methyleneoxy analogue species ($\text{CH}_3\text{-O-CH}_2^{\delta-}\text{-H}^{\delta+}$), and thus, the elongated C–H bond is ready for the C–C coupling with the positively charged methyl group ($\text{CH}_3^{\delta+}$) of $\text{CH}_3\text{-Zeo}$. To our knowledge, this is the first capture of dynamic activation of C1 molecules in zeolite-catalyzed chemistry. The apparent reaction rate of the methanol conversion during the very initial reaction period has been calculated according to the method proposed previously.²⁸ As shown in Figure 1d, the formation rate of initial olefin products is in line with the growth trend of chemical shift values of DME, implying that the progressive activation of approaching DME gives rise to the formation of initial hydrocarbon products with temperature dependence. In view of kinetics and catalysis, the improvement of initial olefin generation could be correlated to the dynamic progressive activation of C1 reactants by the $\text{CH}_3\text{-Zeo}$ catalytic system in the very initial period of the MTH process.

Further, the pivotal role of the $\text{CH}_3\text{-Zeo}$ catalytic system for the activation and transformation of C1 reactants has also been confirmed by studies of the methanol conversion on weakly acidic NaZSM-5 and nonacidic silicate-1 catalysts. In Figure 2a, *in situ* ¹³C ssNMR spectra are recorded during the ¹³C-methanol continuously introduced onto NaZSM-5 at the

programmed temperature increase condition. The signal at 60.5 ppm shows that methanol dehydration to DME can also be realized on NaZSM-5, but of more concern is that the generated DME only presents a slight migration from 60.5 to 62.5 ppm and the signal from SMS is also not detectable during the temperature increase from 373 to 573 K, which is very different from the reaction recorded over HZSM-5. In other words, without $\text{CH}_3\text{-Zeo}$ as the supramolecular catalytic center, the generated DME on NaZSM-5 cannot be well activated in the same way as that on HZSM-5, as indicated by the comparison shown in Figure 2b. Even though the methanol conversion is performed at 573 K for 0.5 h as shown in Figure 2c, there are still no apparent changes, and only trace amounts of hydrocarbons can be detected in the effluent (Figure S6). The ¹³C methanol conversion on silicate-1 gives a better complement. As shown in Figure 2d, neither hydrocarbons nor DME can be detected on the nonacidic catalyst surface and in the effluent (Figure S7) and thus is inactive for the MTH reaction. Additionally, DRIFTS experiments (Figure S8) show that the characteristic peak of SMS at 2977 and 2868 cm⁻¹ can be clearly observed only on HZSM-5 but is not detectable on either the weakly acidic NaZSM-5 or nonacidic silicate-1 samples. In line with the observation on HZSM-5, the studies on NaZSM-5 and silicate-1 also consolidate the indispensable role of the $\text{CH}_3\text{-Zeo}$ catalytic center in C1 reactant activation and transformation during the initial reaction period of the MTH process.

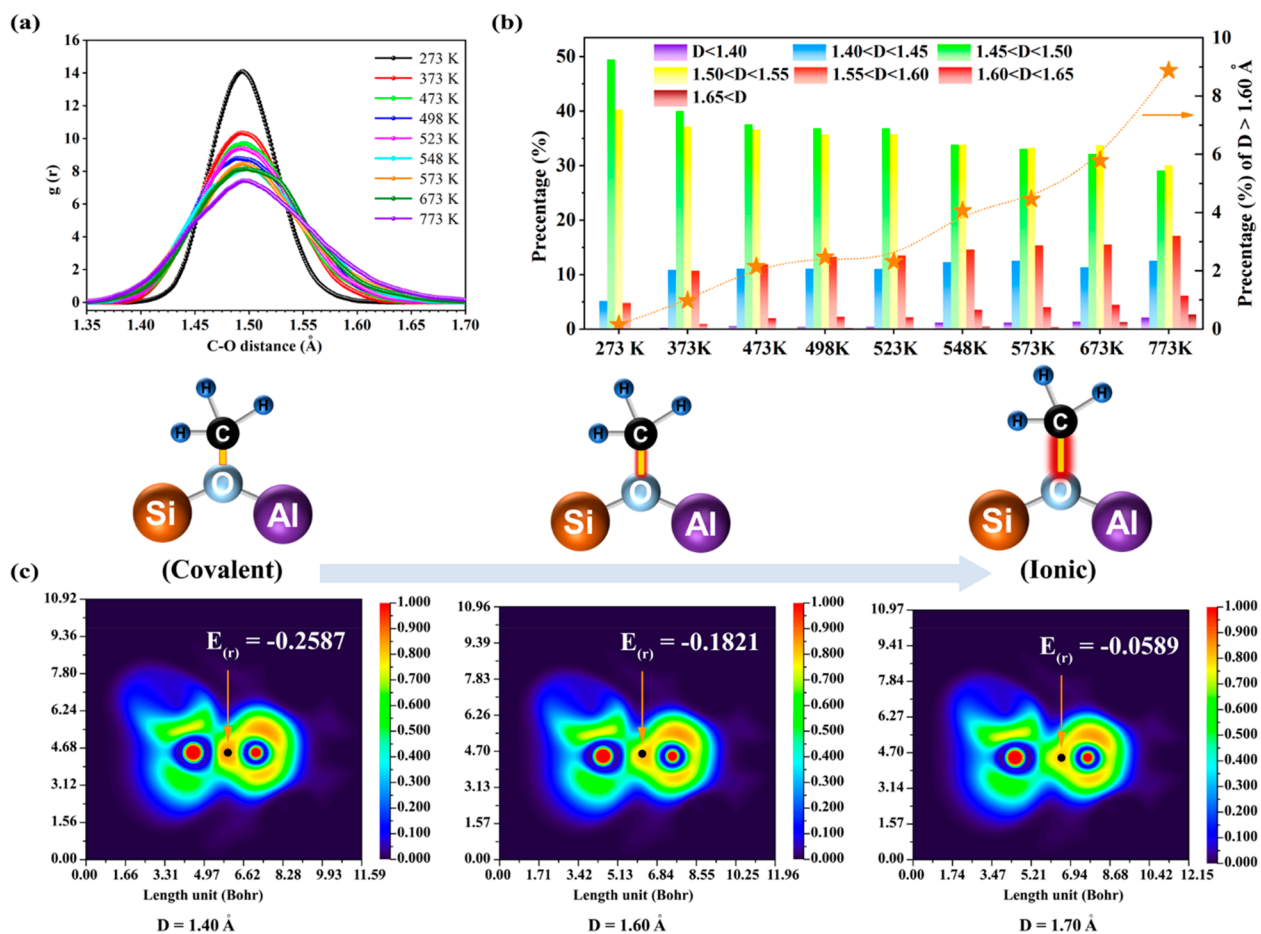
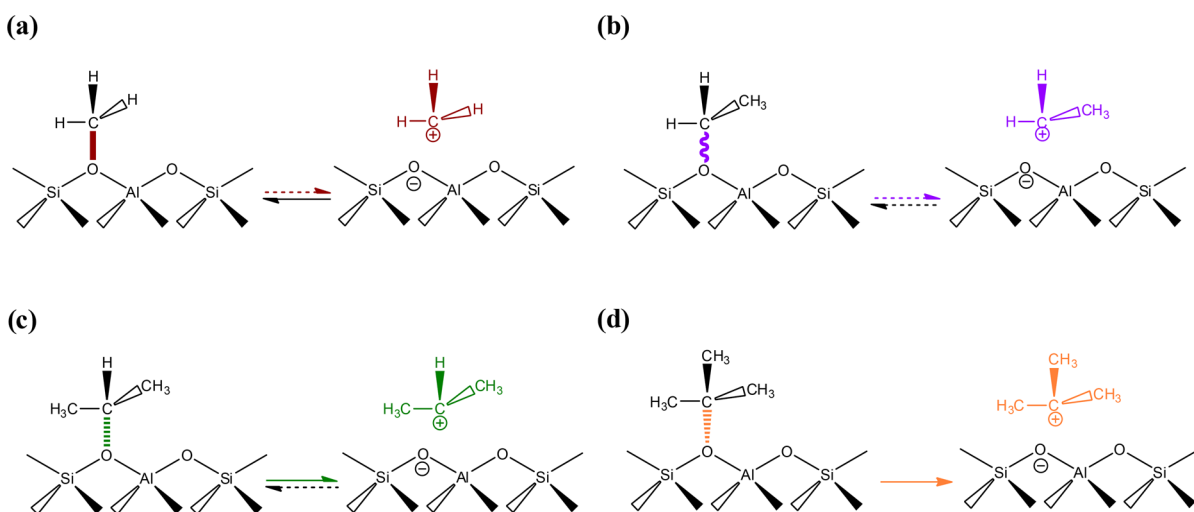


Figure 3. (a) The radial distribution function ($g(r)$) as a function of the C–O bond distance of SMS and (b) the percentage at the different D (D represents the C–O distance) values, based on 50 ps NVT AIMD simulations. (c) Electron localization function (ELF) of the C–O bond from SMS theoretically predicted at 1.40 Å, 1.60 Å, and 1.70 Å and the relevant energy density ($E(r)$) at the bond critical point.

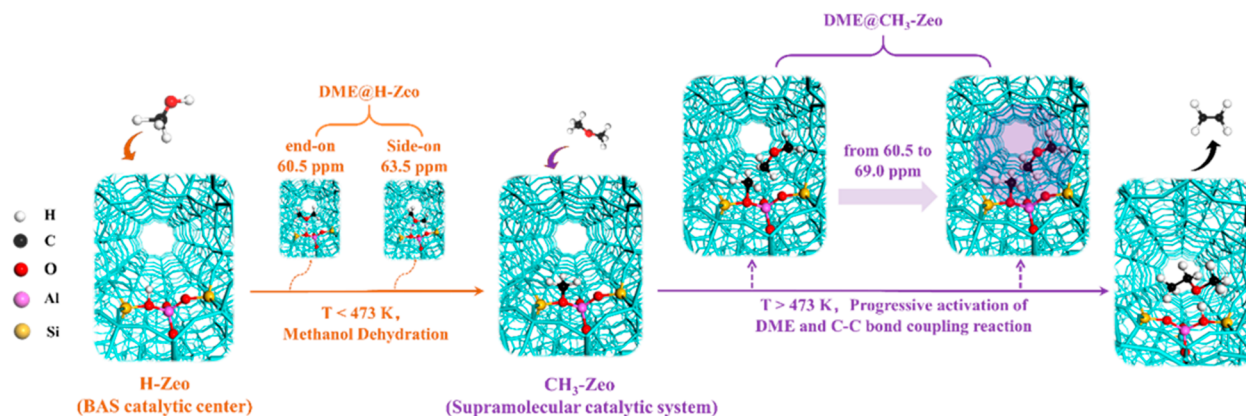
Scheme 1. Covalent-Ionic Transition at the C–O Bond in the Alkyl-Zeo System^a



^a(a) CH₃-Zeo, (b) CH₃CH₂-Zeo, (c) (CH₃)₂CH-Zeo, and (d) (CH₃)₃C-Zeo.

At the molecular level, *operando* simulations on the hybrid supramolecular catalytic system, CH₃-Zeo, have been performed by using AIMD (details about the calculation methods in the Supporting Information). As seen in Figure 3a, the radial distribution $g(r)$ as a function of the C–O bond distance of SMS is plotted in the temperature range from 273

to 773 K. The significant variation of $g(r)$ shows that the amplitude of the C–O bond stretching vibration is enhanced with the temperature increase. The fast-growing percentage of $D_{(C-O)} > 1.60$ Å with the temperature increase shown in Figure 3b also demonstrates that the C–O bond is more reactive at the realistic experimental temperature condition. Once the

Scheme 2. Evolution of the Catalyst Surface during the Methanol Conversion over HZSM-5 with the Temperature Variation^a

^aUnder the low temperature condition, methanol can be dehydrated, and the catalyst surface is occupied by C1 reactants and SMS. Under the high temperature condition, DME can be activated by the CH₃-Zeo supramolecular catalytic system, and the further coupling reaction generates a new C–C bond.

CH₃-Zeo supramolecular catalytic system is established in that confined nanosized space of zeolite channels or cages, either the extension or the delocalization of methyl in CH₃-Zeo will be in favor of the collision with the approaching guest molecules. The electron localization function (ELF) and the energy density ($E_{(r)}$) at the bond critical point of the C–O bond are also measured at 1.40, 1.60, and 1.70 Å, as shown in Figure 3c. With the extended bond length, the C–O bond strength is weakened according to the atoms in molecules theory. Moreover, the bond property variation can be described by the $E_{(r)}$ value of the bond critical point. It is generally accepted that the enlarged value of $E_{(r)}$ signifies the covalency of the chemical bond is decreased, while its ionicity is enhanced. Based on these simulations and theories, one can speculate that the C–O bond in this CH₃-Zeo hybrid system would be varied from covalent-bonding to ionic-bonding when the temperature is increased from 273 to 773 K. Consequently, a more positively charged surface methyl group (i.e., inclining to be carbocation with strengthened electrophilicity) and an enhanced nucleophilicity of the framework oxygen (AlO_4^-) are favorable for the dissociation of the C–H bond in DME and the C–C bond coupling to form MEE. In line with the ssNMR observations, it can be anticipated that the approaching C1 reactant molecule is activated by the CH₃-Zeo catalysis, and the further methylation reaction realizes the first C–C bond coupling under the realistic MTH reaction condition.

Additionally, analogous to the methoxy group, the C–O bond of ethoxy, isopropoxy, and *tert*-butoxy species over the HZSM-5 zeolite was also evaluated theoretically to reach a consensus of dynamic evolution in the alkyl-Zeo system (Scheme 1). The results illustrate the covalent-ionic transition of the C–O bond along with the alkyl groups (see Figure S9, results and discussion also given in the Supporting Information). The ionicity of these alkoxy species, in terms of the percentage of the C–O bond with the bond distance (D) of $D > 1.60$ Å, increases gradually from SMS to surface *tert*-butoxy with the following order: CH₃-Zeo < CH₃CH₂-Zeo < (CH₃)₂CH-Zeo < (CH₃)₃C-Zeo. Compared to methoxy, *tert*-butoxy has presented completely as a surface carbocation without C–O bonding interaction over the zeolite. Temperature effect, steric effect, and substituent effect would dramatically affect the electronic property of surface species and directly determine their stable states. These alkoxy species

or carbocations over the zeolite not only form in the MTH reaction but also serve as important intermediates in cracking, alkylation, dehydration, isomerization, etc.^{29,30} The covalent to ionic bond transition links the covalent alkoxy species to the carbocation species in acid catalysis. The more feasible transition of the C–O bond on the bulky alkoxy groups and the ionicity also rationalizes their role as critical intermediates. The generation and transition procedure of alkoxy groups or carbocations is of great significance to the hydrocarbon-related reactions catalyzed by acid zeolites.

Back to the initial methanol conversion over the acid zeolite, based on the spectroscopic evidence, the evolution of surface species during the methanol conversion over HZSM-5 under the temperature increase condition is depicted in Scheme 2. At the temperature lower than 473 K, BAS behaves as the catalytic center for methanol adsorption and dehydration, and the generated DME can be further stabilized either in forms of end-on and side-on types. Increasing the temperature to higher than 473 K, the CH₃-Zeo supramolecular system forms and succeeds BAS as the new and efficient catalytic center for the activation and methylation of the approaching C1 reactant molecules. Based on the result of ssNMR observations and AIMD simulations in this work, the CH₃-Zeo supramolecular system has been confirmed as the real catalytic center of crucial importance, via which C1 reactant molecules can be progressively activated and have access to the initiation of the MTH reaction.

In conclusion, *in situ* ssNMR spectroscopy reveals the dynamic progressive activation of C1 reactant molecules evoked by the special catalysis from the CH₃-Zeo supramolecular system with the temperature increase. By *operando* simulations, the C–O bond linking the organic methyl group and inorganic zeolite frameworks transforms from covalent to ionic, during which the CH₃-Zeo supramolecular system gains more electrophilic/nucleophilic properties and an improved ionicity, flexibility, and mobility for attacking the approaching C1 reactants, which is responsible for the C1 reactant molecules activation and transformation to realize the first C–C bond coupling. The ionicity and covalent nature of the C–O bond between surface organic species and the zeolite are of universal significance for zeolite acid catalysis, linking the critical intermediates from the covalent role to carbocation chemistry. Therefore, this work consolidates the SMS-

mediated methanol/DME conversion mechanism pathway, and more importantly, the dynamic progressive changes of the CH₃-Zeolite supramolecular system and its catalysis for DME activation remind us of the dynamically variable properties of the catalytic reaction center and catalytic behaviors under the real reaction conditions in zeolite-catalyzed processes.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscentsci.1c00005>.

Characterization of the materials, experimental methods, GC-MS, DRIFTS, and NMR data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are thankful for the financial support from the National Natural Science Foundation of China (Nos. 21902153, 21991090, 21991092, 21972142, 22022202, 22032005, 22002174, 91745109), the Liaoning Revitalization Talents Program (XLYC1807227, XLYC1808014), the Key Research Program of Frontier Sciences, Chinese Academy of Sciences (QYZDYSSW-JSC024, QYZDB-SSW-SLH026), and the International Partnership Program of Chinese Academy of Sciences (121421KYSB20180007).

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