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# A route to form initial hydrocarbon pool species in methanol conversion to olefins over zeolites



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## ABSTRACT

The formation mechanism of the original C–C bond in methanol conversion to hydrocarbons over zeolite catalysts remains a grand challenge, although many researchers have done a lot of work and made significant progress. Here, a convincing route for formation of initial hydrocarbon pool (HCP) species involving original C–C bonds from dimethyl ether (DME) and/or methanol is illustrated by combining coincident experimental and theoretically calculated results. Elaborate experimental results gave strong evidence for predominant direct mechanism in the initial methanol-to-olefins process catalyzed by SAPO-34. A critical intermediate of the methoxymethyl cation was detected and theoretically verified through the reaction of the methoxy group and DME. This intermediate species subsequently reacted with DME or methanol to produce C–C bond-containing compounds 1,2-dimethoxyethane or 2-methoxyethanol. Further formation of oxonium cations led to generation of ethers or alcohols, and further to propene as the primary alkene product that induced the occurrence of the HCP mechanism.

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## 1. Introduction

Methanol is the most important platform compound and energy carrier for conversion of carbon resources such as coal, natural gas, and biomass to fuels and commodity chemicals [1,2]. The principal issue in methanol conversion to hydrocarbons, such as olefins/propene (MTO/MTP), aromatics (MTA), and gasoline (MTG), on solid acid zeolites [1,2] is control of product selectivity. This needs a clear and deep understanding of the catalytic mechanism, particularly of the transformation pathway of C–O bonds to C–C bonds. Although more than 20 direct mechanisms, including oxonium ylide, carbene, carbocation, and methane-formaldehyde mechanisms, have been proposed [2–5], the computed energy barriers are unrealistically high and the proposed intermediates are remarkably unstable [6,7]. Therefore, the hydrocarbon pool (HCP) mechanism has been considered to govern the methanol-tohydrocarbon conversion process because of its reasonable interpretation of the induction period at the early stage [8–19]. Thus, most experimental and theoretical researchers focus on the identity of hydrocarbon pool species and the illustration of their roles, and significant progress has been made, proposing olefinbased and aromatic-based cycles for formation of olefins [17–24].

However, the HCP mechanism did not account for the origin of initial HCP species involving the formation of the first C-C bond. Thus, the organic residual in the calcined zeolite catalyst was assumed to be the initial HCP species [25-28]. Regardless of this, the <sup>13</sup>C MAS NMR and IR spectroscopy results for the conversion of methoxy species over acidic zeolites support the existence of a direct mechanism, although no direct evidence was provided [29–31]. In addition, it was found that propene could be formed from methoxy groups and dimethyl ether (DME), although no evidence was obtained in this case, either [32], and carbene species existed in the methylation of ethene over HZSM-5 [33]. This inconsistency shows that the most active and controversial debate in the last forty years on the formation of the first C-C bond in methanol conversion is still going on. The origin of the HCP species remains a grand challenge due to its extreme complexity and the up-to-date limited characterization techniques. Thus, attempts are made here to show a convincing route for forming the original hydrocarbon pool species at the initial MTO reaction catalyzed by SAPO-34. The direct mechanism predominates the initial MTO process via the formation of CH<sub>3</sub>OCH<sup>+</sup><sub>2</sub> intermediate species and propene is the first alkene product that induces the HCP mechanism.



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## 2. Methods

#### 2.1. Experimental

SAPO-34 with a Si/Al ratio of 0.15 was synthesized with triethylamine as a template. The as-synthesized sample was calcined in air for 5 and 10 h to obtain non-fully-calcined SAPO-34 (NFC-SAPO-34) and fully calcined SAPO-34 (FC-SAPO-34; acid amount: 0.7 mmol/g).

The MTO catalytic properties of these two samples in the induction period were tested in a fixed-bed pulse reactor. Typically, 100 mg of catalyst was loaded and pretreated at 550 °C for 3 h before evaluation. The products were analyzed by a Shimadzu gas chromatograph (GC-2014C) or a Shimadzu gas chromatograph-mass spectrometer (GC-MS QP 2010), both of which were equipped with a HP-PLOT/Q column (30 m × 0.32 mm × 20  $\mu$ m). The IR spectra of the samples were measured on a Bruker TENSOR 27 FT-IR spectrometer equipped with a MCT detector. Before the spectra were recorded, the self-supported SAPO-34 wafer (30 mg) was treated at 500 °C and 0.1 Pa for 2 h.

The procedures for preparing methoxy groups are as follows: the pretreated SAPO-34 first adsorbed methanol at 30 or 50 °C until it was saturated. Then the physically adsorbed methanol was flushed with Ar or pumped out. Finally, the temperature was ramped to 300 °C at a rate of 5 °C/min under flushing (in pulse experiments) or pumping (for IR spectroscopy) conditions.

#### 2.2. Density functional theory calculation methods

Spin-polarized DFT calculations for periodic HSAPO-34 catalysts were carried out with the Vienna ab initio simulation package (VASP) [34,35] using the projector-augmented wave (PAW) method [36,37] and the generalized gradient approximation with the Perdew–Wang exchange-correlation function (GGA-PBE) [38]. Frequency calculations were carried out to verify that the obtained stationary points are minimum structures with real frequencies alone or transition states with only one imaginary frequency along the reaction coordinates. The vibrational frequencies and normal modes were calculated by diagonalization of the mass-weighted force constant matrix, which was obtained using the method of finite differences of force, as implemented in VASP. The ions are displaced in the ± directions of each Cartesian coordinate by 0.02 Å.

The zero-point-energy (ZPE) corrections were calculated using statistical mechanics based on the Boltzmann distribution. The enthalpy, entropy, and Gibbs free energy were derived from the partition functions. Activation energy is attained with the ZPE correction. The partition functions were calculated in the temperature range of 250–400 °C, which was selected on the basis of the experimental conditions. The rate constant *k* obtained using transition-state theory (TST) is defined as follows [39,40]:

$$k = \frac{k_{\rm B}T}{h} e^{-\Delta G_0^{\neq}/RT} = \frac{k_{\rm B}T}{h} e^{\Delta S_0^{\neq}/R} e^{-\Delta H_0^{\neq}/RT},$$

where  $k_{\rm B}$  is Boltzmann's constant, h is Planck's constant, and  $\Delta G_0^{\neq}$ ,  $\Delta H_0^{\neq}$ , and  $\Delta S_0^{\neq}$  are the changes of standard molar Gibbs free energy, enthalpy, and entropy between the transition state (TS) and the initiation state (reactant, IS), respectively.

All the reaction energy barriers over the SAPO-34 were calculated by the nudged elastic band (NEB) method [41] with eight equally spaced images along the reaction pathway. The adsorption energy were calculated with the equation  $E_{ads} = E_{(molecule@HSAPO-34)} - [E_{(molecule)} + E_{(HSAPO-34)}]$ , where  $E_{(molecule@HSAPO-34)}$ ,  $E_{(molecule)}$ , and  $E_{(HSAPO-34)}$  are the total energies of the HSAPO-34 unit cell with adsorbate (methanol) in the pores, free adsorbate (methanol) molecule, and HSAPO-34 unit cell, respectively.

The unit cell of HSAPO-34 (a = b = c = 9.421 Å,  $\alpha = \beta = \gamma = 94.2^{\circ}$ ) was derived from the Silicalite-CHA structure (all Si atoms are symmetrically equivalent), in which all Si atoms are alternatively replaced by P and Al atoms, and one P atom is replaced by one Si atom to generate one Brønsted acid site per cage [42]. This corresponds to a Si/Al ratio of 0.17 in HSAPO-34. In the DFT calculations, the  $p(1 \times 1 \times 1)$  cell was used for C1 reactions such as methoxy and DME formation, while the  $p(2 \times 1 \times 1)$  cell was used for C2 reactions, e.g., C1-C1 coupling, in order to avoid the interaction between molecules, as shown in the Supplementary Material (Fig. S1 in the Supplementary Material). The proton is located at the site of O(884), which refers to the part of 8-, 8-, and 4-membered rings (MR) in the framework. The other sites of O(864) and O(844) are also involved in the reaction of C1-C1 coupling. The calculations show that the relative energy differences of protons bonded to the four nonequivalent O sites are less than 4.0 kI/mol. This indicates that the proton can shift in these four sites. Nevertheless, the acidic strength based on the adsorption energies of NH<sub>3</sub> increases in the order H(864) (-123.5 kJ/mol) > H(884)(-117.7 kJ/mol) > H(844) (-100.3 kJ/mol). In the simulation of all the reactions, all atoms in the cell are allowed to relax with the lattice constants fixed.

#### 3. Results and discussion

#### 3.1. Evidence for the existence of a direct reaction mechanism

In the methanol conversion process, DME is readily produced over the acidic zeolite catalysts [2,43,44]. This is also confirmed by the computational result that the energy barrier for DME formation from two methanol molecules through the interaction with acid sites is not high (95.5 kJ/mol), and the rate constant is  $1.3 \times 10^4$  s<sup>-1</sup> at 400 °C (R6, Fig. S2 in the Supplementary Material). Therefore, we initially compared the reaction behavior of methanol and DME on a fully calcined SAPO-34 (FC-SAPO-34) catalyst (Fig. S3 in the Supplementary Material) using a pulse reactor. The conversion of methanol was only 0.7% in the first injection, while it quickly increased to 44.9% at the fifth pulse (Fig. 1a). This reaction pattern is intimately associated with the accumulation of HCP species, mainly methyl-substituted benzene and naphthalene (Figs. S4 and S5 in the Supplementary Material) in the catalyst. In contrast, when DME was injected, the conversion readily reached 6.8% at the first pulse, but it increased only moderately to 14.5% at the sixth pulse. One might think that this is due to the ready formation of the HCP species from DME at the initial time, but a slow increase in the amount during the reaction process. However, even when the HCP species was first generated in the catalyst by introducing methanol, a much lower conversion was still obtained for DME (Fig. 1a). After five successive injections of methanol, its conversion reached only 23.0%. This suggests that (1) a direct mechanism probably predominates in the conversion of DME in the initial process irrespective of the existence of the HCP mechanism, and/or that (2) DME is converted via another type of HCP mechanism that is largely different from that occurring in the conversion of methanol-namely, the transformation of methanol and DME needs different types of HCP species.

To clarify this point, DME and methanol were pulsed to nonfully-calcined SAPO-34 (NFC-SAPO-34), in which a certain amount of template residue was present (Fig. S3 in the Supplementary Material). It was found that the conversion of methanol reached 4.9% in the first injection, as high as seven times that obtained on the FC-SAPO-34. This indicates that the template residue indeed can act as HCP species. However, a different result was obtained for DME; its conversion in the first pulse was about 7.5%, which is very close to that (6.8%) attained on the FC-SAPO-34. This shows that



Fig. 1. Experimental evidence for the direct mechanism. (a) Methanol and DME conversions obtained at different pulses in the MTO process catalyzed by FC-SAPO-34 and DME conversions attained after successively injecting various times of methanol; e.g., the DME conversions at pulses 3, 4, 5, and 6 refer to the values obtained by pulsing DME after successive injection of 2, 3, 4, and 5 times of methanol. 100 mg of FC-SAPO-34 was first pretreated at 550 °C for 2 h in air before the reaction, which was carried out at 400 °C with Ar as carrier gas, the flow rate of which was 300 mL/min. Every time 0.07 mmol of methanol or 0.035 mmol of DMF was injected. The methanol and DME conversions were calculated by considering both of them in the effluents as unreacted substrates. (b) Reaction results of <sup>13</sup>Cmethanol over NFC-SAPO-34, which was activated at 550 °C under Ar before 0.005 mmol of <sup>13</sup>C-methanol was pulsed. (c) Reaction results of <sup>13</sup>C-methanol over FC-SAPO-34, to which 0.02 mmol of <sup>13</sup>C-methanol was pulsed. (d) Reaction results of <sup>13</sup>C methoxy group (<sup>13</sup>CH<sub>3</sub>O) and 5 µL of H<sub>2</sub>O. The green-bar plots and the red-bar plots in (b-d) are the mass spectra of produced ethene and propene, respectively. The labeled numbers correspond to the mass/charge ratio (m/z). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the template residue has only a marginal effect on the conversion of DME, suggesting that the conversion of DME follows a direct mechanism, instead of the HCP mechanism, in the initial process.

To further confirm this inference, highly purified <sup>13</sup>C methanol was pulsed to the FC-SAPO-34 and NFC-SAPO-34, and the pulse dosages were adjusted to ensure that the amounts of produced olefins were comparable. For the NFC-SAPO-34, a methanol conversion of 47.3% was attained with the formation of <sup>12</sup>C and <sup>13</sup>C olefins (Fig. 1b and Fig. S6 in the Supplementary Material). This indicates that the carbon (C) atoms were transferred from hydrocarbon pool species (template residue) to the product. Over the FC-SAPO-34, however, only <sup>13</sup>C olefins were produced regardless of the relatively low methanol conversion (1.6%) (Fig. 1c). In order to exclude the possible influence of impurities in reagents such as <sup>13</sup>C ethanol. <sup>13</sup>C methanol was prepared in situ by reacting a <sup>13</sup>C methoxy group with H<sub>2</sub>O according to the reported protocol [16,43,44]. As a consequence, a similar product distribution (<sup>13</sup>C olefins only) was observed (Fig. 1d), further verifying the direct mechanism.

## 3.2. Formation of methoxy groups

Upon methanol adsorption on FC-SAPO-34, methoxy groups are readily formed as the first intermediate species and they are reactive for a number of probe molecules such as water, methanol, and aniline [2,43,44]. The asymmetric C–H stretching vibration band of chemisorbed methanol gradually shifted from 2958 to 2977 cm<sup>-1</sup> with the increase of temperature from 50 to 300 °C, showing the formation of methoxy species (Fig. 2a and Fig. S7 in the Supplementary Material) [45,46]. However, the chemisorbed DME cannot be transformed into the methoxy groups; most of the DME are desorbed upon evacuation and increase of temperature due to the lower adsorption energy of DME (33.8 kJ/mol) than of methanol



**Fig. 2.** IR spectra for the formation of methoxy groups from methanol and DME. (a) 200 Pa of methanol or DME was introduced into the IR cell equipped with 30 mg of FC-SAPO-34 self-supported wafer at 50 °C. The spectra were recorded from 50 to 300 °C with a temperature ramp rate of 5 °C/min. (b) DME reacted at 300 °C for 30 s at different pressures.

(67.5 kJ/mol; see Fig. 2a). The methoxy group could only be detected when DME was reacted for more than 30 s at 300 °C and under higher DME pressure (Fig. 2b). Computational results show that the formation of methoxy groups is realized through the decomposition of a trimethyl oxonium (TMO) cation formed from two DME molecules (R1 and R2, Fig. S2 in the Supplementary Material). The energy barriers and rate constants for the formation and decomposition of TMO cations are 101.3 kJ/mol and  $1.3 \times 10^4 \text{ s}^{-1}$  (400 °C) and 59.8 kJ/mol and  $1.9 \times 10^{10} \text{ s}^{-1}$  (400 °C), respectively. In contrast, a remarkably high energy barrier (198.8 kJ/mol) and a very low rate constant  $(8.0 \times 10^{-2} \text{ s}^{-1})$  were obtained for the formation of methoxy groups from a single DME molecule (R5 in Fig. S2 of the Supplementary Material), indicating that it is difficult for this to occur. These calculated results are in good agreement with the dependence of methoxy group formation on the DME pressure (Fig. 2b). This is also supported by the results calculated by Blaszkowski and Lesthaeghe with 1T and 5T cluster models, although much higher energy barriers (141 and 131.3 kJ/ mol) were obtained for generation of TMO species [4,6], which is the rate-determining step for formation of methoxy groups from two DME molecules over zeolite acidic sites. A higher energy barrier (59.8 kJ/mol) obtained by the periodic method for the decomposition of TMO to methoxy groups and DME than those calculated with 1T (27 kJ/mol) and 5T (47.7 kJ/mol) clusters is due to the stabilization of the TMO species by the HSAPO-34 framework.

#### 3.3. Formation of original C-C bond

The much higher reactivity of DME than of methanol in the original MTO process (Fig. 1a) and the conversion of DME via the direct mechanism suggest that methoxy groups and DME may react to form the intermediates for generating hydrocarbons. Computations show that the energy barrier and rate constant of this reaction are 135.1 kJ/mol and  $4.2 \times 10^4 \text{ s}^{-1}$  (400 °C) with the formation of methoxymethyl cations (CH<sub>3</sub>OCH<sub>2</sub><sup>+</sup>) stabilized inside the SAPO-34 framework (Fig. 3a). The stabilization energy of CH<sub>3</sub>. OCH<sub>2</sub><sup>+</sup> species is about 276 kJ/mol (relative to CH<sub>3</sub><sup>+</sup>) [47], being similar to that of tertiary carbocations as a result of lone pair-electron donation from the oxygen to carbon. The distance between H atoms in CH<sub>3</sub>OCH<sub>2</sub><sup>+</sup> and O atoms in the framework is 1.936 Å, indicative of interaction between the zeolite framework and CH<sub>3</sub>OCH<sub>2</sub><sup>+</sup>.

Four types of active carbocations, viz., 1,3-dimethylcyclopentenyl, pentamethylcyclopentenyl, pentamethylbenzenium, and heptamethylbenzenium cations, have been observed in the methanol conversion process over zeolites by Haw and Liu with <sup>13</sup>C MAS NMR spectroscopy [16,23,24,48,49]. This suggests that it is possible to detect active CH<sub>3</sub>OCH<sub>2</sub><sup>+</sup> species since they can be stabilized in the CHA cage of SAPO-34. Indeed, the formation of CH<sub>3</sub>OCH<sub>2</sub><sup>+</sup> intermediate species was experimentally substantiated by IR spectroscopy. When 6.5 Pa of DME was introduced into the IR cell equipped with CH<sub>3</sub>O-formed FC-SAPO-34 self-supported wafers at 30 °C, an intense band at 2964 cm<sup>-1</sup>, attributed to asymmetric C-H stretching vibration in the CH<sub>3</sub> group of DME [50], was observed (Fig. 3b). After the temperature was increased to 180 °C, a new band appeared at 2960  $cm^{-1}$ , while the 2964  $cm^{-1}$ band decreased in intensity. This newly formed 2960 cm<sup>-1</sup> band is characteristic of asymmetric C-H stretching vibration of the  $CH_2$  group in  $CH_3OCH_2OZ$  (Z = zeolite; Fig. S8 in the Supplementary Material) [50]. The absence of this new band in the IR spectrum of the fresh FC-SAPO-34 wafer purged with DME under the same conditions confirms that the CH<sub>3</sub>OCH<sup>+</sup><sub>2</sub> species indeed comes from the reaction of methoxy groups and DME.

The CH<sub>3</sub>OCH<sup>+</sup><sub>2</sub> species further couples with another DME or methanol molecule to give 1,2-dimethoxyethane or 2-methoxyethanol, forming the first C–C bond (Fig. 3a and Fig. S10 in the Supplementary Material). The energy barriers and rate constants of



**Fig. 3.** (a) Route for the formation of the first C–C bond. (b) IR spectra for the formation of CH<sub>3</sub>OCH<sup>2</sup><sub>2</sub> by the reaction of methoxy groups and DME. The blue numbers represent the energy barriers (kJ/mol), while the orange and green numbers in parentheses are the rate constants (s<sup>-1</sup>) at 250 and 400 °C, respectively. 6.5 Pa of DME was introduced into an IR cell equipped with 30 mg of CH<sub>3</sub>O-formed FC-SAPO-34 self-supported wafer at 30 °C. The spectra were recorded from 30 to 180 °C with a temperature ramp rate of 5 °C/min. The spectra recorded at 30 and 180 °C were denoted as CH<sub>3</sub>O + DME (30 °C) and CH<sub>3</sub>O + DME (180 °C), respectively. The spectra of DMM (30 °C) and DMM (180 °C) were obtained by introducing 6.5 Pa of dimethoxymethane into the IR cell equipped with 30 mg of the pretreated FC-SAPO-34 self-supported wafer at 30 °C C, and then increasing the temperature to 180 °C. The spectra of DME (30 °C) and DME (180 °C) were obtained according to the same procedures as those employed for measuring DMM (30 °C) and DMM (180 °C), except that DME was introduced. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

these two reactions are 94.6 kJ/mol and  $2.4 \times 10^5 \, \text{s}^{-1}$  and 102.3 kJ/mol and  $3.7 \times 10^5 \, \text{s}^{-1}$  (400 °C), respectively. To our knowledge, this is the most energetically favorable route reported for the formation of the first C–C bond.

## 3.4. Route for formation of initial olefins

1,2-Dimethoxyethane or 2-methoxyethanol was then methylated by methoxy groups to give 2-methoxyethyldimethyl, 2-hydroxyethyldimethyl, or 2-methoxyethylmethyl oxonium cations, which further decomposed into 2-methoxyethoxy or 2hydroxyethoxy species (Fig. 4 and Fig. S9 in the Supplementary Material). Because these two species have similar reaction processes, the formation of olefin products from 2-methoxyethoxy species will be, as an example, illustrated in the following. The 2methoxyethoxy species was first deprotonated to give methyl vinyl ether (Fig. 4b), which was methylated to generate methyl propenyl ether, resulting in growth of the carbon chain from one to two C-C bonds. This was followed by formation of dimethyl propenyl oxonium cations and subsequent decomposition into propenoxy species, which could easily transform into allyloxy species through spontaneous isomerization. The formation of propenoxy species



**Fig. 4.** Routes for formation of ethene (a) and propene (b). The blue numbers represent the energy barriers (kJ/mol), while the orange and green numbers in parentheses are the rate constants ( $s^{-1}$ ) at 250 and 400 °C, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

was supported by the finding that allyl alcohol promoted methanol conversion more strongly than ethanol and 2-propanol as a result of easier formation of propene (Fig. S10 in the Supplementary Material). The allyloxy species further reacted with DME to produce propene and CH<sub>3</sub>OCH<sup>+</sup><sub>2</sub>. The CH<sub>3</sub>OCH<sup>+</sup><sub>2</sub> species then coupled with DME molecules to maintain the reaction cycle and avoid the repeated generation of methane, while the propene quickly aromatized into the HCP species, and thus greatly accelerated the methanol conversion process (Fig. 5a and Fig. S11 in the Supplementary Material), soon causing the HCP mechanism to dominate the methanol conversion process.

The failure to detect 1,2-dimethoxyethane with GC–MS by adjusting reaction temperature, contact time, and DME amount seems difficult to understand. In fact, the small pore size  $(3.8 \times 3.8 \text{ Å})$  of HSAPO-34 would impose a steric effect on the diffusion of 1,2-dimethoxyethane. This makes its diffusion rate far lower than its rate of transformation to (2-methoxy) ethyl dimethyl oxonium cations (rate constant  $3.6 \times 10^5 \text{ s}^{-1}$  at 400 °C), which converts into (2-methoxy)ethoxyl groups and DME at an extremely high rate (rate constant  $2.7 \times 10^8 \text{ s}^{-1}$  at 400 °C). In addition, the rate of transformation of 1,2-dimethoxyethane is higher than its formation rate. Therefore, 1,2-dimethoxyethane is impossible to detect by GC–MS.

Fig. 4 and Fig. S9 (R3) in the Supplementary Material show that the energy barriers and the rate constants at 400 °C of all the elementary steps for the production of propene are lower than 135.1 kJ/mol and larger than  $4.2 \times 10^4 \text{ s}^{-1}$ , respectively. In contrast, in the pathway to ethene (Fig. 4a), the energy barrier to the

formation of methyl ethyl ether from 2-methoxyethoxy groups and DME molecules reached 163.1 kJ/mol with a rate constant of only  $5.4 \times 10^{1}$  s<sup>-1</sup> at 400 °C. This shows that the formation of ethene is far more difficult than that of propene. Indeed, the first pulse of methanol to FC-SAPO-34 at 400 °C gave a propene selectivity of 72.6%, 13.2 times the ethene selectivity (Table S1a in the Supplementary Material). This difference was more significant when DME was injected, as also observed by Yamazaki and co-workers [32], although the relative propene amount sharply decreased with increasing conversion for both DME and methanol (Table S1 in the Supplementary Material).

However, the selectivity of ethene was unexpectedly higher than that of propene when 1,2-dimethoxyethane reacted with methoxy groups formed in the FC-SAPO-34 (Fig. S12 in the Supplementary Material). This seems to contradict the computational results and the generation of more propene in the initial period. Actually, it does not. A very short contact time of 1,2-dimethoxyethane with the FC-SAPO-34 does not allow it to diffuse into the CHA cage, and consequently, its reaction mainly occurred on the external surface, giving ethene as the major olefin product. Fig. 5b shows that the propene/ethene ratio in the product exponentially increased from 0.05 to 0.22 with decreasing carrier gas flow rate from 300 to 7.1 mL/min (0.03 mmol of 1.2-dimethoxyethane was pulsed), indicating that only 1,2-dimethoxyethane molecules inside the CHA cages may preferentially transform into propene. This is confirmed by the result that a further increase in the propene amount (propene/ethene = 0.31) was achieved by pulsing 0.03 mmol of 1.2-dimethoxyethane and allowing it to



**Fig. 5.** (a) Methanol conversion obtained over FC-SAPO-34 at different pulses before and after injection of propene. At 250 °C, 0.07 mmol of methanol or propene was pulsed into a reactor filled with 100 mg FC-SAPO-34 at a carrier gas (Ar) flow rate of 300 mL min<sup>-1</sup>. (b) Effect of carrier gas flow rate on the propene/ethene ratio in the product obtained in the reaction of 1,2-dimethoxyethane and methoxy groups formed over FC-SAPO-34. 0.03 mmol of 1,2-dimethoxyethane was pulsed into a reactor filled with 100 mg of CH<sub>3</sub>O-formed FC-SAPO-34 at different carrier gas (Ar) flow rates. The effluent gases were analyzed by GC.

adsorb on the  $\text{CH}_3\text{O}\text{-}\text{formed}$  catalyst for 20 min at 50 °C before the reaction.

#### 3.5. Comparison with methane-formaldehyde mechanism

A similar reaction route proposed for the formation of the first C-C bond is the methane-formaldehyde mechanism [3], which is supported by the results of Kubelková and co-workers that DME, methane, and formaldehyde were first formed before generation of aromatics from 2 Pa of methanol on HZSM-5 at 400 °C [5]. According to this mechanism, the CH<sub>3</sub> group of a methanol molecule approaches a surface methoxy group and generates a CH<sub>4</sub> molecule through the hydride transfer reaction, while the H of the OH group in methanol simultaneously transfers to a zeolite surface and gives a formaldehyde molecule. This is followed by the formation of ethanol through the decomposition of methane into  $H^+$  and  $CH_3^-$ , which then transfer to the basic oxygen atom of ZO<sup>-</sup> and the carbon atom of formaldehyde, respectively. Blaszkowski and co-workers reported that formation of CH<sub>4</sub> from methanol and surface methoxy groups (first step) has an energy barrier of 171 kJ/mol (Table 1) [4]. An increase in the cluster model from 1T to 3T decreased the energy barrier to 148.2 kJ/mol. However, the 3T cluster calculation shows that the energy barrier for formation of ethanol (second step) is as high as 185.0 kJ/mol [3]. Similar results were obtained by Lesthaeghe and coworkers with a 5T cluster model [6], showing that it is very difficult for the second step to occur.

In order to reasonably compare our proposed route (designated as a methoxymethyl cation-based mechanism) with the methaneformaldehyde mechanism, the energy barriers and reaction rates of

#### Table 1

Computational results for methane-formaldehyde and methoxymethyl cation-based mechanisms.

Model	1st step		2nd step	
	$E_1 (kJ/mol)^a$	$k_1 (s^{-1})^{b}$	$E_2 (kJ/mol)^a$	$k_2 (s^{-1})^{b}$
Methane–formaldehyde mechanism				
1T [4]	171			
3T [3]	148.2		185.0	
5T [6] <sup>c</sup>	147.1	$4.0 imes10^{0}$	183.1	$1.7 imes 10^{-6}$
Periodic <sup>d</sup>	149.6	$2.1\times10^3$	124.5	$7.4  imes 10^{-1}$
Methoxymethyl cation mechanism				
Periodic <sup>d</sup>	135.1	$1.1\times10^4$	94.6	$\textbf{6.8}\times10^4$

<sup>a</sup> Energy barriers.

<sup>b</sup> Rate constants.

<sup>c</sup> Rate constants were calculated at 447 °C.

<sup>d</sup> Rate constants were calculated at 350 °C.

two steps involved in the methane-formaldehyde mechanism were also calculated by the same periodic method, and the results are listed in Table 1. The calculated energy barrier (149.6 kJ/mol) of the first step is similar to that obtained with the cluster model, but that of the second step significantly decreases to 124.5 kJ/mol due to the stabilization of the transition state by the SAPO-34 framework. Nevertheless, the two steps involved in the methoxymethyl cation-based mechanism not only are energetically more favorable, but also proceed much faster. The formation of methoxymethyl cations from methoxy groups and DME (first step) has an energy barrier lower than that of the formation of methane and formaldehyde by about 14.5 kJ/mol, and the rate constant also increases about four times. This difference is more significant for the second step. The energy barrier for generation of 1,2-dimethoxyethane from methoxymethyl cations and DME (second step) is only 94.6 kJ/mol, lower than that for formation of ethanol from CH<sub>4</sub> and HCHO by about 30 kJ/mol. In particular, the rate constant increases about 10<sup>5</sup> times. This shows that it is much more possible for the methoxymethyl cation-based mechanism to occur than the methane-formaldehyde mechanism.

#### 4. Conclusions

The reaction results of methanol and dimethyl ether (DME) over HSAPO-34 and the isotope labeling experiment on the formation of olefins from methanol evidenced the existence of a direct mechanism in the process of conversion of methanol to olefins. It was identified that the reaction of methoxy groups on SAPO-34 and DME gave methoxymethyl cations (CH<sub>3</sub>OCH<sup>+</sup><sub>2</sub>) that subsequently coupled with DME or methanol to produce C-C bond-containing compounds of 1,2-dimethoxyethane or 2-methoxyethanol. This is followed by the formation of oxonium cations and ethers, which led to generation of propene as the primary product that induced the occurrence of the HCP mechanism. This finding provides new fundamental insights into the mechanism in the formation of initial C-C bonds and original hydrocarbon pool species, and would significantly promote study of the mechanism of methanol to hydrocarbons that facilitates the design of highly selective methanol conversion catalysts.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.05.015.

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