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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.

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-to-hydrocarbon 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 olefin-based 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 ^{13}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 $CH_3OCH_2^+$ 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 μm). 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]:

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

where k_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 $E_{ads} = E_{(molecule@HSAPO\text{-}34)} - [E_{(molecule)} + E_{(HSAPO\text{-}34)}]$, where $E_{(molecule@HSAPO\text{-}34)}$, $E_{(molecule)}$, and $E_{(HSAPO\text{-}34)}$ 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, $\alpha = \beta = \gamma = 94.2°$) 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 kJ/mol. This indicates that the proton can shift in these four sites. Nevertheless, the acidic strength based on the adsorption energies of NH_3 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 1.3×10^4 s^{-1} 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 non-fully-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