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Short communication

Methane formation mechanism in methanol to hydrocarbon process: A periodic density functional theory study

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ABSTRACT

Methane is an important product in methanol to hydrocarbon (MTH) process and its formation mechanism over HZSM-5 was investigated by applying periodic density functional theory. The results show that the carbocations of $C_7H_9^+$–$C_{12}H_{19}^+$ are important intermediates in MTH process and methane is formed via one intramolecular hydrogen transfer reaction of these intermediates from ring carbon to the carbon of methyl group. The activation energies for methane formation increase from 101 to 174 kJ/mol with increasing methyl groups in protonated methylbenzenes. The data indicate that methane has similar formation mechanism as ethene and propene, i.e. via hydrocarbon pool mechanism.

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1. Introduction

As worldwide petroleum reserves are reducing, more and more attentions are devoted to finding alternative ways of producing hydrocarbon products. Methanol has been proposed as a platform for hydrocarbon transformations, as it can be produced from coal, natural gas, biomass and commodity chemicals via syngas (CO, H_2) [1–4]. The conversion of methanol over acid zeolite catalysts to hydrocarbons including light olefins/propene (MTO/MTP), aromatics (MTA) and gasoline (MTG) has been investigated extensively. However, the principal issue of this process is to control product selectivity, which needs a clear and deep understanding of the formation mechanism for each product. At present, the hydrocarbon pool (HCP) mechanism is widely accepted because of its reasonable interpretation of the induction period at the early stage and applicability to explain major products formation [1–8]. In this mechanism, the organic species trapped in the zeolite pores undergo repeated methylation followed by olefin elimination. Two cycles have been identified, distinguished by the active species being either methylbenzenes or alkene [9], and the formation of initial HCP species involving the formation of the first C–C bond is still a hot topic of HCP mechanism investigation [1–4].

Among gaseous effluents in MTH process, ethene and propene are two most important olefins in chemical industry, and their formation mechanism based on HCP mechanism has been investigated extensively [10,11]. Lesthaeghe et al. provided a full theoretical cycle for both ethene and propene formation by the alkene methylation/cracking cycle over HZSM-5 based on the ONIOM approach [10]. The low energy barriers with 60–80 kJ/mol for alkene methylation and cracking into C_3^+ products indicated the plausibility of this catalytic process. In experimental reports, the energy barriers for ethene formation by cracking of higher alkenes were found to be 90–120 kJ/mol [10]. However, the investigations on other gas phase products (i.e. methane, ethane) are rare. Therefore, it is significant to understand methane formation mechanism, such knowledge could provide possibilities to design a catalyst with improved selectivities towards alkenes, while avoiding alkanes in MTH process.

To our best knowledge, no parallel investigation related to methane formation has been reported. In this paper, the possible routes for methane formation over HZSM-5 during MTH process are proposed and calculated by periodic density functional theory (DFT), and the energy barriers are also obtained.

2. Computational methods

The self-consistent density functional calculations were performed using the Vienna Ab Initio Simulation Package (VASP) [12–14]. The projected augmented wave (PAW) method was used to describe electron–ion interactions [15,16]. The generalized gradient approximation PBE functional was employed to describe the exchange and correlation energies [17]. Periodic boundary conditions were applied in all calculations which employed a real-space grid spacing of 0.10 Å except the unit

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cell optimization. In the adsorption calculations, the super cell was identical to the unit cell, and Brillouin zone sampling was restricted to the Γ-point.

The lattice constants of silicalite-1, the purely siliceous version of ZSM-5, were determined using the same approach as Svelle et al. [18]. Geometry optimizations were carried out at a plane wave basis set cutoff energy of 400 eV. The high-temperature structure of ZSM-5 that has an orthorhombic unit cell with lattice constants $a = 20.08$ Å, $b = 19.89$ Å and $c = 13.37$ Å were used [19]. All atomic positions were relaxed, using a force threshold of 0.01 eV/Å and a real-space grid spacing of 0.10 Å. The optimized parameters with $a = 20.32$ Å, $b = 20.16$ Å and $c = 13.46$ Å were used in all subsequent calculations.

Transition state structures were located using the improved-dimer method and were considered converged when forces on all atoms were smaller than 0.03 eV/Å [20]. The frequency calculations employed a partial vibrational Hessian approach, including the atoms in molecules, as well as the H atom of the acid site. This subset of atoms has been shown to be sufficient for calculating thermodynamic quantities of alkanes in HZSM-22 [21]. The numerical differentiation of the forces employed a displacement step of 0.015 Å and an energy convergence threshold of 10^{-6} eV/electron. Each of the aforementioned atoms was displaced $+\delta$ and $-\delta$ from their equilibrium position along each of the three Cartesian coordinates. The zero-point-energy (ZPE) corrections were calculated using statistical mechanics based on the Boltzmann distribution, and the activation energy was obtained with the ZPE correction.

DFT methods are unable to properly describe the van der Waals dispersive contribution, which is critical for the reactions in zeolites [18,22]. Therefore, the total energy of a system (E_{DFT-D}) was obtained by adding a semi empirical dispersion contribution (E_{disp}) to the self-consistent Kohn–Sham energy [23,24]:

$$E_{DFT-D} = E_{DFT} + E_{disp}$$

E_{disp} is obtained with dftd3 program which is available in the authors' website [25].

DFT energy calculations for gas-phase molecules were carried out using cubic boxes with edge lengths of 20 Å to minimize interactions with the periodic images [26]. A force threshold of 0.01 eV/Å was used in these calculations.

To create an acidic site in HZSM-5, one of the 96 Si atoms in the unit cell was replaced by an Al atom in the T12 site [27] and the resulting negative charge was compensated by a proton bonded to one of the neighboring framework oxygen atoms. Specifically the Al12–O (H)–Si (3) site was chosen, because of its location in the intersection of straight and sinusoidal channels which provided maximum available space and creates the most accessible active site to accommodate various guest molecules [26,27]. Our calculations also confirmed the relative stability of this acid site. The established model of HZSM-5 is shown in Fig. S1, which is used in the following investigation.

3. Results and discussion

Arene methylation with methanol reactions have been investigated extensively via both concerted and stepwise pathways [3,28,29]. The stepwise pathway involves a surface bound methoxy group as an intermediate, whereas no such intermediate is involved in the concerted pathway. However, no definitive conclusion regarding the prevailing pathway is warranted. In situ spectroscopic techniques such as FTIR and NMR demonstrate the existence of surface-bound methoxy group, and the fundamental viability of stepwise mechanism has been verified. Brogaard et al. [3] reported the stepwise pathway to prevail at typical MTH reaction temperature, due to higher entropy loss in the concerted pathway than the stepwise pathway. Therefore, the stepwise pathway is primarily considered in this investigation.

In the stepwise pathway, surface-bound methoxy group is an important intermediate, which is readily methylated with arene [28]. The formation of surface-methoxy group originates from the adsorption of methanol in acid site, and the calculated energy barrier is 146 kJ/mol (Fig. S3), which is discussed in detail in Supplementary materials. Take benzene methylation with methanol for example, once the methoxy group has been formed, benzene molecule firstly adsorbed in the vicinity of methoxy group and is pushed to the center of the 10-membered ring owing to the confinement effect of zeolite wall as displayed in Fig. 1(a). The methyl group is almost planar, and parallel with benzene molecule in the transition state geometry as described in Fig. 1(b). The length of the C–C bond being formed is 2.15 Å, while the length of the C–O bond being broken is also 2.15 Å. Once the energy barrier is surmounted, the methyl group (denoted as the attacking methyl group) continues attacking the benzene molecule, eventually causing the formation of protonated toluene as depicted in Fig. 1(c). Because the attacking methyl group is between the benzene molecule and the acid site in the transition state structure, the carbocation with the attacking methyl group in the vicinity of acid site of zeolite is readily formed, while the independent proton is away from acid site. For the same reason, protonated C_8 (typical para-xylene), C_9 (1, 2, 3-trimethylbenzene), C_{10} (1, 2, 4, 5-tetramethylbenzene), C_{11} and C_{12} also could be existing in the zeolite pore in MTH process with the corresponding attacking methyl group in the vicinity of acid site (Fig. 2). In these geometries, all positive center positions of the carbocations are closed to the negative center of acid site caused by electrostatic effect. The energy barrier diagrams of forming these carbocations are presented in Fig. S10, and the activation energies decrease as the number of methyl groups in methylbenzenes increase.

To regenerate the acid site, the charged species should back-donate a proton to zeolite framework. Thus the rotation of the intermediates takes place and obtains a proper geometry for proton back-donation (Fig. 3). Jobic et al. [30] reported that the activation energy barrier for the rotation around the molecular axis C_2 of benzene was between 25 and 105 kJ/mol, with an average of 60 kJ/mol, inside a 8 Å silicalite. Vos et al. [31] estimated the reorientation energy barrier of protonated

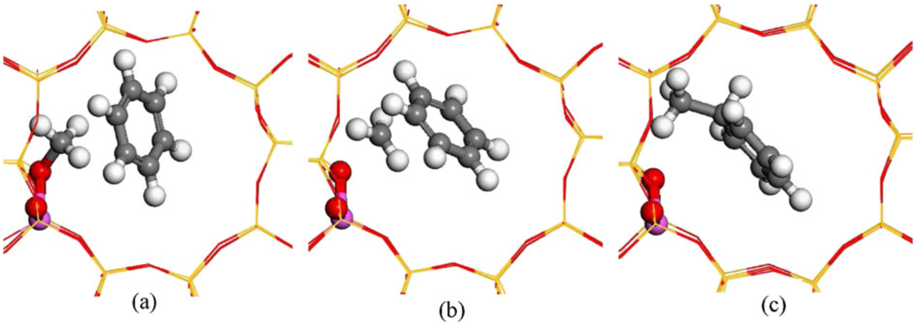

Fig. 1. The geometries involved in benzene methylation with methoxy group. (a) Benzene adsorbed in the vicinity of methoxy group; (b) transition state; (c) the intermediate in benzene methylation (yellow, silicon; red, oxygen; purple, aluminum; white, hydrogen; gray, carbon; similarly hereinafter).

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