Conversion of Methyl Mercaptan to Hydrocarbons over H-ZSM-5 Zeolite: DFT/BOMD Study

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ABSTRACT: Methyl mercaptan— a harmful impurity in natural gas— may be selectively converted into H2S and hydrocarbons [methyl mercaptan to hydrocarbon (M2TH) process], using zeolite catalysts. When M2TH is compared with the well-known MTH (methanol to hydrocarbons) process, significant differences emerge, essentially regarding the formation and distribution of products. Density functional theory (DFT) and Born–Oppenheimer molecular dynamics (BOMD) were employed to reveal possible origins for the experimentally observed differences. We established a close similarity between DFT intrinsic (electronic) reaction profiles in the stepwise mechanism of methanol and mercaptan dehydration, although no variance in reactivity was revealed. BOMD simulations at the experimental temperature of 823 K reveal rapid hydrogen abstraction from the methyl group in mercaptan, adsorbed in the zeolite cavity in the presence of the methoxy intermediate. The formation of •CH3SH radical is 10 times faster than that of •CH3OH at the same temperature. The varied reactivity of methanol and mercaptan in MTH and M2TH processes, respectively, can therefore first be attributed to very rapid hydrogen abstraction in mercaptan, which occurs in the zeolite cavity, following the formation of surface methoxy.

INTRODUCTION

Methyl mercaptan (CH3SH) is invariably an abundant impurity in natural gas. For environmental and industrial reasons, its concentration should be maintained below 5 ppmv; however, CH3SH is one of the most refractory compounds to resist the gas cleanup process. Commercial procedures used to remove mercaptan from gas usually require formulated solvents or include reactions that need additional reagents that often generate waste. We have recently shown that CH3SH can be selectively transformed into hydrocarbons and H2S over H-ZSM-5, H-Y, H-ferrierite, H-BEA, H-MOR, and H-SAPO-34.1,2 The zeolite/zeotypes with diverse topologies, for example, H-ZSM-5, H-ZSM-12, and H-MCM-22, have been found to be effective catalysts for the conversion of CH3SH to hydrocarbons.1,2 Among them, H-ZSM-5 was established as the most active and efficient catalyst.3 To compare M2TH and MTH, the conversion of CH3OH and CH3SH under equivalent conditions was investigated, using H-ZSM-5 zeolite as the catalyst.4 Although similarities exist between M2TH and MTH, significant differences were observed, essentially regarding the catalyst lifetime and the formation of products. In the M2TH process, C1−C3 alkanes (with >90% of CH4) and benzene, toluene, and xylene (BTX) aromatics are the main hydrocarbons formed. Only a very small amount of olefins can be identified among the products. Similarly, in the few reports/patents dedicated to the methyl mercaptan conversion over microporous acid catalysts,5−7 methane appears to be the main product obtained. In contrast, in the MTH process, products obtained are BTX aromatics and alkanes, but large amounts of C2−C4 olefins are also obtained.8 In the MTH process, the catalyst also endured for longer than it did in the M2TH process. Generally, in the MTH process, the formation of lower olefins is assisted by the so-called “dual-cycle hydrocarbon pool” (HP) mechanism.9−12 Accordingly, the aromatic hydrocarbons and olefins present inside the pores/cages of zeolites...
undergo successive methylation steps by methanol, thus eliminating further olefins (Scheme 1).3,12

A similar mechanism has been proposed to explain the formation of olefins, when other C1 functionalized molecules, such as methyl halides (CH3X, X = Cl, Br, I), were converted into hydrocarbons over zeolites (CH3X → hydrocarbons + HX).13–15 A general consensus opines that methylations represent key reaction stages in all these processes. Methanol and methyl halides are known to be efficient methylating agents.16–21 Contrastingly, there is no information in the literature that demonstrates the capability of methyl mercaptan to methylate aromatics/olefins. The absence of olefins in the M2TH process suggests that the HP mechanism (based on methylation steps) is not sustained. Notably, only few theoretical studies have focused on adsorption22,23 and conversion24 of methyl mercaptan on acid zeolites. The most representative is the very recent density functional theory (DFT) study that describes the catalytic CH3SH coupling over chabazite catalyst to form the C–C bond in ethylene.24

We investigated methylation by methyl mercaptan over the H-ZSM-5 catalyst for the first time, using Born–Oppenheimer molecular dynamics (BOMD) in conjunction with methods based on the quantum chemical DFT, to gain more insights into the mechanism of the zeolite-catalyzed M2TH process. We compared our results to those obtained from the methylation reaction with methanol, studied using the same computational methods and models. This report is organized as follows: first, we describe the zeolite models and computational methods used, subsequently we provide an overview of the experimental and theoretical results related to M2TH and MTH processes, and in the following sections, we present and discuss the intrinsic potential energy surface (PES) of dehydration reaction and the BOMD simulation at T = 823 K.

### RESULTS AND DISCUSSION

**M2TH versus MTH—Overview of the Experimental Results.** The experimental studies related to the comparison between M2TH and MTH processes demonstrated that CH3SH can be successfully converted over protonic zeolites (H-ZSM-5, H-Y, and H-ferrierite), without adding any reagent.1 Below 673 K, CH3SH is converted at equilibrium into dimethyl sulfide (DMS) and H2S, and above 773 K, it is selectively converted into H2S and hydrocarbons (essentially light alkanes and aromatics) (see Scheme 2). The conversion of methanol over zeolites is known to follow analogous pathways (see Scheme 3).10,25

In Table 1, we summarize the results from the experimental conversion of methyl mercaptan and methanol, investigated under equivalent conditions: 823 K, WHSV = 0.30 h⁻¹ over H-ZSM-5 as the catalyst,4 reporting the percentage of conversion and amount of products formed during conversion. These results reveal that catalyst lifetime and product distribution constitute the principal differences between M2TH and MTH. In the M2TH process, mercaptan conversion remains at 99% for 8 h, before decreasing smoothly to 75% after 17 h of operation.4 In the case of methanol conversion (the MTH
process), the catalyst exhibits enduring stability. During the first 45 h, methanol is fully converted into hydrocarbons, mainly lower olefins and aromatics.

In terms of the catalyst’s lifetime, differences are associated with deactivation rates related to the amount of coke formed in each process (M2TH produces almost four times more coke than MTH) (Table 1). Concerning product distribution in the M2TH process, the main hydrocarbons that are produced are C1−C3 alkanes (with >90% of CH4) and BTX aromatics. Only very small amounts of olefins are identified among the products. Contrastingly, the MTH process produces aromatics, alkanes, and a large amount of olefins (C2−C4).

According to Scheme 1, light olefins are mainly formed during the methylation cycle of aromatics. Recently, many studies have been published discussing aromatic alkylation with methanol; these are reviewed by Ilias and Bhan.18 Two reaction mechanisms have been recognized: (i) concerted mechanism, in which methanol and aromatic are coadsorbed onto a single acid site and then react in a concerted step, and (ii) stepwise mechanism, in which methanol dehydrates onto an acid site to form a surface-bound methoxide species, which then methylates aromatics by applying an Eley−Rideal-type mechanism.

Theoretical studies remain inconclusive concerning which mechanism is preferable.26 Spectral and kinetic experiments indicate that surface methoxide species are very likely involved as key reactive intermediates in methanol conversion and methylation processes by methanol on zeolite catalysts.27−36 Accordingly, aromatic methylation follows a pathway, as depicted in Scheme 4a, where a model reaction for the methylation of benzene over H-ZSM-5 zeolite is presented. The three main steps of this mechanism are as follows: (i) adsorption of CH3OH on a Bronsted proton; (ii) dehydration of methanol to form surface-bound methoxy species (−OCH3), and (iii) interaction of the methoxy function with an aromatic molecule in the mobile phase (adsorbed or not) to form a methylated hydrocarbon, which then desorbs from the zeolite surface.36 To evaluate the alkylation capability of methyl mercaptan in this theoretical study, both methanol and methyl mercaptan were considered to be methylating agents in the stepwise mechanism of Scheme 4a,b.

In these pathways, whereas the adsorption and dehydration steps are expected to be specific for each methylating molecule, benzene methylation with analogous methoxy species should be independent of the original reactant. Therefore, the present theoretical study at T = 0 K concerns the first two steps of the stepwise mechanism.

**Adsorption of CH3OH and CH3SH on H-ZSM-5 Zeolite.**

In this investigation, we used several H-ZSM-5 models of different sizes (see Figure 1) to compare the influence of model size on adsorption energies.

An embedded cluster was considered for the dehydration reaction, emulating the previously proposed models in the studies of methylation by CH3OH over acid H-ZSM-5.17,37,38 The acidic Bronsted site is represented by one hydrogen atom that is bonded to oxygen at the (Osurf) surface and next to Al3+. A previous theoretical study revealed that H-ZSM-5 structures with Al3+ located at 24 different positions present similar stability.39 Energy differences cannot be used to distinguish between various Al3+ substitution positions. Therefore, Al3+ location does not modify conclusions.

The adsorption of both reactants occurs by means of the H-bond formation between the zeolite surface hydrogen, Hsurf.
and X atom, as shown in Figure 2. The computed minimum energy adsorbate structures with characteristic bond lengths are presented in the same figure. As expected, the methanol adsorbate geometries are characterized by shorter H bonds than the mercaptan adsorbate structures. The adsorption enthalpies and Gibbs free energies for the three zeolite models and exchange−correlation functionals are given in Å.

![Figure 2](image-url)

Table 2. Adsorption Energies (ΔE) and Thermally Corrected Gibbs Free Energies (ΔG) in kcal/mol of CH₃OH and CH₃SH on H-ZSM-5 Models, Computed with PBE, B3LYP, and M06 Functionals

| system     | method | ΔE  | ΔG (T = 298 K) | ΔG (T = 823 K) |
|------------|--------|-----|----------------|----------------|
| CH₃OH/4T   | PBE    | −22.19 | −9.87 | 12.29 |
|            | B3LYP  | −19.09 | −6.70 | 14.31 |
|            | M06    | −19.26 | −6.53 | 12.64 |
| CH₃SH/4T   | PBE    | −11.79 | 0.14  | 20.28 |
|            | B3LYP  | −9.23  | 2.60  | 21.92 |
|            | M06    | −13.09 | −0.15 | 21.99 |
| CH₃OH/10T  | PBE    | −25.26 | −12.43 | 8.92 |
|            | B3LYP  | −21.34 | −9.62  | 9.75 |
|            | M06    | −23.45 | −8.06  | 14.16 |
| CH₃SH/10T  | PBE    | −12.43 | −2.92  | 14.25 |
|            | B3LYP  | −10.76 | 0.52   | 18.57 |
|            | M06    | −17.30 | −2.63  | 18.08 |
| CH₃OH/10T/99T ONIOM | PBE | −28.18 | | |
|            | B3LYP  | −24.42 | | |
|            | M06    | −41.7 | | |
| CH₃SH/10T/99T ONIOM | PBE | −17.32 | | |
|            | B3LYP  | −12.92 | | |
|            | M06    | −22.21 | | |

“Models are included in Figure 1.

Dehydration of Methanol and Mercaptan over H-ZSM-5. Previous theoretical studies concluded that the dehydration of methanol is an endothermic reaction with an energy barrier of ~40 kcal/mol.⁵⁷,⁵⁸,⁵⁹ We studied this using the 10/99T ONIOM model in Figure 1, as described in the “Models and Computational Details” section. The methanol transition-state (TS) structure obtained, shown in Figure 3a, closely resembles the previously described TS complex.37,38 The TS complex in the mercaptan dehydration reaction, shown in Figure 3b, is characterized by a longer C−S separation compared to the C−O distance in Figure 3a. The H bonds formed with Osurf in the mercaptan TS are also longer than in the methanol TS structure. Similar geometric differences can be observed in the methoxy intermediate and adsorbed H₂O and H₂S geometries, presented in Figure 3c,d.
In Figure 4, we present the PBE, B3LYP, and M06 intrinsic PES. The energy barriers, the formation energies of the methoxy intermediate (Int_Met···H2O), and the H2X desorption are reported in Table 3. For methanol dehydration, the energy barriers to Int_Met···H2O are 24.6 (PBE), 22.8 (B3LYP), and 34.8 (M06) kcal/mol. These values are smaller than the ∼40 kcal/mol intrinsic energy barrier reported previously.37,38,45 We also localized TS structures with higher barriers (of ∼50 kcal/mol) and less stable methoxy intermediates, with H2X close to the opposite site of Al3+ that forms H bonds with Osurf of −Si−O−Si− groups. These higher-energy TS geometries are shown in Figure 5. Apparently, PES has several local minima and maxima, with structures that differ mainly in the H2X orientation and in the positions at the zeolite cavity. These small differences in TS geometries can yield TS energies that differ by several tenths of kcal/mol.

Table 3. PBE, B3LYP, and M06 Energies of the Reaction Barrier, ΔE_{TS}, Surface Methoxy Formation, ΔE_{form}, and Desorption of H2X, ΔE_{desorb} of CH3OH/CH3SH Dehydration over H-ZSM-5

|          | CH3OH | CH3SH |
|----------|-------|-------|
| ΔE_{TS}  | PBE   | 24.6  | 26.4  |
|          | B3LYP | 22.8  | 23.9  |
|          | M06   | 34.8  | 26.4  |
| ΔE_{form}| PBE   | 10.9  | 15.5  |
|          | B3LYP | 11.5  | 13.7  |
|          | M06   | 15.4  | 6.5   |
| ΔE_{desorb}| PBE  | 10.0  | 1.5   |
|          | B3LYP | 10.4  | 3.0   |
|          | M06   | 13.9  | 10.8  |

A more significant result is that the energy barriers to the methoxy intermediate, Int_Met···H2X, are very comparable using PBE and B3LYP functionals. In the reaction of mercaptan and methoxy intermediate, the barrier is higher by only 1.5−1.8 kcal/mol. On the contrary, the M06 functional gives an 8 kcal/mol smaller TS barrier for mercaptan versus methanol dehydration (see ΔE_{TS} values in Table 3).

The formation energies of Int_Met···H2X (Table 3) obtained from the equation

ΔE_{form} = ΔE(Int_Met···H2X) − ΔE_{ads}(Ads_CH3,XH)

are similar for both reagents, except with the M06 functional that reveals a nearly two times smaller ΔE_{form} for the CH3SH reagent, which follows from the enhanced M06 adsorption of mercaptan. After H2O/H2S desorption, the relative energy of
surface methoxy resulting from the reaction with mercaptan was smaller by $5\text{−}6$ kcal/mol than that formed from the methanol reagent (see Figure 4). Our computed relative energies of Int_Met···H$_2$O and that of surface methoxy are more negative by $5\text{−}7$ kcal/mol than the previous B3LYP results.\textsuperscript{38} We attribute this difference to slightly different geometrical parameters.

Although the relative energies of the adsorbate, intermediate, and products at the PES of mercaptan to the surface methoxy reaction are higher than those for the methanol reactant, the intrinsic TS barriers are very similar and even smaller for mercaptan as found with the M06 functional. This suggests that the formation of stable surface methoxy following Scheme 4 is energetically favored, immaterial of the use of methanol or methyl mercaptan reagents. Our conclusion corroborates the similarities obtained between the reaction pathways of methanol and mercaptan dehydration in chabazite,\textsuperscript{24} which demonstrates that the DFT approaches and models implemented have little impact on the comparison of methanol/mercaptan reaction pathways, despite some differences in the numerical values of the energies. Moreover, the concerted mechanism and formation of C–C bonds for both CH$_3$XH reagents were shown to be very similar in chabazite from the static DFT reaction barriers. Therefore, we did not attempt computations of intrinsic reaction pathways for the other possible reaction mechanisms in H-ZSM-5 models because we did not anticipate any significant difference of the intrinsic energy barriers that could be useful to answer the questions of the origins for the observed very different reaction mechanisms of both reagents.

Computational results also concur with the experiments reported for both reactants concerning the formation of CH$_3$XCH$_3$ and H$_2$X desorption but at different temperatures, as shown in Scheme 2.\textsuperscript{2,4} For the reaction with methyl mercaptan reagent to continue, an increase in temperature of up to 823 K was necessary.\textsuperscript{4} A detailed explanation of mercaptan conversion at this temperature is still lacking. As mentioned previously, correction of the intrinsic PES at $T = $
823 K by the thermodynamic quantities evaluated in the ideal polyatomic gas approximation posteriori to the DFT electronic structure calculations at T = 0 K produced unrealistic positive adsorption energies and appeared inappropriate for methanol/mercaptan adsorption at high temperatures. We therefore used BOMD to account for the effect of fast rotational and vibrational motions at the experimental temperature.

**BOMD Simulations.** BOMD simulations at T = 823 K were carried out on models of adsorbed methanol/mercaptan in the H-ZSM-5 cavity, as well as on structures containing surface methoxy and one CH₃XH molecule in the cavity. The former model is used to estimate the temperature effect on the adsorption process, which is the first step of the reaction, whereas the latter structure is used to model the reaction between surface methoxy and CH₃XH. According to the experimental study, at temperatures <773 K, the only products are CH₃SH and H₂S (see Scheme 2). Only after increasing the temperature to above 773 K and setting it to T = 823 K in the experiments did we observe total conversion of methyl mercaptan to alkanes, BTX, and H₂S. As the intrinsic TS energy barrier (Figure 4) presents no obstacle for the mercaptan dehydration of surface methoxy, we explicitly considered the rotational and vibrational degrees of freedom along BOMD simulations. The latter are expected to provide initial information about the effect of temperature on the structural evolutions of the reagents in the zeolite cavity. The zeolite model in question is the 20T cluster in Figure 1c, and details of the dynamic simulations are provided in the “Models and Computational Details” section.

First, considering the dynamics of CH₃XH reagents at T = 823 K, prior to the formation of surface methoxy, we found that both molecules adsorb at the zeolite surface via the formation and deformation of hydrogen bond(s). In the left panels in Figure 6a,b, we present the evolution of characteristic structural parameters, such as Hsurf···O(CH₃OH); Osurf···H(HX−); and X−H, X−C, and C−H bond lengths. Methanol forms the shortest H bond with its oxygen and the zeolite hydrogen at the Bronsted site. This bond length oscillates between 1.5 and 2.3 Å. Dynamic H bond(s) with surface oxygen(s) are also formed. The shortest Osurf···H(HO−) is shown in Figure 6a, left panel. Mercaptan predominantly rotates between two surface oxygens, labeled as a and b in Figure 6b (left panel) and indicated on the 20T zeolite structure in Figure 6c. Most of the time, these two dynamic H bonds vary within an interval of 2.0−3.0 Å (Figure 6b, left). Mercaptan H (HS−) tends to dissociate as indicated by the elongation of the S−H bond; however, for the considered simulation time, mercaptan remains intact with the S−H length oscillating between 1.20 and 1.75 Å. The optimized bond length at T = 0 K S−H of the adsorbed mercaptan in the ONIOM 10T/99T structure is 1.36 Å. Contrastingly, the methanol O−H distance remains very close to its optimized value of 0.99 Å. Likewise, the average bond lengths for C−O and C−S over all the snapshots are 1.51 and 1.90 Å, respectively. These values resemble the optimized respective bond distances of 1.44 Å (C−O) and 1.84 Å (C−S). The C−H distance oscillations in the range of 0.9−1.3 Å are obtained for both mercaptan and methanol along the dynamics. This analysis suggests that initially both adsorbed molecules remain intact and undergo similar structural evolution, although subsequently some differences emerge (see Figure 6a,b, left panels).

This also corroborates experimental findings, which indicate that the adsorption on the zeolite catalysts represents a first methylation step on the reaction pathway of methanol and mercaptan (Scheme 4) at T = 823 K.

The presence of surface methoxy and CH₃XH in the zeolite cavity conducted to different dynamics of CH₃OH and CH₃SH. A very fast dissociation of one methyl hydrogen occurred in mercaptan, producing a ●CH₂SH radical. The dissociation occurred after 83 fs simulation time and energy convergence was broken once the methyl hydrogen had dissociated because of the presence of the nonbonded abstracted H atom. The important bond distances in the initial and final snapshot structure are reported in Figure 6c. The C−H and X−C bond evolution along the dynamics are presented in the right panels in Figure 6a,b. The C−X bond length variations remain similar to the isolated adsorbed molecules in the cavity. Elongation of one C−H distance ≥1.34 Å causes hydrogen abstraction. A similar effect of hydrogen abstraction from the methyl group in CH₃OH is established when CH₃OH is adsorbed in the presence of surface methoxy, but this process is roughly 10 times slower than the H dissociation from the coadsorbed methyl mercaptan molecule.

To verify the BOMD results, we repeated the simulations of mercaptan and surface methoxy in the 20T zeolite cluster with larger bases, TZVP, and without constraining the cluster geometry. The ●CH₂SH radical is again obtained after a somewhat longer simulation time of 210 fs. Therefore, larger bases would systematically slow down the processes but with no effect on the resulting trends.

Rapid formation of ●CH₂SH radical from mercaptan in a water solvent was reported previously in electron spin resonance studies. This process was explained with reference to the constraint of free methyl rotation around the C−S bond by the hydrogen bonds between mercaptan and the oxygen of H₂O. Hindered rotation was thought to induce a nonequivalent orbital coupling between the atomic orbitals of carbon and the three hydrogen atoms in the CH₃ group. This promotes coupling between only one or two C−H atoms and causes very rapid dissociation from −CH₃ on the part of the remaining hydrogen. The latter process is known as hydrogen abstraction. An analogous mechanism has been suggested for the formation of CH₃S* and ●CH₃ radicals. Similar to mercaptan in water solvent, C−S rotation is hindered in the zeolite cavity because of the formation of hydrogen bonds between the methyl H···Osurf and H (HS)···Osurf (see Figure 6c). In the initial geometry of the coadsorbed CH₃SH molecule, the three C−H distances are identical, equal to 1.09 Å. In the final snapshot structure in Figure 6c with the ●CH₂SH radical, to the right of the arrow, one C−H distance is shorter, 1.03 Å, and the other two are 1.15 and 1.34 Å. The C−H bonds oscillate between comparable values in the isolated adsorbed molecules (inset in the left panels in Figure 6a,b) without exceeding the dissociation limit of C−H ≥1.34 Å. The very fast hydrogen abstraction from the methyl group in CH₃SH therefore most likely refers to an increase in constraint caused by mercaptan in the presence of surface methoxy. The high reaction temperature seems to favor hydrogen abstraction from the methyl group in mercaptan but not from the S−H group. It cannot be ruled out that other initial geometries may produce other radicals such as CH₃X*. The very complex kinetics in the proposed hydrogen pool mechanism may thus be associated with various speeds and natures of radicals, formed under particular experimental conditions.

One can speculate that the competition between hydrogen abstraction and the C−C bond formation at a given
temperature is likely to be the predominant factor determining the reactivity of methanol and mercapta. Other mechanisms could also be envisaged. A more thorough quantitative biased dynamics study of the free-energy profiles is necessary and will be a subject of future work. Various biased dynamics techniques, such as umbrella sampling or perturbation MD, coupled to QM/MM have been successfully used to unveil catalytic mechanisms at finite temperatures. On the basis of experiments, the occurrence of radical decomposition reactions and hydrogen abstraction was apparent in the mechanism involving the conversion of methanol and mercapta to ethylene over acidic WO3/g-Al2O3 catalysts at T > 327 C, studied by Olah et al.50 In the latter work, the formation of methane as a byproduct was associated with the thermal decomposition of dimethylether (CH3OCH3 → CH4 + CH3O).

The present study demonstrates that the differences in the conversion of mercapta and methanol over acid zeolite catalysts are not related to the electronic structures of CH3SH and CH3OH and the intrinsic pathways. Instead, these differences are determined by the speed and type of radicals arising from CH3SH/CH3OH molecules with constrained motions in the zeolite cavity, where surface methoxy is found.

**CONCLUSIONS**

DFT and BOMD were employed to compare methylation reactions by methanol and methyl mercapta reagents, to reveal the underlying origins of the experimentally established differences between MTH and M2TH processes. For this purpose, we studied the intrinsic PES in the stepwise mechanism and the role of fast rotational and vibrational motions for both reagents.

The DFT intrinsic PESs of the dehydration reactions of CH3XH to surface methoxy do not exhibit any conclusive difference, from which to distinguish between methanol and mercapta.

BOMD simulations at the experimental temperature (823 K) and the analysis of the evolution of molecular bonds reveal initial intact adsorbate structures for the CH3OH and CH3SH molecules. The dynamics of methyl mercapta adsorbed in the cavity with surface methoxy led to the formation of CH3SH radical. A similar phenomenon occurred for the coadsorbed CH3 groups in CH3OH dissolved in the hindered C–X rotation because of the H(CH3)−Osurf and H(XH)−Osurf hydrogen bonds, analogously to the reported hydrogen abstraction from the −CH2 groups in CH3XH dissolved in water. Following our DFT static and BOMD (at T = 823 K) results, it is most probable that the different products observed experimentally from MTH and M2TH processes will relate to the different rate of radical formation under these experimental conditions.

**MODELS AND COMPUTATIONAL DETAILS**

The first two gas-phase 4T and 10T models in Figure 1a are used to compute adsorption energies using DFT methods for the fully optimized structures. The dangling bonds in these clusters are saturated with H atoms. The adsorbate ground-state geometries are confirmed by vibrational frequency analysis. Computed vibrational frequencies are also used to obtain thermal and entropy contributions to the Gibbs free energies of adsorption, ΔG, for T ≠ 0 in the ideal polyatomic gas model.53 Zero-point energy corrections are included in the free energies.

The third 10T/99T model in Figure 1b contains a 10T cluster (Si3AlO12H12), embedded in a 99T-zeolite framework (Si90Al30O120H30). The inner Si3AlO12H12 cluster is treated at the DFT level and the remaining 99T structure is described with the United Force Field (UFF) by using the ONIOM (our own N-layered integrated molecular orbital and molecular mechanics) scheme. This is used to optimize the minima and maxima structures at the PES of CH3XH dehydration reactions. The vibrational frequency computation needed to confirm the minima and the maxima at the PES is also obtained using the ONIOM scheme. We used the two-layer ONIOM scheme with electronic embedding and carried out full geometry optimization of both the QM and MM regions.57 The energies of those optimized with ONIOM structures are subsequently computed at the DFT level that was applied to the entire 109T optimized structures. This approach was employed to avoid inaccurate energy calculations from the molecular UFF in the ONIOM embedding scheme.

The above-described calculations were carried out with Gaussian 09 program with three exchange–correlation DFT functionals that are the PBE,59 the hybrid B3LYP functional,60,61 and M06.52 The atomic wave functions were described with a double-zeta quality basis set, 6-31G(d,p). In all the calculations, the energy convergence was set up to 10−8 au. The Berny63 optimization was used for the localization of the minima, intermediate, and TS structures. The convergence was based on the root-mean-square forces and displacement vectors with a threshold of 3.0 × 10−4 and 1.2 × 10−3, respectively.

There is a fourth model named 20T cluster in Figure 1c that is used in the BOMD calculations, coupled with DFT augmented with an empirical dispersion (DFT-D) method as implemented in deMon2k program.64,65 This approach was employed to study the adsorption processes of CH3XH in H-ZSM-5, before and after the formation of surface methoxy at the experimental temperature.2 The 20T cluster is cut from the 109T optimized structures with the United Force Field (UFF) correlation DFT method.55 with the embedded QM/MM scheme. This is used to optimize the minima and maxima at the PES of CH3XH dehydration reactions. The vibrational frequency computation needed to confirm the minima and the maxima at the PES is also obtained using the ONIOM scheme. We used the two-layer ONIOM scheme with electronic embedding and carried out full geometry optimization of both the QM and MM regions.57 The energies of those optimized with ONIOM structures are subsequently computed at the DFT level that was applied to the entire 109T optimized structures. This approach was employed to avoid inaccurate energy calculations from the molecular UFF in the ONIOM embedding scheme.

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**Notes**

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