

Article

A Theoretical Study on the Hydrolysis of Dimethyl Sulfide (DMS) over Y-FAU Protonated Zeolite

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Abstract

Dimethyl sulfide (DMS) hydrolysis over protonated Y-type faujasite zeolite (H-FAU) was examined using a hybrid density functional theory/molecular mechanics approach. ONIOM2(M06/6-31+G(d,p):UFF) calculations identified stepwise and concerted pathways. In the stepwise route, initial demethylation produces methanethiol and a surface methoxide species; subsequent reaction of the methoxide with water yields methanol. The calculated activation barriers for the demethylation and hydrolysis steps are 36.6 and 25.0 kcal mol⁻¹, respectively. In contrast, the concerted pathway involves simultaneous demethylation and hydrolysis in a single elementary step without formation of a stable intermediate, with a significantly higher activation barrier of 63.8 kcal mol⁻¹. The results suggest that DMS hydrolysis preferentially proceeds via the stepwise mechanism, with the demethylation step being rate-determining. For the preferred stepwise pathway, the apparent activation barrier for the overall hydrolysis reaction, referenced to the initial state, is 23.2 kcal mol⁻¹.

Keywords: hydrolysis of DMS; ONIOM2 methodology; M06 functional; stepwise mechanism

1. Introduction

Natural gas can contain carbon dioxide, hydrogen sulfide, water, carbonyl sulfide (COS), mercaptans, heavy hydrocarbons, and trace mercury [1]. Before distribution or use, these impurities must be reduced to acceptable concentrations by operations such as acid-gas removal, dehydration, molecular-sieve treatment, and hydrocarbon recovery. Even after these operations, treated gas may retain mercaptans and COS at concentrations of several parts per million. Stricter environmental requirements, the sensitivity of downstream catalysts, and the increasing use of reservoirs containing high mercaptan concentrations have therefore created a need for more effective deep-desulfurization technologies. In many industrial and domestic applications, mercaptan concentrations must be reduced to only a few ppmv. Current approaches rely mainly on fixed-bed adsorption and catalytic or chemical conversion, including oxidation, alkaline treatment [2], reaction with olefins [3], and hydrodesulfurization [4]. These processes may require additional reagents and can generate secondary sulfur-containing products, such as dialkyl sulfides and disulfides. In the widely used MEROX process, caustic extraction converts mercaptans to mercaptides, which are subsequently oxidized to dialkyl disulfides while the caustic solution is regenerated [5–8].

Zeolites are important catalytic materials because their ion-exchange capacity, acidity, and hydrophilicity can be tailored for applications that include petroleum refining. These microporous aluminosilicates occur naturally and can also be synthesized with controlled



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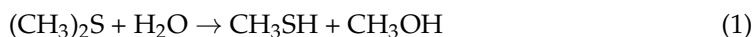
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compositions and structures. Faujasite (FAU) is particularly relevant to industrial catalysis because of its high structural stability and accessible three-dimensional pore system. The FAU framework is represented by synthetic zeolites X and Y, which have the same cage topology but different Si/Al ratios. Zeolite X typically has a Si/Al ratio of 1.0–1.5, whereas the ratio in zeolite Y exceeds 1.5 [9].

Experimental and computational studies have examined the transformations of adsorbed organosulfur compounds (OSCs). Ziolek and Decyk [10], for example, investigated the adsorption and conversion of ethanethiol and diethyl sulfide on faujasite zeolites and showed that protonated frameworks promote sulfur-compound reactivity by stabilizing hydrogen-bonded surface complexes. The hydrogen bond between the sulfur atom of an OSC and a zeolitic Brønsted proton can be modeled effectively with finite cluster representations. Accordingly, *ab initio* and density functional theory (DFT) calculations have been used to characterize OSC-zeolite interactions. Soscun and co-workers studied methanethiol and ethanethiol adsorption on acidic zeolites [11,12], and related calculations have addressed other organosulfur adsorbates [13]. Nevertheless, most theoretical work has emphasized adsorption, whereas the subsequent reaction pathways, transition states, and intermediates remain less thoroughly characterized.

In our previous study, a 38T cluster model showed that an acidic zeolite surface can catalyze the selective conversion of ethanethiol to ethene and H₂S [14]. Because H₂S can be removed efficiently by absorption in conventional solvents such as amines, this transformation could contribute to the near-complete removal of mercaptans (R-SH) from industrial streams and natural gas [15,16]. Recent investigations have also demonstrated that water confined within acidic zeolites strongly affects proton transport, adsorption, and catalytic activity, emphasizing the importance of resolving these processes at the molecular level [17–20].

In the present study, high-level theoretical techniques are used to investigate the catalytic hydrolysis of dimethyl sulfide (DMS) into methanethiol (CH₃SH) and methanol (CH₃OH) over the H-Y zeolite surface, as portrayed in the following scheme,



Both concerted and stepwise pathways have been proposed for dimethyl ether hydrolysis over acidic zeolites [21]. Because dimethyl ether and DMS have analogous structures, the same two pathways were evaluated here for DMS hydrolysis. The direct pathway couples demethylation and hydrolysis in a single elementary step, whereas the stepwise S_N2-type pathway (denoted Sw2) proceeds through a stable surface methoxide intermediate. Elucidating these alternatives can clarify the molecular basis of DMS conversion and support the development of catalysts for removing sulfur compounds from oil- and gas-processing streams. The calculated structures and energetics are compared with available results for related systems.

2. Methods and Computational Details

The application of sophisticated methods, such as the use of periodic boundary conditions, to the study of zeolite crystal systems becomes computationally expensive and, in many cases, impractical for zeolites, which often play a critical role in industrial processes and contain hundreds of atoms in each cell [22–26]. Therefore, their electronic properties are usually modeled with quantum chemical methods for relatively small clusters, where focus lies only on the most important part of the zeolite structure [27–29]. Despite their limited size, such cluster models have provided valuable insights into adsorption processes and catalytic reaction mechanisms. However, due to the small size of the clusters employed, the effect of the framework that plays an important role in the structure and energetics of the

system is not taken properly into account. As a result, the contribution of the van der Waals interactions between adsorbed species and the zeolite walls in the energetics of adsorption/desorption process, is frequently underestimated. The recent development of hybrid approaches, such as the combined quantum mechanics/molecular mechanics (QM/MM) methods, allows the use of much larger model systems with a moderate increase of computational cost. The hybrid QM/MM methods have been shown to provide geometries and reaction energetics in good agreement with periodic DFT calculations while retaining a significantly lower computational cost. Accordingly, the ONIOM methodology adopted in the present work provides a reliable description of the local Brønsted acid site and the elementary reaction steps involved in DMS hydrolysis while remaining computationally tractable. One such method is the original ‘Our-own-N-layer Integrated molecular Orbital + molecular Mechanics (ONIOM) approach, which has been developed by Morokuma and co-workers [30,31] and extended to large chemical and biological systems.

In this study, DMS conversion was modeled on an acidic 38T cluster containing 37 Si atoms and one Al atom in tetrahedral positions representative of Y-type FAU [32,33]. This model represents a high-Si/Al zeolite Y, which can be obtained through dealumination or appropriate synthetic procedures. Such materials exhibit enhanced hydrophobic (organophilic) character, making them particularly suitable for the adsorption of organic molecules. The computational investigation was performed using the ONIOM2 approach [30], which combines density functional theory (DFT) and molecular mechanics (MM) methods. The 38T cluster contains a single Brønsted acid site (BAS) and has the molecular formula $\text{Si}_{37}\text{O}_{56}\text{H}_{38}\text{Al}(\text{OH}_p)$, where H_p denotes the protonic hydrogen, with all terminal bonds saturated by hydrogen atoms, (Figure 1). The inner layer, shown as balls, contains 12 tetrahedral (12T) sites linking two FAU supercages and defines the region in which guest molecules interact with the active site. The remaining framework atoms form the outer layer, shown as sticks, and were fixed at their crystallographic positions. The 12T inner layer and reacting species were treated at the M06/6-31+G(d,p) level [34], whereas the outer layer was described with the Universal Force Field (UFF) [35]. This partitioning incorporates the pore environment without the cost of treating the entire cluster quantum mechanically.

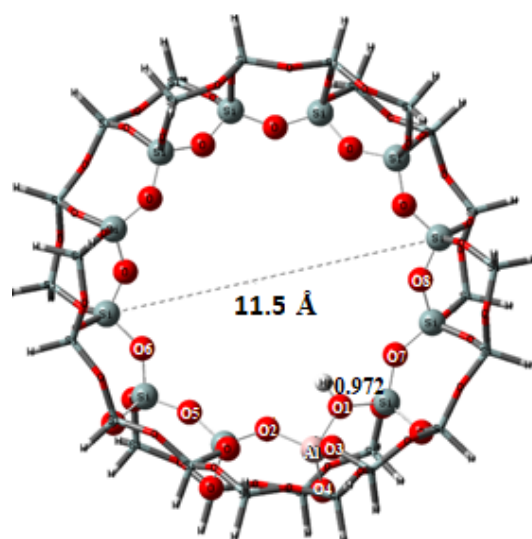


Figure 1. The 38T zeolite cluster optimized at the ONIOM2(M06/6-31+G(d,p):UFF) level of theory. The dotted line indicates the average diameter of the 12-membered-ring (12MR) window, equal to 11.5 Å. The 0.972 Å distance corresponds to the O1–H_p bond length of the hydroxyl group. The 38T zeolite cluster at the ONIOM2(M06/6-31+G(d,p):UFF) level of theory.

In the two-layer ONIOM formulation of Vreven and Morokuma [36], the total energy is assembled from calculations at the high and low levels of theory according to Equation (2).

$$E_{\text{ONIOM2}} = E_{\text{Low}}^{\text{Real}} + E_{\text{High}}^{\text{Model}} - E_{\text{Low}}^{\text{Model}} \quad (2)$$

The full system (real) is evaluated at the low level, whereas the chemically relevant subsystem (model) is calculated at both the high and low levels. The ONIOM energy is obtained by adding the high- minus low-level energy difference for the model subsystem to the low-level energy of the real system. Accuracy therefore depends on the definition of the model region, the levels of theory assigned to the layers, and the embedding treatment used for interlayer interactions. These choices must balance chemical fidelity and computational cost.

The M06/UFF combination within ONIOM2 has previously been applied to structural and energetic problems in zeolites and has produced adsorption energies consistent with published results [37,38]. This multilayer treatment consequently represents both the local reactive center and the confinement imposed by the surrounding FAU cavity.

The ONIOM2 protocol was used to optimize the DMS-38T adsorption complex, reaction intermediates, transition states, and product complexes. Within the local 3T Brønsted-acid fragment [$\equiv\text{OSiOAl}(\text{O})_2\text{O}(\text{Hp})\text{SiO}\equiv$], the terminal hydrogen atoms and adsorbed species were allowed to relax, while the remaining framework atoms were held at their crystallographic coordinates. Harmonic vibrational-frequency calculations were performed at the same level as the geometry optimizations to classify the stationary points and obtain zero-point-energy (ZPE) corrections. Each transition state exhibited exactly one imaginary frequency whose normal mode corresponded to the expected motion along the reaction coordinate. All calculations were performed with Gaussian 09 [39], and structures were examined using GaussView [40].

This study addresses the intrinsic elementary mechanism of DMS hydrolysis at a single Brønsted acid site in zeolite Y under standard theoretical conditions. The model does not explicitly include elevated temperature, reactant partial pressures, or the full network of competing reactions that may occur under industrial conditions. The calculated pathway should therefore be interpreted as a plausible elementary mechanism rather than a complete kinetic description of catalytic DMS conversion. Quantitative comparison with competing routes that form additional methanethiol, H_2S , or hydrocarbons will require further computational and experimental work.

3. Results and Discussion

In this work, we used the ONIOM2(M06/6-31+G(d,p):UFF) methodology to investigate the reaction mechanism of DMS hydrolysis over Y-FAU protonated zeolite and understand its catalytic function in this specific molecular transformation. Thus, by further exploiting the information obtained from the catalytic decomposition of DMS into CH_3SH and CH_3OH , we can design a candidate catalyst that converts an unwanted pollutant into commercially valuable products. The initial step of demethylsulfidation to methanethiol and methanol removal occurs when DMS is diffused into the pores of H-FAU zeolite and adsorbed on both acidic and basic sites to form the adsorption complex, DMS_ads. Starting from the adsorption complex DMS_ads, the conversion of DMS into methanethiol (MeSH) and methanol (MeOH) proceeds through two alternative reaction pathways. One pathway involves a stepwise $\text{S}_{\text{N}}2$ ($\text{S}_{\text{w}}2$) mechanism with the formation of intermediate species (Figure 2), whereas the other follows a direct (t_2) route (Figure 3). The corresponding transition states were identified and fully characterized for both mechanisms: TS1 associated with MeSH and alkoxide formation, TS2 leading to MeOH formation, and TS corresponding to the direct production of MeSH and MeOH. The relative electronic energy (ΔE , including

ZPE corrections) profile comparing the two reaction pathways is shown in Figure 4, while the corresponding Gibbs free-energy (ΔG) profile is presented in Figure 5.

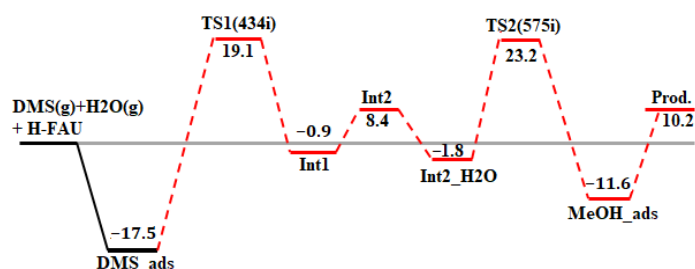


Figure 2. Reaction energy profile indicating the catalytic stepwise mechanism for DMS hydrolysis on the 38T cluster of H-FAU calculated at the ONIOM2(M06/6-31+G(d,p):UFF) level of theory. Relative energies are in kcal mol^{-1} . Adsorbed dimethyl sulfide (DMS) on the 38T cluster of H-FAU zeolite functions as the initial reactant complex.

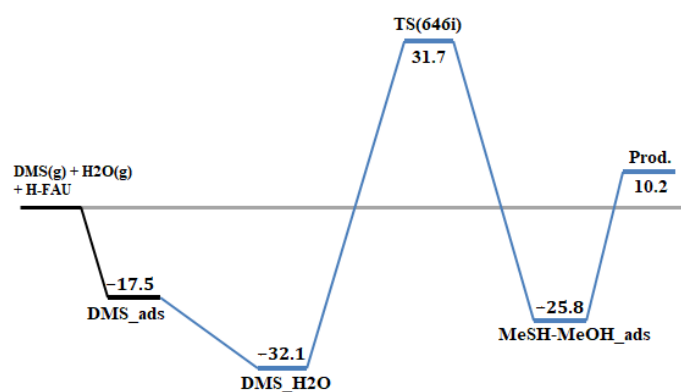


Figure 3. Reaction energy profile indicating the catalytic concerted mechanism for DMS hydrolysis on the 38T cluster of H-FAU calculated at the ONIOM2(M06/6-31+G(d,p):UFF) level of theory. Relative energies are in kcal mol^{-1} .

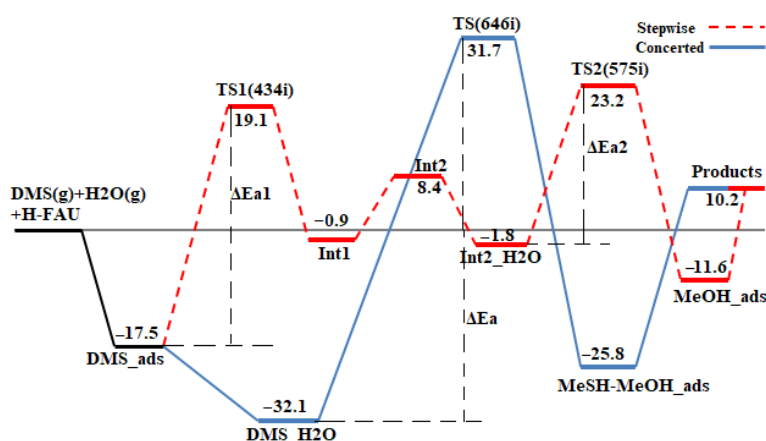


Figure 4. Reaction energy profiles for the stepwise (dashed line) and concerted (solid line) mechanisms. Relative energies are in kcal mol^{-1} .

The separated gas-phase products lie $10.2 \text{ kcal mol}^{-1}$ above the separated reactants, whereas the surface pathway contains strongly stabilized adsorbed intermediates and products. The positive overall reaction energy mainly reflects the energy required for product desorption from the zeolite surface and does not preclude the catalytic reaction under practical operating conditions.

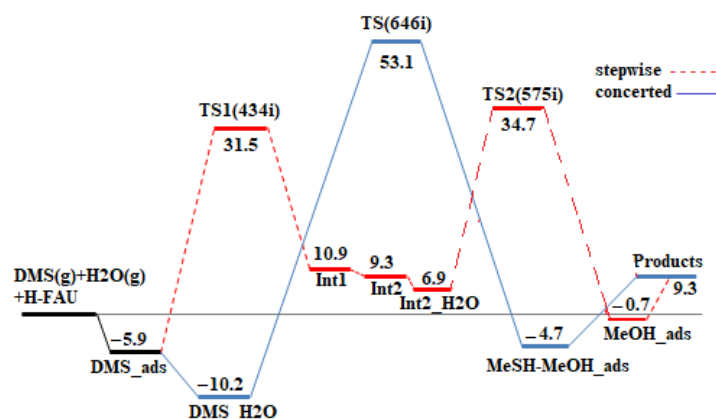
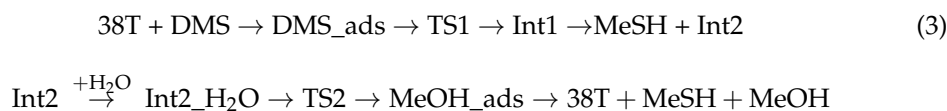


Figure 5. Relative Gibbs free-energy profile (ΔG) for DMS hydrolysis over protonated H-FAU through the stepwise (Sw2) and concerted (t2) pathways.

3.1. Stepwise Mechanism

Figure 1 shows the optimized 38T cluster, which comprises two FAU supercages connected through a 12-membered-ring window with an average diameter of 11.5 Å. DMS adsorption at the Brønsted acid site forms the DMS-38T complex (DMS_{ads}). The calculated adsorption energy is $-17.5 \text{ kcal mol}^{-1}$ (Table 2, improving the description obtained from smaller cluster models [11]).

Overall, the hydrolysis of DMS to methanethiol (MeSH) and methanol (MeOH) via a stepwise Sw2-type mechanism proceeds through the formation of a surface methoxide intermediate, followed by hydrolysis of the methoxide species by water (Figure 6), and can be summarized as follows:



The first step involves an Sw2-type demethylation of DMS, leading to methanethiol formation and the generation of a surface methoxide species. In the optimized DMS adsorption complex shown in Figure 6, the framework O1-H_p bond lengthens from 0.972 Å in the bare cluster to 1.063 Å. The intermolecular distance, between the sulfur atom of DMS and the Brønsted proton (S...H_p) is calculated to be 1.874 Å (Table 1a), and the two methyl groups interact weakly with framework oxygen atoms at 2.241 and 2.298 Å. The calculated adsorption energy of DMS at the H-FAU Brønsted acid site is $-17.5 \text{ kcal mol}^{-1}$ (Table 2). This value is not corrected for basis-set superposition error (BSSE) and is therefore reported as uncorrected adsorption energy. Although the absolute magnitude of the adsorption energy may be affected by basis-set effects associated with the finite QM basis set, the calculated value falls within the range reported for related organosulfur compounds on Brønsted-acid zeolites [13,41] and is consistent with the reported adsorptive affinity of FAU materials for sulfur compounds [42]. These comparisons indicate that the calculated DMS adsorption energy is consistent with previously reported values for related sulfur compounds, although they do not eliminate the possibility of a BSSE contribution.

A comparable initial demethylation step was proposed for dimethyl ether hydrolysis over H-ZSM-5 [21]. Starting from DMS_{ads}, C1-S bond cleavage and transfer of H_p to sulfur generate MeSH and the surface-methoxide intermediate Int1. Frequency analysis identified TS1 as a first-order saddle point with one imaginary frequency at 434i cm⁻¹. Its normal mode combines proton transfer to sulfur, C1-S bond cleavage, and C1-O2 bond formation. From DMS_{ads} to TS1, the C1-S distance increases from 1.869 to 2.404 Å, whereas C1...O2 decreases from 3.199 to 1.997 Å. Concurrently, H_p...S decreases from

1.874 to 1.392 Å (Table 1a). The activation barrier for this demethylation step (ΔE_{a1}) is 36.6 kcal mol⁻¹.

After MeSH desorbs, Int2 remains as a surface methoxide species. Adsorption of water next to the methoxide forms Int2_H₂O with an adsorption energy of -10.2 kcal mol⁻¹. The second transition state, TS2, has one imaginary frequency at 575i cm⁻¹. Its normal mode describes simultaneous C1-O2 bond cleavage and C1-O_w bond formation, where O_w is the oxygen atom of water. The C1-O2 distance increases from 1.484 Å in the intermediate to 2.042 Å in TS2, while C1-O_w decreases from 3.185 to 1.923 Å (Table 1a). Completion of this step produces MeOH with an activation barrier (ΔE_{a2}) of 25.0 kcal mol⁻¹.

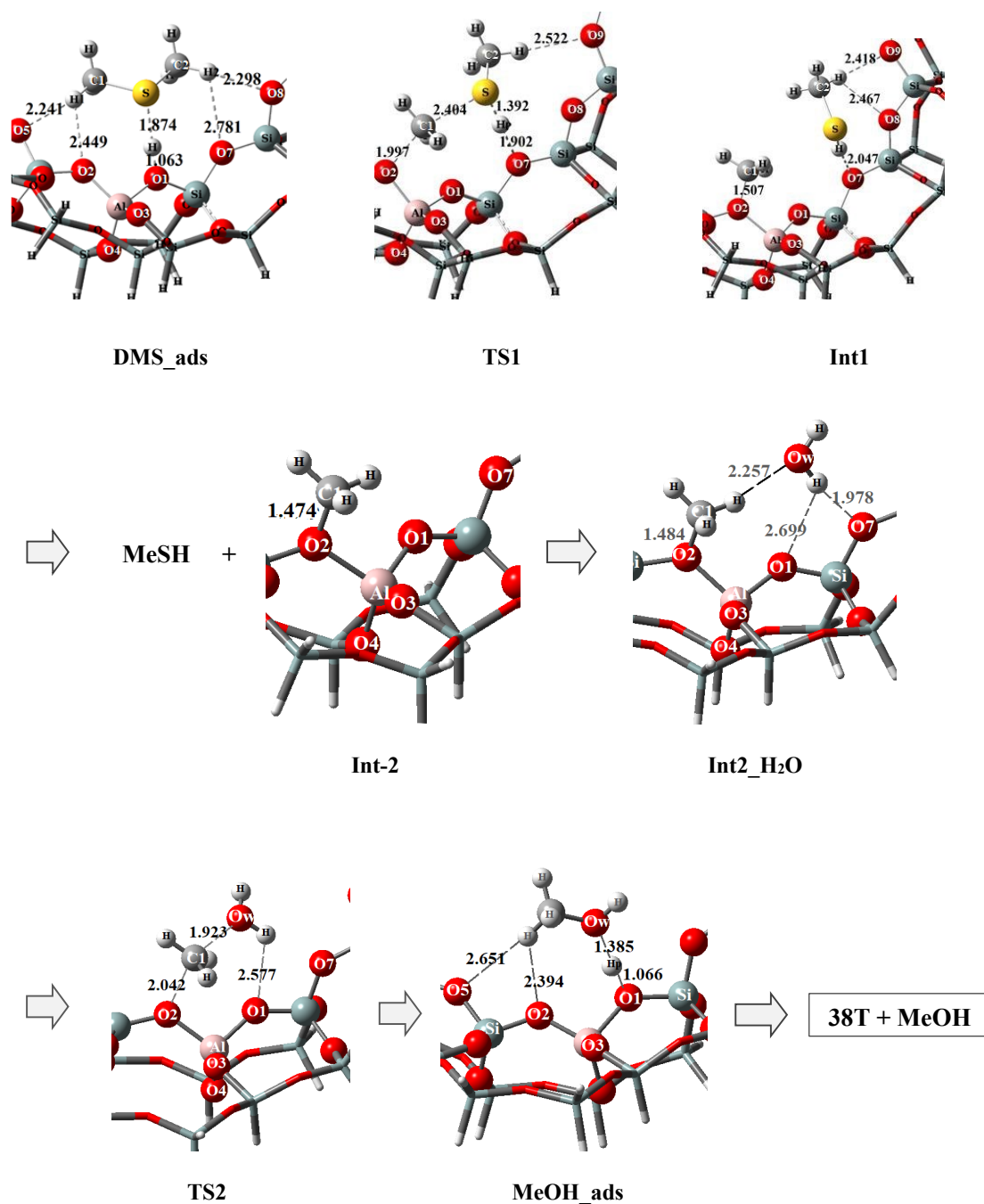


Figure 6. Optimized structures of adsorption complexes, transition states, and product complexes for the stepwise mechanism were obtained using a 38T zeolite cluster model at the ONIOM2(M06/6-31+G(d,p):UFF) level of theory. Dotted lines indicate bond distances.

Table 1. Selected interatomic distances (Å) for the stationary points along (a) the stepwise (Sw2) and (b) the concerted (t2) pathways of DMS hydrolysis over H-FAU, calculated at the ONIOM2(M06/6-31+G(d,p):UFF) level.

<i>(a) Stepwise (Sw2) Pathway</i>								
<i>Geometry</i>	<i>C1...O2</i>	<i>C1...S</i>	<i>S...H_p</i>	<i>O1...H_p</i>	<i>O7...H_p</i>	<i>H_w...O_w</i>	<i>H_w...O1</i>	<i>C1...O_w</i>
DMS_ads	3.199	1.869	1.874	1.063				
TS1	1.997	2.404	1.392	2.901	1.902			
Int1	1.507	3.669	1.351		2.047			
Int2	1.474							
Int2_H ₂ O	1.484						2.699	3.185
TS2	2.042						2.577	1.923
MeOH_ads	3.204					1.385	1.066	1.433
<i>(b) Concerted (t2) Pathway</i>								
<i>Geometry</i>	<i>C1...O2</i>	<i>C1...S</i>	<i>S...H_p</i>	<i>O1...H_p</i>	<i>O_w...S</i>	<i>H_w...O_w</i>	<i>H_w...O2</i>	<i>C1...O_w</i>
DMS_ads	3.199	1.869	1.874	1.063				
DMS_H ₂ O	3.410	1.819	1.899	1.057	3.715	0.973	1.784	3.428
TS		2.646	1.435	1.625	3.200	0.991	1.724	2.174
MeSH-MeOH_ads		3.749	1.356		3.926	1.448	1.046	1.429

3.2. Concerted (Direct) Mechanism

An alternative pathway for DMS hydrolysis involves a concerted mechanism in which demethylation and hydrolysis occur simultaneously, leading directly to the formation of methanol and methanethiol without the formation of a methoxide intermediate (Figure 7). The overall reaction sequence can be summarized as follows:



The process begins with the adsorption of DMS on the Brønsted acidic site of the zeolite, leading to the formation of the DMS_{ads} complex. Subsequently, a water molecule is weakly adsorbed near the adsorbed DMS through a hydrogen-bond interaction between one of its hydrogen atoms (H_w) and the zeolitic O2 atom (H_w...O2 = 1.784 Å; Table 1b) forming the DMS_{H₂O} complex, which is stabilized by an adsorption energy of −32.1 kcal mol^{−1} relative to the separated reactants (Table 2). The reaction then proceeds via a concerted demethylation and hydrolysis pathway via the transition state TS which has one imaginary frequency at 646i cm^{−1}, directly yielding methanol and methanethiol. Relative to DMS_{H₂O}, the calculated activation barrier is 63.8 kcal mol^{−1}. This value differs from the transition-state energy in Table 2, which is referenced to separated DMS, H₂O, and H-FAU. In addition to the relative electronic energies (ΔE), Table 2 also summarizes the corresponding Gibbs free energies (ΔG) for all stationary points.

The transition state structures have been identified by one imaginary frequency as first-order saddle points using the Synchronous Transit-Guided Quasi-Newton (STQN) method via the QST3 option [43,44]. The corresponding intrinsic reaction coordinate (IRC) calculations successfully connected each transition state to the respective reactant (co-adsorbed) and product minima without any intermediate structural collapse, confirming the proposed reaction pathways. Zero-point energy (ZPE) corrections were obtained from the frequency calculations and were found to be relatively small (typically 1.0–1.5 kcal mol^{−1}) for both minima and transition states.

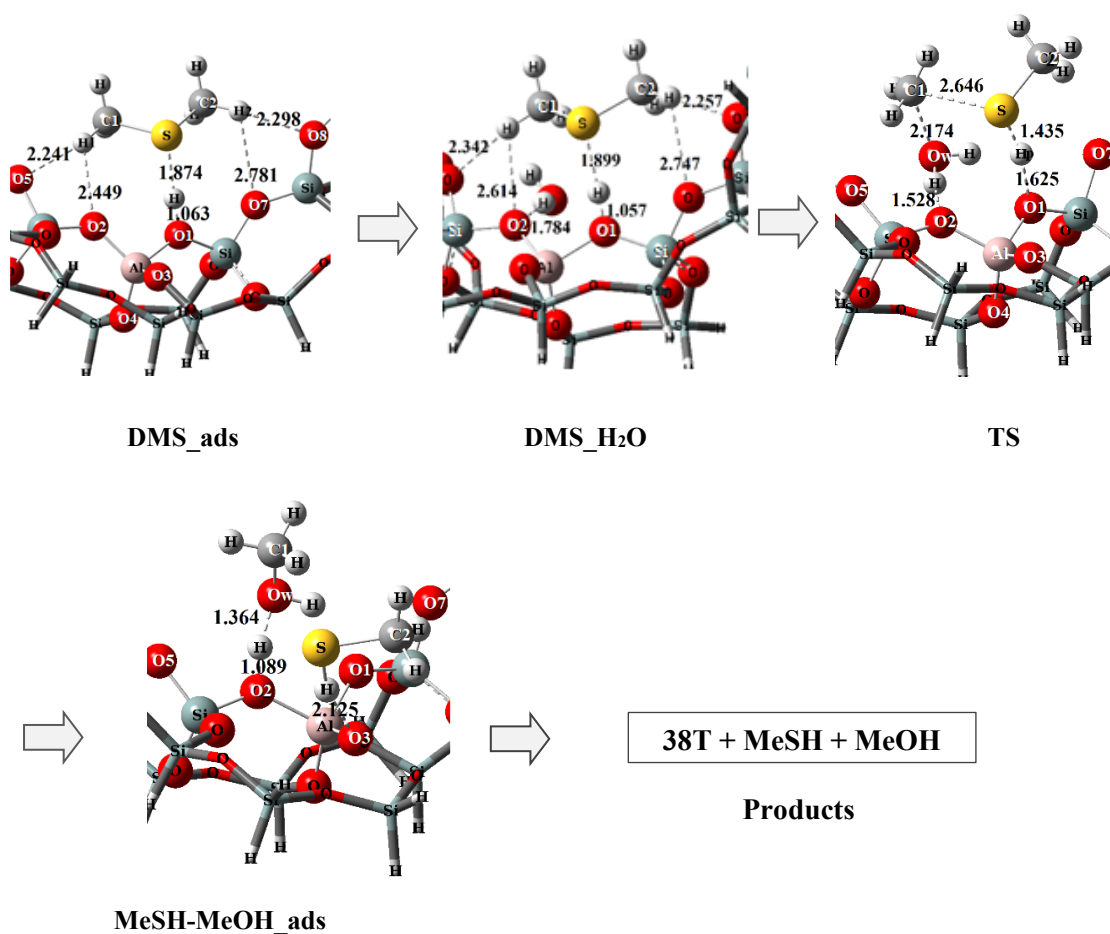


Figure 7. Optimized structures of 38T zeolite cluster model adsorption complexes, transition states and product complexes for the concerted mechanism at the ONIOM2(M06/6-31+G(d,p):UFF) level of theory.

Table 2. Relative ZPE-corrected electronic energies (ΔE , kcal mol^{−1}) and Gibbs free energies (ΔG , kcal mol^{−1}) for DMS conversion via the stepwise (Sw2) and concerted (t2) pathways.

Stationary Points	$\Delta E_{(Sw2)}$	$\Delta G_{(sw2)}$	$\Delta E_{(t2)}$	$\Delta G_{(t2)}$
DMS(g) + H ₂ O(g) + H-FAU	0.0	0.0	0.0	0.0
DMS_ads	−17.5	−5.9	−17.5	−5.9
DMS_H ₂ O			−32.1	−10.2
TS			31.7	53.2
MeSH-MeOH_ads			−25.8	−4.7
TS1	19.1	31.5		
Int1	0.9	10.9		
Int2	8.4	9.3		
Int2_H ₂ O	−1.8	6.9		
TS2	23.2	34.7		
MeOH_ads	−11.6	−0.7		
Products	10.2	9.3	10.2	9.3

(Sw2), (t2) Relative energies and Gibbs free energies with respect to the gas-phase reactants for the stepwise and concerted mechanisms, respectively.

3.3. Comparison Between Stepwise and Concerted Mechanisms

The profiles in Figure 4 show that the stepwise route is kinetically favored. Using the separated reactants as a common reference, TS1, TS2, and the concerted transition state are located at 19.1, 23.2, and 31.7 kcal mol⁻¹, respectively. Thus, the concerted transition state is substantially higher in energy than either transition state along the stepwise pathway. The intrinsic activation barriers of the individual elementary steps are 36.6 kcal mol⁻¹ for TS1, 25.0 kcal mol⁻¹ for TS2, and 63.8 kcal mol⁻¹ for the concerted transition state, each referenced to its corresponding preceding minimum (Table 2). Demethylation is therefore the rate-determining elementary step of the stepwise pathway.

The apparent activation barrier for the overall stepwise pathway is 23.2 kcal mol⁻¹, corresponding to the energy difference between the highest transition state along the stepwise pathway (TS2) and the separated reactants in the gas phase. For comparison, the corresponding apparent barrier for the concerted pathway is 31.7 kcal mol⁻¹. Thus, on a common reference, the concerted pathway remains kinetically less favorable than the stepwise pathway. Although the concerted route forms the more stable adsorbed product complex (MeSH–MeOH_{ads}), the lower barriers of the methoxide-mediated pathway indicate that the stepwise mechanism is kinetically preferred. DMS hydrolysis over H-FAU is therefore predicted to occur predominantly by the stepwise route. This result contrasts with calculations for dimethyl ether hydrolysis on acidic zeolites, for which the concerted pathway was preferred [21]. The difference may be related to the distinct electronic properties of sulfur and oxygen, which influence C–S bond activation and intermediate stabilization. NBO analysis supports this interpretation by showing a substantial increase in the antibonding $\sigma^*(\text{C}–\text{S})$ population from ~0.015 in the pre-TS structure to 0.256 at TS1, indicating significant electronic destabilization of the C–S bond during demethylation.

To assess the effect of thermal and entropic contributions, Gibbs free energies were calculated for all stationary points. As expected, the adsorbed intermediates become less stabilized when Gibbs free energies are considered because adsorption is accompanied by a significant loss of entropy. Nevertheless, the intrinsic activation free-energy barriers relative to the corresponding preceding minima remain consistent with the corresponding ZPE-corrected electronic-energy barriers. The intrinsic activation free-energy barriers are 37.4 and 27.8 kcal mol⁻¹ for TS1 and TS2, respectively, while the concerted pathway has an intrinsic activation free-energy barrier of 63.3 kcal mol⁻¹. Consequently, both the electronic-energy and Gibbs free-energy profiles consistently predict that the stepwise pathway is kinetically favored over the concerted mechanism.

4. Conclusions

DMS hydrolysis over H-FAU was investigated with the ONIOM2(M06/6-31+G(d,p):UFF) hybrid QM/MM method. Two pathways were characterized: a stepwise mechanism involving surface methoxide and a concerted mechanism in which demethylation and hydrolysis occur in one elementary step.

DMS adsorption at the H-FAU Brønsted acid site is energetically favorable. Along the stepwise route, demethylation forms MeSH and surface methoxide, after which water converts the methoxide to MeOH. The demethylation step is rate-determining. The concerted route has a substantially higher activation barrier, even though it produces a more stable adsorbed product complex.

Comparison of the energy profiles predicts that DMS hydrolysis proceeds preferentially through the methoxide-mediated stepwise mechanism. This preference may be related to the distinct electronic properties of sulfur compared with oxygen, which influence C–S bond activation and intermediate stabilization. NBO analysis indicates significant electronic destabilization of the breaking C–S bond during demethylation. Reducing the

demethylation barrier should therefore be a central objective when optimizing H-FAU-based catalysts for DMS hydrolysis.

These results provide a molecular-level account of DMS hydrolysis at a zeolitic Brønsted acid site and a theoretical basis for designing more effective catalysts for sulfur-compound conversion. Because the model represents an intrinsic elementary pathway, validation under realistic temperatures, pressures, and water loadings remains an important direction for future work.

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