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THESIS

DEHYDRATION OF ETHANOL TO ETHYLENE OVER H-MOR INVESTIGATED BY THE ONIOM METHOD

JITTIMA MEEPRASERT

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
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The conversion of ethanol to ethylene is of particular interest as an alternative method for production of petrochemical feedstock. In this study, two mechanisms, stepwise and concerted, of the ethanol dehydration to ethylene in H-MOR zeolite were theoretically investigated using the ONIOM(B3LYP/6-31g(d,p):UFF) method. The effect of water on the reaction mechanism is also considered because water is commonly found in ethanol produced from biomass. In the stepwise mechanism, the reaction proceeds via dehydration of ethanol to form the surface ethoxide intermediate which is found to be the rate determining step. Then the surface ethoxide is transformed to ethylene. In the concerted mechanism, ethanol dehydrated to ethylene directly without the formation of surface ethoxide. The presence of coadsorbed water is found to reduce the activation energy by 2-3 kcal mol^{-1}. The dehydration of ethanol preferentially takes place via the stepwise mechanism. The first step has an activation energy of 41.2 kcal mol^{-1} and, then, the transformation of ethoxide species to ethylene has an activation energy of 22.2 kcal mol^{-1}. In addition, the presence of coadsorbed water prevents the direct access of the ethylene product to the Brønsted acid site. Therefore, the reverse reaction of ethylene to ethoxide requires a higher activation energy of 34.1 kcal mol^{-1} (compared to 25.1 kcal mol^{-1} without coadsorbed water).

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First of all, I would like to grateful thanks to Asst. Prof. Dr. Piboon Pantu my thesis advisor, who provided me with many helpful suggestions, important advice and encouragement during the completion of this thesis. I wish to express my sincere gratitude to my committees, Prof. Dr. Jumras Limtrakul who made many valuable suggestions and constant encouragement for completely research, and also Dr. Pimpa Hormnirun for hers extremely helpful advice and suggestion. Special thanks also go to Dr. Somkiat Nokbin and Dr. Piti Treesukol for their valuable comments and suggestion. In addition, I am grateful to all my teachers for the excellent knowledge that I received.

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Finally, I would like to express special thanks and dedicate this thesis to my parents for their love and encouraging me to pursue this degree.

Jittima Meeprasert
May 2009

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LIST OF ABBREVIATIONS

Å = Ångström (1 x 10^{-10} metres)
B3LYP = Becke's three parameters hybrid function using the Lee-Yang-Parr correlation functional
C = Concerted pathway
DFT = Density functional theory
Ea = Activation energy
Ed = Desorption energy
ETX = surface ethoxide
FAU = Faujasite zeolite
K = Kelvin
kcal = kilocalories
kJ = kilojoules
MM = Molecular Mechanics
MR = Membered-ring
MOR = Mordenite zeolite
ONIOM = Our own N-layered Integrated molecular Orbital and molecular Mechanics
PRD = product structure
QM = Quantum Mechanics
RT = reactant structure
S = Stepwise pathway
T = tetrahedral
TS = transition state structure
UFF = Universal Force Fields
ZSM-5 = Zeolite Socony Mobil 5

DEHYDRATION OF ETHANOL TO ETHYLENE OVER H-MOR INVESTIGATED BY THE ONIOM METHOD

INTRODUCTION

Currently, petroleum is still the most important energy resource and the most important feedstock for many chemical products. It is predicted that petroleum resources will inevitable by depleted. Therefore, there are concerted attentions, efforts and research to develop alternative hydrocarbon resources.

Biomass, is one such alternative. It is a usable and renewable resource mostly derived from plants. Biomass can be converted to more valuable chemical compounds, an example of which is bio-ethanol, produced through the microbial fermentation of agricultural feedstock such as corn, sugarcane and cassava. Bio-ethanol has now become a highly attractive product in many countries with abundant agricultural resources (Farber, 2005; Earth Sciences Division NASA, n.d.).

Not only ethanol used as a fuel but also can be used to produce more valuable hydrocarbon compounds, especially ethylene. This hydrocarbon compound is very important and is used industrially to synthesize a wide range of organic compounds. Acidic solution was found to be a catalyst for this conversion. Solid acid catalysts such as silica-alumina (SiO_2/Al_2O_3) and zeolites have also been used (Phillips and Datta, 1997). Zeolite has the advantage that it is environmentally friendly and can be reused and reactivated. Mordenite (H-MOR) and H-ZSM5 zeolite types are frequently used in ethanol dehydration (Costa et al., 1985; Le Van Mao and Dao, 1987; Phillips and Datta, 1997; Talukdar *et al*., 1997; Takahara *et al*., 2005; Barthos *et al*., 2006; Inaba *et al*., 2006; Ermakov *et al*., 2008; Zhang *et al*., 2008). Inaba *et al*. (2006) found that H-MOR has a high selectivity for ethylene formation by intramolecular dehydration at the temperature of 400 °C, while H-ZSM-5 is effective for the formation of aromatics, parafins and C3+olefins.

Two reaction pathways for the dehydration of ethanol to ethylene over zeolite are reported (Inaba *et al.*, 2006). At low temperatures, ethylene is produced via diethyl ether dehydration process (equation 1). At high temperatures, it is formed directly by intramolecular dehydration (equation 2):

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O \rightarrow 2C_2H_4 + 2H_2O \qquad (1)$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad (2)$$

It has been found that the selectivity to ethylene increases as the reaction temperature increases (Phillips and Datta, 1997; Talukdar *et al.*, 1997; Takahara *et al.*, 2005; Barthos *et al.*, 2006; Inaba *et al.*, 2006;). It is, therefore, more interesting to study in detail of the direct ethanol dehydration. So far, there has been only a limited amount of research reported concerning the mechanism of ethanol dehydration to ethylene over zeolite.

Generally, the dehydration of alcohol over zeolite is considered to start with the direct interaction of the hydroxyl group of alcohol with the Brønsted acid sites of zeolite (Haase and Sauer, 1995; Limtrakul, 1995; Blaszkoski and van Santen, 1996, 1997; Phillips and Data, 1997a; Barthos et al., 2006). In a previous theoretical study, density functional theory (DFT) calculations with small quantum clusters were employed to investigate the dehydration mechanism and proposed that the reaction proceeds via an intermediate ethoxide surface species (Blazkoski and van Santen, 1997). This suggestion was later confirmed by the experimental study which observed the presence of a stable ethoxy intermediate in this reaction (Kondo *et al.*, 2005; Barthos *et al.*, 2006). It is currently well known that the shape and pore size of zeolite have significant effects on adsorptions and reactions (Jansang *et al.*, 2007; Pantu *et al.*, 2007). Therefore, it is necessary to use a sufficiently large model to have a good representation of the complex zeolite structure.

In this study we use a 120T cluster representing the H-MOR framework and use the ONIOM (our Own N-layered-Integrated molecular Orbital and molecular Mechanics) method which has been successfully utilized to investigate the reaction mechanisms inside the zeolite framework (Jansang *et al.*, 2007; Pantu *et al.*, 2007). Two different mechanisms for the dehydration of ethanol to ethylene are considered. One is a concerted mechanism and another one is a stepwise mechanism which proceeds in two steps via ethoxide intermediate. Additionally, the experimental results indicated that water in ethanol feed enhances the catalytic activity and selectivity for ethylene formation (Costa *et al.*, 1985; Phillips and Datta, 1997; Talukdar *et al.*, 1997). Thus it is necessary to study all mechanisms in the absence and presence of water.

OBJECTIVES

1. To investigate the reaction mechanism of dehydration of ethanol to ethylene over H-MOR using the ONIOM method.

2. To study the effect of water in ethanol dehydration over zeolites.

LITERATURE REVIEW

The dehydration of ethanol is one of the reactions that require an acidic catalyst (Phillips and Datta, 1997). But recent studies on the selective catalytic dehydration of ethanol have focused on the solid acid catalysts such as γ-alumina (Al_2O_3), perfluorinated sulfonated cation exchangers, polyphosphoric acid, heteropoly acids and zeolites (Ermakov, 2008). Among these, zeolite which is an aluminosilicates molecular sieve catalyst have received considerable attention because of their catalytic activities and environmentally friendly materials (Weitkamp, 2000).

The dehydration of ethanol on zeolite-type catalysts yield ethylene, diethyl ether, ethane, acetaldehyde, propene, butenes and small amounts of aromatics (Takahara *et al.,* 2005; Brathos *et al.,* 2006; Inaba *et al.,* 2006). Ethylene is the dominant product of this reaction to produce higher hydrocarbons (Talukdar *et al.*, 1997):

$$C_2H_5OH \rightarrow C_2H_4 \rightarrow C_2H_{4n} \rightarrow \text{parafins} + \text{aromatics} \qquad (1)$$

The zeolite H-ZSM5 and H-MOR have frequently been used for the dehydration of ethanol (Costa *et al.*, 1985; Le Van Mao and Dao 1987; Phillips and Datta 1997; Talukdar et al., 1997; Takahara *et al.*, 2005; Barthos *et al.*, 2006; Inaba *et al.*, 2006; Ermakov *et al.*, 2008; Zhang *et al.*, 2008). Inaba and co-worker (2006) studied the conversion of ethanol over several zeolite catalysts. The catalytic activity of H-ZSM5, USY, H-Beta, and H-MOR were investigated by using a fixed-bed reactor. At 400°C, H-ZSM5 zeolite (190 Si/Al_2 ratio) gave the highest ethanol conversion (96.41%) and ethylene selectivity (97.51%). However, at above 400°C, they found that the selectivity of ethylene was decreased and higher hydrocarbons were predominantly formed over H-ZSM5, while other zeolites showed that the selectivity of ethylene increased with increasing the reaction temperature. *In* 2008, Zhang *et al.* studied the activity and stability of γ-Al_2O_3, H-ZSM5, SAPO-34 and NiAPSO-34 catalysts for the dehydration of ethanol to ethylene. H-ZSM5 showed the highest conversion of ethanol, up to 97.3% at 325^{0}C. However, in H-ZSM5 the yield of ethylene decreased rapidly after reaction for 60 hours because of its strong acidity can convert ethylene product to higher hydrocarbons and lead to deactivation of catalyst by coke formation.

For the H-MOR zeolite, Takahara and co worker (2005) reported that it was the most active catalyst for the dehydration of ethanol when compared with other solid acid catalysts (silica-alumina, H-Y, H-Beta, and H-ZSM5) at temperatures in range of 453-573 K under atmospheric pressure. H-MOR zeolite exhibited greater ethylene yield (99.9%) than any catalysts. The catalytic activity decreases in the following order: H-MOR ($Si/Al_2 = 20$) > H-MOR (90) > H-ZSM5 (25) > H-Beta (25) > H-ZSM5 (90) > H-Y (5.5) > silica-alumina. Morover, H-MOR (90) showed a very low amount of carbonaceous deposits, while ethanol conversion and ethylene selectivity were almost constant for 40 hours.

Many researchers studied the effect of SiO_2/Al_2O_3 ratio of zeolites for the dehydration. H-zeolite with lower SiO_2/Al_2O_3 ratio (high Bronsted acid site) was preferable to form aromatics while the higher SiO_2/Al_2O_3 ratio (low Brønsted acid site) observed ethylene is the dominant products. This results indicated that the number of acid site was important as well as the acid strength to catalytic activity for the dehydration of ethanol to ethylene (Costa *et al.*, 1985; Talukdar *et al.*, 1997; Takahara *et al.*, 2005; Brathos *et al.*, 2006; Inaba *et al.*, 2006).

Generally, ethanol obtained from biomass fermentation (bio-ethanol) is a mixture of ethanol and water with the molar ratio of 1:13 (about 12 wt% ethanol). Then, it can be concentrated by distillation to produce up to 96% ethanol (hydrated ethanol). Removal of remaining 4% water to produce anhydrous ethanol requires a special treatment (Ni *et al.*, 2007; Demirbas 2008). More importantly, water is the by-product from the ethanol dehydration. Therefore the effect of water on this reaction was studied intensively. Talukdar *et al.* (1997) reported that ethylene showed a rapid decrease as the water content decreased from 50% to 20% while paraffins and aromatics showed an increasing trend with decrease in water content. In the work of

Phillips and Datta (1997), the presence of water in ethanol feed enhances the steady state catalytic activity of zeolites and the selectivity for ethylene formation.

It is generally agreed that the dehydration of ethanol to ethylene can take place by two reaction pathways (Inaba *et al.*, 2006). In the first path, two ethanol molecules interact with each other to form diethyl ether, which then dehydrates to ethylene.

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O \quad (2)$$

$$C_2H_5OC_2H_5 \rightarrow 2C_2H_4 + 2H_2O \quad (3)$$

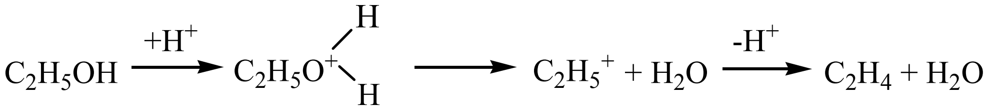
In the second path, ethylene is formed by the intramolecular dehydration.

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad (4)$$

At low temperatures, diethyl ether is produced in significant quantities whereas at high temperatures, ethylene is the dominant product. In addition, ethanol is dehydrogenated to acetaldehyde as a side reaction at high temperatures (Phillips and Datta 1997; Barthos *et al.*, 2006). Ermakov *et al.* (2008) estimated the heats of ethanol conversion to ethylene on acid-base catalysts from the calculated values of the equilibrium constants and enthalpies at 700 K. They found that this reaction was endothermic with a heat of 46.90 kJ mol^{-1}.

The mechanism of heterogeneously catalyzed dehydration of alcohols over zeolites obtained from calculations reveals that the reaction is initiated with the direct interaction of the hydroxyl group of the alcohol with the Brønsted-acid sites of zeolites (Haase and Sauer 1995; Limtrakul 1995; Blaszkoski and van Santen 1996, 1997). Infrared spectroscopy showed that ethanol strongly interacts with the OH groups of the zeolites (Barthos *et al.,* 2006). This result agrees with experimental heats of adsorption for ethanol in H-ZSM-5, 130 ± 5 kJ mol^{-1} (Lee *et al.,* 1997). However, one of the key steps to understand the mechanism of any reactions is the observation and identification of intermediates. For the dehydration of ethanol in the acidic solution, it is well known that the carbenium cationic species is a reaction intermediate (see Figure 1a). In the case of zeolites, Kondo and co-worker (2005) studied this reaction intermediate on H-MOR zeolite using infrared spectroscopy and concluded that ethanol dehydrated to ethylene via a covalent ethoxy group (C_2H_5O) on a zeolite which is a stable intermediate for this reaction (see Figure 1b).

(a) Conversional mechanism through cationic intermediate



$$C_2H_5OH \xrightarrow{+H^+} C_2H_5\overset{H}{\underset{H}{O^+}} \longrightarrow C_2H_5^+ + H_2O \xrightarrow{-H^+} C_2H_4 + H_2O$$

(b) Mechanism on zeolite through covalent intermediate

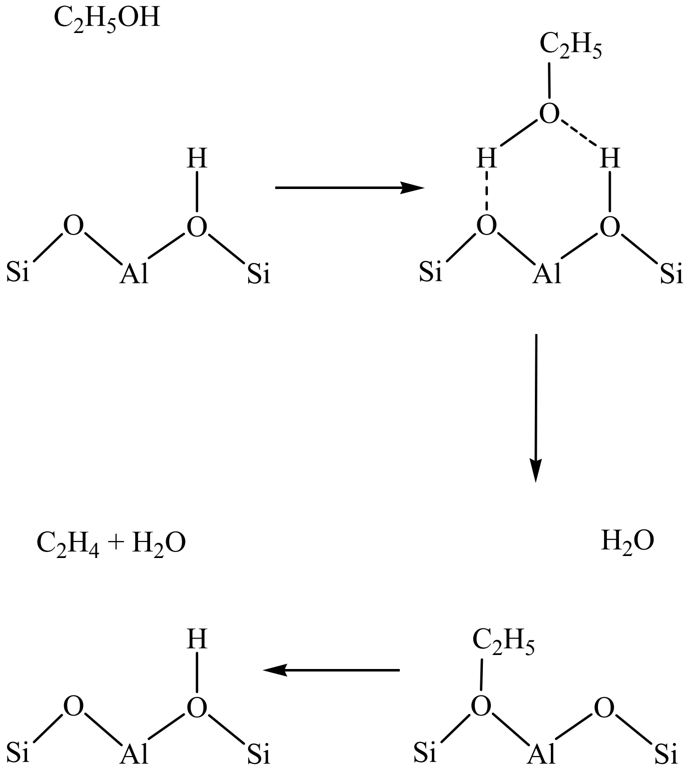


Figure 1 Mechanisms of ethanol dehydration (a) in acidic solutions and (b) on zeolites.

Source: Kondo *et al.* (2005)

Density functional theory (DFT) calculations with small quantum clusters were used extensively for studying alcohol adsorption and dehydration on zeolites (Blaszkoski and van Santen 1996, 1997). *In* 1997, Blaszkoski and van Santen using HOHAl(OH_2)OH cluster and local density approximation with nonlocal exchange and correlation corrections to study the methanol-to-gasoline process.. In that study, three different mechanisms were proposed for the dehydration of ethanol to ethylene. The first path was the concerted mechanism, anhydrous ethanol dehydration. The activation energy for the first path was 171 kJ mol^{-1}. The second path was the stepwise mechanism of anhydrous ethanol dehydration involving two elementary steps via ethoxy surface species. The first step was ethanol dehydration to ethoxide and water with the activation energy of 187 kJ mol^{-1}. The second step, the ethoxide was transformed to ethylene. The activation energy was 123 kJ mol^{-1}. The last path was the stepwise mechanism of hydrous ethanol dehydration which was found that this mechanism was significantly influenced by coadsorbed water in both steps. The activation energies of first step and second step were 164 and 125 kJ mol^{-1}, respectively.

Recently, the theoretical studies of the adsorption and reaction mechanisms over zeolites, are more commonly performed on large models. In addition, hybrid methods such as the embedded cluster, the combined quantum mechanics/molecular mechanics (QM/MM) method or our-Own-N-layered-Integrated molecular orbital + molecular mechanics (ONIOM) method (Greatbangs *et al.*, 1996; Brandle *et al.*, 1998; Limtrakul *et al.*, 2000) have been developed to describe the zeolite framework effect at the affordable computational cost. The ONIOM method has been successfully used to investigate the adsorption of hydrocarbons and reaction mechanism over zeolites. Kasuriya and co-worker (2003) studied the adsorption of ethylene, benzene and ethylbenzene on H-FAU zeolites with three different cluster sizes (3T, 20T and 84T) and methods comprising various two-level ONIOM2 schemes. They found that the extended framework significantly enhances their adsorption energy of adsorbed to the zeolites. Raksakoon and Limtrakul (2003) used four different cluster sizes (10T, 14T, 18T and 46T) and methods comprising various two-level ONIOM2 schemes to investigate the adsorption of benzene on H-ZSM5 zeolites. Their results also showed the strong effect of extender framework on the adsorption of probe molecules.

In 2007, Pantu and co-worker reported the study on the adsorption of light alkanes and alkenes on H-FAU and H-MOR zeolites ~~by~~ using the ONIOM approach. They used the B3LYP/6-31G(d,p) level of theory to apply for the 14T tetrahedral quantum cluster and 120T extended framework connecting the quantum region was treated with the universal force field (UFF). They concluded that this ONIOM scheme was a practical method for investigating the adsorption of unsaturated and saturated hydrocarbons on these zeolites. Moreover, many reaction mechanisms over zeolites such as, the dimerization of ethylene over H-FAU zeolite (Namuangruk *et al.*, 2005) and the hydration of ethylene oxide over H-ZSM5 zeolite (Maihom *et al.*, 2008) were investigated using the ONIOM method and agreed well with the experimental results.

MATERIALS AND METHODS

The topology of the crystal lattice of mordenite (H-MOR) zeolite is an orthorhombic space group Cmcm with unit cell parameters a = 18.09 Å, b = 20.52 Å and c = 7.52 Å. The framework system consists of two types of one-dimensional channel: the straight 12-membered ring (6.5 x 7.0 Å) and crossed 8-membered ring (2.6 x 5.7 Å) channels, running parallel to the *c*-axis (Figure 2).

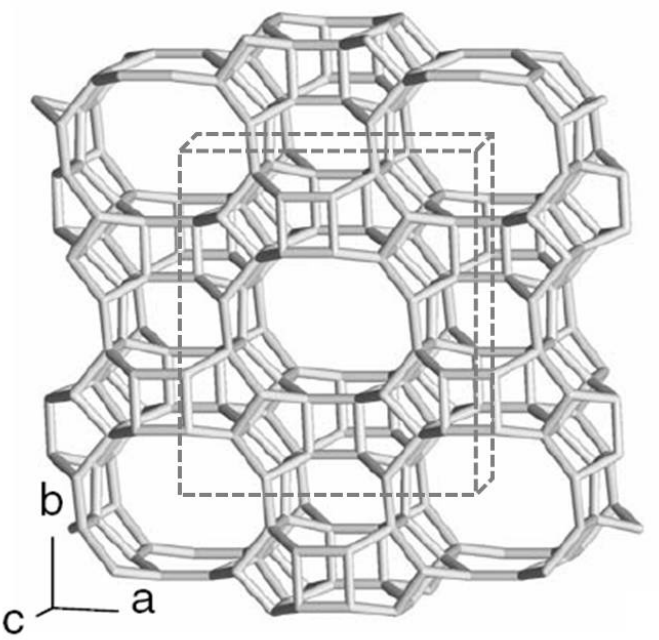


Figure 2 The framework structure of mordenite zeolite in the highest possible topological symmetry Cmcm.

Source: Baur and Fischer (2006)

The structure of the 120T cluster (119 tetrahedral atoms of Si and 1 tetrahedral atoms of Al) was taken from the lattice of mordenite zeolite as shown in Figure 3. The dangling bonds resulting from cutting the Si-O bonds were terminated by the H atoms with the Si-H bond distances of 1.47 Å and pointed in the same direction as the crystallographic Si-O bonds. This cluster was modeled to cover an ample portion of the straight channel with the crossed windows opening to the side pockets. To increase the computational efficiency, the 120T cluster was subdivided to two layers of calculation methods according to the two-layer ONIOM (ONIOM2 scheme). The inner layer was a fourteen-tetrahedral (14T) cluster consisting of the 12-membered-ring (MR) window of the straight channel of 6.5 Å × 7.0 Å and a silicon atom was substituted by an aluminum atom to form the Brønsted acid site. This layer and the reacting molecules were treated with the B3LYP/6-31G(d,p) method. The rest of the model was treated with the Universal Force Field (UFF) to represent the confinement effect of the zeolite pore structure and to reduce the required computational time. All calculations were performed using the Gaussian 03 code (Frisch *et al.*, 2004). Geometry optimizations of all structures were performed at the ONIOM(B3LYP/6-31G(d,p):UFF) level of theory where only the active site region 5T, $[(\equiv SiO)_3Al(OH)Si\equiv]$ and the adsorbate were allowed to relax. In addition, the vibrational spectra were performed at the same level of theory to ensure that each transition state structure has only one imaginary frequency which corresponds to the expected vibration of the transition state structure.

(a)

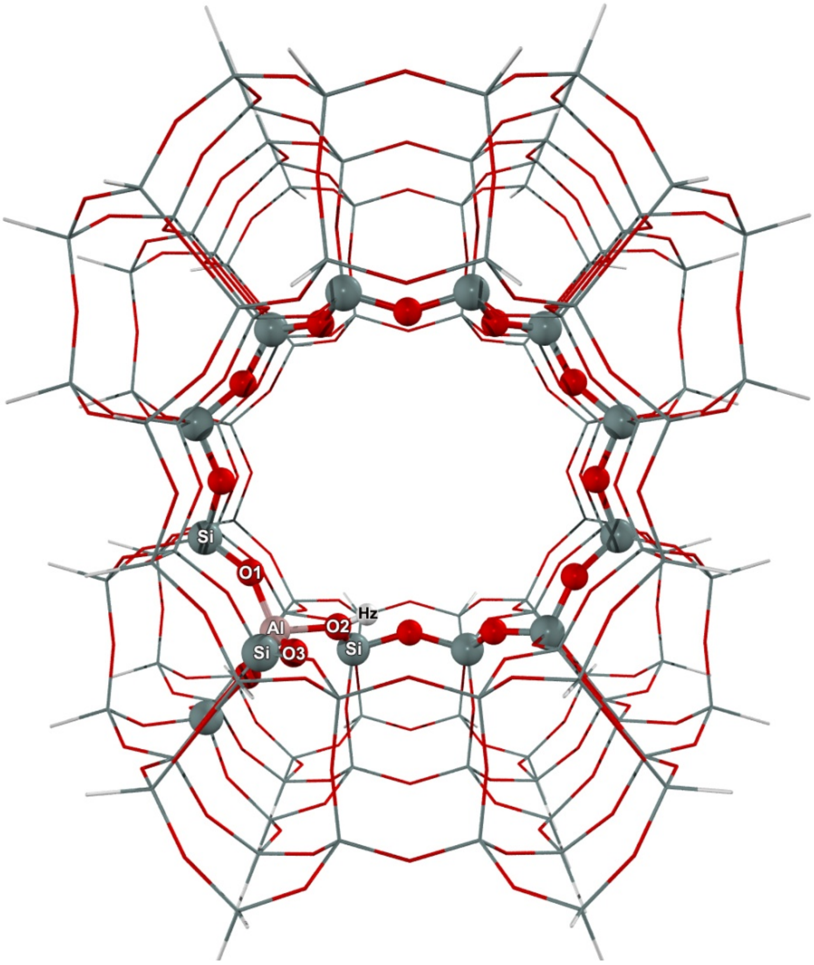


Figure 3 The ONIOM model of the 120T cluster of the H-MOR zeolite. Atoms belonging to the quantum region are drawn as balls and sticks while the lines represent universal force field (UFF): (a) front view shows the 12-membered-ring window of the straight channel (b) side view of the 12-membered-ring straight channel.

(b)

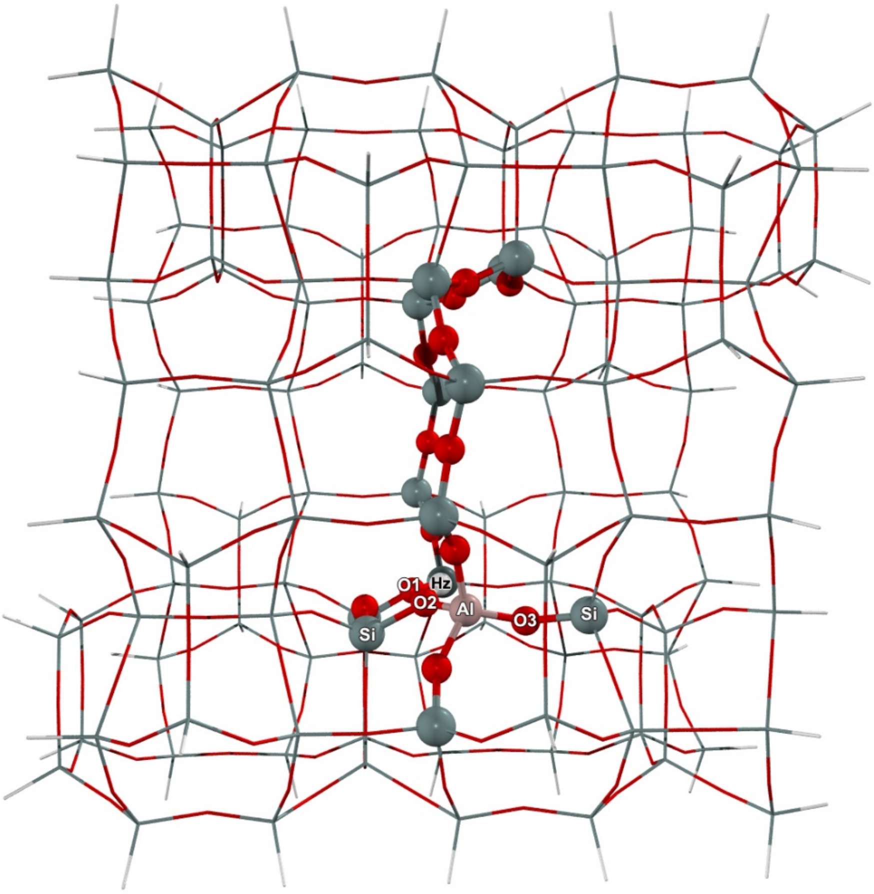


Figure 3 (Continued)

The total energy of the whole system can be expressed by within the framework of the ONIOM methodology (Jansang *et al.*, 2007; Pantu *et al.*, 2007) by:

$$E_{ONIOM2} = E_{Low}^{REAL} + \left(E_{High}^{CLUSTER} - E_{Low}^{CLUSTER}\right)$$

The superscript REAL means the whole system and the superscript CLUSTER means the active region. The subscripts High and Low mean high- and low-level methodologies used in the ONIOM calculation.

RESULTS AND DISCUSSION

In this study, the dehydration of ethanol to ethylene over H-MOR zeolite is investigated using the ONIOM method. The reaction is considered to proceed through the concerted and stepwise pathways. Additionally, the effects of coadsorbed water are studied in the part of hydrous ethanol dehydration.

1. Ethanol dehydration

1.1 Concerted mechanism

The ethanol dehydration to ethylene starts with the adsorption of an ethanol molecule on the active site of H-MOR zeolite. Then, the ethanol C-O bond cleavage to generate water and C=C double bond formation to generate an ethylene molecule are occurred in one step (equation 1):

$$C_2H_5OH + \text{H-MOR} \rightleftharpoons C_2H_4 + \text{H-MOR} + H_2O \qquad (1)$$

Figure 4 and Table 1 show the optimized structures and selected geometric parameters of the reactant, transition state and products. The reaction starts with the adsorption of an ethanol molecule on the acidic proton at the active site of H-MOR zeolite. The adsorption energy is computed to be -28.7 kcal mol^{-1}, which is reasonable compared with the experimental measurement of ethanol adsorption in H-ZSM5 of -31.1 kcal mol^{-1} (Lee *et al.,* 1997). This strong interaction is the result of two hydrogen bonds: one between the oxygen atom of ethanol and the zeolite proton (O4-Hz), with a distance of 1.37 Å, and another between the ethanol proton and the adjacent oxygen atom from the Al tetrahedron (O3-H1) with a distance of 1.89 Å. The acidic O2-Hz bond distance of zeolite is increased from 0.97 to 1.09 Å. At the transition state, the acidic proton of the zeolite (Hz) is protonated to the oxygen atom of the ethanol molecule (O4), as indicated by the distance of Hz proton to the ethanol oxygen atom (O4) 0.97 Å and the breaking C1-O4 bond of ethanol molecule (2.50 Å).

Simultaneously the C-C bond is contracted to 1.38 Å and the C2-H2 bond distance is elongated from 1.09 to 1.30 Å leading to the C-C double bond formation and the creation of ethylene molecule. This transition state is confirmed by the frequency calculation with one imaginary frequency at -740.58 cm^{-1}. The activation energy for this step is calculated to be 48.8 kcal mol^{-1}. The produced ethylene molecule is adsorbed on the acid site via the π-interaction. Finally, ethylene and water are desorbed and the acid site is regenerated by requiring energy of 17.3 kcal mol^{-1}. The evaluated energy profile of all species involved in this mechanism is illustrated in Figure 5.

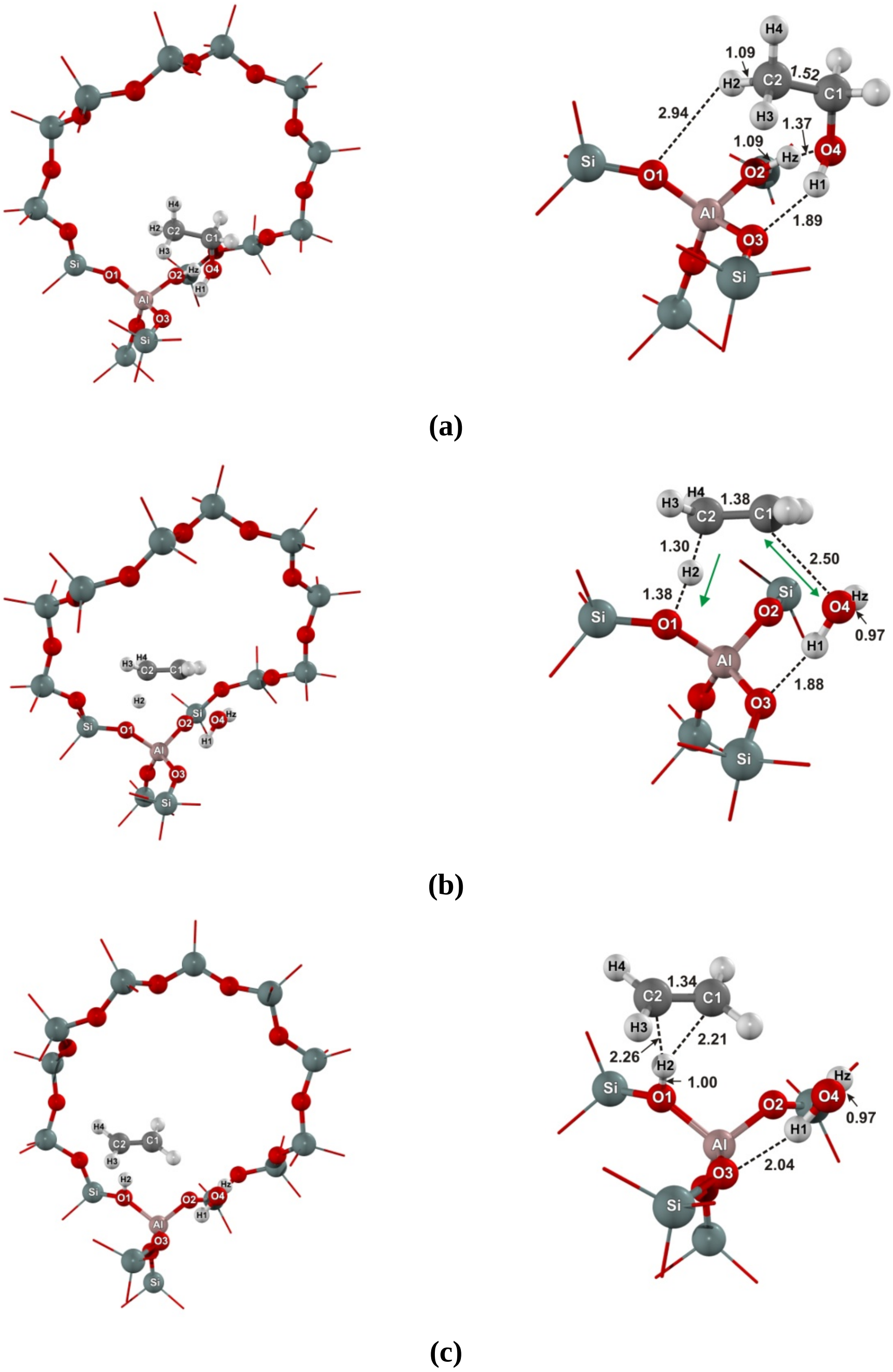


Figure 4 Optimized complexes on 14T/120T H-MOR zeolite (Concerted A): (a) ethanol adsorption complexes; RT_CA, (b) transition state complexes; TS_CA, and (c) ethylene and water adsorption complexes; PRD_CA.

Table 1 The optimized geometric parameters of isolated molecule, ethanol adsorption complexes (RT_CA), transition state (TS_CA), and ethylene & water adsorption complexes (PRD_CA) of concerted ethanol dehydration mechanism without co-adsorb water (Concerted A).

	Isolated cluster	RT_CA	TS_CA	PRD_CA
Distances				
C1-C2	1.52^{EtOH*} ; 1.33^{C2H4*}	1.52	1.38	1.34
C1-O4	1.42	1.45	2.50	3.32
O4-Hz	-	1.37	0.97	0.97
O2-Hz	0.97	1.09	2.53	2.54
C2-H2	1.10	1.09	1.30	2.26
C1-H2	-	-	2.18	2.21
O1-H2	0.97	2.94	1.38	1.00
O4-H1	0.97^{EtOH*} ; 0.96^{H2O*}	0.98	0.98	0.97
O3-H1	-	1.88	1.88	2.04
Al-O1	1.65	1.65	1.74	1.81
Al-O2	1.80	1.76	1.67	1.65
Al-O3	1.65	1.67	1.67	1.65
Si1-O1	1.57	1.57	1.62	1.67
Si2-O2	1.68	1.65	1.58	1.59
Si3-O3	1.60	1.61	1.60	1.60
Angles				
Si1-O1-Al	149.2	149.3	139.5	138.4
Si2-O2-Al	127.2	127.2	131.5	130.3
Si3-O3-Al	129.5	130.3	134.6	136.7
H3-C2-H4	108.2^{EtOH*} ; 116.2^{C2H4*}	107.6	116.1	116.9

^{EtOH*} = optimized geometric parameter of ethanol molecule

^{C2H4*} = optimized geometric parameter of ethylene molecule

^{H2O*} = optimized geometric parameter of ethanol molecule

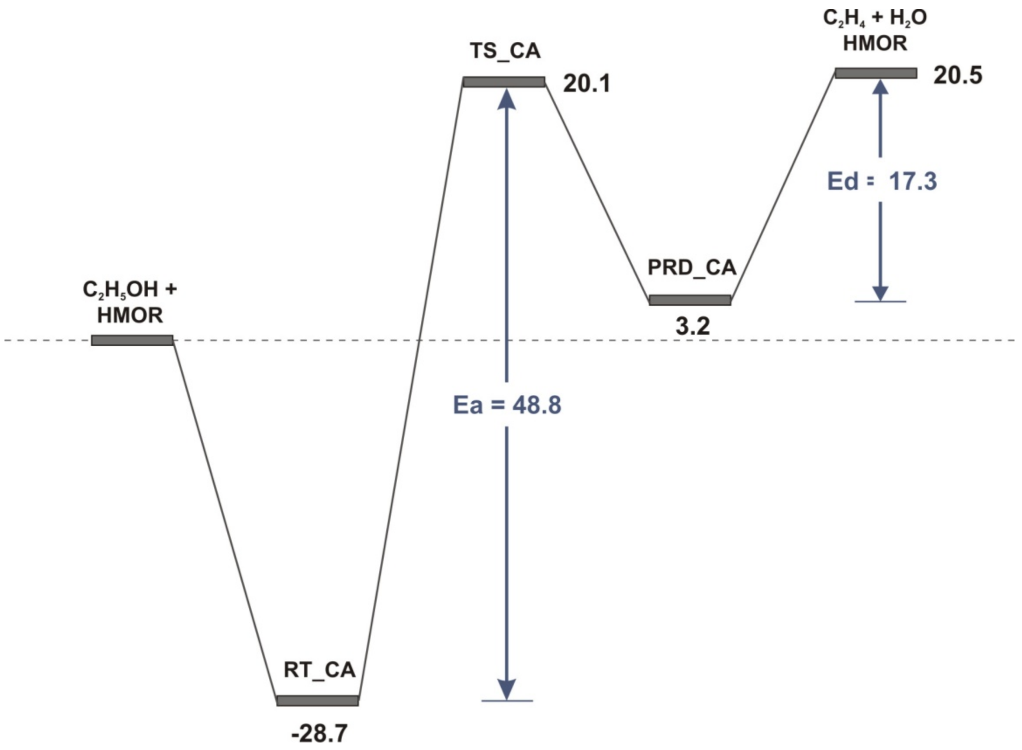


Figure 5 The energy profile for concerted mechanism A.

1.2 Stepwise mechanism

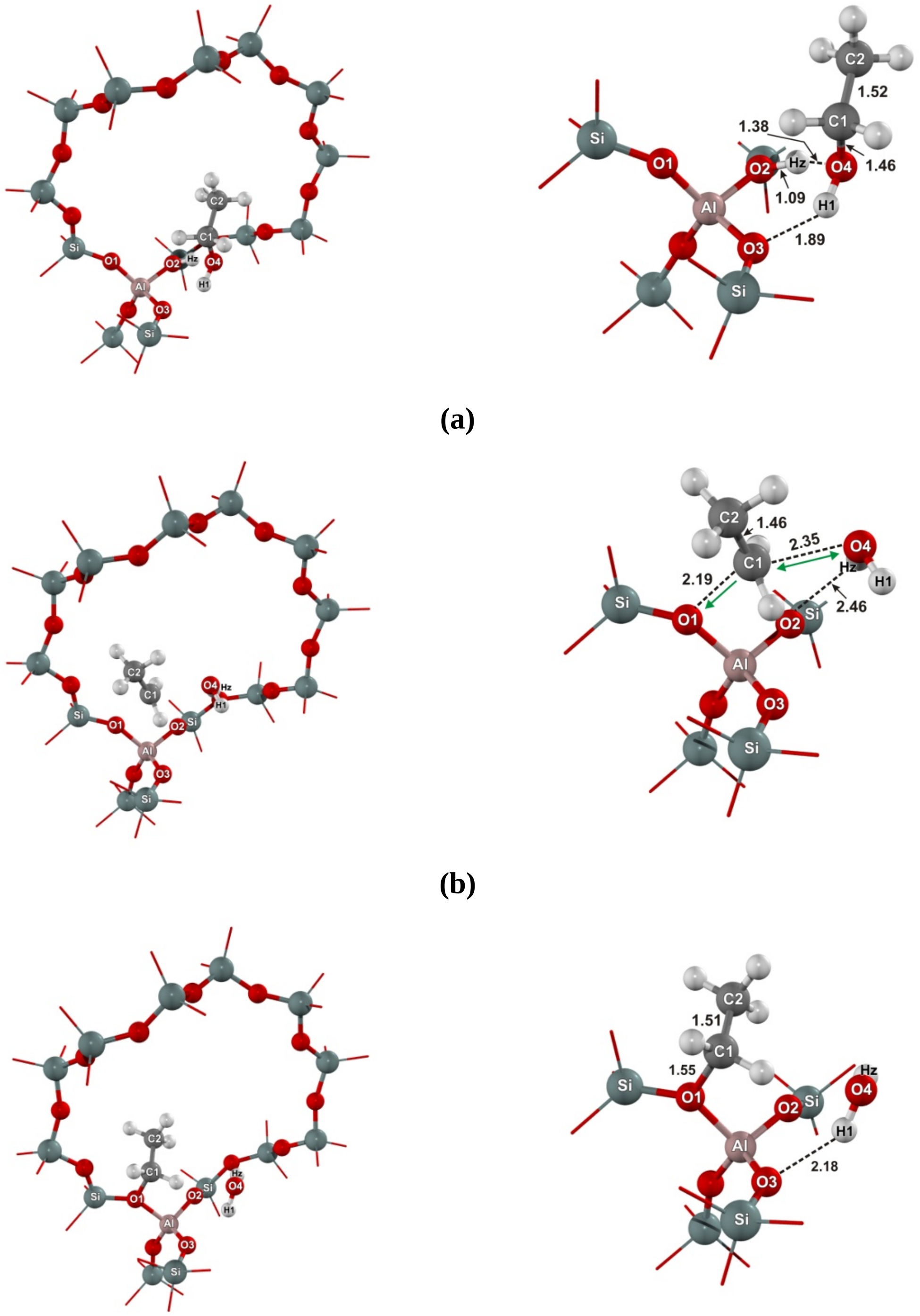
Alternatively, the dehydration of ethanol to ethylene can be considered to proceed in a stepwise mechanism through the formation of ethoxide intermediate that was been experimentally observed (Kondo *et al.*, 2005; Barthos *et al.*, 2006). The stepwise mechanism consists of two steps: the dehydration of ethanol to ethoxide and the deprotonation of ethoxide to ethylene.

1.2.1 The dehydration of ethanol to ethoxide

In this step (Step 1A), an adsorbed ethanol molecule is dehydrated, forming an ethoxide group attached to the basic oxygen of the zeolite and a water molecule (equation 2):

$$C_2H_5OH + H\text{-}MOR \rightleftharpoons C_2H_5\text{-}MOR + H_2O \qquad (2)$$

Figure 6 and Table 2 show the optimized structures and selected geometric parameters of the reactant, transition state and intermediates. The starting adsorption complex for this step is somewhat different from the adsorption complex (RT_CA) for the concerted mechanism by the rotation of the ethyl group of the ethanol molecule to approach the oxygen atom of zeolite (O1). The adsorption energy is calculated to be -27.6 kcal mol^{-1} which is slightly less than that of the RT_CA complex. Then, the surface ethoxy species is formed through the transition state (TS_S1A). At the transition state, the acidic proton of the zeolite is protonated to the oxygen atom of ethanol, and the C1-O4 bond is broken to form a water molecule and an ethyl group which moves toward the basic oxygen of zeolite. This transition state is confirmed by the frequency calculation with the imaginary frequency at -247.0 cm^{-1}. The calculated activation barrier is 45.0 kcal mol^{-1}. Subsequently, the ethyl group is attached by forming covalent bond to the basic oxygen atom of zeolite (C1-O1 1.55 Å). The reaction energy for this step of reaction is almost thermo neautral (-3.5 kcal mol^{-1}). Then the desorption of water require an energy of 14.3 kcal mol^{-1}.



(a)

(b)

(c)

Figure 6 Optimized complexes on 14T/120T H-MOR zeolite (Step 1A): (a) ethanol adsorption complexes; RT_SA, (b) transition state complexes; TS_S1A, and (c) ethoxide and water adsorption complexes; ETX_1W.

Table 2 The optimized geometric parameters of isolated molecule, ethanol adsorption complexes (RT_SA), transition state (TS_S1A), and ethoxide & water adsorption complexes (ETX_1W) of ethanol dehydration to ethoxide process over H-MOR using ONIOM2 (Step 1A).

	Isolated cluster	RT_SA	TS_S1A	ETX_1W
Distances				
C1-C2	1.52^{EtOH*}	1.52	1.46	1.51
C1-O4	1.42^{EtOH*}	1.46	2.35	3.32
C1-O1	-	4.16	2.19	1.55
O4-Hz	0.96^{H2O*}	1.38	0.98	0.97
O2-Hz	0.97	1.09	2.46	2.56
H1-O3	-	1.89	3.59	2.18
Al-O1	1.65	1.65	1.73	1.80
Al-O2	1.80	1.76	1.68	1.66
Si1-O1	1.57	1.57	1.61	1.68
Si2-O2	1.68	1.65	1.59	1.58
Angles				
Si1-O1-Al	149.3	149.8	139.5	133.6
Si2-O2-Al	127.2	126.7	130.1	132.4
Hz-O4-H1	103.7^{H2O*}	92.7	102.8	102.9

^{EtOH*} = optimized geometric parameter of ethanol molecule

^{H2O*} = optimized geometric parameter of ethanol molecule

1.2.2 The deprotonation of ethoxide to ethylene process

In this step, the deprotonation of the surface ethoxy species to form adsorbed ethylene (equation 3) is considered.

$$C_2H_5\text{-MOR} \rightleftharpoons C_2H_4 + \text{H-MOR} \qquad (3)$$

Figure 7 and Table 3 show the optimized geometries and selected geometric parameters of the intermediate, transition state and product. The surface ethoxide species (ETX_0W) has a relative energy of 10.8 kcal mol^{-1}compared to the isolated reactants. At the transition state (TS_S2A), there is one imaginary frequency at -275.9 cm^{-1} that corresponds to the proton of ethoxide being transferred back to the zeolite, thereby regenerating the acidic site, while the C1-C2 bond of the ethoxide is shortened from 1.51 to 1.42 Å and the covalent C1-O1 bond of the surface ethoxide is simultaneously breaking (2.27 Å). The energy barrier for the deprotonation is calculated to be 23.4 kcal mol^{-1}. The product of this step is an ethylene molecule adsorbed on the acidic site of H-MOR zeolite via the π-interaction (PRD_SB). Finally, the ethylene product is desorbed by requiring desorption energy of 11.4 kcal mol^{-1}. The evaluated energy profile of all species involved in the ethanol dehydration to ethoxide and the deprotonation of ethoxide to ethylene is illustrated in Figure 8.

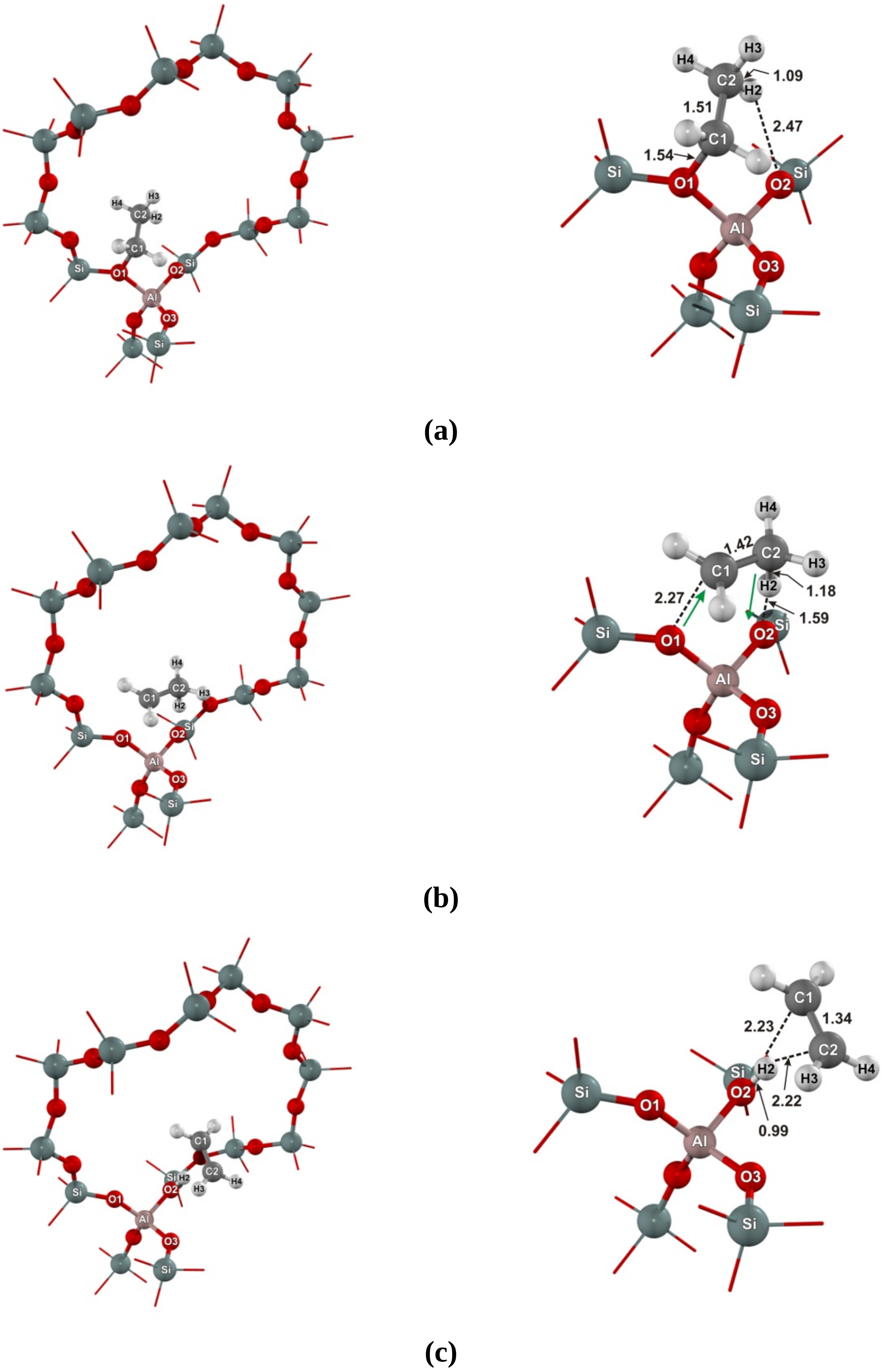


Figure 7 Optimized complexes on 14T/120T H-MOR zeolite (Step 2A): (a) ethoxide adsorption complexes; ETX_0W, (b) transition state complexes; TS_S2A, and (c) ethylene adsorption complexes; PRD_SA.

Table 3 The optimized geometric parameters of isolated molecule, ethoxide adsorption complexes (ETX_0W), transition state (TS_S2A), and ethylene adsorption complexes (PRD_SA) of ethylene formation process over H-MOR using ONIOM2 (Step 2A).

	Isolated cluster	ETX_0W	TS_S2A	PRD_SA
Distances				
C1-C2	1.33^{C2H4*}	1.51	1.42	1.34
C1-O1	-	1.54	2.27	4.21
H2-C2	1.10^{EtOH*}	1.09	1.18	2.22
H2-C1	-	-	2.05	2.23
H2-O2	0.97	2.47	1.59	0.99
Al-O1	1.65	1.82	1.72	1.65
Al-O2	1.80	1.65	1.69	1.79
Al-O3	1.65	1.64	1.66	1.65
Si1-O1	1.57	1.68	1.61	1.57
Si2-O2	1.68	1.58	1.60	1.67
Si3-O3	1.60	1.58	1.59	1.60
Angles				
Si1-O1-Al	149.3	133.8	139.2	149.2
Si2-O2-Al	127.2	132.0	131.2	127.3
Si3-O3-Al	103.7	138.2	134.8	130.5
H3-C2-H4	116.2^{C2H4*}	107.8	115.0	116.3

^{EtOH*} = optimized geometric parameter of ethanol molecule

^{C2H4*} = optimized geometric parameter of ethylene molecule

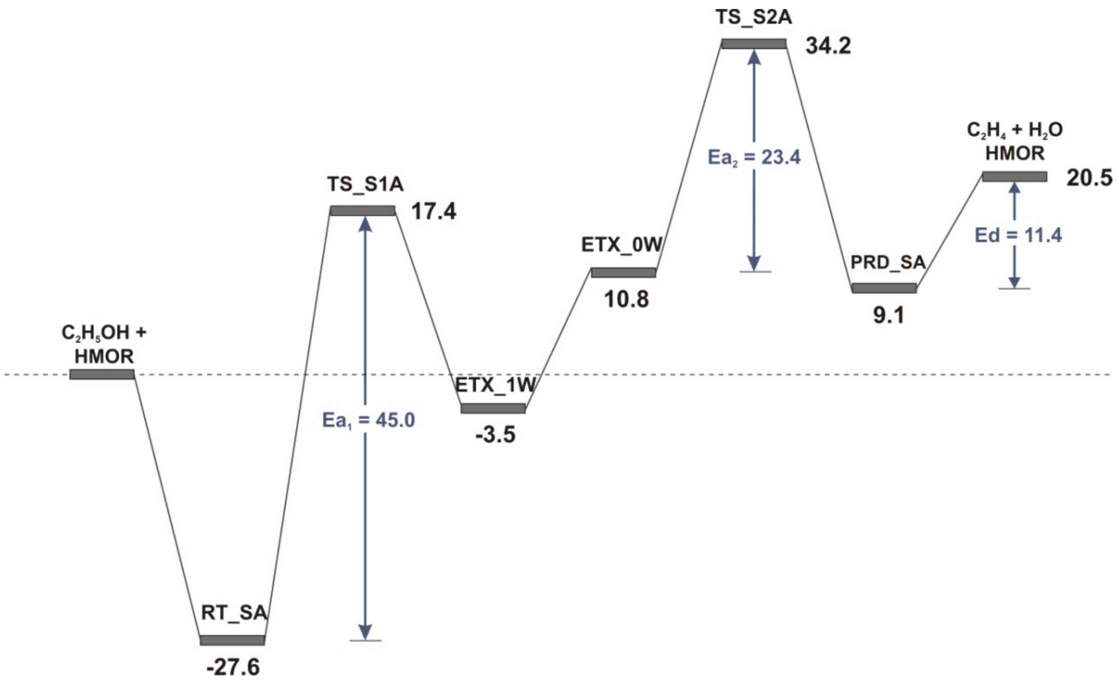


Figure 8 The energy profile for stepwise mechanism A.

1.3 Comparison of concerted and stepwise mechanism pathways

The complete energetic profiles of both concerted and stepwise mechanisms are shown on the same diagram in Figure 9. For the concerted mechanism, the activation barrier is 48.8 kcal mol^{-1}. For the stepwise mechanism the rate determining step is the first step of dehydration of ethanol to ethoxide with an activation barrier of 45.0 kcal mol^{-1}. The subsequent deprotonation step requires a less activation energy of 23.4 kcal mol^{-1}. Therefore, the dehydration of ethanol to ethylene slightly favors the stepwise mechanism. This is also in line with the experiment that has detected a stable ethoxide intermediate for ethanol dehydration on zeolite.

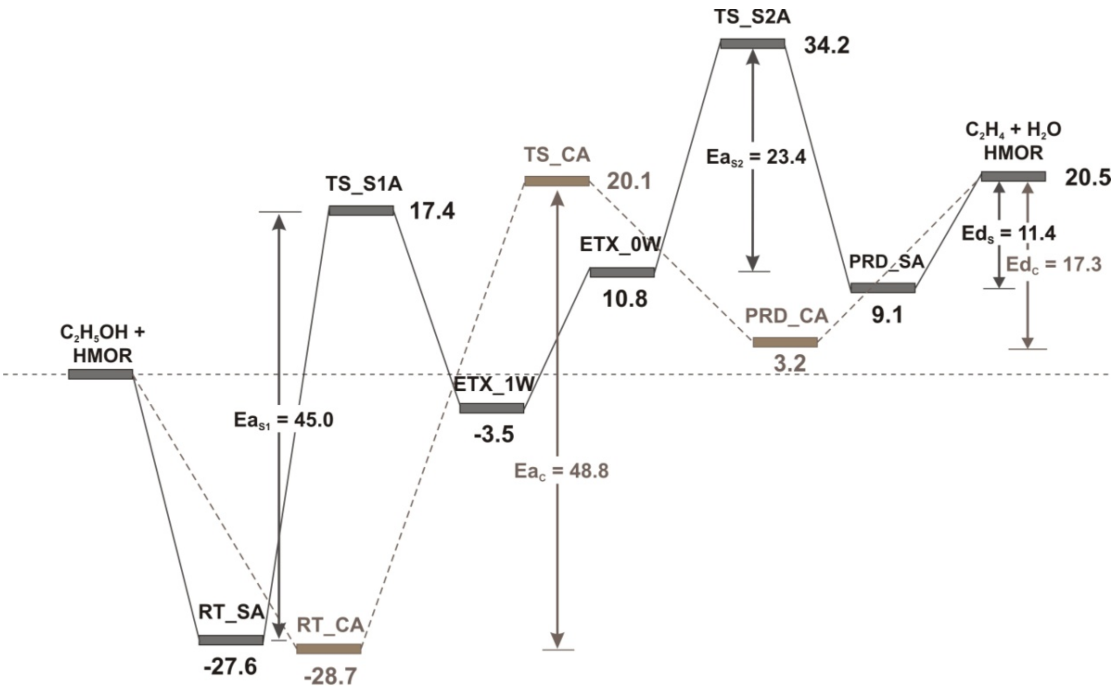


Figure 9 Relative energies (kcal mol^{-1}) of concerted (dash line) and stepwise (solid line) mechanisms of ethanol dehydration to ethylene over H-MOR zeolite in the absence of water.

2. Hydrous ethanol dehydration

In industrial processes, hydrous ethanol is almost always used because complete removal of water from ethanol feed would require an additional costly process. Bio-ethanol which usually has a high water content is favored as the reactant. Thus water could play an important role in the dehydration of ethanol to ethylene.

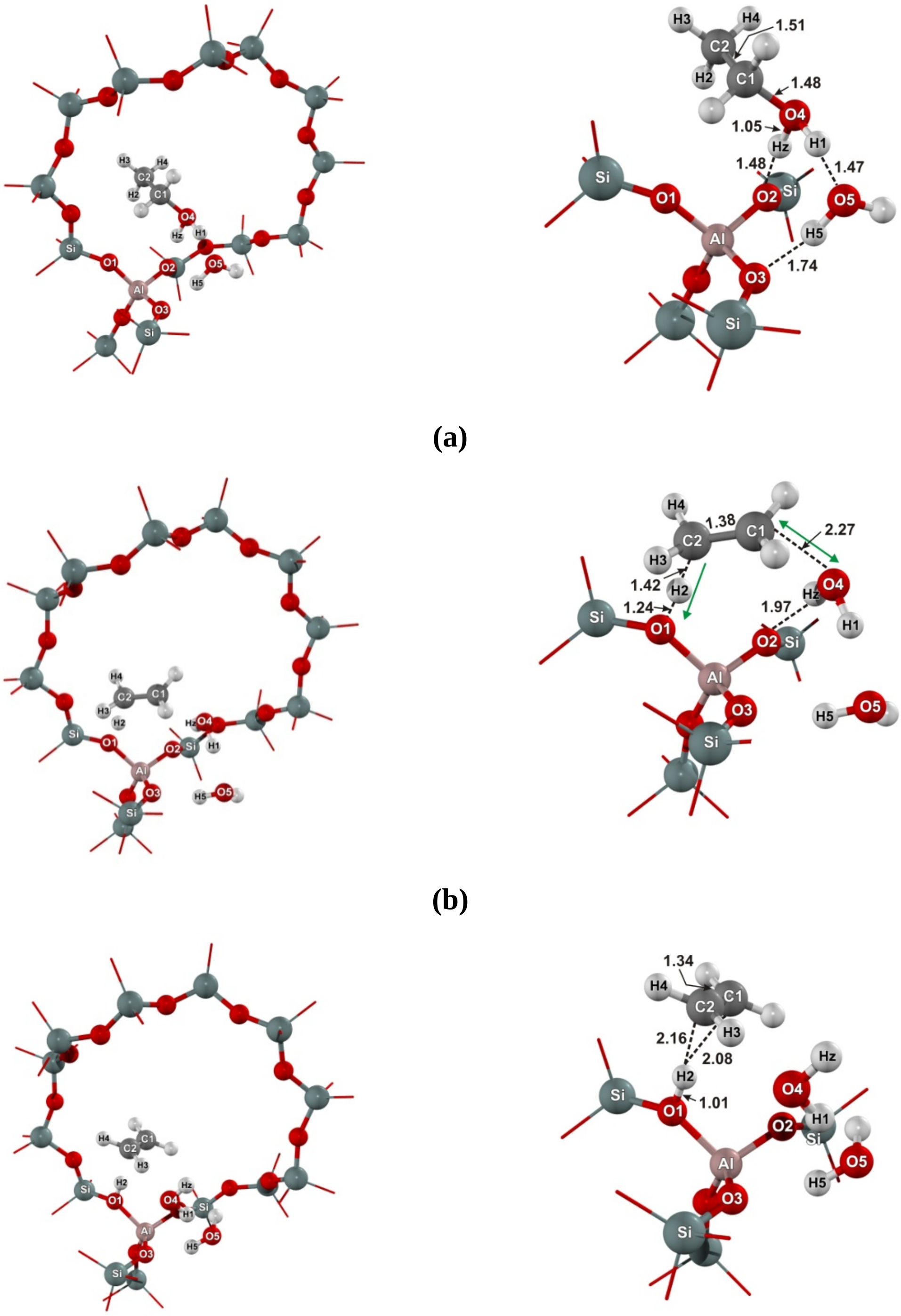
The initial step of ethanol dehydration to ethylene in the presence of water starts with the adsorption of a water molecule on H-MOR zeolite and then the ethanol molecule comes to coadsorb on the same site (Figure 10a). The calculated adsorption energy of ethanol is -24.0 kcal mol^{-1}. It can be noted that in the presence of water, the adsorbed ethanol molecule is protonated by the acidic proton of zeolite to form the ethoxonium ion ($CH_3CH_2OH_2^+$) which does not occur in the case of ethanol adsorption without water. Due to the formation of three hydrogen bonds in the coadsorption complex, the structures of ethanol and the active site of H-MOR zeolite change considerably. In addition to the O4-Hz bond (1.05 Å), H1-O5 and H5-O3 hydrogen bonds with distances of 1.47 and 1.74 Å, respectively, are formed. The C1-C2 and C1-O4 bond distances of ethanol are 1.51 and 1.48 Å, respectively while, the O2-Hz and O4-Hz bond distances are 1.48 and 1.05 Å, respectively. After the adsorption process has taken place, the ethoxonium ion is converted to ethylene via the dehydration that can proceed through either a concerted or a stepwise mechanism.

2.1 Concerted mechanism

In this mechanism, the deprotonation and the C-O bond destruction of the ethanol molecule occur simultaneously to give the ethylene product (equation 4):

$$C_2H_5OH + H_2O\cdots H\text{-}MOR \rightleftharpoons C_2H_4\cdots H\text{-}MOR + 2H_2O \qquad (4)$$

Figure 10 and Table 4 show the optimized structures and selected geometric parameters of the reactant, transition state and products, respectively. The coadsorbed water molecule is associated with the ethoxonium ion ($CH_3CH_2OH_2^+$) on the active site of zeolite. At the transition state, the C1-O4 bond of the ethoxonium breaking (2.27 Å) to form water and ethylene molecule simultaneously with the C2-H2 bond distance of ethyl group is elongated from 1.09 to 1.42 Å while the new bond between O1 and H2 is forming (1.24 Å). This transition state can be confirmed by the frequency calculation with one imaginary frequency at -1,106.68 cm^{-1}. The activation barrier for this step is calculated to be 54.8 kcal mol^{-1}, ethylene and water molecules are formed (PRD_CB) as the products. Finally, ethylene and water molecules are desorbed from the active site by requiring energy of 7.3 kcal mol^{-1}. The evaluated energy profile of all species involved in this mechanism is illustrated in Figure 11.



(a)

(b)

(c)

Figure 10 Optimized complexes on 14T/120T H-MOR zeolite (Concerted B): (a) ethanol and water adsorption complexes; RT_CB, (b) transition state complexes; TS_CB, and (c) ethylene and waters adsorption complexes; PRD_CB.

Table 4 The optimized geometric parameters of isolated molecule, ethanol & water adsorption complexes (RT_CB), transition state (TS_CB), and ethylene & water adsorption complexes (PRD_CB) of concerted ethanol dehydration mechanism with co-adsorb water (Concerted B).

	Isolated cluster	H_2O/H-MOR	RT_C2	TS_C2	PRD_C2
Distances					
C1-C2	1.52	-	1.51	1.38	1.34
C1-O4	1.42	-	1.48	2.27	3.22
C2-H2	1.10	-	1.09	1.42	2.16
C1-H2	-	-	-	2.43	2.08
O1-H2	0.97	-	3.23	1.24	1.01
O4-Hz	-	-	1.05	0.97	0.96
O2-Hz	0.97	1.05	1.48	1.97	5.82
O5-H1	-	-	1.47	1.82	1.83
O3-H5	-	1.80	1.74	1.85	1.96
O4-H1	0.97^{EtOH*} ; 0.96^{H2O*}	-	1.05	0.98	0.98
Al-O1	1.65	1.65	1.67	1.75	1.80
Al-O2	1.80	1.77	1.71	1.67	1.66
Al-O3	1.65	1.68	1.68	1.67	1.65
Si1-O1	1.57	1.57	1.57	1.64	1.66
Si2-O2	1.68	1.66	1.61	1.59	1.59
Si3-O3	1.60	1.61	1.61	1.60	1.60
Angles					
Si1-O1-Al	149.3	149.7	148.9	137.4	138.6
Si2-O2-Al	127.2	126.8	128.3	130.8	130.4
Si3-O3-Al	129.5	129.9	130.6	134.8	136.0
H3-C2-H4	108.2^{EtOH*} ; 116.2^{C2H4*}	-	109.1	116.0	117.5

^{EtOH*} = optimized geometric parameter of ethanol molecule

^{C2H4*} = optimized geometric parameter of ethylene molecule

^{H2O*} = optimized geometric parameter of ethanol molecule

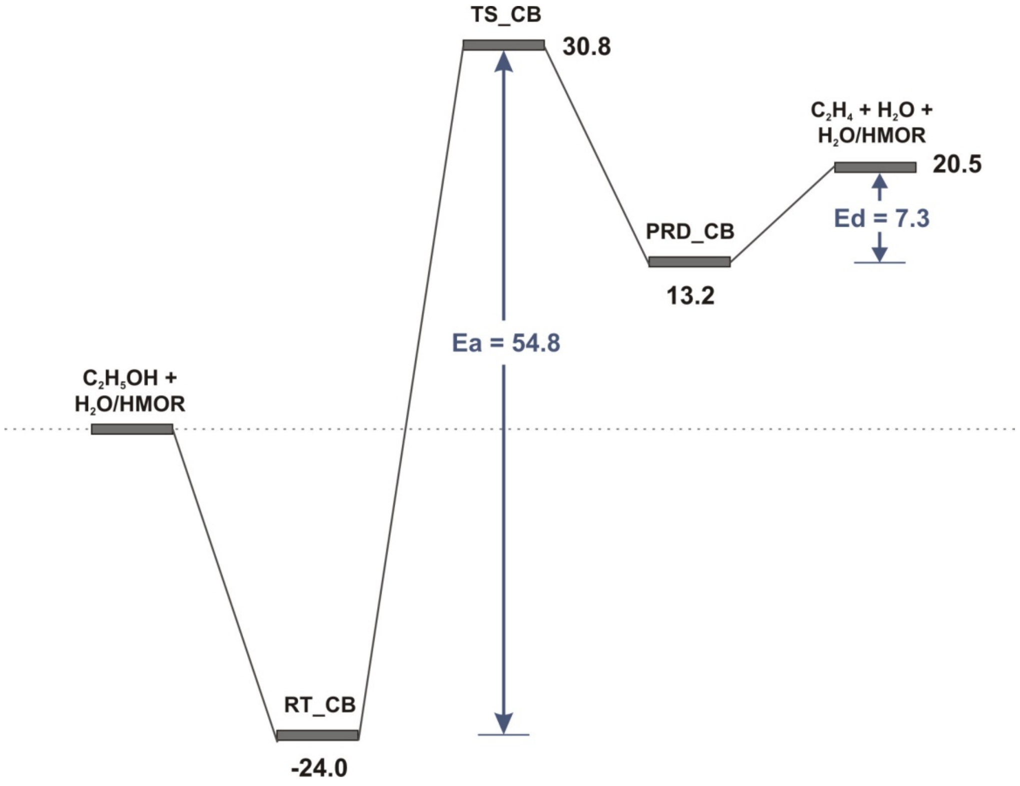


Figure 11 The energy profile for concerted mechanism B.

2.2 Stepwise mechanism

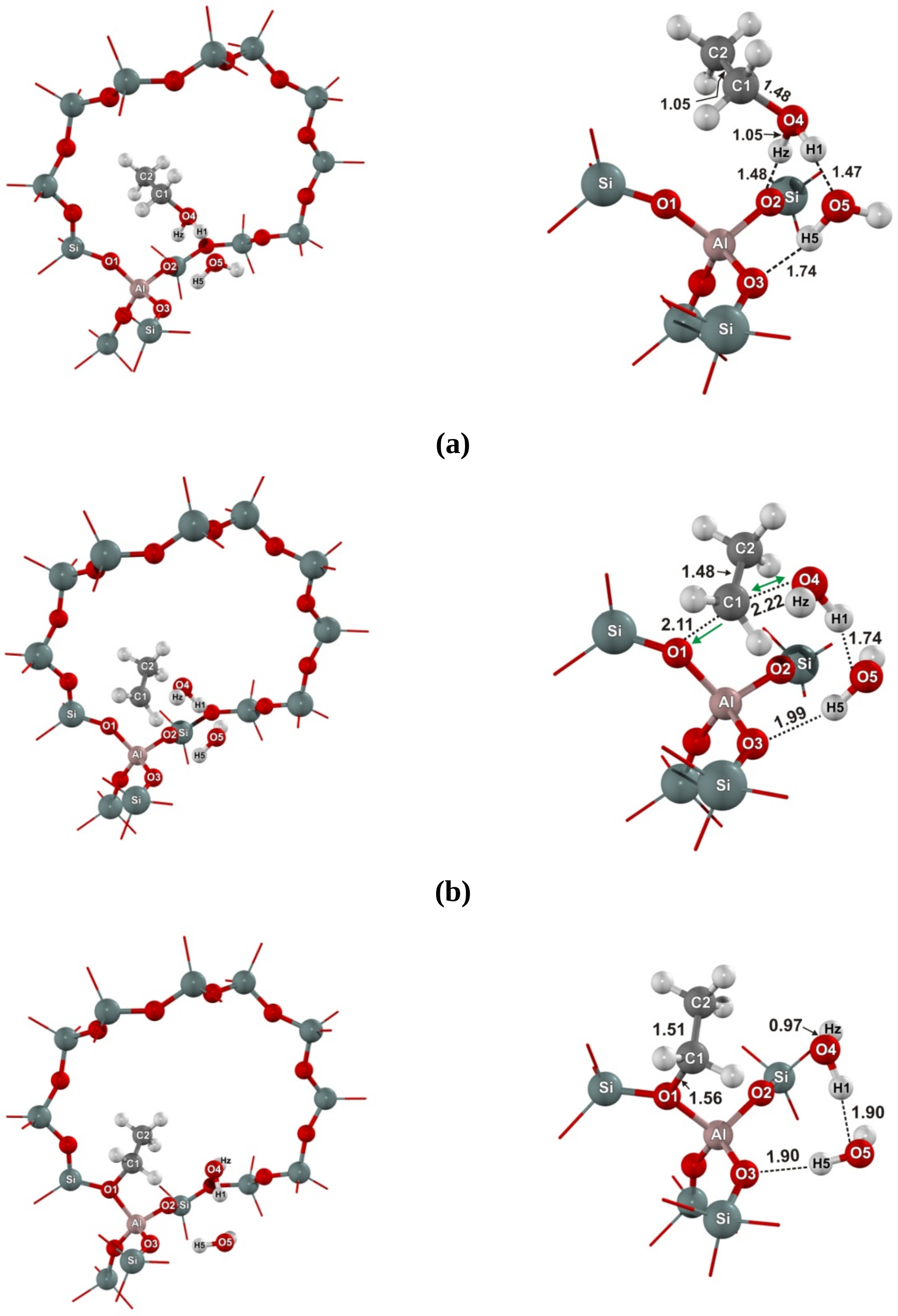
Alternatively, the dehydration of ethanol to ethylene can proceed in a stepwise mechanism through the formation of ethoxide intermediates that have also been observed in experiments (Kondo *et al.*, 2005; Barthos *et al.*, 2006). The two processes involved are the dehydration of ethanol to ethoxide and the deprotonation of ethoxide to ethylene similar to the case without water.

2.2.1 The dehydration of ethanol to ethoxide process

In this process, the ethanol molecule is dehydrated and an ethyl group is attached to the basic site of the zeolite. From there, the surface ethoxy species is formed within the presence of two water molecules (equation 5):

$$C_2H_5OH + H_2O + H\text{-}MOR \rightleftharpoons C_2H_4\text{-}MOR + 2H_2O \qquad (5)$$

Figure 12 and Table 5 show the optimized structures and selected geometric parameters of the reactant, transition state and intermediates, respectively. The starting coadsorbed structure (RT_SB) is the same as the starting structure of concerted mechanism (RT_CB). At the TS_S1B transition state, the C1-O4 bond of ethoxonium (2.22 Å) is breaking to form a water molecule (Hz-O3-H1) while the ethyl group gets closer to the basic oxygen of zeolite with an O1-C1 distance of 2.06 Å. The O4-C1-O1 bond angle is 154.4°. The imaginary frequency of this transition state is 348 cm^{-1}. The activation barrier is calculated to be 41.2 kcal mol^{-1}. After the transition state, the ethoxide intermediate and a water molecule (ETX_2W) are formed. Their relative energy is 6.8 kcal mol^{-1}.



(a)

(b)

(c)

Figure 12 Optimized complexes on 14T/120T H-MOR zeolite (Step 1B): (a) ethanol and water adsorption complexes; RT_SB, (b) transition state complexes; TS_S1B, and (c) ethoxide and two water adsorption complexes; ETX_2W.

Table 5 The optimized geometric parameters of isolated molecule, ethanol & water adsorption complexes (RT_SB), transition state (TS_S1B), and ethoxide & two water adsorption complexes (ETX_2W) of ethanol dehydration to ethoxide process over H-MOR using ONIOM2 (Step 1B).

	Isolated cluster	H_2O/H-MOR	RT_SB	TS_S1B	ETX_2W
Distances					
C1-C2	1.52^{EtOH*}	-	1.51	1.48	1.51
C1-O4	1.42^{EtOH*}	-	1.48	2.22	3.22
C1-O1	-	-	3.32	2.11	1.56
O4-Hz	0.96^{H2O*}	-	1.05	0.97	0.97
O2-Hz	0.97	1.05	1.48	5.02	3.03
O4-H1	0.96^{H2O*}	-	1.05	1.00	0.98
O5-H1	-	-	1.47	1.74	1.90
O3-H5	-	1.80	1.74	1.99	1.90
Al-O1	1.65	1.65	1.67	1.73	1.79
Al-O2	1.80	1.77	1.71	1.67	1.66
Al-O3	1.65	1.68	1.68	1.68	1.66
Si1-O1	1.57	1.57	1.57	1.61	1.68
Si2-O2	1.68	1.66	1.61	1.59	1.58
Si3-O3	1.60	1.61	1.61	1.60	1.60
Angles					
Si1-O1-Al	149.3	149.7	148.9	139.9	133.5
Si2-O2-Al	127.2	126.8	128.3	130.4	132.7
Si3-O3-Al	129.5	129.9	130.6	134.8	136.2
Hz-O4-H1	103.7^{H2O*}	-	99.2	106.3	102.2

^{EtOH*} = optimized geometric parameter of ethanol molecule

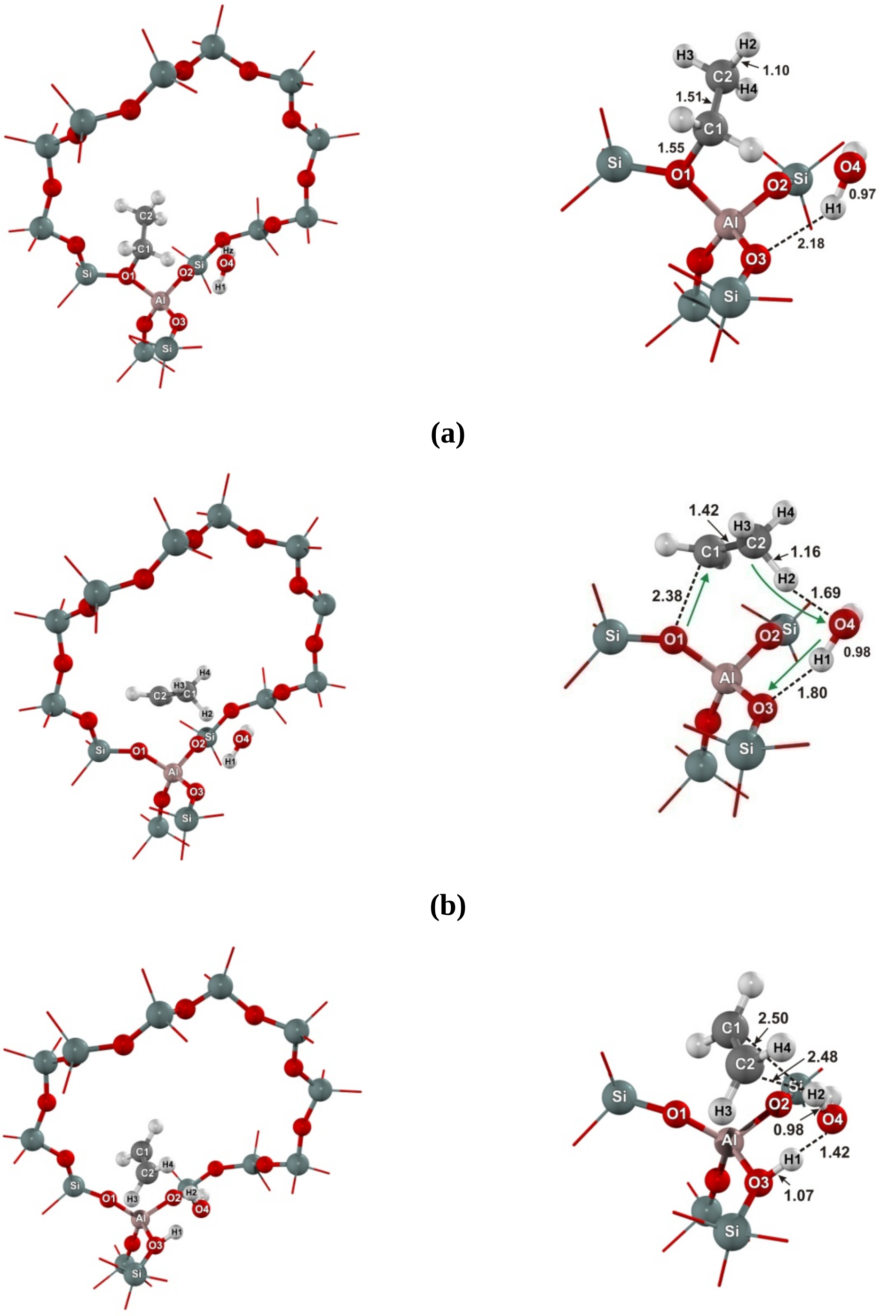
^{H2O*} = optimized geometric parameter of ethanol molecule

2.2.2 The deprotonation of ethoxide to ethylene process

In this process, the water-assisted deprotonation of ethoxide leads to the formation of ethylene (equation 6):

$$C_2H_5\text{-MOR} + H_2O \rightleftharpoons C_2H_4 + H_2O + \text{H-MOR} \qquad (6)$$

Figure 13 and Table 6 show the optimized structures and selected geometric parameters of the intermediates, transition state and products, respectively. The reaction starts with ethoxide and a water molecule (ETX_1W). In the transition state (TS_S2B), the proton of ethoxide is transferred to the oxygen of the water molecule that is hydrogen-bound to an oxygen atom of zeolite. The C1-C2 bond distance is slightly shortened by about 0.09 Å and the proton of the water molecule is transferred to the zeolite regenerating the acidic site (O3-H1 bond). This transition state is confirmed by the imaginary frequency at 248 cm^{-1}. The calculated energy barrier is 22.2 kcal mol^{-1}. The ethylene product is formed and adsorbed via the π-interaction (PRD_SB). The adsorption energy of this complex is 9.4 kcal mol^{-1}. The desorption of ethylene and one water molecules from the pore of H-MOR zeolite requires 11.1 kcal mol^{-1}. The evaluated energy profile of all species involved in the ethanol dehydration to ethoxide and the deprotonation of ethoxide to ethylene is illustrated in Figure 14.



(a)

(b)

(c)

Figure 13 Optimized complexes on 14T/120T H-MOR zeolite (Step 2B): (a) ethoxide and water adsorption complexes; ETX_1W, (b) transition state complexes; TS_S2B, and (c) ethylene and water adsorption complexes; PRD_SB.

Table 6 The optimized geometric parameters of isolated molecule, ethoxide & water adsorption complexes (ETX_1W), transition state (TS_S2B), and ethylene & water adsorption complexes (PRD_SB) of ethylene formation process over H-MOR using ONIOM2 (Step 2B).

	Isolated cluster	ETX_1W	TS_S2B	PRD_SB
Distances				
C1-C2	1.33^{C2H4*}	1.51	1.42	1.34
C1-O1	-	1.55	2.38	3.73
H2-C2	1.10^{EtOH*}	1.10	1.16	2.48
H2-C1	-	-	2.16	2.50
H2-O4	0.96^{H2O*}	3.71	1.69	0.98
O4-H1	0.96^{H2O*}	0.97	0.98	1.42
O3-H1	0.97	2.18	1.80	1.07
Al-O1	1.64	1.80	1.71	1.65
Al-O2	1.66	1.66	1.68	1.67
Al-O3	1.80	1.65	1.68	1.76
Si1-O1	1.58	1.68	1.60	1.58
Si2-O2	1.60	1.58	1.59	1.60
Si3-O3	1.68	1.59	1.60	1.66
Angles				
Si1-O1-Al	143.3	133.6	140.0	145.6
Si2-O2-Al	126.2	132.4	131.1	127.8
Si3-O3-Al	132.3	136.5	133.6	131.1
H3-C2-H4	116.2^{C2H4*}	110.6	112.9	116.4

^{EtOH*} = optimized geometric parameter of ethanol molecule

^{C2H4*} = optimized geometric parameter of ethylene molecule

^{H2O*} = optimized geometric parameter of ethanol molecule

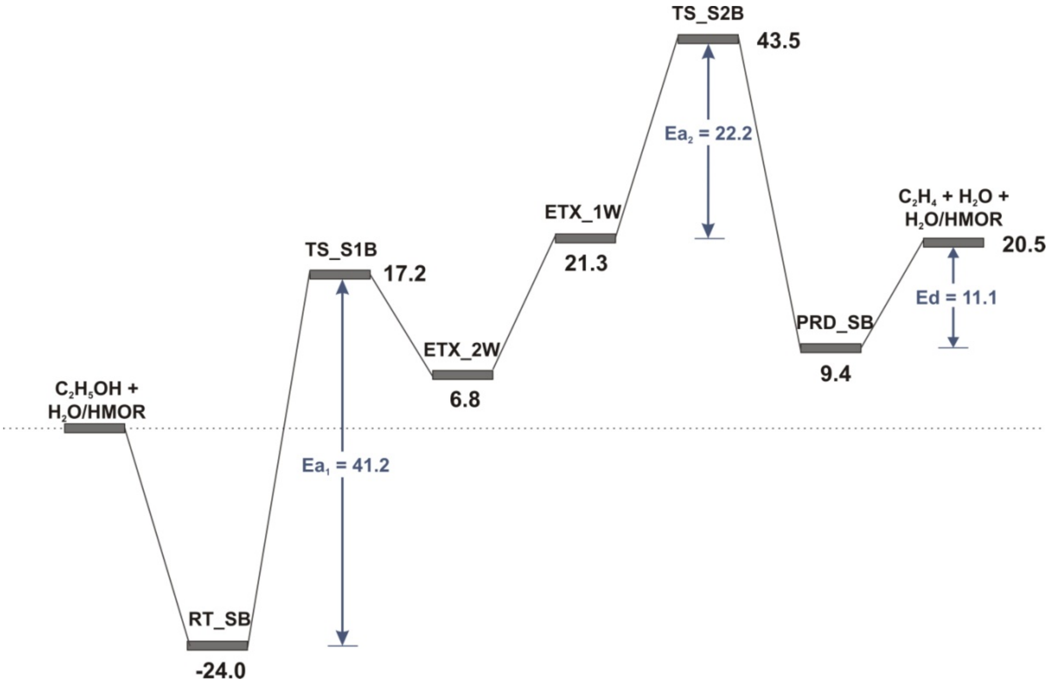


Figure 14 The energy profile for stepwise mechanism B.

2.3 Comparison of concerted and stepwise mechanism pathways

The complete energetic profiles for concerted and stepwise reaction pathways of the dehydration of ethanol to ethylene in the presence of water are illustrated in Figure 15. For the concerted mechanism, the activation barrier is 54.8 kcal mol^{-1}. In the stepwise mechanism the rate determining step is the dehydration of ethanol to ethoxide with an activation barrier of 41.2 kcal mol^{-1}. When the ethoxide intermediate is generated, it can be transformed to ethylene in the deprotonation process. This step requires activation energy of 22.2 kcal mol^{-1}. Since the relative energy of the transition state of the concerted mechanism is higher than that of both transition states of the stepwise mechanism, therefore the dehydration of hydrous ethanol to ethylene favors the stepwise mechanism.

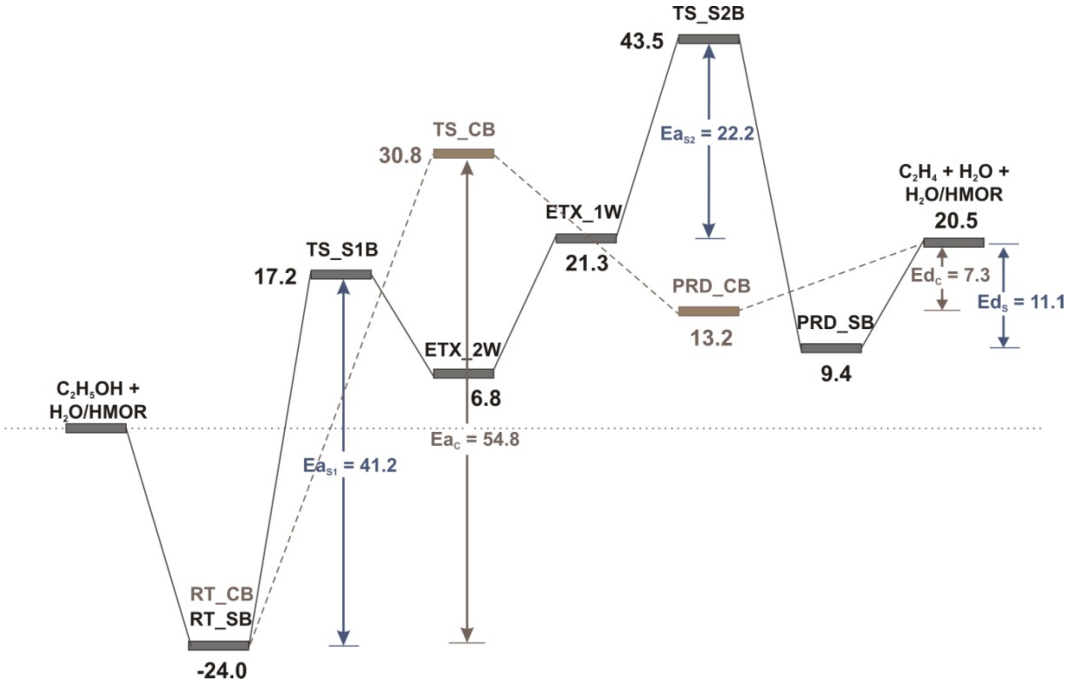


Figure 15 Relative energies (kcal mol^{-1}) of concerted (dash line) and stepwise (solid line) mechanisms of ethanol dehydration to ethylene over H-MOR zeolite in the presence of water.

CONCLUSION

The dehydration of ethanol to ethylene over the mordenite zeolite in the absence and presence of water has been investigated by using the ONIOM2 method with two different pathways: the stepwise and concerted mechanisms. The stepwise mechanism proceeds via 2 elementary steps, the dehydration of ethanol to ethoxide and the deprotonation of ethoxide to ethylene. The first step is the protonation and dehydration of adsorbed ethanol on the Bronsted acid site to form ethoxide surface species. This step is found to be the rate determining step of the reaction with the activation energy of 45.0 kcal mol^{-1}. For the concerted mechanism, the reaction occurs in a single step of simultaneous dehydration and deprotonation. The calculated activation energy is 48.8 kcal mol^{-1}.

In the presence of water, the dehydration of hydrous ethanol to ethylene shows the similar trend to the anhydrous ethanol dehydration. For the stepwise mechanism the calculated activation energy are 41.2 and 22.2 kcal mol^{-1} for the dehydration and the deprotonation steps, respectively. For the concerted mechanism, the activation energy is 54.8 kcal mol^{-1}. On the basis of our calculations it can be concluded, that the dehydration of ethanol to ethylene over H-MOR zeolite in the both of absence and presence of water preferably proceed via the stepwise.

Additionally, from the results it appears that water has a little effect on decreasing the activation energy by a few of kcal mol^{-1}. However, in the deprotonation step, it is more difficult to reverse the reaction when the water exists in this step. The activation barriers for the transformation of ethylene to ethoxide (reverse reaction) are 25.1 and 34.1 kcal mol^{-1} for the absence and presence of water, respectively. So, it is possible that water is the inhibitor for the reverse reaction.

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