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THESIS

STRUCTURES AND MECHANISMS INVESTIGATION ON ETHERIFICATION OF ISOBUTENE WITH ETHANOL CATALYZED BY ACIDIC BEA ZEOLITE

PANIDA SINGRA

A Thesis Submitted in Partial Fulfillment of
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Ethyl *tert*-butyl ether (ETBE) can be considered as a prime candidate for high-octane additive due to its outstanding environmentally friendly properties. ETBE easily mixes with gasoline, to make gasoline burn cleanly and completely, and reduce the vehicle’s greenhouse gas emission from the exhaust. In this work, the reaction mechanisms for ETBE production via the etherification reaction of isobutene and ethanol catalyzed by the H-BEA zeolite were investigated by using the full quantum calculations at the M06-2X/6-311+G(2df,2p) level of theory. A catalyzed reaction was proposed to occur via stepwise and concerted reaction mechanisms. The stepwise mechanism starts with the formation of a *tert*-butyl carbenium ion intermediate and then the intermediate reacts with ethanol yielding an ETBE product. The concerted reaction mechanism occurs in one step through the coadsorption of isobutene and ethanol leading to the ETBE formation. Besides the catalyzed reaction, an uncatalyzed reaction was investigated by the bare model system with the same level of theory as the catalyzed reaction. The overall reaction is found to be exothermic and this study gives the calculated reaction energy of -18.4 kcal/mol. The H-BEA zeolite is demonstrated to be an efficient catalyst in the etherification of isobutene with ethanol due to it having a lower energy barrier (8.7 kcal/mol for the concerted reaction mechanism and 9.6 kcal/mol for the stepwise reaction mechanism) as compared to that of the bare model system (53.3 kcal/mol).

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Finally, I would like to inscribe this thesis to my father, grandfather, grandmother, brother and especially, my mother who was a driving force me to accomplish. Although she would not be in today, I hope she would be proud of me.

Panida Singra
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LIST OF ABBREVIATIONS

Ads = Adsorption structure
BEA, B = Beta zeolite
BDE = Binding energy
DFT = Density functional theory
ETBE = Ethyl *tert*-butyl ether (2-Ethoxy-2-methylpropane)
e.g. = exempli gratia (example)
E_a = Activation energy
E_{des} = Desorption energy
FAU, Y = Faujasite zeolite
FER = Ferrierite zeolite
FTIR = Fourier transform infrared spectroscopy
GGA = Generzalized Gradient Approximation
HF = Hartree-Fock
IB = Isobutene
Int = Intermediate structure
K = Kelvin
kcal = Kilocalories
kJ = Kilojoules
LHSV = Liquid Hourly Space Velocity
MM = Molecular Mechanics
mm = Millimeter
MO = Molecular Orbital
MOR = Mordenite zeolite
MR = Membered ring
M06 = Minnesota 06
MPa = Mega Pascal
MP2 = The second-order Møller-Plesset perturbation theory
MTBE = Methyl *tert*-butyl ether (2-Methoxy-2-methylpropane)

LIST OF ABBREVIATIONS (Continued)

ONIOM = Our own N-layered Integrated Molecular Orbital and molecular Mechanics

pbc = Periodic Boundary Condition

PBE = Perdew-Burke-Ernzerhof

Prod = Product structure

pw = Plane wave basis set

PW91 = Perdew-Wang 91 functional

QM/MM = Quantum Mechanical/Molecular Mechanical

T = Tetrahedral

tert- = tertiary

TS = Transition State structure

UFF = Universal Force Fields

ZSM-5 = Zeolite Socony Mobil 5

STRUCTURES AND MECHANISMS INVESTIGATION ON ETHERIFICATION OF ISOBUTENE WITH ETHANOL CATALYZED BY ACIDIC BEA ZEOLITE

INTRODUCTION

Nowadays, the world is encountering a global warming crisis where greenhouse gas emission from vehicles is one of the important causes of problem. Increasing gasoline efficiency by raising the octane number leads to a clean and complete combustion of gasoline in engines, which, in turn, can reduce greenhouse gas emission.

Ethyl *tert*-butyl ether, ETBE (2-Ethoxy-2-methylpropane) is known as an antiknock additive reagent that blends with gasoline to increase the octane number. This is extensively brought into replace the toxic lead alkyl antiknock agents. Typically mixing of alkyl *tert*-butyl ethers with gasoline makes the fuel burn completely, thus it reduces the emission of unburned hydrocarbons from vehicle exhausts. In earlier times, Methyl *tert*-butyl ether, MTBE (2-Methoxy-2-methylpropane) was widely used in the production of high-octane gasoline. However, due to high solubility of MTBE in water makes it easily contaminated with groundwater making it difficult to be detoxified by a biodegradation process (Reuter *et al.*, 1998; Nadim *et al*., 2001). Therefore, at the present time, ETBE is more preferable because of its environmental advantages such as less soluble in water and using bio-ethanol, a renewable source, as a reagent. Moreover, the other advantages such as highest-octane blending values, lowest oxygen content, and low vapor pressure also made it a wise choice for being the most promising antiknock additive.

ETBE is straightforwardly synthesized by the etherification reaction of isobutene (2-methyl-1-propene) with ethanol (Ethyl alcohol). This reaction can be carried out both in liquid and vapor phase conditions. Conventionally, sulfonated acidic ion-exchange resin catalysts, such as Amberlyst-15, Amberlyst-35, and Lewatit

K2631 were used to catalyze the reaction for the synthesis of the ETBE. Although these catalysts are very efficient, they have some disadvantages such as low thermal stability and activity loss due to the leak of sulfuric acid and sulfonic groups from the catalyst, and consecutively cause corrosion problems to the reactor (Collignon *et al.*, 1997; Aboul-Fotouh, 2004). Therefore, zeolite catalysts become more practical because of their high thermal and chemical stability, convenience in separating the catalyst and product and ability to be recycled. From a previous experimental study on the vapor phase synthesis of MTBE and ETBE, it was found that H-BEA is as active as Amberlyst-15. The order for the activity of commonly used zeolites decreases as follow: H-BEA > H-Y > H-ZSM-5 (Collignon *et al.*, 1997, 2001)

To the best of our knowledge, there is no previous study on this subject matter. In this work, the density functional theory with the M06-2X functional was employed to investigate the fundamental details of the ETBE formation via the etherification of isobutene with ethanol over H-BEA zeolite. Two possible reaction pathways can be considered to occur; either a stepwise reaction mechanism through the formation of a *tert*-butyl carbenium ion intermediate or by a concerted reaction mechanism through one-step leading to the ETBE formation.

We suggest the elementary steps of the stepwise reaction mechanism as follow:

$$C_4H_8 + \text{H-zeolite} \longrightarrow C_4H_8@\text{H-zeolite} \quad (1)$$

$$C_4H_8@\text{H-zeolite} \longrightarrow C_4H_9@\text{zeolite} \quad (2)$$

$$C_4H_9@\text{zeolite} + C_2H_5OH \longrightarrow C_6H_{15}O@\text{zeolite} \quad (3)$$

$$C_6H_{15}O@\text{zeolite} \longrightarrow C_6H_{14}O + \text{H-zeolite} \quad (4)$$

Step (1) is the adsorption of isobutene on the acid site of the zeolite. Then, in step (2), a protonation of the adsorbed isobutene occurs, leading to the *tert*-carbenium ion intermediate formation. Step (3) involves the interaction of the *tert*-carbenium ion intermediate with the ethanol molecule, resulting in adsorbed ETBE, which is desorbed in the final step.

The concerted reaction mechanism is proposed as follows:

$$C_2H_5OH + C_4H_8 + \text{H-zeolite} \longrightarrow \{C_2H_5OH + C_4H_8\}@\text{H-zeolite} \quad (5)$$

$$\{C_2H_5OH + C_4H_8\}@\text{H-zeolite} \longrightarrow C_6H_{15}O@\text{zeolite} \quad (6)$$

$$C_6H_{15}O@\text{zeolite} \longrightarrow C_6H_{14}O + \text{H-zeolite} \quad (7)$$

The reaction is initiated by a co-adsorption of ethanol and isobutene molecules on the acid site of the zeolite in step (5). Then, in step (6), protonation of the adsorbed isobutene and an ethanol molecule attraction to isobutene take place simultaneously, resulting in an adsorbed ETBE, which is desorbed in the final step. The computational model for investigation of the reaction on the H-BEA zeolite is illustrated in Figure 1.

Besides the catalyzed reaction, the uncatalyzed reaction has been investigated with the M06-2X functional at the same level of theory of the catalyzed reaction.

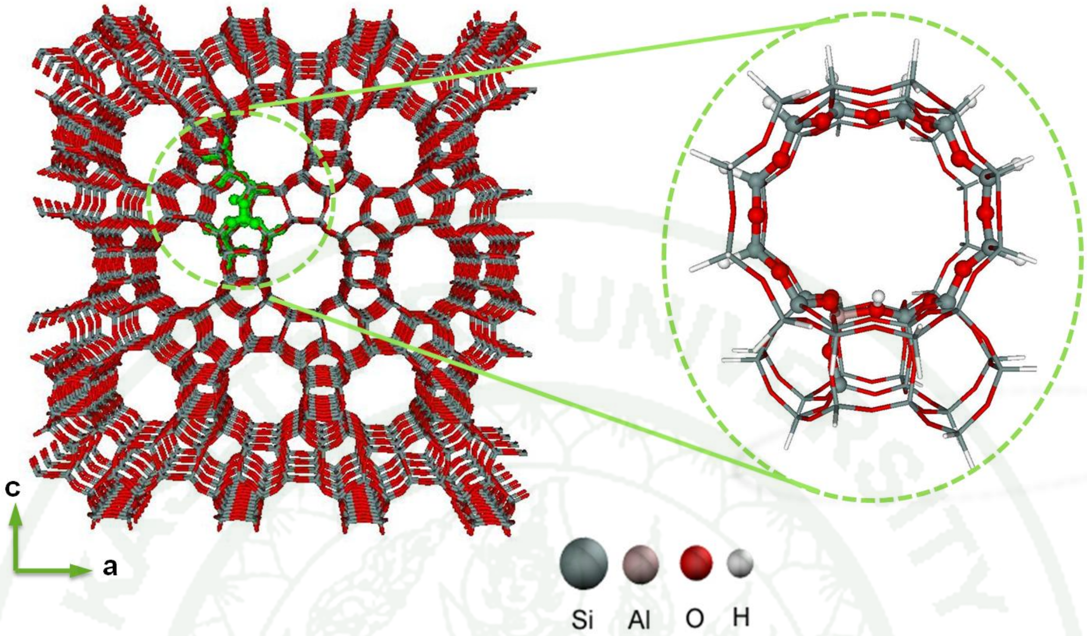


Figure 1 Illustration of BEA zeolite framework; inset is the 54T cluster of H-BEA zeolite being selected to represent the acid site of the catalyst. This cluster covers the 12-membered ring (12MR) representing the main gateway to the intersection of two perpendicular 12MR channel systems (6.6 Å × 6.7 Å), where the reactions normally take place, where T is an Al or Si atom.

OBJECTIVES

1. To investigate the structures and reaction mechanisms of the etherification of isobutene with ethanol to produce ethyl *tert*-butyl ether, ETBE over H-BEA zeolites by using the ONIOM(M06-2X/6-31G(d,p):UFF) method for geometry optimization calculations and the M06-2X/6-311+G(2df,2p) method for single point calculation

2. To compare the uncatalyzed and H-BEA zeolite catalyzed reactions

LITERATURE REVIEW

Oxygenated compounds are blended with gasoline to increase the octane number, as an antiknock additive in gasoline to replace lead alkyl antiknock agents, which are toxic and nondegradable. Two types of oxygenates are commonly used in gasoline; alcohols e.g. methanol, ethanol and ethers e.g. methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), isopropyl *tert*-butyl ether (IPTBE) and *tert*-amyl methyl ether (TAME). However, ethers have advantages over alcohols due to the fact that the alcohol addition to gasoline tend to make the blend very volatile and water-soluble, possibly creating problems in the fuel distribution system and vehicle engine (McGregor *et al.,* 2007; Cataluña *et al.,* 2008). Particularly, Alkyl *tert*-butyl ethers easily mix with gasoline, to make gasoline burn cleanly and completely, reducing emission of unburned hydrocarbons from car exhausts.

In the last decade, MTBE has become the major option for an automotive gasoline additive worldwide. MTBE is produced commercially from methanol and isobutene by liquid-phase or vapor-phase reactions. There are a number of studies on the reaction of MTBE (Collignon *et al.,* 1997; Knifton *et al.,* 1999; Salomón *et al.,* 2000; Díaz *et al.,* 2001; Aboul-Fotouh *et al.,* 2004). However, due to its high solubility in water and high resistance to biodegradation, it can readily transfer to groundwater and cause contamination problems when fuel spills and leaks occur (Kharoune *et al.,* 2001; Reuter *et al.,* 1998; Nadim *et al.*, 2001). Thus, ETBE is more attractive because of it is less water solubility, has the highest-octane blending values, the lowest oxygen content, and low vapor pressure. Moreover, ETBE can be produced from low cost bio-ethanol, a renewable energy source (Malça *et al.,* 2006), which is produced from many sources of agriculture products such as cassava, molasses and sugarcane.

The etherification reaction of isobutene with ethanol to ETBE is carried out both in liquid and vapor phase conditions. A wide range of catalysts has been tested for ETBE synthesis such as heteropolyacids (Kovalchuk *et al*., 2009; Bielański *et al*., 2010), phosphoric acid activated carbons (Puziy *et al.,* 2010), ion-exchange resins

(Fite *et al.,* 1994; Sola *et al.,* 1996; Tanabe *et al.,* 1999; Dogu *et al.,* 2001; Umar *et al.,* 2009 and Degirmenci *et al.,* 2009), and zeolites (Larsen *et al.,* 1995; Alcántara *et al.,* 2000; Collignon *et al.,* 2001; Kochkin *et al.,* 2002; Vlasenko *et al.,* 2006). Synthesis of ETBE using the sulfonated acidic ion-exchange resin catalysts was previously studied and found that the catalysts were active and selective catalysts. However, these conventional catalysts have disadvantages such as inability to tolerate temperatures above 100 °C and releasing sulfonic compounds and sulfuric acid, which cause a loss of activity and corrosion problems (Collignon *et al.*, 2001; Aboul-Fotouh 2004). Hence, zeolites become more advantageous because of high thermal and chemical stability, easy separation between catalyst and product, and ability to be recycled. There are many investigations of ETBE production by using zeolites as catalysts. From previous experimental studies on the vapor phase synthesis of MTBE and ETBE, it was found that the activity of the different zeolites followed the sequence: H-BEA > H-Y ≥ H-MOR > H-ZSM-5 (Collignon *et al.*, 1997, 2001). Iborra *et al.*, (2005) investigated the liquid-phase synthesis of isopropyl *tert*-butyl ether (IPTBE) from 2-propanol and isobutene over H-BEA, H-ZSM-5, and H-Y zeolites. The results showed that H-BEA is the most active and selective catalyst with the activation energy of 92 ± 12 kJ/mol (22 ± 3 kcal/mol).

The synthesis of ETBE from isobutene and ethanol occurs via the following reaction namely etherification reaction, taking place in the presence of acid catalysts:

$$(CH_3)_2C{=}CH_2 + C_2H_5OH \xrightleftharpoons{H^{-}} (CH_3)_3C\text{-}O\text{-}C_2H_5 \qquad (8)$$

The ETBE reaction is reversible and exothermic, the increasing temperature makes the rate constant for the forward reaction to increase until the optimum temperature is reached. However, at a temperature higher than the optimum, a decrease in the ETBE yield was found (Alcántara *et al.*, 2000; Collignon *et al.*, 2001). A previous experimental investigation of the thermodynamic equilibrium for the ethanol-isobutene-ETBE system in the vapor phase predicted the values of ΔH_r^0 = −14.9 ± 0.5 kcal/mol and the enthalpy of formation, ΔH_f^0 = −75.0 ± 0.5 kcal/mol at 298 K (Iborra *et al.*, 1989). As for the liquid phase, the value of ΔH_r^0 was estimated to be −32.0 kcal/mol (Sola *et al.*, 1995). Moreover, several side reactions, dimerization of isobutene producing *di*-isobutene and dehydration of ethanol producing *di*-ethyl ether were observed. If water is present in reactants, the competitive reaction, specifically the *tert*-butyl alcohol formation was found to be dominated (Vlasenko *et al.,* 2006).

In additionto the above mentioned, the synthesis of ETBE can be obtained by the reaction of *tert*-butyl alcohol and ethanol as follows:

$$(CH_3)_3COH + C_2H_5OH \rightleftharpoons (CH_3)_3C\text{-}O\text{-}C_2H_5 + H_2O \qquad (9)$$

The etherification reaction of isobutene with ethanol to ETBE can be considered to occur through the concerted route or stepwise route. If it takes place through the concerted route, it will process via one-step by the coadsorption of isobutene with ethanol and convert directly to the ETBE product. However, many references in literature have reported the existence of the *tert*-butyl carbenium ion intermediate during the etherification process. Alcántara *et al.* (2000) proposed mechanism for the gas-phase synthesis of ETBE from ethanol and isobutene on the H-ZSM-5 catalyst (shown in Figure 2). The first step is the protonation of isobutene over the H-ZSM-5 catalyst, to give a *tert*-butyl carbenium ion. In a second step, an ethanol molecule reacts with the adsorbed *tert*-butyl carbenium ion resulting in an adsorbed intermediate adduct. The third step is the desorptive step, the intermediate adduct is converted into ETBE.

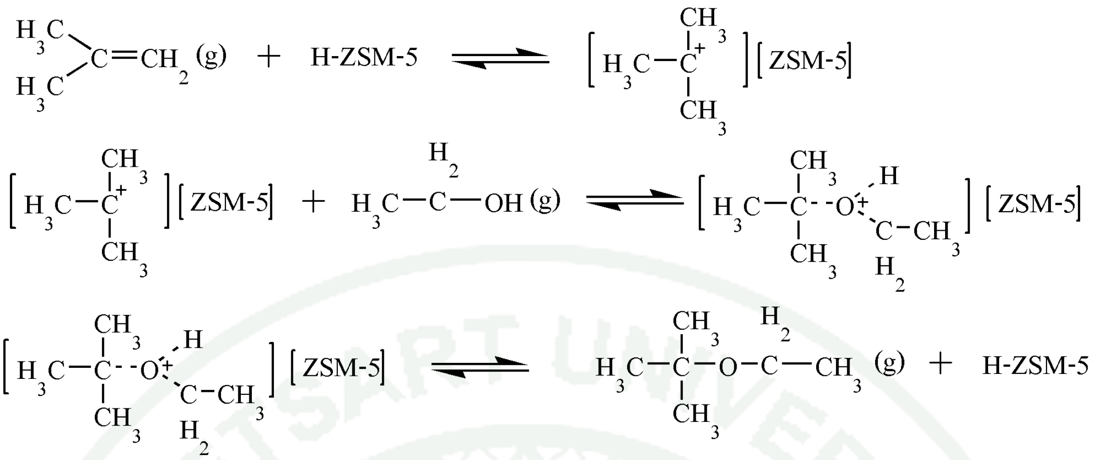


Figure 2 Schematic diagram the mechanisms of the gas-phase synthesis of ETBE from ethanol and isobutene on zeolite H-ZSM-5

Source: Alcántara *et al.* (2000)

Adams *et al.,* (1986) investigated MTBE formation over both over Amberlyst 15 and Al^{3+} exchanged montmorillonite catalysts. They found that the rate-determining step of both catalysts appears to be the alkene protonation to form the *tert*-carbocation with the activation energy of 44 ± 3 kJ/mol (10 ± 1 kcal/mol) and 25 ± 13 kJ/mol (6 ± 3 kcal/mol), respectively.

Theoretical studies have confirmed that the *tert*-butyl carbenium ion intermediate is stable inside the zeolite pores, depending on its stability in the position and local geometry of the active site. This intermediate is found to be a reactive intermediate (Rozanska *et al.,* 2003 and Boronat *et al.,* 2004, 2008). Boronat, Viruela and Corma (2004) investigated the mechanism of protonation of ethene, propene, and isobutene by seven different Brønsted acid sites in H-MOR zeolite by using the B3PW91/6-31G(d,p)//ONIOM(B3PW91/6-31G(d,p):MNDO method. The results showed the order of activation energies as follows: isobutene < propene < ethene, reflecting the order of stability of primary, secondary, and tertiary carbenium ions. Moreover, the protonation of ethene and propene cause them to convert into stable covalent alkoxide intermediates through carbenium ion-like transition states. In contrast, a protonation of isobutene always results in a formation of a free *tert*-butyl carbenium ion intermediate, whether it can be converted to *tert*-butoxide or not, depending on the location of the acid site in the zeolite. For the system in which the Al atom occupies the T4A positions of H-MOR zeolite; isobutene protonation to give the adsorbed *tert*-carbenium ion is endothermic with an activation energy of 7.4 kcal/mol. This finding is reasonable and compared well with the periodic DFT approach by VASP program reported by Rozanska *et al.* (2003). They investigated this reaction by the generzalized gradient approximation (GGA) with the Perdew-Wang 91 functional. The results showed that the activation energy of the protonation of isobutene to *tert*-butoxide in H-MOR is 7.2 kcal/mol. This reaction follows transformation through *tert*-carbocation-like transition states and the energy difference between the physisorbed isobutene and *tert*-butyl carbocation state is 6.0 kcal/mol.

Tuma and Sauer (2005) investigated the isobutene protonation in H-FER and found that formation of the π complex of isobutene with the Brønsted acidic site is an exothermic process. In contrast, chemisorption of isobutene (the protonation of isobutene to *tert*-butyl carbocation, isobutoxide and *tert*-butoxide formation) is an endothermic process. Besides, at temperatures higher than about 120 K, the *tert*-butyl cation complex becomes favored over the alkoxides. In the following year, Tuma and Sauer (2006) investigated the effects of the dispersion force correction for “ extended systems” by hybrid MP2:DFT calculations (the second-order Møller-Plesset perturbation theory, MP2, for the active site with DFT for the full periodic model). This calculation combines with three steps for estimation; the first step is the structure optimization of a $16T_{16H}$ cluster embedded in the periodic model, the second step is extrapolation of the MP2 energy to the complete basis set limit and the final step is the extrapolating the high-level (MP2) correction to the limiting case of the full periodic structure. The result of the final estimate showed that adsorption of isobutene in zeolite H-FER, the π-complex, the isobutoxide, the tert-butoxide, and the *tert*-butyl carbenium ion, are −78 (-19 kcal/mol), −73, −48 and −21 (−5.0 kcal/mol) kJ/mol, respectively. Recently, Tuma *et al.*, (2010) investigated the deprotonation of *tert*-butyl carbenium ion to isobutene and conversion of *tert*-butyl carbenium ion into surface alkoxides over zeolite H-FER. They investigated by using a hybrid *16T*$_{16H}$ MP2/TZVP(P):PBE/pw that comprises five steps for the best estimate which is improved from previous work in 2006. The best estimate was reported that adsorption of isobutene in zeolite H-FER, the π-complex, the isobutoxide, the tert-butoxide, and the *tert*-butyl carbenium ion, are −77 (−18 kcal/mol), −68, −41 and −17 (−4 kcal/mol) kJ/mol, respectively. Moreover, the results showed that the lowest energy barrier of 14 kJ/mol (3 kcal/mol) is found for the conversion of the tert-butyl carbenium ion to isobutene whereas energy barriers of 31 and 61 kJ/mol (7 and 15 kcal/mol) are found for conversion into isobutoxide and *tert*-butoxide, respectively.

The adsorption energy is one of the most valuable data obtained from experimental observation which can be used to validate the theoretical data. Eder *et al.* (1997) and Yoda *et al.* (2005) reported that heat of adsorption for *n*-butane over H-FER zeolite of −59 and −63 kJ/mol (−14 and −15 kcal/mol), respectively. From theoretical calculations, Namuangruk *et al.* (2006) reported the trend of the calculated adsorption energies (kcal/mol) for the butene isomers over H-ZSM-5 as follows: 1-butene (−16.06) > *cis*-2-butene (−13.62) ≅ *trans*-2-butene (−13.25) > isobutene (−6.96). On the other hand, Pantu *et al.* (2007) reported the adsorption energies of alkenes on acidic zeolites which were predicted to be −9.4, −11.3, and −12.5 kcal/mol for ethene, propene, and 1-butene in H-FAU, respectively and −10.1, −13.8, and −17.4 kcal/mol for ethene, propene, and 1-butene in H-MOR, respectively. Unfortunately, experimental heats of adsorption for unsaturated hydrocarbons in Brønsted acid zeolite could not so far be measured because C3–C4 unsaturated hydrocarbons rapidly oligomerize on zeolite catalysts even at room temperature (Yoda *et al.*, 2005). However, the experimental observation of Cant and Hall (1972) estimated the heat of adsorption for ethene on H-FAU zeolite of −9.0 kcal/mol.

We approach the reaction mechanisms on quantum chemical calculations. Only a small part of the zeolite framework affects the electronic properties of the reactive site, thus modeling is facilitated using quantum chemical methods. To account for the effects of the zeolite framework, various techniques such as periodic ab initio calculations and quantum mechanics/molecular mechanics (QM/MM) hybrid methods have been widely used. The former approach is computationally too expensive and impractical for studying the large unit cell zeolites. The recent development of QM/MM hybrid methods, such as the embedded cluster or combined quantum mechanics/molecular mechanics (QM/MM) methods (Brandle *et al.*, 1998; Khaliullin *et al.*, 2001; Limtrakul *et al.*, 2000) as well as the ONIOM schemes, were employed to keep the calculations feasible. These methods can properly describe the effect of the zeolite framework. Especially, the ONIOM method has been used successfully to investigate the adsorption of hydrocarbons such as ethene, benzene, and ethylbenzene over acidic and alkaline faujasite and ZSM-5 zeolites (Kasuriya *et al.*, 2003 and Namuangruk *et al.*, 2004) and several important reaction mechanisms over zeolites (Jansang *et al.*, 2008; Kumsapaya *et al.*, 2009; Maihom *et al.*, 2009).

Furthermore, among several known density functionals used in quantum chemistry investigations, the M06−2X functional has been proved to show excellent performance for main group thermochemistry and kinetics, predicting accurate valence and Rydberg electronic excitation energies, and noncovalent interactions (Zhao *et al.*, 2008, 2011). This functional is successfully applied to the studies of various organic reactions in zeolite pores (Boekfa *et al.*, 2009; Wannakao et al., 2010; Maihom *et al.*, 2010; Bobuatong *et al.*, 2010; Kongpatpanich *et al.*, 2011).

MATERIALS AND METHODS

Materials

Hardwares

1. LCAC super computer cluster (Chemistry Department, Faculty of Science, Kasetsart University, Bangkok).
2. HP workstations; Intel Pentium 4 CPU 2.40 GHz, RAM 512 MB (Chemistry Department, Faculty of Science, Kasetsart University, Bangkok).

Softwares

1. Gaussian 03 program
2. Gaussian View 03 program
3. Accelrys DS ViewerPro 5.0
4. POV−ray for Windows
5. Endnote X3
6. Chemcraft 1.5
7. Accelrys Material studio 4.3
8. EditPlus 3.0

Methods

The uncatalyzed reaction

The uncatalyzed reaction, the bare model system, is investigated with M06−2X/6−311+G(2df,2p)//M06−2X/6−31G(d,p) calculations. This method gives good the reaction energies for the etherification reaction of isobutene with ethanol (as shown in Appendix Table A2)

The catalyzed reaction

The BEA zeolite is selected as the catalyst for this study. The crystal lattice structure of BEA zeolite was taken from the Accelrys Material studio program. The topology is a tetragonal system with unit cell parameters a = b = 12.661 Å, c = 26.406 Å and $\alpha = \beta = \gamma = 90°$. The BEA zeolite has three-dimensional channels. It has two perpendicular 12MR channel systems with the pore diameter of about 6.6 Å × 6.7 Å and a helical channel of about 5.6 Å × 5.6 Å along the c-axis. (as shown in Figure 3).

The structure of the 54T model is used to represent the Brønsted acid site in the BEA zeolite framework (the acid site of the catalyst), where T is an Al or Si atom. The 54T model is taken from the H-BEA zeolite crystal lattice structures (de Vries *et al.*, 1999; Rungsirisakun *et al.*, 2005). This cluster model covers the 12-MR representing the main gateway to the intersection of two perpendicular 12-MR channel systems, where the reactions normally take place (Kumsapaya *et al., 2009*). A silicon atom at a T5 position in the BEA zeolite is replaced with an aluminum atom to generate the Brønsted acid site. Furthermore, the terminal Si atoms are terminated by the H atoms with the Si–H bond distances of 1.47 Å, pointed in the same direction as the crystallographic Si–O bonds.

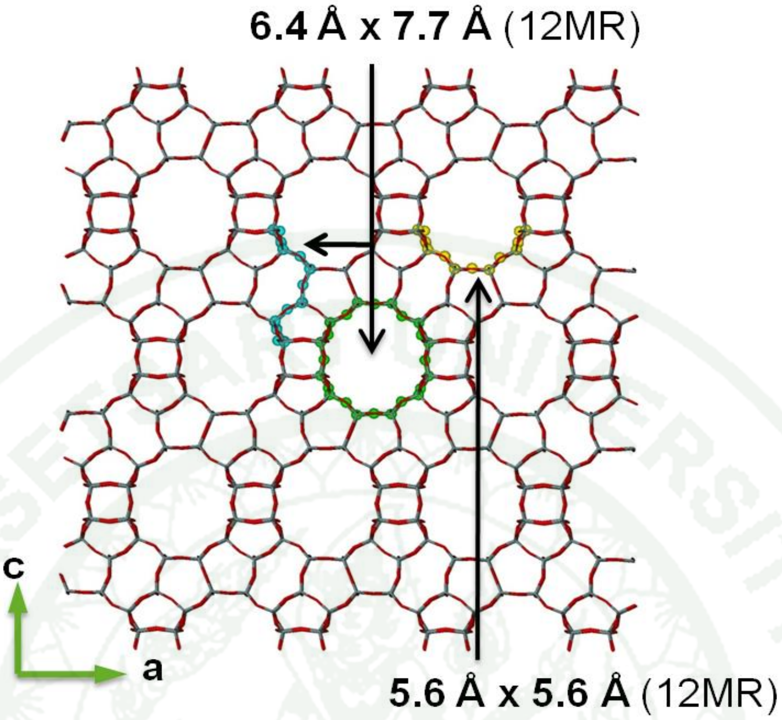


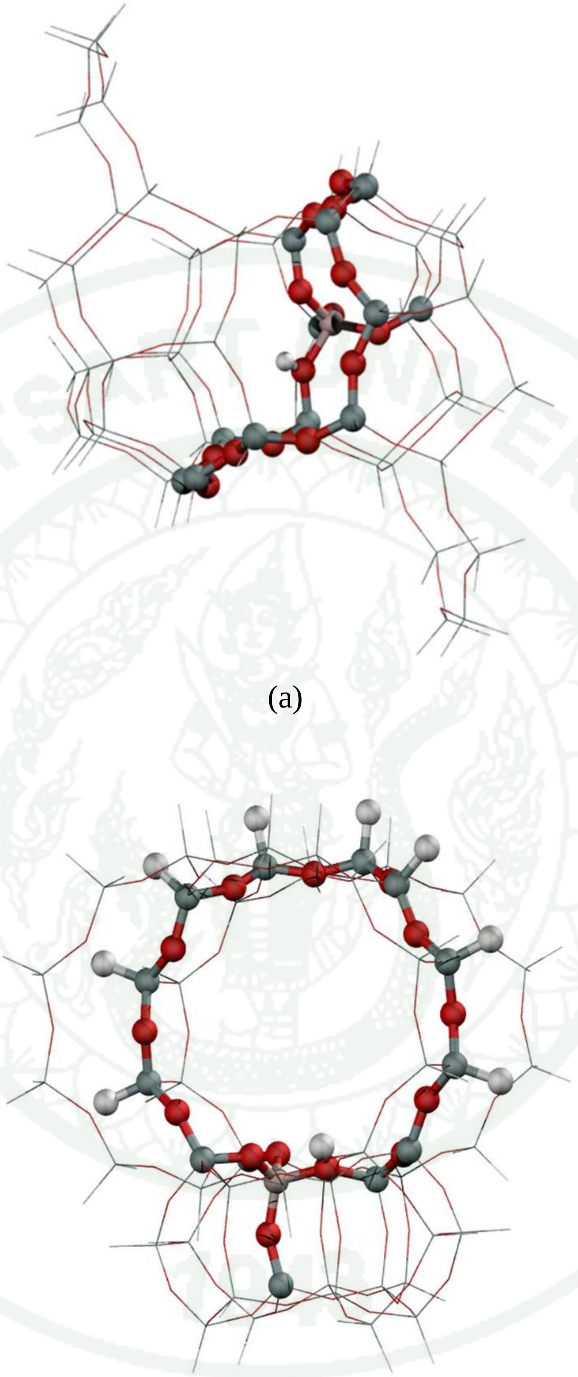
Figure 3 Illustration of the channel of BEA zeolite viewed in b-axis.

All geometries are optimized by using the Our own N−layered Integrated molecular Orbital and molecular Mechanics (ONIOM) method. In the ONIOM model (shown in Figure 4), The inner layer that contains the 14T cluster as the active site region is treated with the recently developed density functional, namely M06−2X with the 6−31G(d,p) basis set. The outer layer is the rest of 54T cluster and treated with the universal force field (UFF) to account for the short-range van der Waals interactions with the surrounding pore walls. In the structure optimization, only the 5T cluster of the active site region, [(≡SiO)$_3$Al(OH)Si≡], and the probe molecule are allowed to relax while the rest is fixed at the crystallographic coordinates. Frequency calculation at the same level of the active site region was carried out to verify the transition states structure with only one imaginary frequency.

In order to improve the quality of those relative energies in the reaction coordinate, single point calculations are performed using full quantum calculations at the M06−2X/6−311+G(2df,2p) level of theory with a large quantum cluster model

(54T). The M06−2X/6−311+G(2df,2p) level of theory with a cluster model can account for two important interactions that are short-range van der Waals interactions and long-range electrostatic interactions that were diminished in the UFF level. Moreover, the high basis set, 6−311+G(2df,2p) that included diffuse functions and extended polarization functions, would account for more accuracy on the short-range electrostatic contributions which are important to the stabilization of all the intermediate and transition states.

All calculations were performed by using the Gaussian 03 code (Frisch *et al.,* 2004) incorporated with the Minnesota density functional module 3.1 by Yan Zhao and Donald G. Truhlar.



(a)

(b)

Figure 4 Extended 54T cluster model of H-BEA framework; inner layer (the active site region) is represented in the ball-bond view and the outer layer is represented by the line view (a) An intersection of two perpendicular 12-MR channel systems which serve as a nanoreactor (b) View along the main channel.

RESULTS AND DISCUSSION

1. The uncatalyzed reaction

The uncatalyzed reaction is performed by the bare model system. The energy profile of the reaction computed at the M06−2X/6−311+G(2df,2p)//M06−2X/6−31G(d,p) level of theory, is shown in Figure 5. Energies obtained at the M06−2X/6−31G(d,p) level of theory are shown in Appendix Table A1. The optimized geometric parameters of all species involved in the etherification of isobutene with ethanol are shown in Table 2.

In this referenced system, isobutene and ethanol are initially bound together with a weak interaction (–4.5 kcal/mol). The geometric parameters of those two reactant molecules are barely changed at this adsorption state. At the transition state, the intermolecular proton transfer from the hydroxyl group of ethanol to the first carbon atom of unsaturated isobutene takes place. At the same time, the oxygen atom of ethanol moves toward another carbon atom of unsaturated isobutene. In comparing the isobutene and ethanol molecules (IB_EtOH), it is noted that the C1−H distance decreases from 2.57 to 1.40 Å, and the O−H bond length increases from 0.97 to 1.24 Å, meanwhile the C2−O distance decreases to 1.92 Å and the C1−C2 double bond is elongated from 1.34 to 1.42 Å.

Table 1 M06-2X/6−311+G(2df,2p) energies of the uncatalyzed reaction mechanism.

Reaction coordinate	Relative energy (kcal/mol)
IB_EtOH	−4.5
TS1	48.8
ETBE	−18.4

Table 2 Optimized geometric parameters of all species involved in the ETBE formation of the uncatalyzed reaction, the bare model system.

Parameter	**IB_EtOH**	**TS1**	**ETBE**
Distance (Å)			
C1−H	2.57	1.40	1.09
C2−H	2.35	1.74	2.16
H−O	0.97	1.24	2.64
C2−O	3.00	1.92	1.43
C1−C2	1.34	1.42	1.53
Angle (°)			
C2−C1−H	65.1	76.3	109.7
C1−C2−H	83.8	51.2	28.4
C1−H−O	155.5	130.2	67.0
C1−C2−O	99.2	90.4	110.6

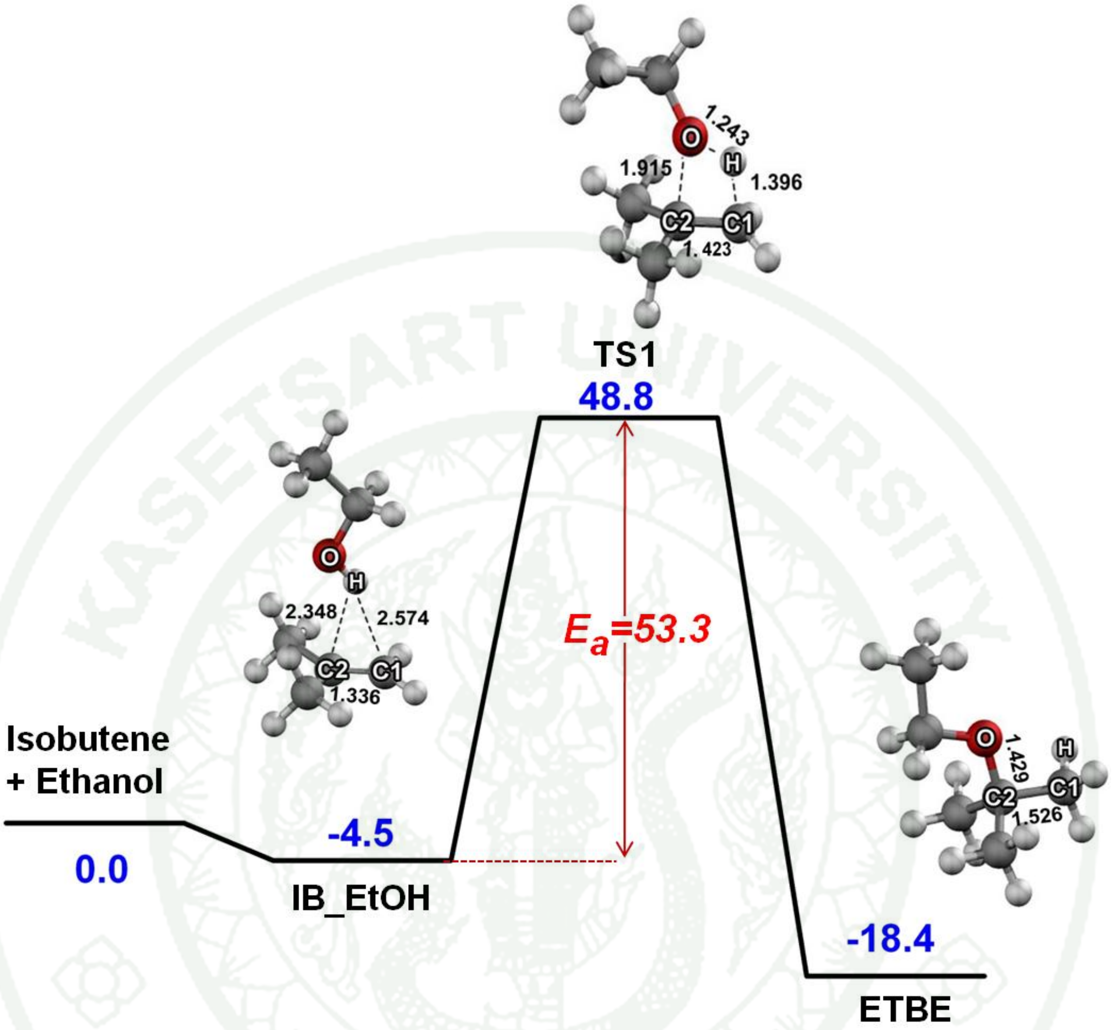


Figure 5 M06−2X/6−311+G(2df,2p) relative energies of all reaction coordinates in the etherification reaction of isobutene with ethanol to ETBE uncatalyzed reaction, the bare model system. Distances and energies are given in Å and kcal/mol.

The unanalyzed gas phase reaction mechanism concerns the O−H bond dissociation, O−C and H−C bond formation. The activation energy is calculated to be 53.3 kcal/mol, and the overall reaction is estimated to be an exothermic reaction by –18.4 kcal/mol. The calculated reaction energy in this study is in reasonable agreement with the experimental results of –15 ± 1 kcal/mol (Iborra *et al.*, 1989 and Alcántara *et al.*, 2000).

2. The catalyzed reaction

In the zeolite catalyzed system, two possible reaction pathways for the etherification of isobutene with ethanol can be considered to occur either by a stepwise reaction mechanism through the formation of a *tert*-butyl carbenium ion as intermediate or by a concerted reaction mechanism through one-step leading to the ETBE formation (Shown in Figure 6).

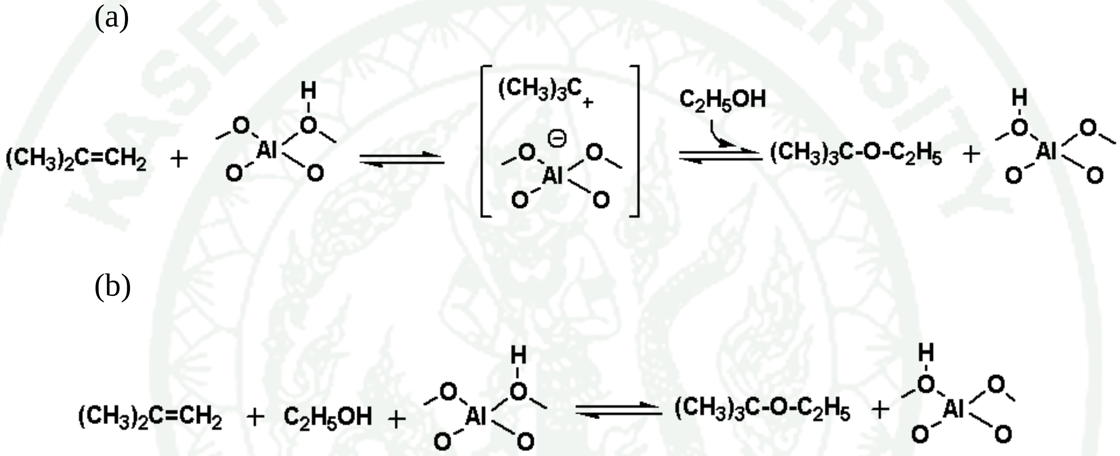


Figure 6 Schematic diagrams the reaction mechanisms of ETBE formation from ethanol and isobutene on H-BEA zeolite (a) stepwise reaction mechanism (b) concerted reaction mechanism.

2.1 Stepwise reaction mechanism

The relative energies of all species involved in the stepwise reaction mechanism are shown in Figure 7, and selected geometrical parameters are listed in Table 4. In this stepwise mechanism, the reaction can be considered to occur through two steps;

Table 3 M06-2X/6−311+G(2df,2p) energy of the stepwise reaction mechanism on H−BEA zeolite.

Reaction coordinate	Relative energy (kcal/mol)
B_Ads1	−18.5
B_TS1	−8.9
B_Int1	−12.5
B_Ads2	−26.6
B_TS2	−26.2
B_Ads3	−48.6

2.1.1 The *tert*-butyl carbenium ion intermediate formation step

This step is started by the adsorption of isobutene with acidic H-BEA zeolite. In the adsorption complex, **B_Ads1**, the main contribution in the interactions between isobutene and acidic H-BEA zeolite is the orbital interaction between the π bonding orbital of the C1=C2 bond of isobutene with the σ*antibonding orbital of O1−Hz bond zeolite. The calculated adsorption energy is –18.5 kcal/mol. Unfortunately, there is no experimental data to compare with our obtained value directly because heats of adsorption for unsaturated hydrocarbons in Brønsted acid zeolite cannot yet be measured due to C3−C4 unsaturated hydrocarbons rapidly oligomerizing on zeolite catalysts even at room temperature (Yoda *et al.*, 2005). However, there are the experimental data of the heat of ethene adsorption on H-FAU zeolite of −9.0 kcal/mol (Cant and Hall, 1972) and the heat of isobutane adsorption on H-BEA zeolite of –11.0 kcal/mol (Yoda *et al.*, 2005), which corresponds to alkene adsorption because the π-adsorption complex is much stronger than the alkyl interactions with the acid site. Besides the experimental observation, the theoretical calculations were investigated. Tuma *et al.* (2010) reported the adsorption energies of –18.4 kcal/mol for isobutene, –4.1 kcal/mol for *tert*-butyl carbenium ion in H-ferrierite (H-FER) and the conversion of the *tert*-butyl carbenium ion into adsorbed isobutene by proton transfer to the zeolite with the lowest barrier (3.3 kcal/mol). They investigated by using a hybrid MP2:DFT method that combines second-order Møller-Plesset perturbation theory (MP2) for the reaction site with DFT for the full periodic structure. On the other hand, Pantu et al. (2007) reported the adsorption energies of 1−butene on the acidic MOR zeolites, 12 MR window of the straight channel of 6.5 Å ×7.0 Å that is similar to the acidic BEA zeolites (6.6 Å ×7.7 Å). The adsorption energy of 1−butene on the acidic MOR zeolites was predicted to be −18.5 kcal/mol, which is comparable to the adsorption energy of **B_Ads1**. In the adsorption complex, **B_Ads1**, the O1−Hz bond length of zeolite was lengthened from 0.97 Å to 1.01 Å. The distances of C1…Hz and C2…Hz were 2.00 Å and 2.20 Å, respectively.

The adsorbed isobutene is then protonated by the acidic proton leading to the "*tert*−butyl carbenium ion" intermediate with an activation energy of 9.6 kcal/mol. In a previous theoretical study, using periodic calculations with the generzalized gradient approximation (GGA) and the Perdew−Wang 91 functional (Rozansaka *et al. 2003*), the activation energy of the protonation of isobutene to *tert*-butoxide in H-MOR is 7.2 kcal/mol. Our predicted activation energy also compared well with the value obtained from the B3PW91/6−31G(d,p)//ONIOM(B3PW91/6−31G(d,p):MNDO) method reported by Boronat *et al.* (2004).

At the first transition state **(B_TS1)** of the proton transfer, there is one imaginary frequency at −435 cm^{-1} corresponding to the following movements: the zeolite proton (Hz) moves toward a carbon atom (C1) of isobutene while the C1=C2 bond of isobutene is elongated from 1.34 Å to 1.40 Å. Following, the formation of the *tert*-butyl carbenium ion intermediate, **B_Int1**, to bring about bond length between C1 and C2 is lengthened from 1.40 Å to 1.45 Å. The *tert*-butyl carbenium ion structure is planar (Shown in Appendix Figure B2) and the three methyl group interacts with the zeolite framework through intermolecular forces. The central carbon atom (C2) is now sp^2 hybridized with an empty *p* orbital.

The partial positive charge on the C2 atom (as shown in Appendix Table B3) of the active carbocation intermediate should interact with one of the negative charged-neighboring atoms, such as oxygen atoms of the active site. However, previous studies found that, the *tert*−butyl carbocation could be stable inside the zeolite pores without any interactions with basic oxygen of zeolite (Boronat *et al.*, 2004 and 2008).

The relative energy of adsorption complex, **B_Ads1**, and *tert*−butyl carbenium ion intermediate, **B_Int1**, was computed to be −18.5 and −12.5 kcal/mol respectively, which is endothermic by 6.0 kcal/mol, corresponding well with previous studies (Boronat *et al.*, 2004 and Tuma *et al.*, 2005).

2.1.2 The ethyl *tert*−butyl ether formation step

An ethanol molecule was inserted into the zeolite intersection channel and was adsorbed with the *tert*−butyl carbenium ion intermediate. The relative energy of this co−adsorption complex **(B_Ads2)** was calculated to be −26.6 kcal/mol.

In the transition state, **B_TS2**, the *tert*−butyl carbenium ion intermediate interacts with an ethanol molecule. The positive charge of the unsaturated carbon C2 atom of *tert*−butyl carbenium ion intermediate interacts with the negative charge of the O atom of the ethanol molecule leading to the formation of ethyl *tert*-butyl ether. In this case, the ethanol molecule acts as a nucleophile and interacts with the *tert*−butyl carbenium ion intermediate to generate ethyl *tert*-butyl ether. The activation energy for this transition state is predicted to be 0.4 kcal/mol. The very low energy barrier (E_a^2) of 0.4 kcal/mol implies that the *tert*-butyl carbocation is highly reactive and it is ready to react with the ethanol molecule.

Therefore, the activation barrier of the first step is 9.6 kcal/mol, higher than that of the second step (0.4 kcal/mol) and it is expected to be the rate-determining step. There is good agreement from available experimental observations for the etherification of isobutene with methanol to produce methyl *tert*-butyl ether (MTBE) formation. The reaction occurs with the protonation of isobutene by the acidic zeolite to give the "*tert*-butyl carbenium ion" intermediate. Subsequently, intermediate interacted methanol leads to the MTBE formation. Adams *et al.,* (1986) found that the rate determining step of MTBE formation over both Amberlyst 15 and Al^{3+} exchanged montmorillonite catalysts appears to be the alkene protonation to form the *tert*-butyl carbenium ion with the activation energy of 11±1 kcal/mol and 6 ± 3 kcal/mol, respectively. The relative energies of the co-adsorption complex **(B_Ads2)** and product adsorption **(B_Ads3)** were calculated to be −26.6 and −48.6 kcal/mol, respectively. The results indicate that the etherification of isobutene with ethanol over H-BEA is considered to be exothermic with the reaction energy of −14.1 kcal/mol.

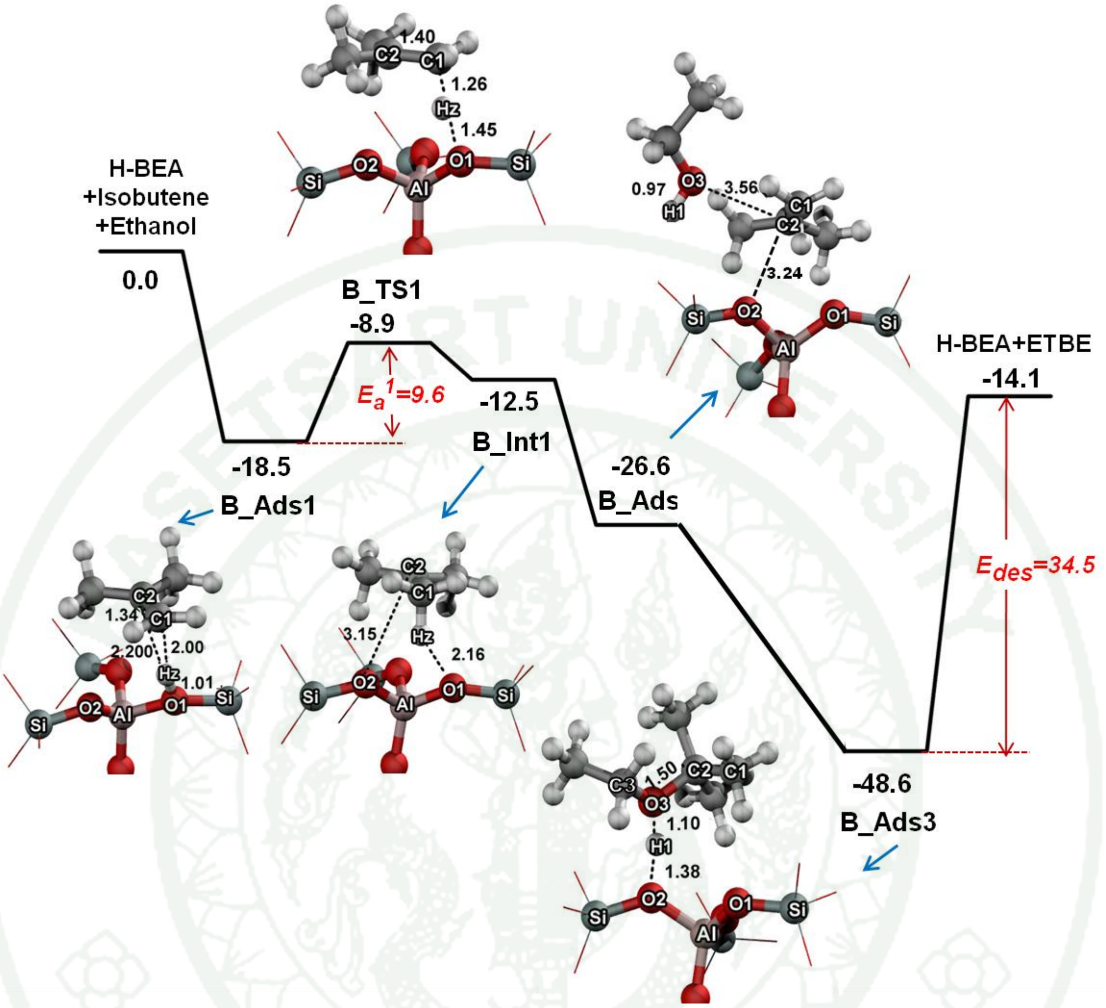


Figure 7 M06−2X/6−311+G(2df,2p) energy profiles for the stepwise mechanisms of the etherification of isobutene with ethanol catalyzed by H−BEA. Distances and energies are given in Å and kcal/mol.

Table 4 Optimized geometric parameters of all species involved in the etherification of isobutene with ethanol of the stepwise reaction mechanism catalyzed by H-BEA.

Parameter	**Isobutene**	**Ethanol**	**Zeolite**	**B_Ads1**	**B_TS1**	**B_Int1**	**B_Ads2**	**B_TS2**	**B_Ads3**	**ETBE**
Distance (Å)										
O1−Hz	−	−	0.97	1.01	1.45	2.16	2.14	2.28	2.35	−
C1−Hz	−	−	−	2.00	1.26	1.12	1.12	1.10	1.09	1.09
C2−Hz	−	−	−	2.20	1.99	1.96	1.96	2.12	2.16	2.16
C1−C2	1.33	−	−	1.34	1.40	1.45	1.45	1.47	1.52	1.53
C2−O2	−	−	−	3.34	2.88	3.15	3.24	2.31	2.35	−
O3−C3	−	−	−	−	−	−	1.42	1.44	1.46	1.42
O3−C2	−	−	−	−	−	−	3.27	2.31	1.50	1.43
O3−H1	−	0.96	−	−	−	−	0.97	1.00	1.10	−
H1−O2			−	−	−	−	3.38	1.76	1.38	−
Angle (°)										
Al−O1−Si	−	−	131.8	130.3	130.0	131.4	131.6	131.0	130.0	−
Al−O2−Si	−	−	129.8	132.0	133.7	135.4	135.3	133.2	129.8	−
O1−Hz−C1	−	−	−	172.4	165.5	136.7	137.7	159.0	161.6	−
Hz−C1−C2	−	−	−	79.6	96.8	98.7	98.6	110.2	110.5	109.9
O2−H1−O3	−	−	−	−	−	−	107.1	167.5	168.0	−
C3−O3−C2	−	−	−	−	−	−	151.7	121.1	118.2	118.0

2.2 Concerted reaction mechanism

In this mechanism, isobutene protonation and C–O bond formation between the carbon atom of the π−bonded adsorbed isobutene molecule and the oxygen atom of the ethanol molecule occur simultaneously to give the ETBE product without formation of the *tert*−butyl carbenium ion intermediate. The energy profile of the reaction catalyzed by H-BEA is shown in Figure 8, and optimized geometric parameters of all species involved in the reaction are listed in Table 6.

Table 5 M06-2X/6−311+G(2df,2p energy of the concerted reaction mechanisms on H−BEA zeolite.

Reaction coordinate	Relative energy (kcal/mol)
B_Ads4	−27.9
B_TS3	−19.2
B_Ads3	−48.6

The initial step is started by the co-adsorption of isobutene and ethanol over acidic H-BEA **(B_Ads4).** In this co-adsorption complex, the main interactions are the π interaction between the C1=C2 bond of isobutene with acidic H-BEA zeolite and hydrogen bond interaction between the H atom of ethanol and the O atom of zeolite. The C1–Hz, C2–Hz and H1–O2 distances are calculated to be 1.97, 2.28 and 2.20 Å, respectively. The interaction energy of the co-adsorption complex is calculated to be −27.9 kcal/mol, which is lower than the binding energy of the π-adsorption complex of isobutene −18.5 kcal/mol. It should be noted that the emerging ethanol molecule makes the system more stable.

At the transition state of the concerted mechanism, **B_TS3,** a protonation of the π-adsorbed isobutene molecule by the zeolite proton and simultaneous formation of a C2–O3 bond between the adsorbed isobutene molecule and ethanol molecule take place simultaneously. The transition state is verified by frequency calculation with one imaginary frequency corresponding to the following movements: the zeolite proton (Hz) moves toward a carbon atom (C1) of adsorbed isobutene bringing about the O1−Hz bond and the C1=C2 bond lengths increase from 1.01 and 1.34 Å to 1.34 and 1.38 Å, respectively. At the same time, the oxygen atom of ethanol is adducting to the carbon atom (C2) of adsorbed isobutene resulted in the O3…C2 and O2…H1 distance contracting from 3.67 and 2.20 Å to 2.66 and 1.97 Å, respectively. The activation energy in this mechanism is calculated to be 8.7 kcal/mol, which is lower than the stepwise mechanisms by ~ 10%.

Table 6 Optimized geometric parameters of all species involved in the etherification of isobutene with ethanol of the concerted reaction mechanisms catalyzed by H-BEA zeolite.

Parameter	**Zeolite**	**B_Ads4**	**B_TS3**	**B_Ads3**
Distance (Å)				
O1−Hz	0.97	1.01	1.34	4.43
C1−Hz	−	1.97	1.35	1.09
C2−Hz	−	2.28	2.12	2.19
C1−C2	−	1.35	1.38	1.52
O3−C2	−	3.67	2.66	1.50
O3−C3	−	1.42	1.42	1.46
O3−H1	−	0.97	0.97	1.10
H1−O2	−	2.20	1.97	1.38
Angle (°)				
Al−O1−Si	131.8	130.2	129.2	130.0
Al−O2−Si	129.8	130.5	133.4	129.8
O1−Hz−C1	−	172.4	156.2	51.7
Hz−C1−C2	−	163.9	102.0	112.9
O2−H1−O3	−	173.3	156.1	168.0
C3−O3−C2	−	121.6	126.0	118.2

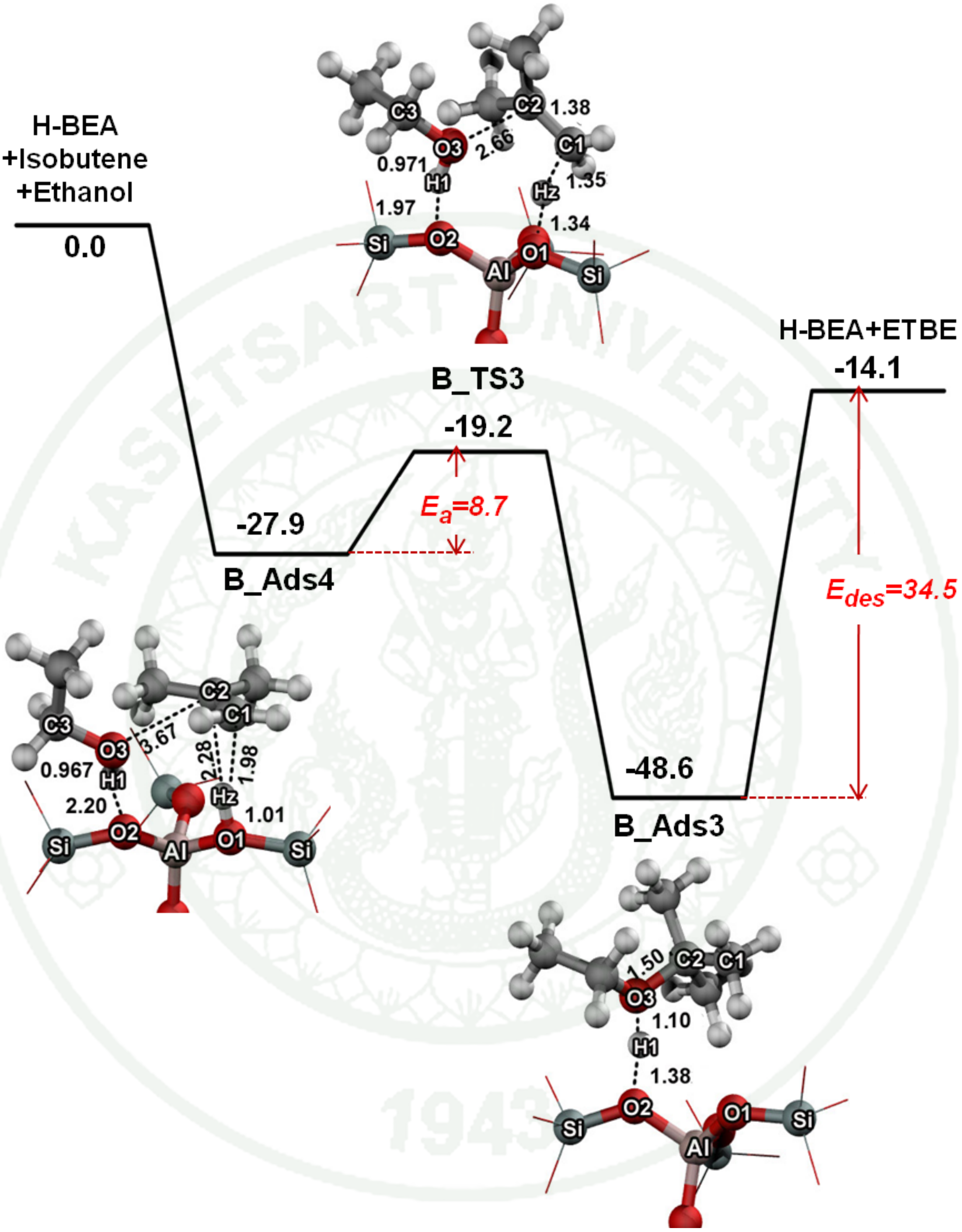


Figure 8 M06−2X/6−311+G(2df,2p) energy profiles for the concerted reaction mechanism catalyzed by H-BEA. Distances and energies are given in Å and kcal/mol.

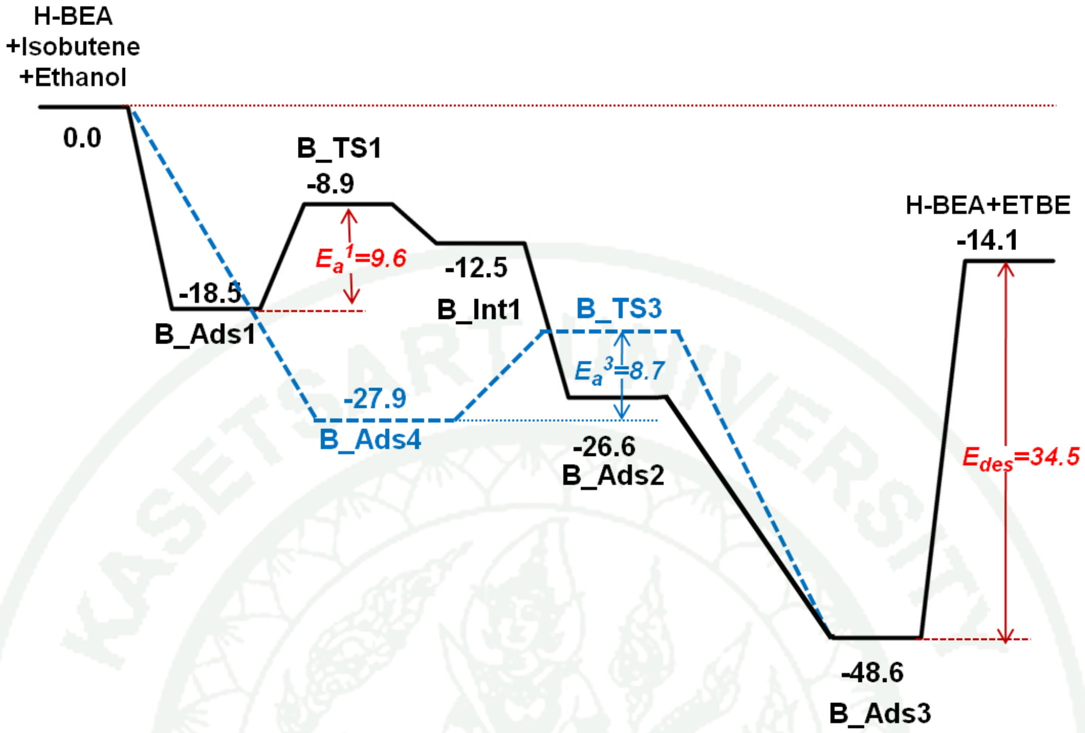


Figure 9 Energy profiles for the stepwise (———) and concerted (– – –) reaction mechanisms of the etherification of isobutene with ethanol catalyzed by H−BEA.

2.3 Comparison of stepwise and concerted reaction mechanisms

The complete energetic profiles of both possible mechanisms are shown in Figure 9. In the stepwise mechanism, the protonation of the adsorbed isobutene is the rate-determining step with the activation energy of 9.6 kcal/mol, resulting from *tert*-butyl carbenium ion being destabilized by both short-range interactions with the active site zeolite and long-range interactions with the zeolite walls. Thus, the *tert*-butyl carbenium ion is rather reactive and readily reacts with the ethanol molecule with very low activation energy. For the concerted mechanism, the ETBE formation can proceed in a single step via the concerted interactions in the coadsorbed complex of isobutene with ethanol, without the formation of the *tert*-butyl carbenium ion intermediate. The activation energy is calculated to be 8.7 kcal/mol, which is slightly lower than the activation energy of the rate-determining step of the stepwise mechanisms. Thus, the reaction mechanisms for the ETBE production via the etherification reaction of isobutene and ethanol catalyzed by the H−BEA zeolite prefer to occur through both stepwise and concerted reaction mechanisms.

In this work, the H-BEA zeolite could stabilize the reaction systems leading to an increase of the binding energy (more negative value). The H-BEA zeolite, as the catalyst changes the reaction path by lowering the energy barrier from 53.3 kcal/mol to 8.7 kcal/mol for the concerted reaction mechanism and 9.6 kcal/mol for the stepwise reaction mechanism, which leads to increase the rate of the reaction.

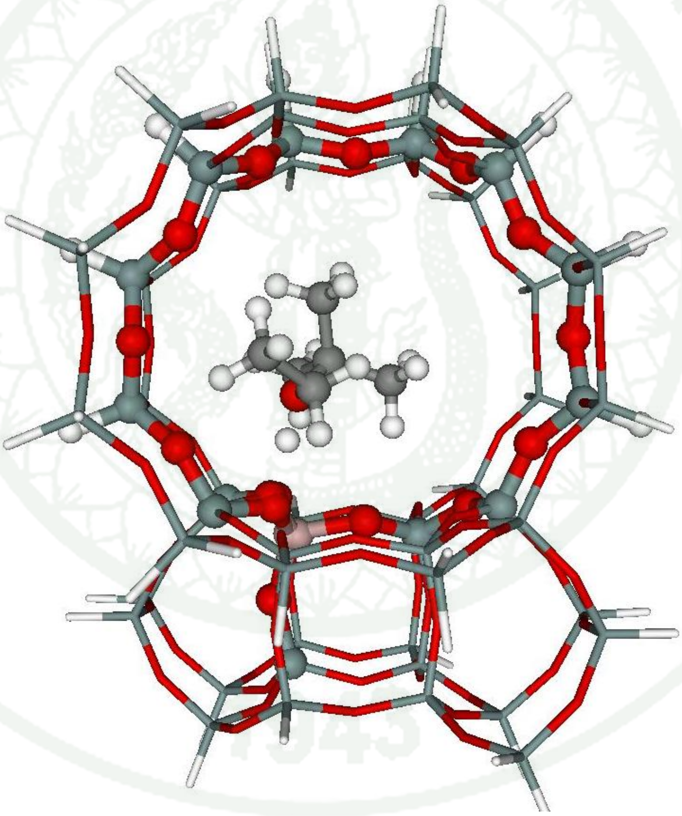


Figure 10 Product adsorption on the Brønsted acid of BEA zeolite along the 12MR straight channel.

CONCLUSION AND RECOMMENDATIONS

Conclusion

The reaction mechanisms for the ETBE production via the etherification reaction of isobutene and ethanol both the uncatalyzed and the catalyzed by the H-BEA zeolite were investigated using the full quantum calculations at the M06−2X/6−311+G(2df,2p) level of theory. The uncatalyzed reaction mechanism concerns the O−H bond dissociation and O−C, H−C bond formations. At the transition state, the hydroxyl bond of the ethanol molecule dissociates, the proton of the hydroxyl group transfers to the first carbon atom of unsaturated isobutene and the oxygen atom of ethanol attaches to another carbon atom of unsaturated isobutene. The activation energy is calculated to be 53.3 kcal/mol. For the catalyzed reaction mechanism, the reaction was proposed to occur via both stepwise and concerted reaction mechanisms. The stepwise reaction mechanism starts with a *tert*-butyl carbenium ion intermediate formation step and then the intermediate reacts with ethanol to generate the ETBE product. The activation energy is calculated to be 9.6 kcal/mol. The concerted reaction mechanism occurs via a single step through the co-adsorption of isobutene and ethanol without formation of the *tert*-butyl carbenium ion intermediate. Isobutene protonation and bond formation between the carbon atom of the π-bonded adsorbed isobutene molecule and the oxygen atom of the ethanol molecule occur simultaneously to give the ETBE product. The activation energy is calculated to be 8.7 kcal/mol, which is slightly lower than the activation energy of the rate-determining step of the stepwise mechanisms.

The uncatalyzed reaction for the ETBE production was exothermic and this study provides the calculated reaction energy of −18.4 kcal/mol. The H-BEA zeolite is found to be an efficient catalyst in the etherification of isobutene with ethanol, culminating in a lower energy barrier (8.7 kcal/mol for the concerted reaction mechanism and 9.6 kcal/mol for the stepwise reaction mechanism) as compared to that of the bare model system (53.3 kcal/mol).

Recommendations

1. The Density Functional Theory calculation with M06−2X can be used to analyze the reaction mechanism in deep detail and provides the results that agree well the thermodynamic and kinetic data obtained from the experiment.

2. The ONIOM method has been used successfully to optimize structures for all species and has been used appropriately for studying the long reaction mechanism and the large unit cell of zeolite.

3. The etherification of isobutene with ethanol to produce ETBE can use the H-BEA zeolite as the catalyst.

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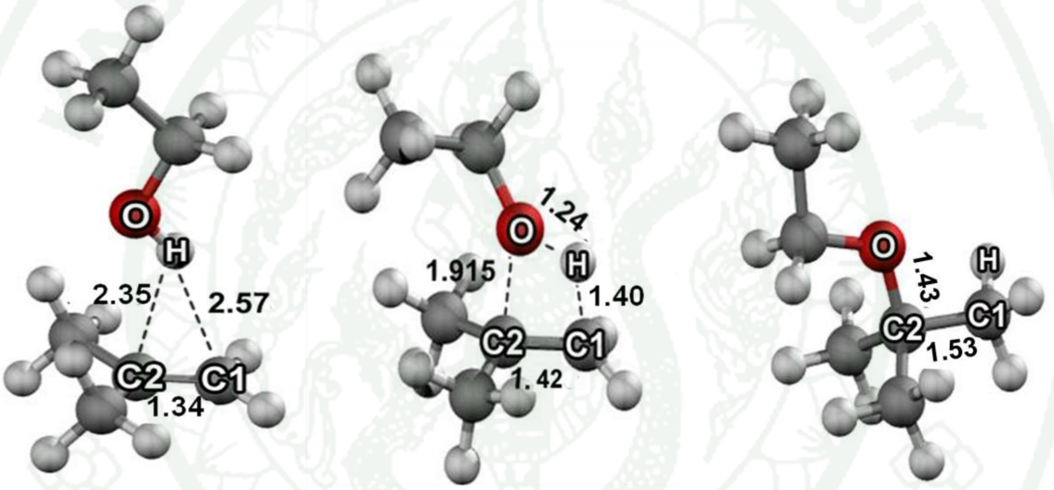
APPENDICES

Appendix A

Structures and energies optimization with the M06−2X/6−31G(d,p) of all species involved in the uncatalyzed reaction.

Appendix Table A1 Optimization energies with M06−2X/6−31G(d,p) of all species involved in the uncatalyzed reaction.

Reaction coordinate	Relative energy (kcal/mol)	Activation energy (kcal/mol)
IB_EtOH	−6.1	_
TS1	43.9	50.0
ETBE	−24.3	_



IB_EtOH **TS1** **ETBE**

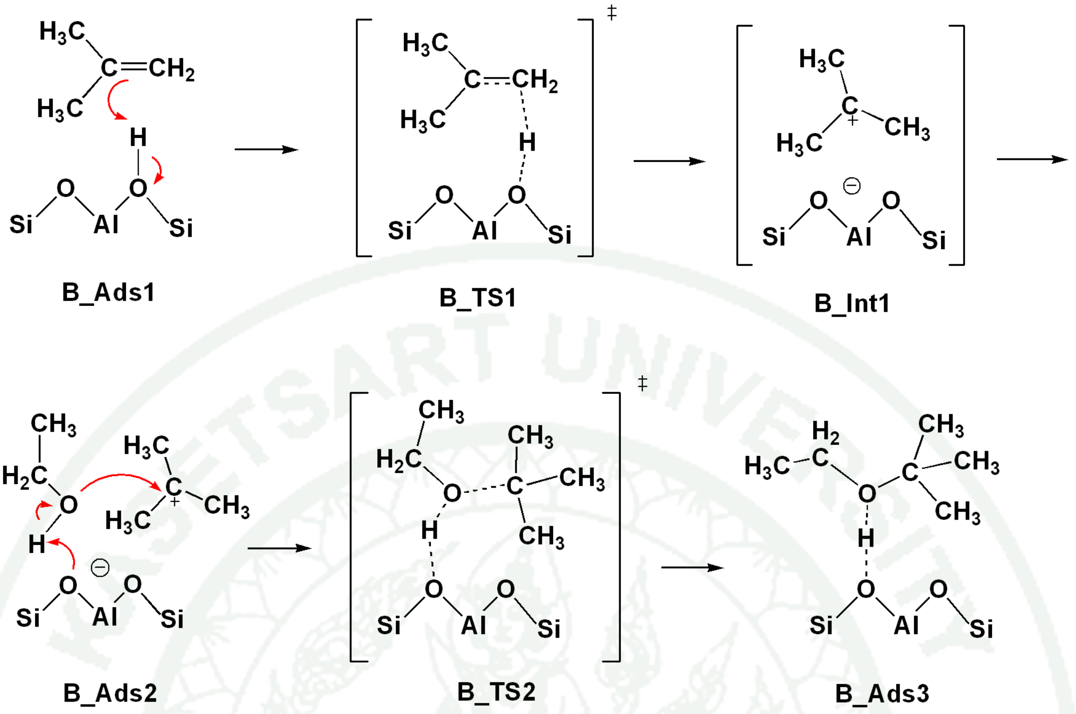
Appendix Figure A1 Optimized structure of all species involved in the uncatalyzed reaction.

Appendix Table A2 Reaction energies of the etherification of isobutene with ethanol to ETBE in gas phase which are computed with different methods.

Method	Reaction energy	
	kcal/mol	**kJ/mol**
B3LYP/6−31g(d,p)	−17.7	−74.0
M06L/6−31g(d,p)	−20.5	−85.7
M06−2X/6−31g(d,p)	−24.3	−101.5
MP2/6−31g(d,p)	−14.8	−61.9
B3LYB/6−311+g(2df,2p)	−10.5	−43.9
M06L/6−311+g(2df,2p)	−24.5	−102.4
M06−2X/6−311g(2df,2p)	−20.4	−85.4
M06−2X/6−311+g(2df,2p)	−18.3	−76.6
M06−2X/6−311++g(3df,3pd)	−18.3	−76.8
MP2/6−311+g(2df,2p)	−10.2	−42.6

Appendix B

Structures and energies optimization with the ONIOM(M06−2X/6−31G(d,p):UFF) method of all species involved in the stepwise reaction mechanism catalyzed by H−BEA zeolite.



Appendix Figure B1 The reaction pathway of stepwise mechanism for the ETBE formation via the etherification of isobutene and ethanol on acidic BEA zeolite.

In the ONIOM calculations, the inner layer contains the cluster model as the active site region is treated with the high level quantum mechanical calculation whereas the rest of framework is treated by the low level. The ONIOM energy of the whole system is as follows:

$$E^{ONIOM} = E_{low}^{real} + E_{high}^{cluster} - E_{low}^{cluster} \tag{10}$$

E_{low}^{real} : Energy of real system is calculated with the low level of theory

$E_{high}^{cluster}$: Energy of cluster model system is calculated with the high level of theory

$E_{low}^{cluster}$: Energy of cluster model system is calculated with the low level of theory

Substituent values (S−values) are defined as the energy difference between the real system and the cluster model system (Vreven and Morokuma., 2002).

$$S(level) = BDE(level, real) - BDE(level, cluster) \tag{11}$$

BDE(level, real) : Binding energy of real system
BDE(level, cluster) : Binding energy of cluster model system

Appendix Table B1 The ONIOM(M06-2X/6−31G(d,p):UFF) energy of the stepwise reaction mechanisms on H−BEA zeolite.

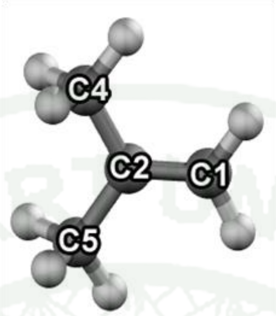
Reaction coordinate	**Relative energy (kcal/mol)**
B_Ads1	−25.0
B_TS1	−15.2
B_Int1	−17.0
B_Ads2	−38.2
B_TS2	−36.7
B_Ads3	−64.7

Appendix Table B2 Substituent values (S−values) and their differences between the real and model system at the M06−2X/6−31G(d,p) and UFF levels for the stepwise reaction mechanisms on H−BEA zeolite.

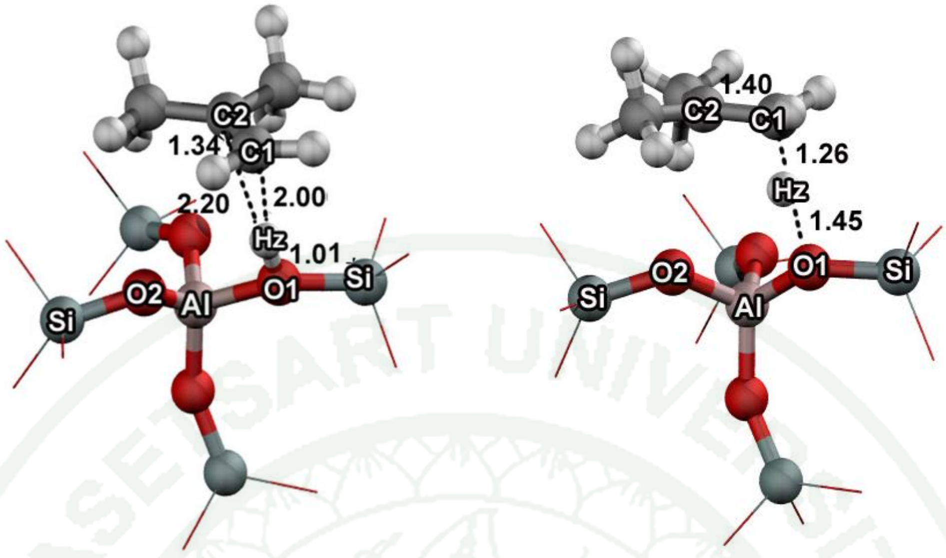
Reaction coordinate	M062X(kcal/mol)	UFF(kcal/mol)	ΔS(kcal/mol)	ΔS(au)
B_Ads1	−3.5	−7.1	3.6	0.00574893
B_TS1	−9.2	−10.5	1.3	0.00201723
B_Int1	−11.8	−10.9	−0.8	0.00130410
B_Ads2	−13.9	−16.6	2.8	0.00442671
B_TS2	−13.0	−14.8	1.9	0.00296637
B_Ads3	−8.1	−12.8	4.7	0.00743784

From Appendix Table B2 it can be seen that both of the substituent values at M06−2X/6−31G(d,p) and UFF have the same trend of the results which is a negative binding energy, to stabilize system. However, there are different substituent values between M06−2X/6−31G(d,p) and UFF. In particular the adsorption complex, UFF gives the over−binding energy compared to M06−2X/6−31G(d,p). Therefore, in order to make the results from ONIOM calculations more reliable, single point calculations at the higher level of theory are required.

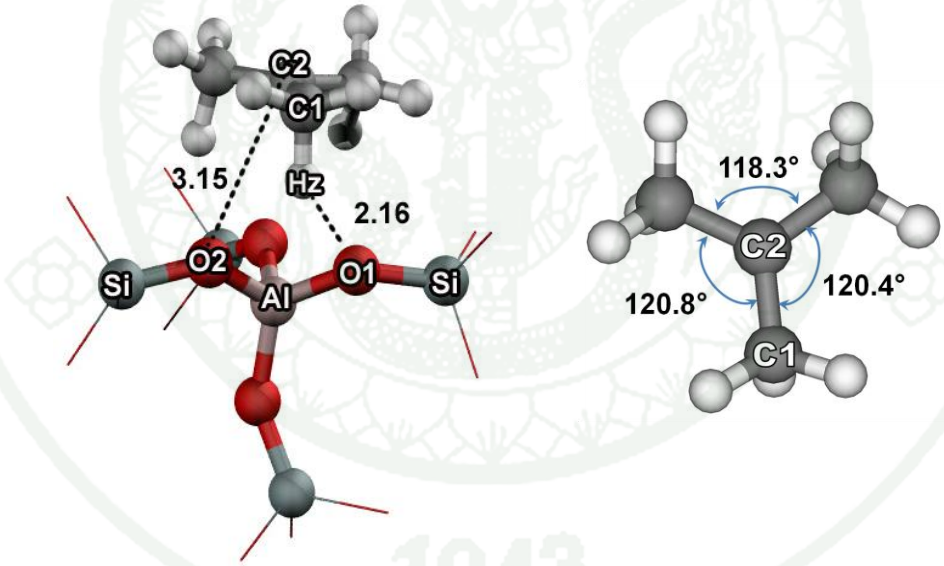
Appendix Table B3 The charged form NBO population analysis using the 54T model with the M06-2X/6-31G (d,p) level of theory.



Reaction coordinate	**NBO population analysis**			
	q(C1)	**q(C2)**	**q(C4)**	**q(C5)**
isobutene	-0.312	0.120	-0.397	-0.397
B_Ads1	-0.369	0.063	-0.406	-0.378
B_TS1	-0.469	0.211	-0.400	-0.429
B_Int1	-0.431	0.214	-0.438	-0.413
B_Ads2	-0.440	0.217	-0.437	-0.423
B_TS2	-0.402	0.251	-0.424	-0.409
B_Ads3	-0.341	0.160	-0.358	-0.349

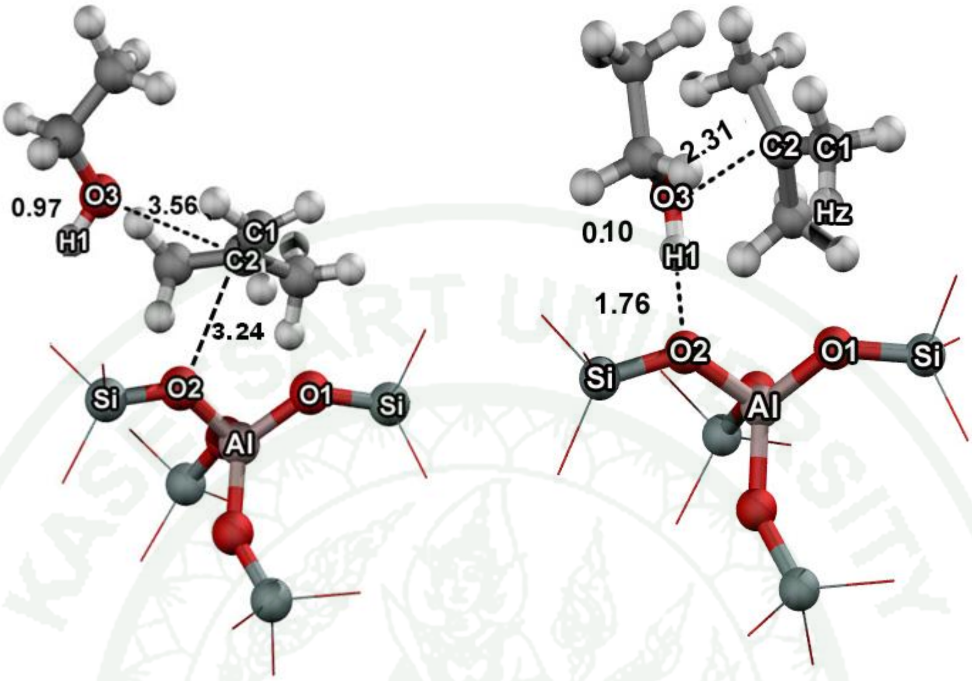


B_Ads1 B_TS1

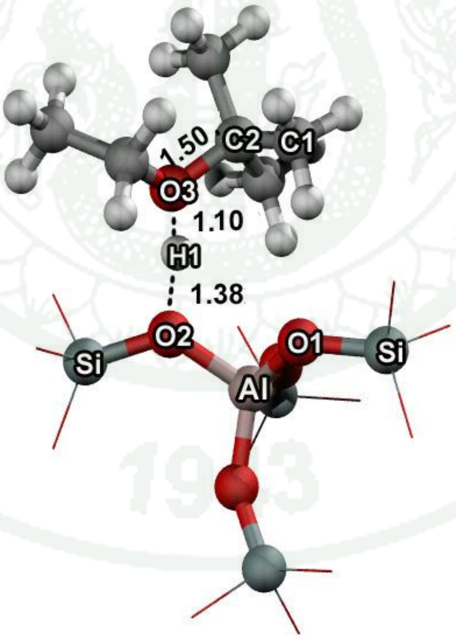


B_Int1

Appendix Figure B2 Optimized structure of all species involved in the etherification of isobutene with ethanol of the *tert*−butyl carbenium ion intermediate formation step of the stepwise reaction mechanism.



B_Ads2 B_TS2

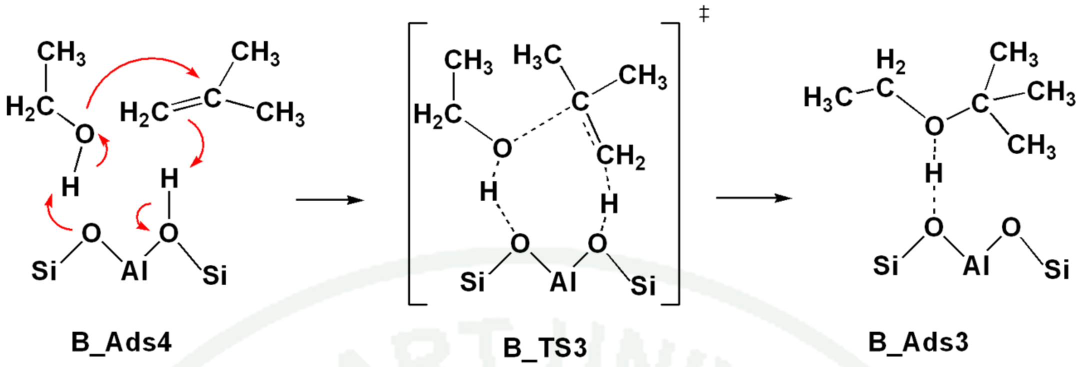


B_Ads3

Appendix Figure B3 Optimized structure of all species involved in the etherification of isobutene with ethanol of the ethyl *tert*−butyl ether formation step of the stepwise reaction mechanism.

Appendix C

Structures and energies optimization with the ONIOM(M06−2X/6−31G(d,p):UFF) method of all species involved in the concerted reaction mechanism catalyzed by H−BEA zeolite.



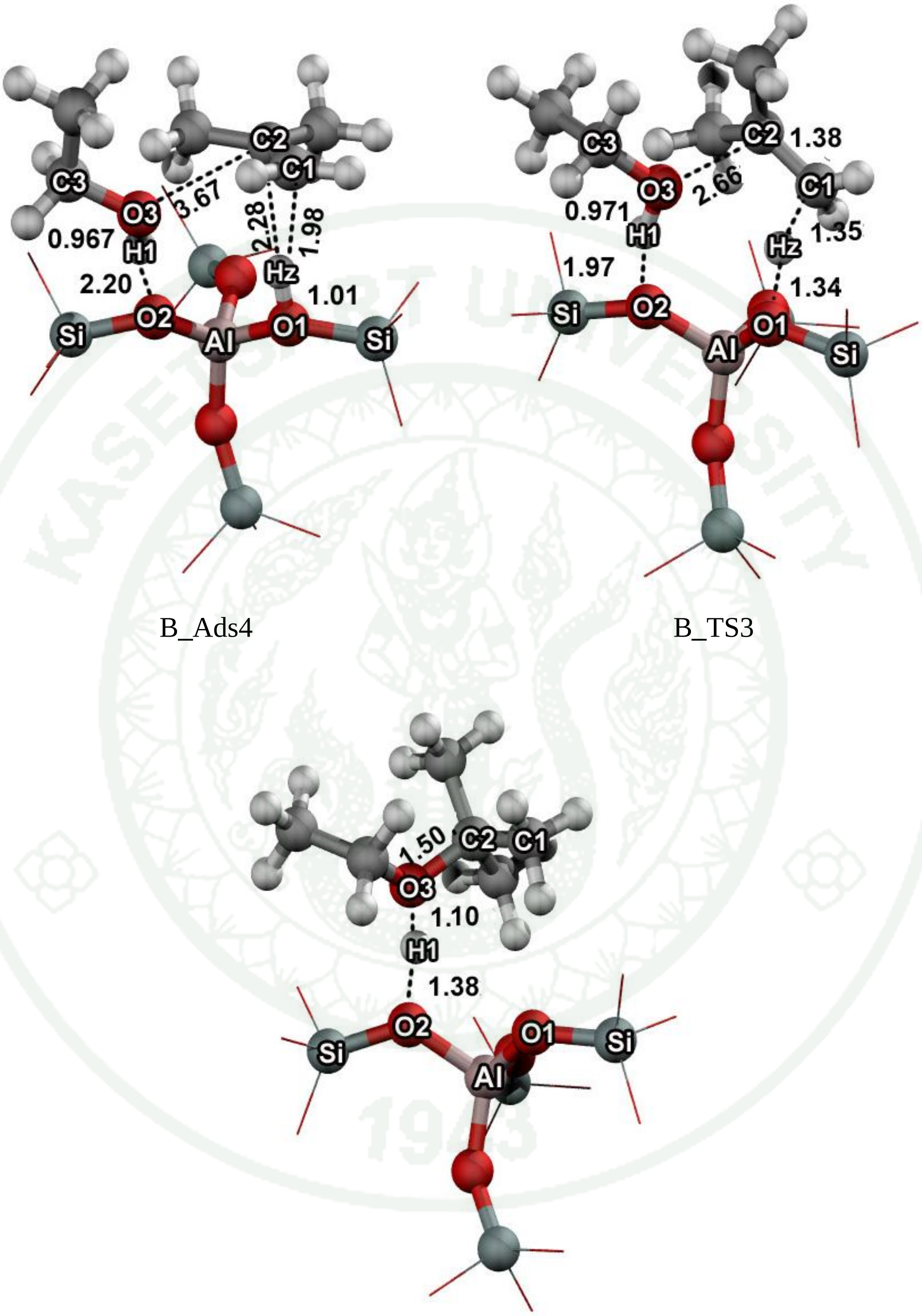
Appendix Figure C1 The reaction pathway of concerted mechanism for the ETBE formation via the etherification of isobutene and ethanol on acidic BEA zeolite.

Appendix Table C1 The ONIOM(M06-2X/6−31G(d,p):UFF) energy of the concerted reaction mechanisms on H−BEA zeolite.

Reaction coordinate	**Relative energy (kcal/mol)**
B_Ads4	−39.3
B_TS3	−29.5
B_Ads3	−64.7

Appendix Table C2 Substituent values (S−values) and their differences between the real and model system at the M06−2X/6−31G(d,p) and UFF levels for the concerted reaction mechanisms on H−BEA zeolite.

Reaction coordinate	**M062X(kcal/mol)**	**UFF(kcal/mol)**	**ΔS(kcal/mol)**	**ΔS(au)**
B_Ads4	−6.3	−12.0	5.7	0.00907320
B_TS3	−10.3	−12.3	2.0	0.00324901
B_Ads3	−8.1	−12.8	4.7	0.00721228



B_Ads4

B_TS3

B_Ads3

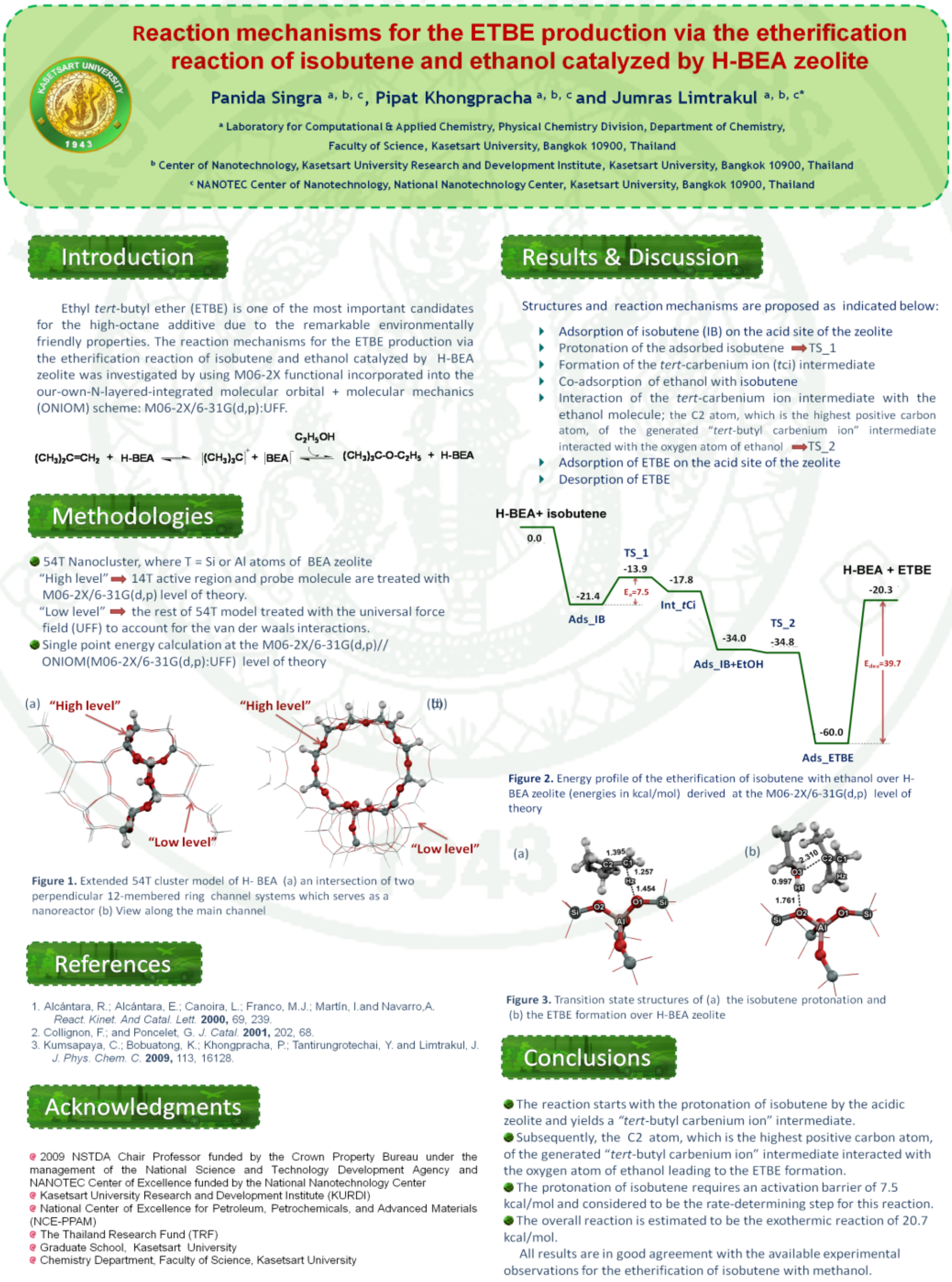
Appendix Figure C2 Optimized structure of all species involved in the etherification of isobutene with ethanol of the concerted reaction mechanism.

Appendix D

Poster and oral presentations, and proceeding publications

Poster Presentations

1. <u>Panida Singra</u>, Pipat Khongpracha, and Jumras Limtrakul. **Reaction Mechanisms Investigation on Etherification of Isobutene with Ethanol to ETBE Catalyzed by Acidic BEA Zeolite.** The 1st National Research Symposium on Petroleum, Petrochemicals and Advanced Materials and The 16th PPC Symposium on Petroleum, Petrochemicals and Polymers, Bangkok, Thailand, 22 April 2010.



Reaction mechanisms for the ETBE production via the etherification reaction of isobutene and ethanol catalyzed by H-BEA zeolite

Panida Singra [a, b, c], **Pipat Khongpracha** [a, b, c] **and Jumras Limtrakul** [a, b, c*]

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Introduction

Ethyl *tert*-butyl ether (ETBE) is one of the most important candidates for the high-octane additive due to the remarkable environmentally friendly properties. The reaction mechanisms for the ETBE production via the etherification reaction of isobutene and ethanol catalyzed by H-BEA zeolite was investigated by using M06-2X functional incorporated into the our-own-N-layered-integrated molecular orbital + molecular mechanics (ONIOM) scheme: M06-2X/6-31G(d,p):UFF.

$$(CH_3)_2C{=}CH_2 + \text{H-BEA} \rightleftharpoons |(CH_3)_3C|^+ + |BEA|^- \xrightleftharpoons{C_2H_5OH} (CH_3)_3C\text{-}O\text{-}C_2H_5 + \text{H-BEA}$$

Methodologies

- 54T Nanocluster, where T = Si or Al atoms of BEA zeolite
  "High level" ➡ 14T active region and probe molecule are treated with M06-2X/6-31G(d,p) level of theory.
  "Low level" ➡ the rest of 54T model treated with the universal force field (UFF) to account for the van der waals interactions.
- Single point energy calculation at the M06-2X/6-31G(d,p)//ONIOM(M06-2X/6-31G(d,p):UFF) level of theory

Figure 1. Extended 54T cluster model of H- BEA (a) an intersection of two perpendicular 12-membered ring channel systems which serves as a nanoreactor (b) View along the main channel

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- National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials (NCE-PPAM)
- The Thailand Research Fund (TRF)
- Graduate School, Kasetsart University
- Chemistry Department, Faculty of Science, Kasetsart University

Results & Discussion

Structures and reaction mechanisms are proposed as indicated below:

- Adsorption of isobutene (IB) on the acid site of the zeolite
- Protonation of the adsorbed isobutene ➡ TS_1
- Formation of the *tert*-carbenium ion (*t*ci) intermediate
- Co-adsorption of ethanol with isobutene
- Interaction of the *tert*-carbenium ion intermediate with the ethanol molecule; the C2 atom, which is the highest positive carbon atom, of the generated "*tert*-butyl carbenium ion" intermediate interacted with the oxygen atom of ethanol ➡ TS_2
- Adsorption of ETBE on the acid site of the zeolite
- Desorption of ETBE

Figure 2. Energy profile of the etherification of isobutene with ethanol over H-BEA zeolite (energies in kcal/mol) derived at the M06-2X/6-31G(d,p) level of theory

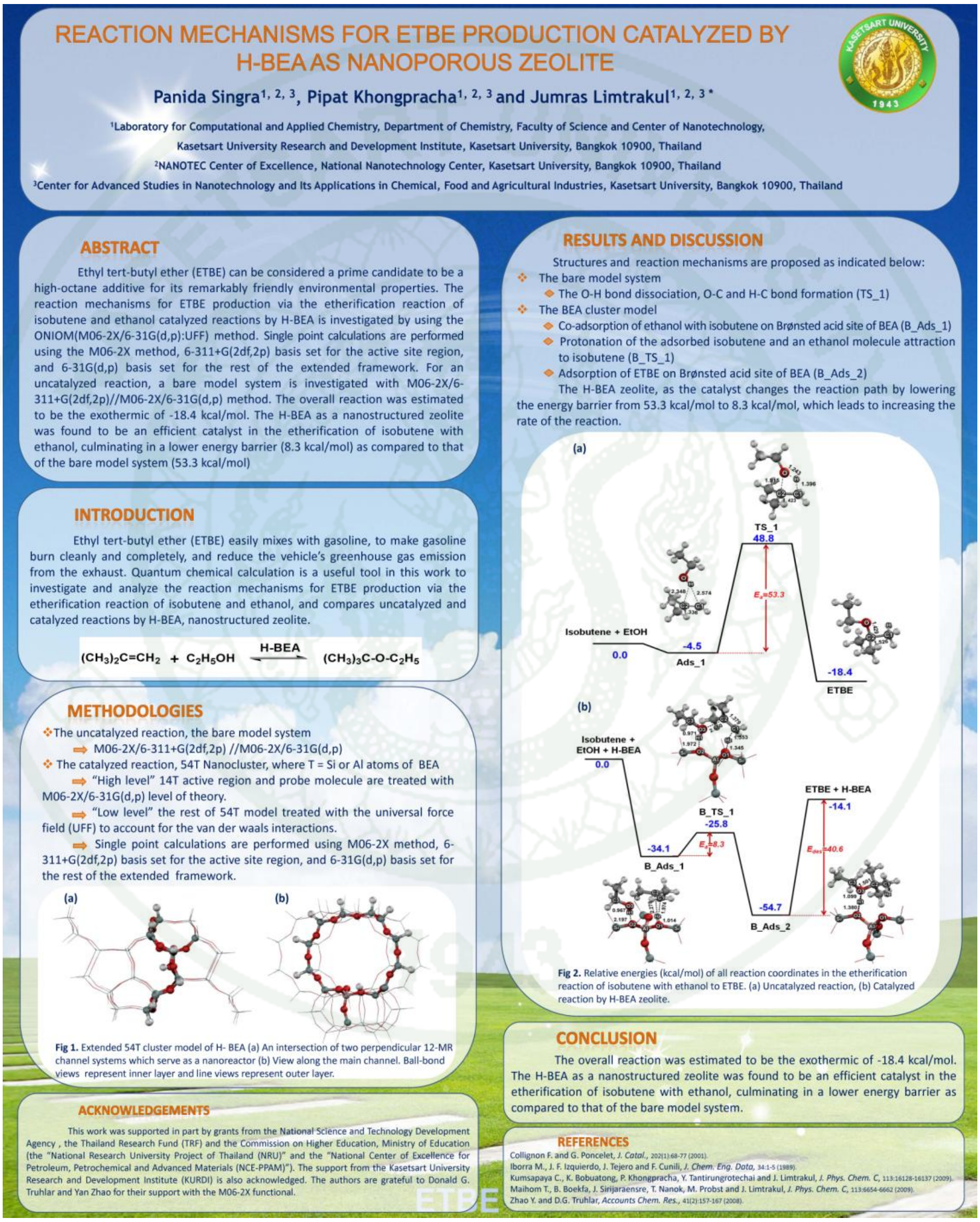
Figure 3. Transition state structures of (a) the isobutene protonation and (b) the ETBE formation over H-BEA zeolite

Conclusions

- The reaction starts with the protonation of isobutene by the acidic zeolite and yields a "*tert*-butyl carbenium ion" intermediate.
- Subsequently, the C2 atom, which is the highest positive carbon atom, of the generated "*tert*-butyl carbenium ion" intermediate interacted with the oxygen atom of ethanol leading to the ETBE formation.
- The protonation of isobutene requires an activation barrier of 7.5 kcal/mol and considered to be the rate-determining step for this reaction.
- The overall reaction is estimated to be the exothermic reaction of 20.7 kcal/mol.

All results are in good agreement with the available experimental observations for the etherification of isobutene with methanol.

2. Panida Singra, Pipat Khongpracha, and Jumras Limtrakul. **Reaction Mechanisms for ETBE Production Catalyzed by H-BEA as Nanoporous zeolite.** NanoThailand 2010, Phatumthani, Thailand, 18-20 November 2010.



REACTION MECHANISMS FOR ETBE PRODUCTION CATALYZED BY H-BEA AS NANOPOROUS ZEOLITE

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ABSTRACT

Ethyl tert-butyl ether (ETBE) can be considered a prime candidate to be a high-octane additive for its remarkably friendly environmental properties. The reaction mechanisms for ETBE production via the etherification reaction of isobutene and ethanol catalyzed reactions by H-BEA is investigated by using the ONIOM(M06-2X/6-31G(d,p):UFF) method. Single point calculations are performed using the M06-2X method, 6-311+G(2df,2p) basis set for the active site region, and 6-31G(d,p) basis set for the rest of the extended framework. For an uncatalyzed reaction, a bare model system is investigated with M06-2X/6-311+G(2df,2p)//M06-2X/6-31G(d,p) method. The overall reaction was estimated to be the exothermic of -18.4 kcal/mol. The H-BEA as a nanostructured zeolite was found to be an efficient catalyst in the etherification of isobutene with ethanol, culminating in a lower energy barrier (8.3 kcal/mol) as compared to that of the bare model system (53.3 kcal/mol)

INTRODUCTION

Ethyl tert-butyl ether (ETBE) easily mixes with gasoline, to make gasoline burn cleanly and completely, and reduce the vehicle's greenhouse gas emission from the exhaust. Quantum chemical calculation is a useful tool in this work to investigate and analyze the reaction mechanisms for ETBE production via the etherification reaction of isobutene and ethanol, and compares uncatalyzed and catalyzed reactions by H-BEA, nanostructured zeolite.

$$(CH_3)_2C{=}CH_2 + C_2H_5OH \xrightleftharpoons{\text{H-BEA}} (CH_3)_3C\text{-}O\text{-}C_2H_5$$

METHODOLOGIES

- The uncatalyzed reaction, the bare model system
  - M06-2X/6-311+G(2df,2p) //M06-2X/6-31G(d,p)
- The catalyzed reaction, 54T Nanocluster, where T = Si or Al atoms of BEA
  - "High level" 14T active region and probe molecule are treated with M06-2X/6-31G(d,p) level of theory.
  - "Low level" the rest of 54T model treated with the universal force field (UFF) to account for the van der waals interactions.
  - Single point calculations are performed using M06-2X method, 6-311+G(2df,2p) basis set for the active site region, and 6-31G(d,p) basis set for the rest of the extended framework.

Fig 1. Extended 54T cluster model of H- BEA (a) An intersection of two perpendicular 12-MR channel systems which serve as a nanoreactor (b) View along the main channel. Ball-bond views represent inner layer and line views represent outer layer.

RESULTS AND DISCUSSION

Structures and reaction mechanisms are proposed as indicated below:

- The bare model system
  - The O-H bond dissociation, O-C and H-C bond formation (TS_1)
- The BEA cluster model
  - Co-adsorption of ethanol with isobutene on Brønsted acid site of BEA (B_Ads_1)
  - Protonation of the adsorbed isobutene and an ethanol molecule attraction to isobutene (B_TS_1)
  - Adsorption of ETBE on Brønsted acid site of BEA (B_Ads_2)

The H-BEA zeolite, as the catalyst changes the reaction path by lowering the energy barrier from 53.3 kcal/mol to 8.3 kcal/mol, which leads to increasing the rate of the reaction.

Fig 2. Relative energies (kcal/mol) of all reaction coordinates in the etherification reaction of isobutene with ethanol to ETBE. (a) Uncatalyzed reaction, (b) Catalyzed reaction by H-BEA zeolite.

CONCLUSION

The overall reaction was estimated to be the exothermic of -18.4 kcal/mol. The H-BEA as a nanostructured zeolite was found to be an efficient catalyst in the etherification of isobutene with ethanol, culminating in a lower energy barrier as compared to that of the bare model system.

ACKNOWLEDGEMENTS

This work was supported in part by grants from the National Science and Technology Development Agency , the Thailand Research Fund (TRF) and the Commission on Higher Education, Ministry of Education (the "National Research University Project of Thailand (NRU)" and the "National Center of Excellence for Petroleum, Petrochemical and Advanced Materials (NCE-PPAM)"). The support from the Kasetsart University Research and Development Institute (KURDI) is also acknowledged. The authors are grateful to Donald G. Truhlar and Yan Zhao for their support with the M06-2X functional.

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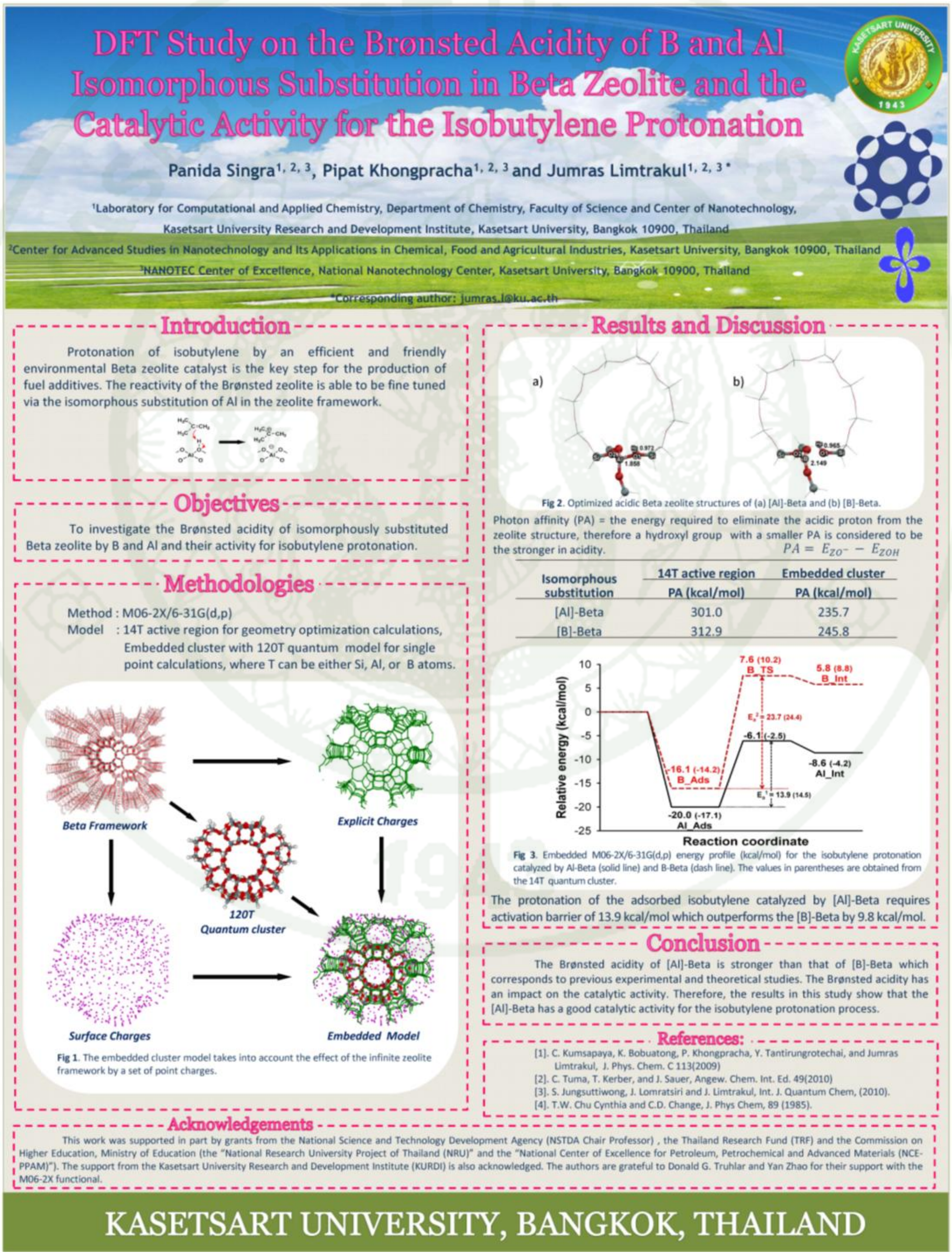
Kumsapaya C., K. Bobuatong, P. Khongpracha, Y. Tantirungrotechai and J. Limtrakul, *J. Phys. Chem. C*, 113:16128-16137 (2009).
Maihom T., B. Boekfa, J. Sirijaraensre, T. Nanok, M. Probst and J. Limtrakul, *J. Phys. Chem. C*, 113:6654-6662 (2009).
Zhao Y. and D.G. Truhlar, *Accounts Chem. Res.*, 41(2):157-167 (2008).

3. Panida Singra, Pipat Khongpracha, and Jumras Limtrakul. **DFT Study on the Brønsted Acidity of B and Al Isomorphous Substitution in Beta Zeolite and the Catalytic Activity for the Isobutylene Protonation.** The winter School of SOKENDAI/Asian CORE Program, “Frontiers of Molecular Science-Life, Material, Energy, and Space”, Okazaki, Japan, 19-22 February 2011.



DFT Study on the Brønsted Acidity of B and Al Isomorphous Substitution in Beta Zeolite and the Catalytic Activity for the Isobutylene Protonation

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Introduction

Protonation of isobutylene by an efficient and friendly environmental Beta zeolite catalyst is the key step for the production of fuel additives. The reactivity of the Brønsted zeolite is able to be fine tuned via the isomorphous substitution of Al in the zeolite framework.

Objectives

To investigate the Brønsted acidity of isomorphously substituted Beta zeolite by B and Al and their activity for isobutylene protonation.

Methodologies

Method : M06-2X/6-31G(d,p)
Model : 14T active region for geometry optimization calculations, Embedded cluster with 120T quantum model for single point calculations, where T can be either Si, Al, or B atoms.

Fig 1. The embedded cluster model takes into account the effect of the infinite zeolite framework by a set of point charges.

Results and Discussion

Fig 2. Optimized acidic Beta zeolite structures of (a) [Al]-Beta and (b) [B]-Beta.

Photon affinity (PA) = the energy required to eliminate the acidic proton from the zeolite structure, therefore a hydroxyl group with a smaller PA is considered to be the stronger in acidity.

$$PA = E_{ZO^-} - E_{ZOH}$$

Isomorphous substitution	14T active region	Embedded cluster
	PA (kcal/mol)	PA (kcal/mol)
[Al]-Beta	301.0	235.7
[B]-Beta	312.9	245.8

Fig 3. Embedded M06-2X/6-31G(d,p) energy profile (kcal/mol) for the isobutylene protonation catalyzed by Al-Beta (solid line) and B-Beta (dash line). The values in parentheses are obtained from the 14T quantum cluster.

The protonation of the adsorbed isobutylene catalyzed by [Al]-Beta requires activation barrier of 13.9 kcal/mol which outperforms the [B]-Beta by 9.8 kcal/mol.

Conclusion

The Brønsted acidity of [Al]-Beta is stronger than that of [B]-Beta which corresponds to previous experimental and theoretical studies. The Brønsted acidity has an impact on the catalytic activity. Therefore, the results in this study show that the [Al]-Beta has a good catalytic activity for the isobutylene protonation process.

References:

[1]. C. Kumsapaya, K. Bobuatong, P. Khongpracha, Y. Tantirungrotechai, and Jumras Limtrakul, J. Phys. Chem. C 113(2009)
[2]. C. Tuma, T. Kerber, and J. Sauer, Angew. Chem. Int. Ed. 49(2010)
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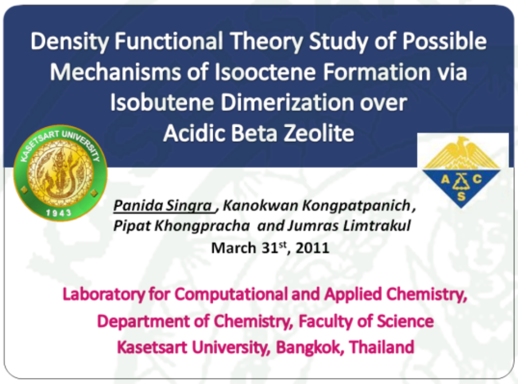
Acknowledgements

This work was supported in part by grants from the National Science and Technology Development Agency (NSTDA Chair Professor) , the Thailand Research Fund (TRF) and the Commission on Higher Education, Ministry of Education (the “National Research University Project of Thailand (NRU)” and the “National Center of Excellence for Petroleum, Petrochemical and Advanced Materials (NCE-PPAM)”). The support from the Kasetsart University Research and Development Institute (KURDI) is also acknowledged. The authors are grateful to Donald G. Truhlar and Yan Zhao for their support with the M06-2X functional.

KASETSART UNIVERSITY, BANGKOK, THAILAND

Oral Presentation

1. Panida Singra, Kanokwan Kongpatpanich, Pipat Khongpracha, and Jumras Limtrakul. **Density Functional Theory Study of Possible Mechanisms of Isooctene Formation via Isobutene dimerization over Acid Beta Zeolite.** The 241st ACS National Meeting & Exposition, Anaheim, California, USA, 27-31 March 2011.



Density Functional Theory Study of Possible Mechanisms of Isooctene Formation via Isobutene Dimerization over Acidic Beta Zeolite

Panida Singra , Kanokwan Kongpatpanich , Pipat Khongpracha and Jumras Limtrakul

March 31st, 2011

Laboratory for Computational and Applied Chemistry, Department of Chemistry, Faculty of Science Kasetsart University, Bangkok, Thailand

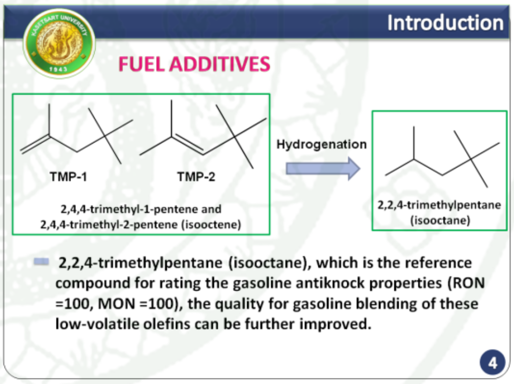
Outlines

- Introduction
- Objective
- Methodology
- Results and Discussion
- Conclusions

Introduction

ISOOCTENE

- An intermediate of a surface-active agent
- A starting chemical in the production of fuel additives



Introduction

FUEL ADDITIVES

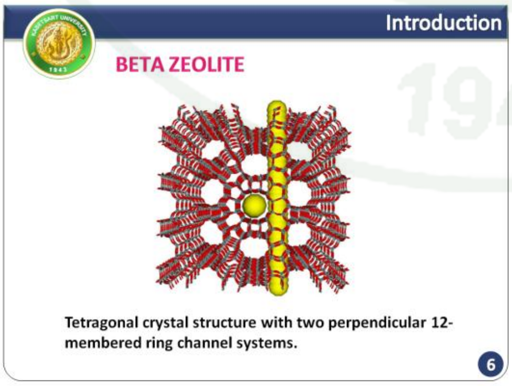
TMP-1 TMP-2

2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene (isooctene)

Hydrogenation

2,2,4-trimethylpentane (isooctane)

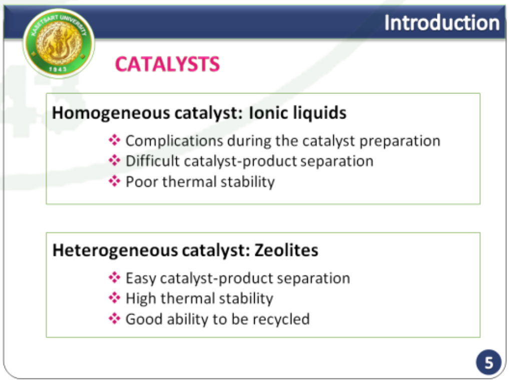
- 2,2,4-trimethylpentane (isooctane), which is the reference compound for rating the gasoline antiknock properties (RON =100, MON =100), the quality for gasoline blending of these low-volatile olefins can be further improved.



Introduction

BETA ZEOLITE

Tetragonal crystal structure with two perpendicular 12-membered ring channel systems.



Introduction

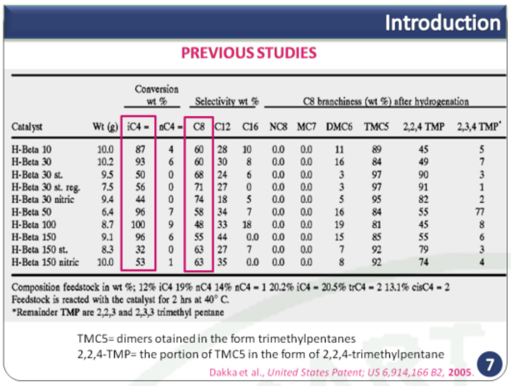
CATALYSTS

Homogeneous catalyst: Ionic liquids

- Complications during the catalyst preparation
- Difficult catalyst-product separation
- Poor thermal stability

Heterogeneous catalyst: Zeolites

- Easy catalyst-product separation
- High thermal stability
- Good ability to be recycled



Introduction

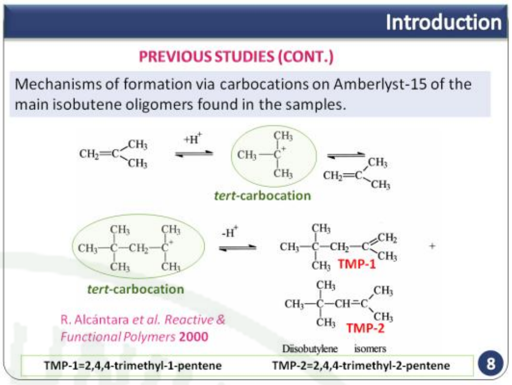
PREVIOUS STUDIES

Catalyst	Wt (g)	Conversion wt %		Selectivity wt %			C8 branchiness (wt %) after hydrogenation					
		iC4 =	nC4 =	C8	C12	C16	NC8	MC7	DMC6	TMC5	2,2,4 TMP	2,3,4 TMP*
H-Beta 10	10.0	87	4	60	28	10	0.0	0.0	11	89	45	5
H-Beta 30	10.2	93	6	60	30	8	0.0	0.0	16	84	49	7
H-Beta 30 st.	9.5	50	0	68	24	6	0.0	0.0	3	97	90	3
H-Beta 30 st. reg.	7.5	56	0	71	27	0	0.0	0.0	3	97	91	1
H-Beta 30 nitric	9.4	44	0	74	18	5	0.0	0.0	5	95	82	2
H-Beta 50	6.4	96	7	58	34	7	0.0	0.0	16	84	55	77
H-Beta 100	8.7	100	9	48	33	18	0.0	0.0	19	81	45	8
H-Beta 150	9.1	96	6	55	44	0.0	0.0	0.0	15	85	55	6
H-Beta 150 st.	8.3	32	0	63	27	7	0.0	0.0	7	92	79	3
H-Beta 150 nitric	10.0	53	1	63	35	0.0	0.0	0.0	8	92	74	4

Composition feedstock in wt %; 12% iC4 19% nC4 14% nC4 = 1 20.2% iC4 = 20.5% trC4 = 2 13.1% cisC4 = 2
Feedstock is reacted with the catalyst for 2 hrs at 40° C.
*Remainder TMP are 2,2,3 and 2,3,3 trimethyl pentane

TMC5= dimers otained in the form trimethylpentanes
2,2,4-TMP= the portion of TMC5 in the form of 2,2,4-trimethylpentane

Dakka et al., *United States Patent; US 6,914,166 B2*, **2005**.



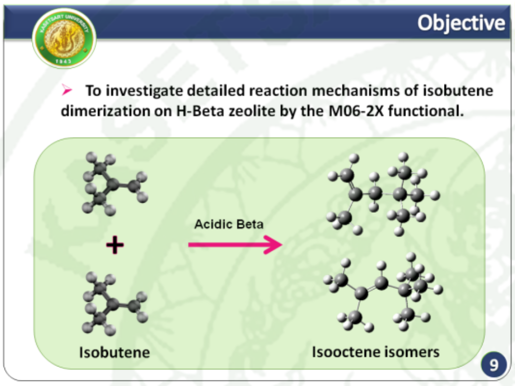
Introduction

PREVIOUS STUDIES (CONT.)

Mechanisms of formation via carbocations on Amberlyst-15 of the main isobutene oligomers found in the samples.

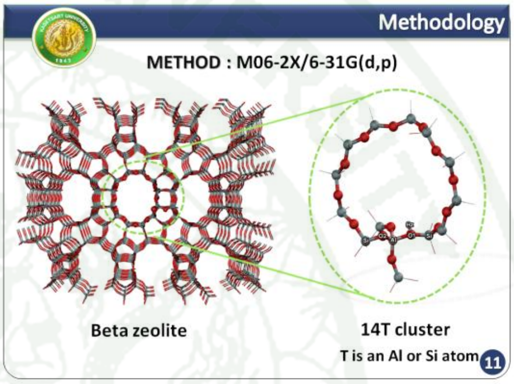
R. Alcántara *et al. Reactive & Functional Polymers* **2000**

TMP-1=2,4,4-trimethyl-1-pentene
TMP-2=2,4,4-trimethyl-2-pentene



Objective

- To investigate detailed reaction mechanisms of isobutene dimerization on H-Beta zeolite by the M06-2X functional.

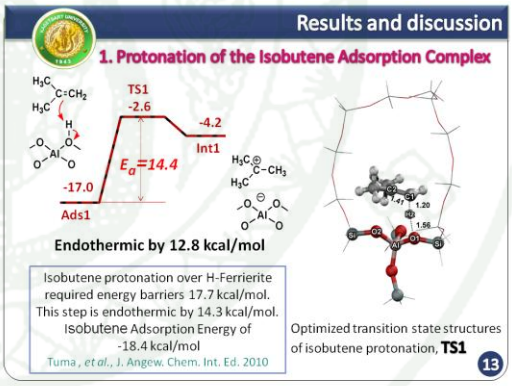


Methodology

METHOD : M06-2X/6-31G(d,p)

T is an Al or Si atom

Results and Discussion



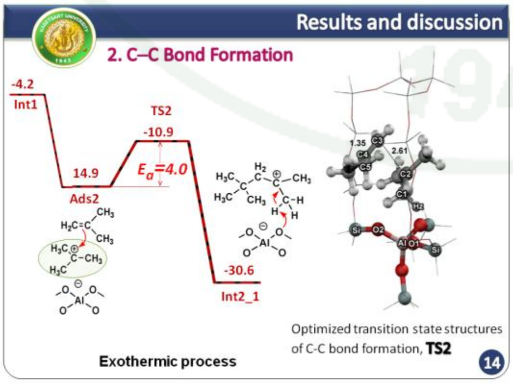
Results and discussion

1. Protonation of the Isobutene Adsorption Complex

Endothermic by 12.8 kcal/mol

Isobutene protonation over H-Ferrierite required energy barriers 17.7 kcal/mol. This step is endothermic by 14.3 kcal/mol. Isobutene Adsorption Energy of -18.4 kcal/mol
Tuma , *et al.*, J. Angew. Chem. Int. Ed. 2010

Optimized transition state structures of isobutene protonation, **TS1**

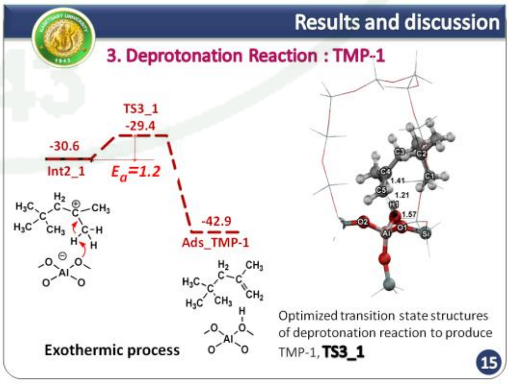


Results and discussion

2. C–C Bond Formation

Optimized transition state structures of C-C bond formation, **TS2**

Exothermic process

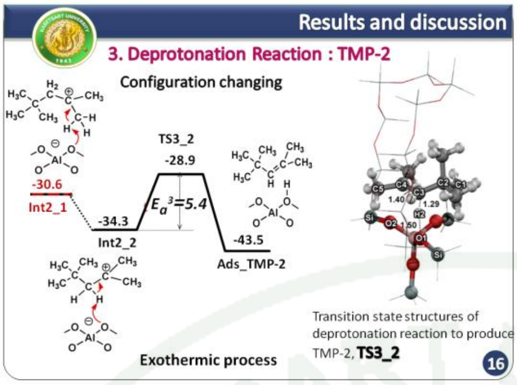


Results and discussion

3. Deprotonation Reaction : TMP-1

Exothermic process

Optimized transition state structures of deprotonation reaction to produce TMP-1, **TS3_1**



Results and discussion

3. Deprotonation Reaction : TMP-2

Configuration changing

Exothermic process

Transition state structures of deprotonation reaction to produce TMP-2, **TS3_2**

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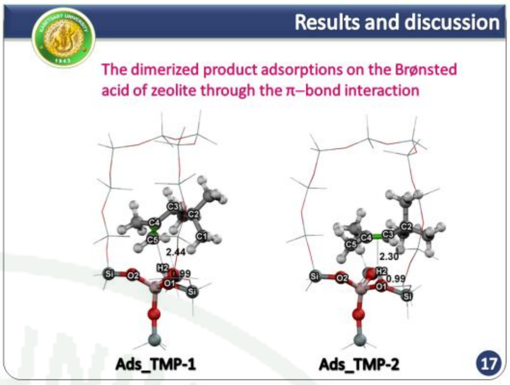
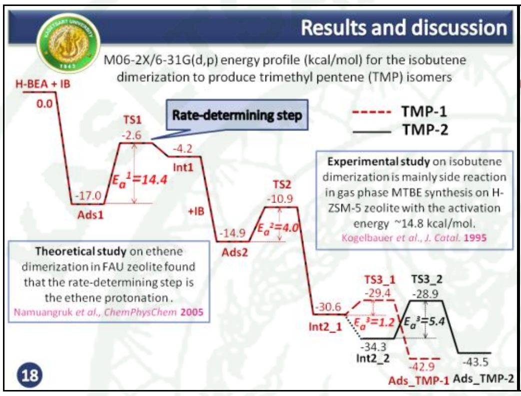


Results and discussion

The dimerized product adsorptions on the Brønsted acid of zeolite through the π–bond interaction

Ads_TMP-1 **Ads_TMP-2**

17



Results and discussion

M06-2X/6-31G(d,p) energy profile (kcal/mol) for the isobutene dimerization to produce trimethyl pentene (TMP) isomers

Rate-determining step

Experimental study on isobutene dimerization is mainly side reaction in gas phase MTBE synthesis on H-ZSM-5 zeolite with the activation energy ~14.8 kcal/mol.
Kogelbauer *et al.*, *J. Catal.* **1995**

Theoretical study on ethene dimerization in FAU zeolite found that the rate-determining step is the ethene protonation.
Namuangruk *et al.*, *ChemPhysChem* **2005**

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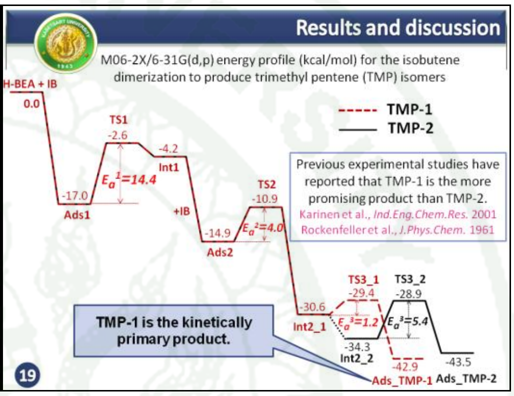

Results and discussion

M06-2X/6-31G(d,p) energy profile (kcal/mol) for the isobutene dimerization to produce trimethyl pentene (TMP) isomers

Previous experimental studies have reported that TMP-1 is the more promising product than TMP-2.
Karinen et al., *Ind.Eng.Chem.Res.* 2001
Rockenfeller et al., *J.Phys.Chem.* 1961

TMP-1 is the kinetically primary product.

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Acknowledgements

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- National Research University Project of Thailand (NRU)
- National Nanotechnology Center under the National Science and Technology Development Agency (NSTDA)
- National Center of Excellence for Petroleum, Petrochemical and Advanced Materials (NCE-PPAM)
- Commission on Higher Education (CHE)
- Kasetsart University Research and Development Institute (KURDI)

Proceeding publications

1. Panida Singra, Pipat Khongpracha, and Jumras Limtrakul. **Reaction Mechanisms for ETBE Production Catalyzed by H-BEA as Nanoporous zeolite.** NanoThailand 2010, Phatumthani, Thailand, 18-20 November 2010.

Reaction Mechanisms for ETBE Production Catalyzed by H-BEA as Nanoporous Zeolite

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Keywords Zeolite, Etherification reaction, Octane booster, Ethyl tert-butyl ether (ETBE)

Introduction

Ethyl tert-butyl ether (ETBE) can be considered a prime candidate to be a high-octane additive for its remarkably friendly environmental properties. ETBE easily mixes with gasoline, to make gasoline burn cleanly and completely, and reduce the vehicle's greenhouse gas emission from the exhaust.

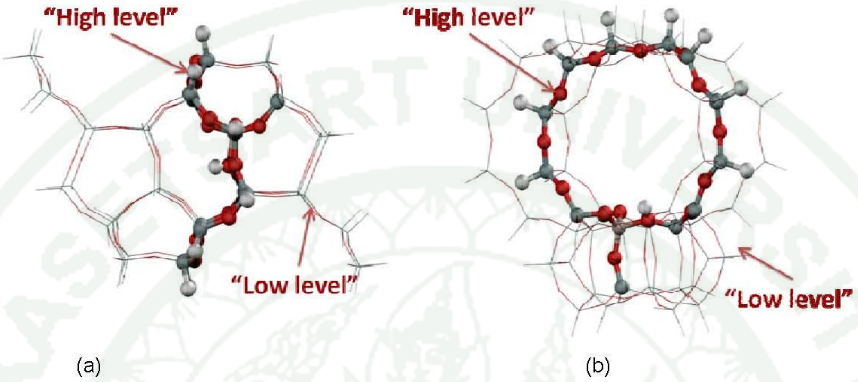
ETBE is readily synthesized by the etherification reaction of isobutene with ethanol. Conventionally, sulfonated acidic ion-exchange resin catalysts, such as Amberlyst-15 and Lewatit K2631 were used to catalyze the reaction for synthesis of the ETBE. Although these catalysts are very efficient, they have some disadvantages, such as low thermal stability and corrosion problems in the reactor. Hence, zeolites become more advantageous because of high thermal and chemical stability, and their ability to be recycled result in there being many investigations on zeolite catalysts. From a previous experimental study on the vapor phase synthesis of MTBE and ETBE, it was found that H-BEA is as active as Amberlyst-15. The order for the activity of commonly used zeolites decreases as follow: H-BEA > H-Y ≥ H-mordenite > H-ZSM-5.

Quantum chemical calculation is a useful tool in this work to investigate and analyze the reaction mechanisms for ETBE production via the etherification reaction of isobutene and ethanol, and compares uncatalyzed and catalyzed reactions by H-BEA, nanostructured zeolite.

Methodology

The uncatalyzed reaction, the bare model system, is investigated with M06-2X/6-311+G(2df,2p) //M06-2X/6-31G(d,p) calculations.

For the catalyzed reaction, the 54T nanocluster is used as the model of the Brønsted acid site in the H-BEA zeolite framework. This model is taken from the BEA zeolite crystal lattice structures. For computational efficiency, the 54T nanocluster model is subdivided into two layers according to the Our-own-N-layered-integrated molecular orbital + molecular mechanics (ONIOM) scheme. An inner layer, high level, consists of a 14T cluster including the 12-membered ring and the other two Si atoms around the Al atom, as the active site region, is treated with the density function, namely M06-2X with the 6-31G(d,p) basis set. An outer layer, low level, consists of the rest of the extended framework, is treated with the universal force field (UFF). This force field has been found to provide a good description of the long-range van der Waals (vdW) interactions. In the structure optimization, only the 5T cluster of the active site region, [(≡SiO)$_3$ Al(OH)Si≡], and the probe molecule are allowed to relax while the rest is fixed at the crystallographic coordinates. Frequency calculation at the same level of the active site region was carried out to verify transition states structure with only one imaginary frequency. In order to make the results more reliable, single point calculations are performed using M06-2X method, 6-311+G(2df,2p) basis set for the active site region, and 6-31G(d,p) basis set for the rest of the extended framework. All calculations were performed using the Gaussian 03 code.



(a) (b)

Fig. 1 Extended 54T cluster model of H- BEA (a) An intersection of two perpendicular 12-membered ring channel systems which serve as a nanoreactor (b) View along the main channel.

Results and Discussion

The etherification reaction of isobutene and ethanol to ETBE catalyzed by H-BEA. The reaction is initiated by the coadsorption between isobutene and ethanol over the Brønsted acid site of BEA, the coadsorption complex (B_Ads_1), was stabilized by orbital interaction between the π bonding orbital of the C1=C2 bond of isobutene with the σ*-antibonding orbital of O1-Hz bond zeolite and interaction between H atom of ethanol with the O atom of zeolite. This was followed by the concerted transition state (B_TS_1), a protonation of the adsorbed isobutene and an ethanol molecule attraction to isobutene occurs simultaneously, resulting in adsorbed ETBE (B_Ads_2), which is desorbed in the final step. The uncatalyzed reaction is from the bare model system. The transition state concerns the O-H bond dissociation, O-C and H-C bond formation. The optimized geometric parameters of all species involved in the etherification of isobutene with ethanol are showed in Tables1 and 2.

Table 1 Optimized geometric parameters of all species involved in the ETBE formation of the uncatalyzed reaction, the bare model system.

Parameter	Ads_1	TS_1	Ads_2
Distance (Å)			
C1-H	2.57	1.40	1.09
C2-H	2.35	1.74	2.16
H-O	0.97	1.24	2.64
C1-C2	1.34	1.42	1.53
Angle (°)			
C2-C1-H	65.1	76.3	109.7
C1-C2-H	83.8	51.2	28.4
C1-H-O	155.5	130.2	67.0
C1-C2-O	99.2	90.4	110.6

Table 2 Optimized geometric parameters of all species involved in the ETBE formation of the catalyzed reaction by H-BEA zeolite.

Parameter	**zeolite**	**B_Ads_1**	**B_TS_1**	**B_Ads_2**
Distance (Å)				
O1-Hz	0.97	1.01	1.34	2.35
C1-Hz	-	1.97	1.35	1.09
C2-Hz	-	2.28	2.12	2.16
C1-C2	-	1.35	1.38	1.52
O3-C2	-	3.67	2.66	1.50
O3-C3	-	1.42	1.42	1.46
O3-H1	-	0.97	0.97	1.10
H1-O2	-	2.20	1.97	1.38
Angle (°)				
Al-O1-Si	131.8	130.2	129.2	130.0
Al-O2-Si	129.8	130.5	133.4	129.8
O1-Hz-C1	-	172.4	156.2	161.6
Hz-C1-C2	-	163.9	102.0	110.5

The H-BEA zeolite, as the catalyst changes the reaction path by lowering the energy barrier from 53.3 kcal/mol to 8.3 kcal/mol, which leads to increasing the rate of the reaction. The reaction for the ETBE production was exothermic and this study provides the calculated reaction energy of –18.4 kcal/mol. This result is reasonable and compares well with the experimental study of the enthalpy of reaction by –14.9±0.5 kcal/mol. The calculated relative energies of all reaction coordinates are summarized in Fig. 2.

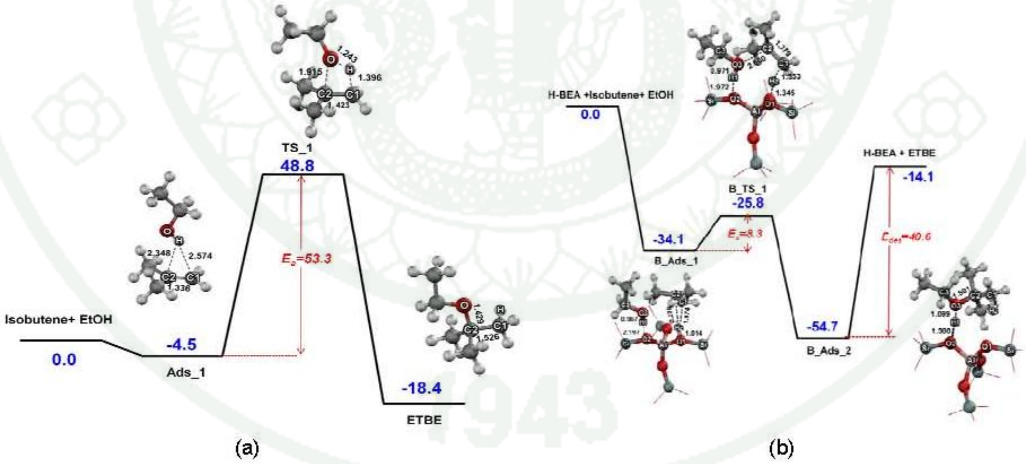


Fig. 2 Relative energies (kcal/mol) of all reaction coordinates in the etherification reaction of isobutene with ethanol to ETBE. (a) Uncatalyzed reaction, the bare model system, (b) Catalyzed reaction by H-BEA zeolite.

Conclusion

The reaction mechanisms for ETBE production via the etherification reaction of isobutene and ethanol catalyzed reactions by H-BEA is investigated by using the ONIOM(M06-2X/6-31G(d,p):UFF) method. Single point calculations are performed using the M06-2X method, 6-311+G(2df,2p) basis set for the active site region, and 6-31G(d,p) basis set for the rest of the extended framework. For the uncatalyzed reaction, the bare model system is investigated with M06-2X/6-311+G(2df,2p)//M06-2X/6-31G(d,p) method. The overall reaction was estimated to be the exothermic of −18.4 kcal/mol. The H-BEA as a nanostructured zeolite was found to be an efficient catalyst in the etherification of isobutene with ethanol, culminating in a lower energy barrier (8.3 kcal/mol) as compared to that of the bare model system (53.3 kcal/mol).

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2. Panida Singra, Kanokwan Kongpatpanich, Pipat Khongpracha, and Jumras Limtrakul. **Density Functional Theory Study of Possible Mechanisms of Isooctene Formation via Isobutene dimerization over Acid Beta Zeolite.** The 241st ACS National Meeting & Exposition, Anaheim, California, USA, 27-31 March 2011.

DENSITY FUNCTIONAL THEORY STUDY OF POSSIBLE MECHANISMS OF ISOOCTENE FORMATION VIA ISOBUTENE DIMERIZATION OVER ACIDIC BETA ZEOLITE

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Introduction

Dimerization and further oligomerization reactions are among the most important reactions in petrochemical industries. Isobutene oligomerization is a very useful process for the preparation of a range of products that are of commercial interest, such as isoparaffins, higher alcohols or aldehydes. Highly branched trimethylpentanes (isooctanes) are among several chemicals that are of particular interest as gasoline octane number enhancers. Such octanes can be obtained through the hydrogenation of trimethylpentenes (isooctenes) which are the main products of isobutene dimerization. The isooctene chemical is also used as a versatile intermediate of a surface-active agent, a starting chemical in the production of fuel additives[1-2]. A wide range of catalysts has been tested for isobutene dimerization such as ionic liquids[3] and sulfonic acid resins[4]. However these catalysts have some limitations resulting from complications during the catalyst preparation, notably, the catalyst-product separation step and their poor thermal stability. Acidic zeolite catalysts would seem to be a good candidate for catalyzing this reaction due to their size and shape-selective properties, high thermal stability as well as the ability to be recycled. It is well-known that heterogeneous catalysts have been used in petroleum refineries and petroleum chemical industries for many years[5-6]. Previous experimental studies on oligomerization of isobutene suggested that the beta zeolite catalytic membrane provides a high activity towards trimethyl pentene isomers. Moreover, the coke deposition which would cause fast deactivation of applied beta zeolite was not detected in the zeolite pore[7-8].

The general reaction mechanisms of isobutene dimerization are considered to proceed via isobutene protonation by acidic catalyst to generate a first carbocation (C_4^+) intermediate. The newly formed carbocation subsequently reacts with another isobutene molecule yielding a bigger carbocation (C_8^+) and finally the deprotonation of carbocation to the catalyst regenerating a promptly reused acid site and giving trimethyl pentene products. Typically, the main trimethylpentene isomers obtained upon the reaction are 2,4,4-trimethyl-1-pentene (TMP-1) and 2,4,4-trimethyl-2-pentene (TMP-2).

The experimental study on alkene dimerization or oligomerization reaction over solid acid catalysts is rather complicated. It is a highly exothermic reaction that is very difficult to control and can rapidly occur to form higher oligomer products and bring about the deactivation of catalysts by coke formation[9-10]. Therefore, a theoretical study based on quantum chemical calculation is a useful tool to analyze the reaction mechanisms in deep detail and can fulfill the experimental study. The aim of the present work is to investigate detailed reaction mechanisms of isobutene dimerization on acidic beta zeolite by employing the well-calibrated model of the M06-2X functional[11].

Methods

Quantum cluster models for representing the structure of beta zeolite were taken from its crystallographic structure[12]. A 14T quantum cluster of beta zeolite was selected to represent the acid site of the catalyst, where T is an Al or Si atom. This cluster covers the 12-membered ring (12MR) representing the main gateway to the intersection of two perpendicular 12MR channel systems, where the reactions normally take place[13-14]. A silicon atom at a T5 position in the beta zeolite was replaced with an aluminum atom to generate the Brønsted acid site. All geometry optimizations were performed by the M06-2X functional with the 6-31G(d,p) basis set. With this well-calibrated method, one of the important interactions, namely the van der Waals interaction, is taken into account. During the optimization, only the active site of the catalyst $[(\equiv SiO)_3Al(OH)Si\equiv]$, and the probe molecule are allowed to relax, while the rest is fixed at the crystallographic coordinates. Frequency calculation at the same level of theory was carried out to verify transition state structures with only one imaginary frequency. This method is successfully applied to the studies of various organic reactions in the zeolite pores[15-18]. All calculations were performed by using the Gaussian 03 code[19] incorporated with the Minnesota density functions module 3.1 by Yan Zhao and Donald G. Truhlar.

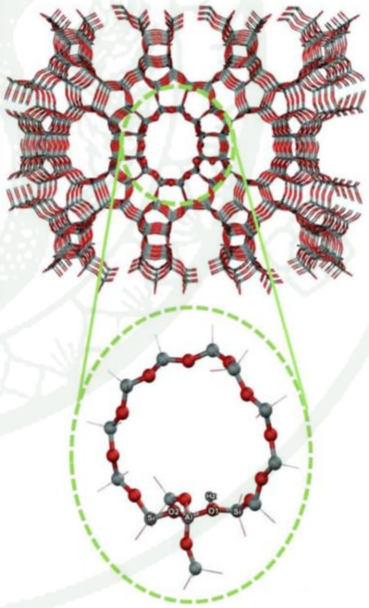


Figure 1. Illustration of H-beta zeolite framework; inset is the 14 T quantum cluster of beta zeolite being selected to represent the acid site of the catalyst, where T is an Al or Si atom.

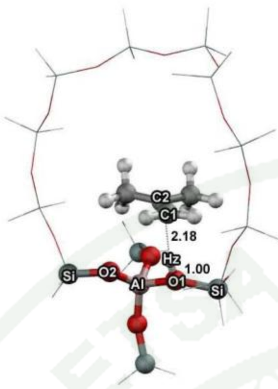
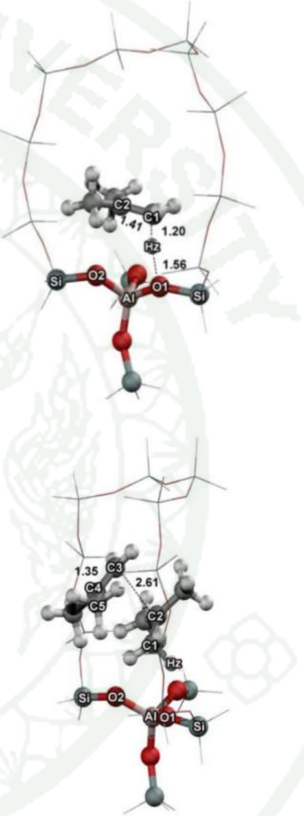


Figure 2. Presentation of an isobutene molecule adsorbed on acidic beta zeolite, Ads1.

Results and Discussion

Reaction mechanisms of isobutene dimerization. In the details of the mechanisms, isobutene is first adsorbed at the Brønsted acid site by the π–bond interaction between the double bond of isobutene with the acidic proton of beta zeolite. Then the adsorbed complex is protonated to give a *tert*-butyl carbocation intermediate. Subsequently, a second isobutene molecule interacts with the *tert*-butyl carbocation intermediate to form the *tert*-octyl carbocation (diisobutene carbocation) and finally the *tert*-octyl carbocation returns a proton back to the catalyst yielding the dimerized products, namely 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene.

1. Protonation of the isobutene adsorption complex. This step is started by the absorption of isobutene with acidic beta zeolite. The adsorption complex mode, Ads1, takes place with the C1=C2 bond interacting with the acidic proton (Hz) by C1–Hz and C2–Hz with an average distance of 2.18 Å, and the O1–Hz bond length increased from 0.97 to 1.00 Å (shown in Figure 2.). The isobutene molecule was slightly perturbed by the zeolite cavity when adsorbed at the Brønsted acid site. The calculated adsorption energy is −17.0 kcal/mol. Unfortunately, there is no available experimental data to make a comparison of the calculated adsorption. It is due to the fact that in the real experiment condition the adsorption complexes of unsaturated C3–C4 hydrocarbons cannot be achieved in zeolite catalysts. It goes to dimerization and oligomerization rapidly[20]. However, there is the experimental data of the heat of isobutane adsorption on beta zeolite of −11.0 kcal/mol[21], which corresponds with the calculated isobutene adsorption in this work due to the π-adsorption complex being much stronger than the alkyl interactions with the acid site. In the next step, the protonation of the adsorbed isobutene complex takes place at the C1 position (shown in Figure 3(a)). At the first transition state (TS1), involving the proton transfer, there is one imaginary frequency at −435 cm^{-1} corresponding to the following movements: the zeolite proton (Hz) is moving toward a carbon atom (C1) of isobutene while the C1=C2 bond of isobutene is elongated from 1.34 to 1.41 Å. The adsorbed isobutene is protonated leading to the "*tert*-butyl carbocation" intermediate with the activation energy of 14.4 kcal/mol. The *tert*-butyl carbocation intermediate, Int1, structure is planar and the methyl group interacts with the zeolite framework through intermolecular forces. The partial positive charge on the C2 atom of the active carbocation intermediate should interact with one of the negative charge-neighboring atoms, such as oxygen atoms of the active site. However, previous studies found that, the *tert*-butyl carbocation is stable inside the zeolite pores without any interactions with the basic oxygen of zeolite[22-23]. The relative energies of the adsorption complex, Ads1, and the *tert*-butyl carbocation intermediate, Int1, are calculated to be −17.0 and −4.2 kcal/mol, respectively. The relative reaction energy in this step is endothermic by 12.8 kcal/mol, which is in accordance with previous studies[23-25].


(a)

(b)

Figure 3. Optimized transition state structures of (a) isobutene protonation, TS1 and (b), C-C bond formation, TS2.

2. C–C Bond Formation and Deprotonation Reaction. The second isobutene molecule diffuses into the zeolite pore and adsorbs on the reactive *tert*-butyl carbocation intermediate by a π–bond interaction between the C3=C4 bond of the second isobutene molecule with the C2 atom of the *tert*-butyl carbocation. The relative energy of the coadsorption complex over deprotonated zeolite (Ads2) is estimated to be −14.9 kcal/mol. Next, the reaction proceeds via the second transition state, TS2, that involves the formation of the C2–C3 bond and simultaneously the weakening of the C3=C4 bond to the C3–C4 bond. The C2···C3 distance shortens from 2.93 to 2.61 Å and C3=C4 bond length increases by 0.02 Å. The low energy barrier (E_a^2) of 4.0 kcal/mol implies that the *tert*-butyl carbocation is highly reactive and it is ready to react with another isobutene molecule. The *tert*-octyl carbocation intermediate over deprotonated zeolite possesses a relative energy of –30.6 kcal/mol. In the last step, 2,4,4-trimethyl-1-pentene (TMP-1), one of the trimethyl pentene isomers, can be directly formed via the deprotonation transition state. The proton transfers from *tert*-octyl carbocation to the oxygen-bridging atom of zeolite. This step can simultaneously occur with the activation energy of 1.2 kcal/mol. After the proton back-donation to the zeolite framework, TMP-1 is formed and adsorbed on the acidic site of the zeolite through the π–bond interaction by C4–H2 and C5–H2 with an average distance of 2.44 Å. This state has a relative energy of –42.9 kcal/mol.

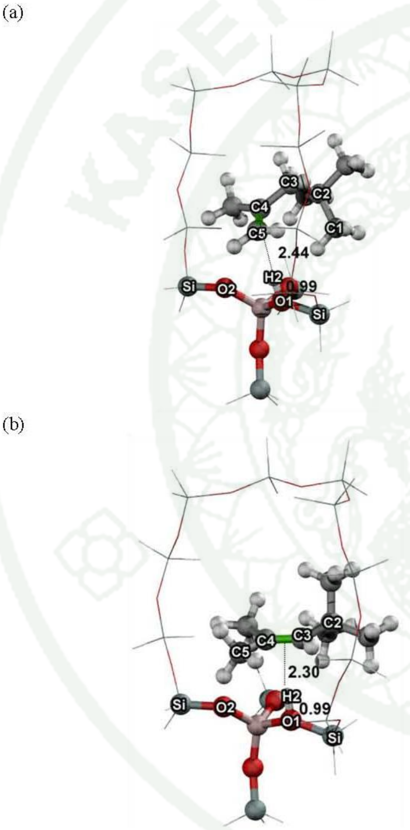


Figure 4. The dimerized product adsorptions on the brønsted acid of zeolite through the π–bond interaction; (a), the TMP-1 formation and (b), the TMP-2 formation.

Besides TMP-1, another trimethyl pentene product called 2,4,4-trimethyl-2-pentene (TMP-2) can be generated via the configuration changing of the *tert*-octyl carbocation intermediate complex to another stable adsorption configuration. Subsequently, the intermediate is deprotonated to yield 2,4,4-trimethyl-2-pentene. The activation energy of this step is 5.4 kcal/mol, which is 4.2 kcal/mol or ~78% higher than the one for the deprotonation transition state of TMP-1. Then, TMP-2 is formed and adsorbed on the zeolite surface by the π–bond interaction with the relative stability of –43.5 kcal/mol. The dimerized products, TMP-1 and TMP-2, adsorbed on the brønsted acid of zeolite through the π–bond interaction are shown in Figures 4(a) and (b), respectively.

From the energetic point of view, the dimerization of isobutene catalyzed by beta zeolite is an exothermic reaction. The protonation of the adsorbed isobutene is considered to be the rate-determining step with the activation barrier of 14.4 kcal/mol (shown in Figure 5.) which corresponds well with the experimental study of 14.8 kcal/mol over H-ZSM-5 zeolite[26]. Moreover the theoretical study on the mechanisms of small alkene dimerization in faujasite zeolite found that the rate-determining step is the alkene protonation to form surface alkoxide[27]. The protonation of the adsorbed isobutene is the rate-determining step that implies that the *tert*-butyl carbocation intermediate is rather reactive and ready to react with another isobutene molecule with a low activation barrier and the proton back-donation to the zeolite framework is also the fast step with the activation energies of 1.2 and 5.4 kcal/mol for TMP-1 and TMP-2, respectively. From these results, TMP-1 was the kinetically primary product. Many previous experimental studies have reported that TMP-1 is the more promising product than TMP-2[3,28-29].

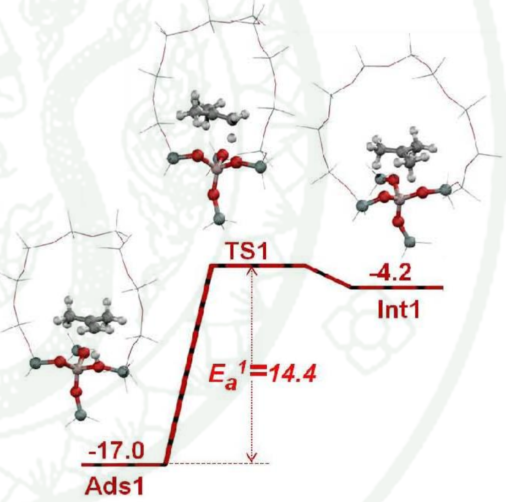


Figure 5. M06-2X/6-31G(d,p) energy profile (kcal/mol) for the rate-determining step of isobutene dimerization.

Conclusions

Possible reaction mechanisms of isobutene dimerization on acidic beta zeolite were investigated by means of the density functional theory (DFT) at the M06-2X/6-31G(d,p) level of theory. A quantum cluster containing 14 tetrahedral units from the beta zeolite structure was selected to be a model for the active catalyst. The reaction starts with the protonation of isobutene by the acidic zeolite and yields a "*tert*-butyl carbocation" intermediate. Subsequently, the C–C bond formation between the *tert*-butyl carbocation intermediate and the second isobutene molecule to form a "*tert*-octyl carbocation" intermediate and then proton back-donation to the zeolite framework leads to trimethyl pentene isomers (isooctene). The protonation of isobutene is considered to be the rate-determining step with the activation energy of 14.4 kcal/mol. Whereas the C–C bond formation is the fast step with the activation energy of 4.0 kcal/mol and the deprotonation reaction was also the fast step with the activation energies of 1.2 and 5.4 kcal/mol for 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, respectively. In this reaction, it was found that 2,4,4-trimethyl-1-pentene was the kinetically primary product.

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