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THESIS

QUANTUM EFFECT ON THE REACTION MECHANISM OF PROPENE OXIDE ISOMERIZATION IN H-ITQ-22: A DFT INVESTIGATION

KULWADEE THEANNGERN

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
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Kulwadee Theanngern 2013: Quantum Effect on the Reaction Mechanism of Propene Oxide Isomerization in H-ITQ-22: A DFT Investigation. Master of Science (Chemistry), Major Field: Chemistry, Department of Chemistry. Thesis Advisor: Mr. Pipat Khongpracha, Ph.D. 60 pages.

The selective isomerization of propene oxide over multi-nanopore zeolite, H-ITQ-22, has been investigated with the M06-2X/6-31G(d,p) method. 14T and 58T quantum cluster covered the intersection 12 membered ring was used to represent the acid site, where T is Si or Al atoms. The reaction were proposed through a stepwise mechanism: the ring opening and the 1,2 hydride rearrangement. Two different pathways were systematically examined leading to the two products, namely propanal and propanone. The ring-opening step of these mechanisms is found to be the rate-determining step with an activation barrier of 24.4 kcal/mol for the propanal and of 38.4 kcal/mol for the propanone. Therefore, the propanal is predicted to be the main product for this reaction. With chemically realistic and well-calibrated models together with an accurate DFT method, our findings clearly demonstrate that H-ITQ-22 zeolite is one of the good catalysts for the selective isomerization of propene oxide for the production of propanal.

Student’s signature

Thesis Advisor’s signature

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I would like to thank my supervisor, Dr. Pipat Khongpracha for their excellent supervision, encouragement, continuous support and constant inspiration throughout the span of my study and research. He was always there to listen and to give advice. I would like to express my appreciation to my co-advisor, Prof. Jumras Limtrakul, who showed me the different ways to approach a research problem and the need to be persistent to accomplish any goals. I am also appreciative to my co-advisor, Dr.Bundet Boekfa, for his helpful guidance and advantageous suggestions on the quantum chemical calculations to fulfill this thesis work. Many thanks also to Dr.Chompunuch Warakulwit and Dr.Potjaman Poolmee for agreeing to be a chairperson and an external examiner in my final examination.

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I am especially appreciative of my parents for continuously boosting my morale, encouraging me to overcome the obstacles facing me in my life and giving me financial assistance.

Kulwadee Theanngern
April, 2013

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LIST OF ABBREVIATIONS

ABS = Absorption Complex Structure
B3LYP = Becke's Three Parameters Hybrid Functional Using The Lee-Yang-Parr Correlation Functional
DFT = Density Functional Theory
E_a = Activation Energy
E_{des} = Desorption Energy
HF = Hartree-Fock
INT = Intermediate
ITQ-22 = Instituto de Tecnologia Quimica Valencia 22
kcal = Kilocalories
M06 = Minnesota 2006 Functional
ONIOM = Our own N-layered Intergrated molecular Orbital and molecular Mechanics
QM = Quantum Mechanics
TS = Transition State Structure
ZSM-5 = Zeolite Socony Mobil 5

QUANTUM EFFECT ON THE REACTION MECHANISM OF PROPENE OXIDE ISOMERIZATION IN H-ITQ-22: A DFT INVESTIGATION

INTRODUCTION

Epoxides are major chemical intermediates used in organic synthesis and petrochemical industries. The reactive epoxide, driven from the constraint of the three-membered ring, makes it suitable to be a building block in the synthesis of organic compounds and polymers.

Propene oxide (see the structure of propene oxide in Figure 1) is one of the most important epoxides with a huge consumption for application in polymer industry including polyether polyols, propene glycols and propene glycol ethers productions.(Carlier, 2004; Cheng *et al.*, 2005; Katsuki and Sharpless, 1980; Smith, 1984).

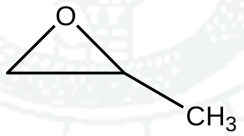

Figure 1 Structure of propene oxide

One interesting reaction of propene oxide is the “ring-opening isomerization”. The epoxide ring can be opened by either homogeneous or heterogeneous catalysts such as Al_2O_3, Al_2O_3-SiO_2, ZnO (Molnár *et al.*, 1991), Nafion-H, and zeolites (Fási *et al.*, 2001; Fási *et al.*, 2004). It can provide various oxygenated products such as carbonyl compounds or allylic alcohols depending on the reaction conditions as shown in Figure2. Under acidic reaction conditions, epoxides primarily isomerize to carbonyl compounds, especially propanal and acetone.(Karamé *et al.*, 2003; Procopio *et al.*, 2004; Ranu and Jana, 1998)

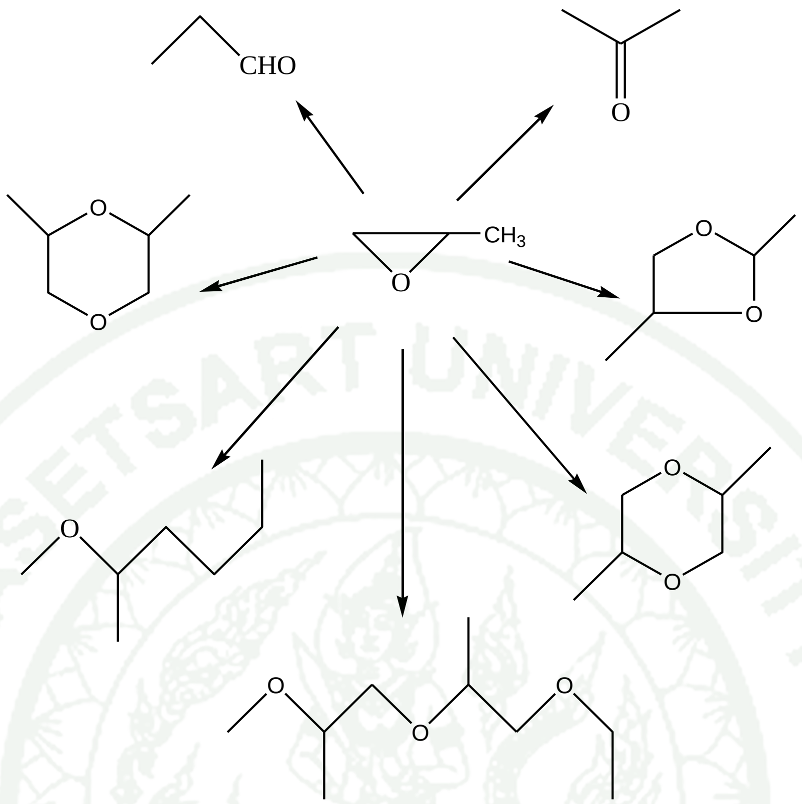

Figure 2 Viable transformation pathways of propene oxide over acid–base catalysts

The most current catalysts for this process are deficient in the versatility to be selective for the desired products. It is desirable to develop a catalytic process which is able to handle and give a beneficial selectivity.

During the past decades, zeolites have been successfully applied as catalysts for intermediate and fine chemical synthesis. While the relatively small pores of the zeolites limit their utilization to the synthesis of small molecules, the well-defined and narrow pore size distribution can be used to induce shape selectivity by allowing only certain reactants to reach the active sites (reactant selectivity), imposing diffusional constraints on bulkier reaction products (product selectivity), or excluding the formation of certain products due to spatial constraints (restricted transition state selectivity).

Zeolites are crystalline aluminosilicates which serve as potential solid catalysts for chemical processes involving in proton transfer and also use in chemical separations. This type of catalysts is one of the most important catalysts widely used in petroleum refinery industries and for the production of fine chemicals (Andy *et al.*, 1998; Bhan and Iglesia, 2008; Corma, 2003; Hsia Chen and Bridger, 1996; Luzgin *et al.*, 2008; Smit and Maesen, 2008; Venuto, 1994; Yaluris *et al.*, 1995). Zeolites consist of tetrahedral SiO_4 and AlO_4 units connected through shared oxygen sites to form porous frameworks. Zeolites have attracted great attention because of their high surface area, uniform pore structure, intrinsic acidity, thermal stability and shape selectivity resulting in the superior catalytic activity. The catalytic activity originates from the presence of the Brønsted acid site in the confined space (Van Santen and Kramer, 1995). Its acidity, and, therefore performance, can be controlled by tuning the Si/Al ratio.

AndrasFasi and co-workers studied the ring-opening isomerization of epoxide in various zeolites (Fási *et al.*, 2001; Fási *et al.*, 2004), including H-ZSM-5. Their results showed that the reaction of epoxide in zeolite lead to the carbonyl compounds and propanal was the major product when H-ZSM-5 was employed as a catalyst. The comprehensive mechanistic study of this reaction in zeolite was initiated with the quantum chemical calculation (Namuangruk *et al.*, 2006a). Propene oxide isomerization over H-ZSM-5 zeolite was proposed in two mechanisms based on the reaction products, propanal and acetone. The ring-opening step was found to be the rate-determining step with activation barriers of 38.5 kcal/mol and 42.4 kcal/mol for propanal and acetone, respectively.

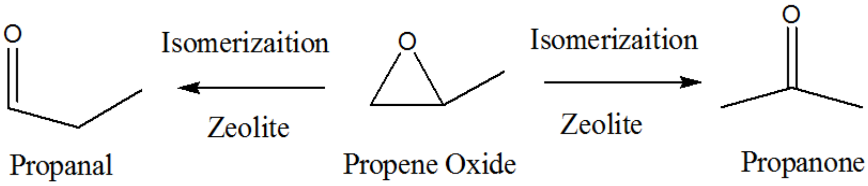

Figure 3 The products of propene oxide over zeolite catalyst isomerizes to propanal and acetone.

Despite the large number of new zeolites are reported as a new material with unique structural characteristics, such as pore shape, size and channel dimensionality. Moreover, it’s always attractive because of potential new and improved applications. In this sense, the new zeolites with intersecting channels of different sizes allows the selective diffusion of reactants with different dimensions, with potential unique molecular transport through the zeolite, and inducing more favorable orientations to react and give the desired product.

Corma et al. synthesized the new zeolite (ITQ-22) with Multiple channel dimensionality (channels interconnected in 2-D or 3-D systems) (Corma *et al.*, 2003b). It is an important requirement for many reactions that find a benefit from the larger diffusivity that is allowed when channels intersect each other (Corma *et al.*, 2009). ITQ-22 (IWW) is the synthetic multipore zeolite with the dimension 8 x 10 x 12 membered ring pore structure. Conventionally, this novel zeolite is applied for the isomerization of m-xylene, the disproportionation of m-xylene and the alkylation of benzene with isopropanol or propene. The catalytic selectivity toward these reactions has proved to be better than ZSM-5 zeolite.

The aim of this work is to study the propene oxide isomerization reaction and the effects of confinement over ITQ-22 zeolite by using the M06-2X method. The detailed reaction mechanism of propene oxide to propanal and acetone have been discussed.

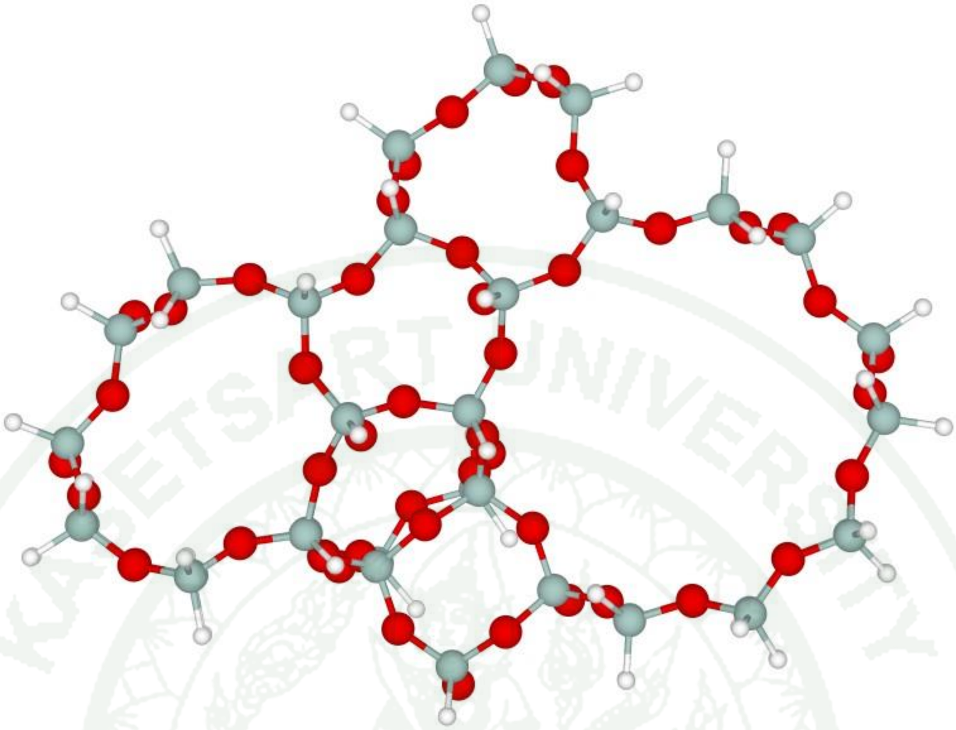

Figure 4 The selected structure of the 58T cluster of H-ITQ-22 zeolite.

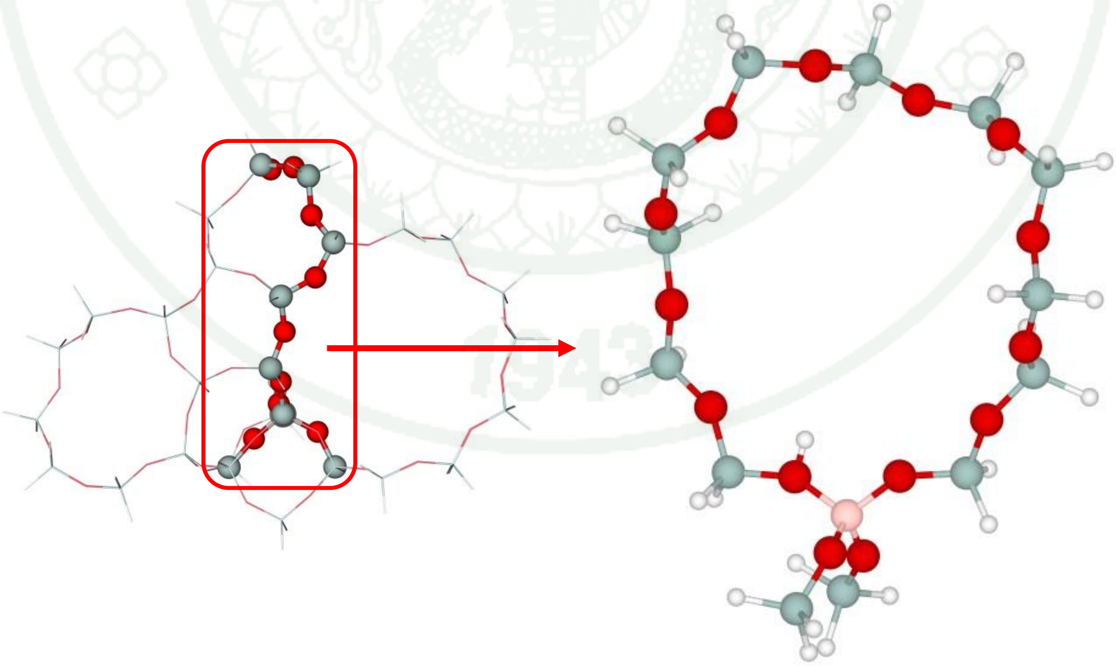

Figure 5 The selected structure of the 14T cluster of H-ITQ-22 zeolite.

OBJECTIVES

1. To investigate the reaction mechanism of propene oxide isomerization reaction over acidic ITQ-22 zeolite by using the M06-2X/6-31G(d,p) method.

2. To investigate the influence of the zeolite framework on the reaction mechanisms.

LITERATURE REVIEW

In the recent years, numerous experimental and theoretical studies have investigated the reactions and mechanisms of the propene oxide isomerization to various oxygenated products, especially propanal and acetone (Karamé *et al.*, 2003; Procopio *et al.*, 2004; Ranu and Jana, 1998). The propene oxide isomerization is based on the ring opening by the scission of either C-O bond. Various acid catalysts, including homogeneous and heterogeneous, have been investigated for propene oxide isomerization to various products, especially propanal and acetone in the liquid phase and in the gas phase as described below.

Lifshitz (Lifshitz and Tamburu, 1994) studied The thermal reactions of propene oxide at high temperatures (850-1250 K) using the experimentally single-plus shock tube technique. The mechanisms of propene oxide isomerization were described. The products of shock heating reaction consist of four isomerization products, acetone, propanal, methyl vinyl ether, and allyl alcohol, and a large number of decomposition products.

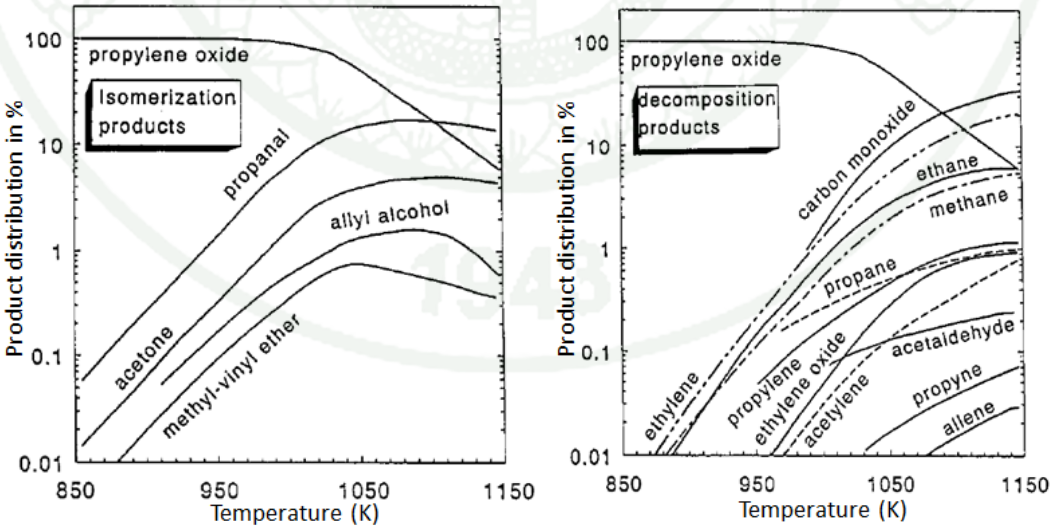

Figure 6 Products distribution in propylene oxide isomerization and decomposition.

From products distribution, the major product of isomerization is propanal and the major product of decomposition is carbon monoxide. The propene oxide isomerization is based on the ring opening by the dissociation of either C-O bond. The production of both propanal and acetone are rather simple. The isomerization channels for propanal, acetone, and allyl alcohol involve the dissociation of one of the two nonequivalent C-O bonds, followed by 1,2-H-atom migration for propanal and acetone and 1,4-H-atom migration for allyl alcohol. The channel for the production of methyl vinyl ether is associated with the dissociation of the C-C bond, followed by 1, 4-H-atom migration.

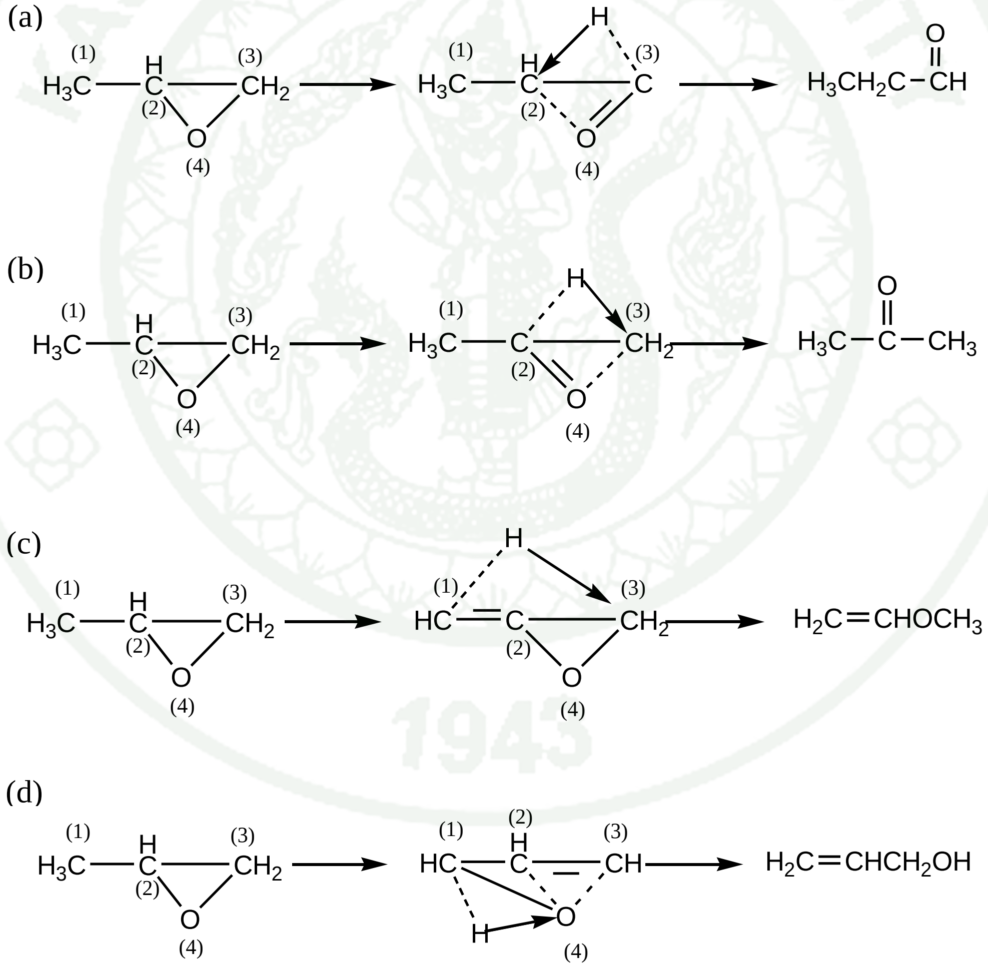

Figure 7 Schematic descriptions of the four-isomerization reactions ; (a) propanal, (b) acetone, (c) methyl vinyl ether, (d) allyl alcohol.

Dubnikova (Dubnikova and Lifshitz, 2000) investigated the mechanism of propene oxide isomerization, to yield four isomerization products by the B3LYP/cc-pVDZ method. The potential energy surfaces for four isomerization pathways corresponding to the production of acetone, propanal, methyl vinyl ether, and allyl alcohol were calculated.

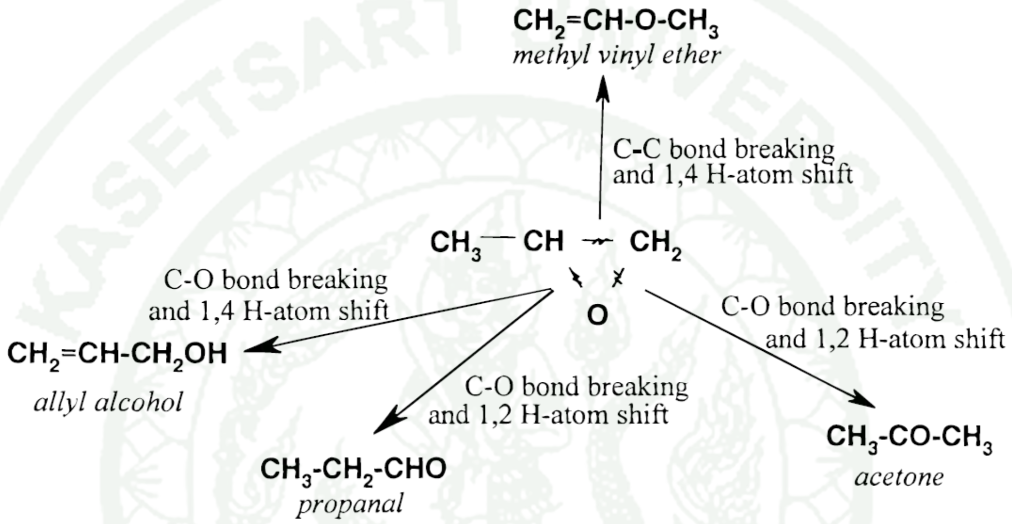

Figure 8 The reaction scheme provides a schematic description of the four-isomerization reactions.

Three products of the isomerization, acetone, propanal, and allyl alcohol are produced by concerted mechanism. Methyl vinyl ether is formed via stepwise mechanism. The activation energy of the four-isomerization products, propanal, acetone, allyl alcohol and methyl vinyl ether are 54.99, 54.18, 60.17 and 71.49 kcal/mol respectively. The theory shows a fair agreement with the experimental values (Lifshitz and Tamburu, 1994).

For increasing the selectivity of products, these reactions were conventionally catalyzed by Lewis acid catalysts ($AlCl_3$, and BF_3, etc.) because under acidic reaction conditions, there are two mechanisms for the isomerization of propene oxide to carbonyl compounds. Unfortunately, the catalysts are highly toxic and corrosive and, consequently, present a serious waste disposal problem. To substitute the conventional catalysts to reduce these problems, solid catalysts, for example, Al_2O_3, Al_2O_3-SiO_2, ZnO (Molnár *et al.*, 1991), Nafion-H (Fási *et al.*, 2004), zeolites (Fási *et al.*, 2001).

Zeolites are crystalline aluminosilicate which serve as potential solid catalysts for chemical processes involving in proton transfer and also use in chemical separations. This type of catalysts is one of the most important catalysts widely used in petroleum refinery industries and for the production of fine chemicals. Zeolites consist of tetrahedral SiO_4 and AlO_4 units connected through shared oxygen sites to form porous frameworks. Zeolites have attracted great attention because of their high surface area, uniform pore structure, intrinsic acidity, thermal stability and shape selectivity resulting in the superior catalytic activity. The catalytic activity originates from the presence of the Brønsted acid site in the confined space (Van Santen and Kramer, 1995). Its acidity, and, therefore performance, can be controlled by tuning the Si/Al ratio.

Supawadee Namuangruk et al. studied the methyl oxirane reaction mechanism on H-ZSM-5 using the computational method the mechanism is considered to proceed through a stepwise mechanism. The reaction mechanism is proposed to proceed via two consecutive steps: (1) the epoxide ring protonation, and concurrently, the ring-opening, and (2) the 1, 2-hydride shift forming the adsorbed carbonyl compound. Because of the asymmetric structure of propene oxide, two different C-O bonds (more or less substituted carbon atom sides) can be broken leading to propanal and acetone. The ring-opening step of this mechanism is the rate-determining step with an activation barrier of 38.5 kcal/mol for the propanal and of 42.4 kcal/mol for the acetone.

Multiple channel dimensional (channels interconnected in 2-D or 3-D systems) is an important requirement for many reactions that find a benefit from the larger diffusivity that is allowed when channels intersect each other. Examples of zeolites containing connected pores with different dimensions include: Ferrierite (FER, 8 × 10 MR) (Vaughan, 1966), ITQ-13 (ITH, 9 × 10 MR) (Corma *et al.*, 2003a), Mordenite (MOR, 8 × 12 MR) (Meier, 1961), ITQ-22 (IWW, 8 × 10 × 12 MR) (Corma *et al.*, 2003b). The catalytic benefit of zeolites containing more than one type of pores within the same structure has been shown for reactions such as the isomerization of 1-butene into isobutene in ferrierite, (Domokos *et al.,* 2000).

ITQ-22 (IWR) is the synthetic multipore zeolite with the dimension 8 x 10 x 12 membered ring pore structure (Corma *et al.*, 2003b). From a catalytic point of view, the ITQ-22 structure presented a behavior different from that of 10- or 12MR pore zeolites. Indeed, in the case of ITQ-22, the reactant molecules will see not only one 10MR window that connects two adjacent 12MR channels, but a continuous 10MR channel that communicates between two neighboring 12MR channels. This means that, from a catalytic point of view, ITQ-22 should fill the gap between 10MR and 12MR zeolites. This novel zeolite is applied for the isomerization of m-xylene, the disproportionation of m-xylene and the alkylation of benzene with isopropanol or propene. The catalytic selectivity toward these reactions has proved to be better than ZSM-5 zeolite.

It is quite difficult to get comprehensive information about the detailed mechanism of propene oxide isomerization in zeolites from experiments. This is due to the complexity of their nanoporous structures that prevents them from being investigated by conventional techniques. Although there are some theoretical studies of propene oxide isomerization over ZSM-5 zeolite but, the small quantum cluster is not able to represent the confinement effect of the zeolite framework.(Namuangruk *et al.*, 2006b; Pantu *et al.*, 2007; Pantu *et al.*, 2008). To the best of our knowledge, there are no theoretical studies reported about the detailed reaction mechanism of propene oxide isomerization over the new synthetic multipore zeolite, which may offer lower activation energy from the conventional ones. Therefore, a computational investigation of the reaction mechanisms with a reliable method should be useful. In this work we investigate the reaction mechanisms by means of cluster calculations using a density functional theory with the M06-2X functional.

The M06-2X functional is early developments of DFT by Zhao and Thrular (Zhao and Truhlar, 2008a; b) which focused on the most basic challenges in chemistry such as the ability to give a reasonable description of both the geometries and dissociation energies of molecules and accurately predict reaction barrier heights in order to determine the kinetics of chemical reactions as well as to describe van der Waals interactions. This functional has been successfully applied to study the adsorption and reaction mechanisms of non-polar and aromatic molecules on zeolites (Boekfa *et al.*, 2009; Kumsapaya *et al.*, 2009; Maihom *et al.*, 2009; Maihom *et al.*, 2010).

In this work, the full quantum chemical calculation was employed to study the isomerization of propene oxide over H-ITQ-22 zeolite in order to better understand its chemistry and further control the industrial operating conditions.

MATERIALS AND METHODS

1. Materials and Equipment

1.1. Hardware

1) LCAC super computer cluster (Chemistry Department, Faculty of Science, Kasetsart University, Bangkok)

2) HP workstations; Intel Core 2 QUAD Q9550 2.83 GHz, RAM 4 GB (Chemistry Department, Faculty of Science, Kasetsart University, Bangkok)

1.2. Software

1) Gaussian 03 program
2) Gaussian View 03 program
3) Accelrys Material studio 4.3

2. Computational details

The two different computational models have been employed to study the H-ITQ-22 zeolite and their adsorption complexes with propene oxide. The first model 14T where T means the tetrahedral unit of Si or Al atoms was taken from the crystal structure of ITQ-22 lattice. The cluster covers the 12-membered ring at the intersection cavity between 10-membered ring and 12-membered ring. One Si atom was replaced with an Al atom at the most appropriate T1 position and subsequently one proton was added to the system yielding a Brønsted acid site. Within the cluster approach, the catalytic active site model is the small neutral zeolite fragment, terminated with hydrogen atoms or hydroxyl group. The terminated H atoms are fixed along the Si-O bonds of H-ITQ-22 framework. This cluster represents the Brønsted acid site in the interaction with propene oxide. All geometries were optimized with the M06-2X functional using the 6-31G(d,p) basis set. Only the 5T cluster of active region, $[\equiv SiO(H)Al(OSi)_3\equiv]$, and the probe molecule were allowed to relax while the rest was kept fixed with the crystallographic structure. Only one imaginary frequency with its vibration corresponding to the transition structure was confirmed by frequency calculation. The cluster consisting of 14 tetrahedral atoms is illustrated in Figure 9 and Figure 10.

In order to examine the effect of the extended framework, the 58T quantum cluster covered intersection and 8-, 10- and 12-MR windows of ITQ-22 is treated with the M06-2X functional using the 6-31G(d,p) basis set as shown in Figure 9 and Figure 10. During optimization, only 5T cluster of the active region and the probe molecules were allow to relax. The frequency calculations were performed at the same level of theory to ensure that the transition state structure has only one imaginary frequency. All calculations were carried out by the Gaussian 03 package (Frisch *et al.*, 2003) incorporated with the Minnesota Density Functionals module 3.1 by Zhao and Truhlar.

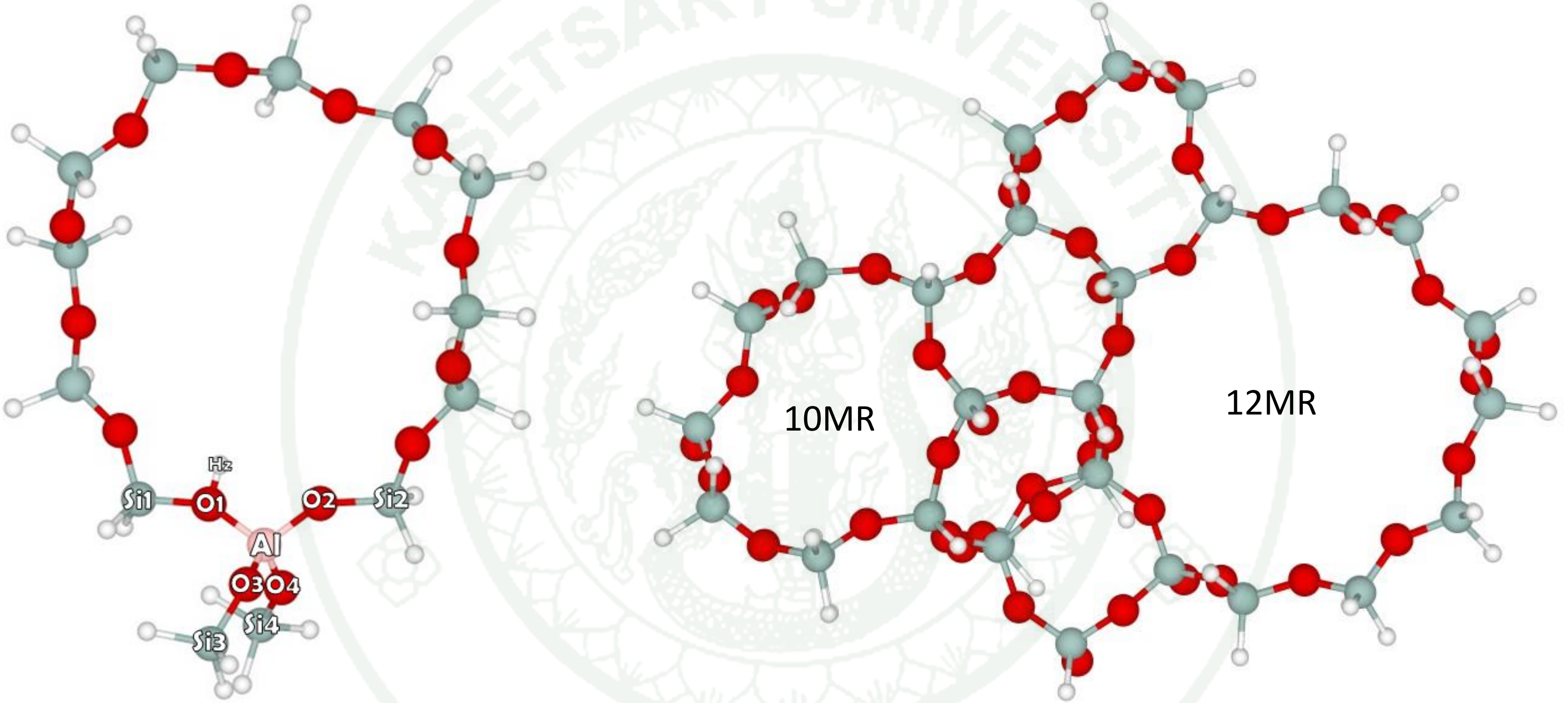

Figure 9 The selected cluster model of H-ITQ-22 zeolite. (a) 14T cluster covers the 12-membered ring at the intersection cavity between 10-membered ring and 12-membered ring of 58T cluster, (b) the 58T cluster of H-ITQ-22 zeolite covers the 12-membered ring and 10-membered ring.

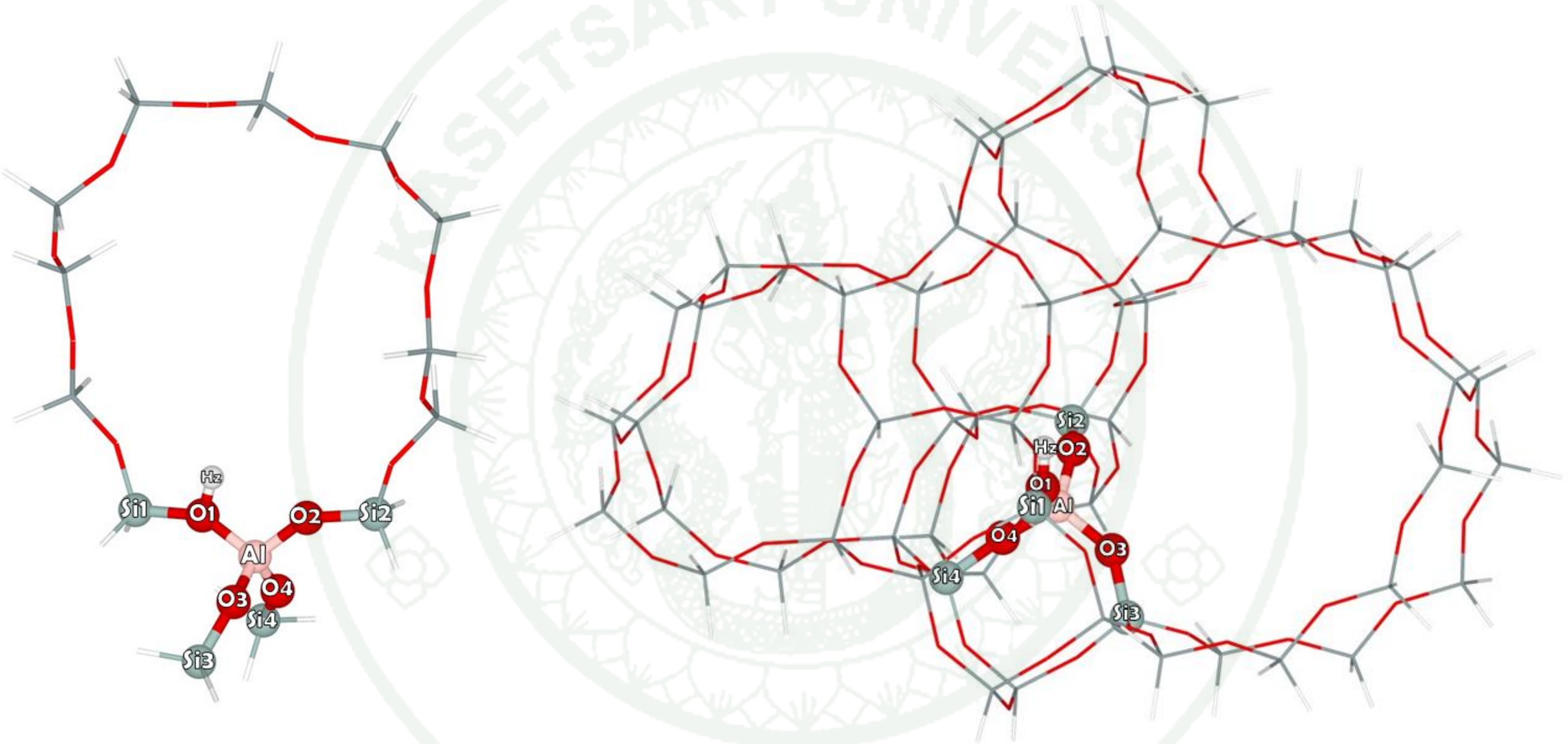

Figure 10 The model of 14T and 58T clusters represent the active site of ITQ-22 zeolite. The ball-and-stick graphics illustrates the relaxed geometry resulting from calculations at M06-2X/6-31G(d,p), while the rest was kept fixed with the crystallographic structure.

RESULTS AND DISCUSSION

This chapter is separated into 3 sections. In the first section, we discuss the zeolite model and adsorption complexes of propene oxide onto the brønsted acid site. In section 2, the reaction mechanisms of propene oxide isomerization to two products are described. In section 3, we make the comparisons of the two products.

1. The Zeolite Models and the Adsorption complexes of Propene Oxide onto the Brønsted acid site

Propene oxide is chiral epoxide that has equal amounts of left- and right-handed enantiomers. This compound is called 1,2-propene oxide to distinguish it from its isomer 1,3-propene oxide, better known as oxetane. The optimized structure of propene oxide molecules is shown in Figure 11.

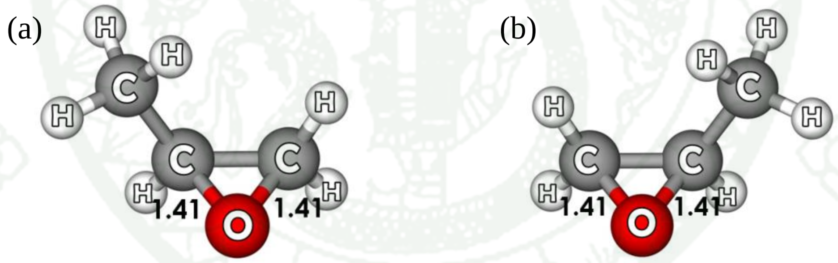

Figure 11 Conformational of the Propene oxide isomer; (a) 1,2-propene oxide (b) 1,3-propene oxide.

The 14T and 58T cluster of H-ITQ-22 are shown in Figure 12 while their geometric parameters are tabulated in Table 1**.** To observe the catalytic framework effect on the reaction over the active site, the atoms in the 5T region in both clusters have been optimized with the exception of the atoms in the extended framework of the 58T quantum cluster, which were fixed. Comparison of the 14T quantum cluster and the 58T quantum cluster reveals little difference in the geometric parameters. As the extended framework has only a small effect on the active site geometry, the indication is that the active site in the 58T quantum cluster might be more acidic than that in the 14T quantum cluster, which, in turn, leads to the prediction that the adsorption energy of adsorbates on the 58T quantum cluster should also be higher.

Table 1 The optimized geometric parameters (distances in pm and angles in degrees) of the 14T and 58T clusters of H-ITQ-22 zeolite calculated using the M06-2X/6-31G(d,p) method.

Parameters	14T	58T
Distance (pm)		
O1-Hz	0.972	0.973
O1-Si1	1.691	1.682
Al-O1	1.886	1.875
O2-Al	1.696	1.688
O2-Si2	1.617	1.597
Al···Hz	2.348	2.362
Angles (degrees)		
∠Si1-Al-O1	135.75	136.37
∠Si2-Al-O2	124.28	125.80

The optimized geometric parameters from the 58T quantum cluster are tabulated in Table 1. The Brønsted acid O1-Hz bond distance is 0.97 Å. The Al···Hz distance is 2.36 Å, which compared well with the experimental value (2.38-2.48 Å).

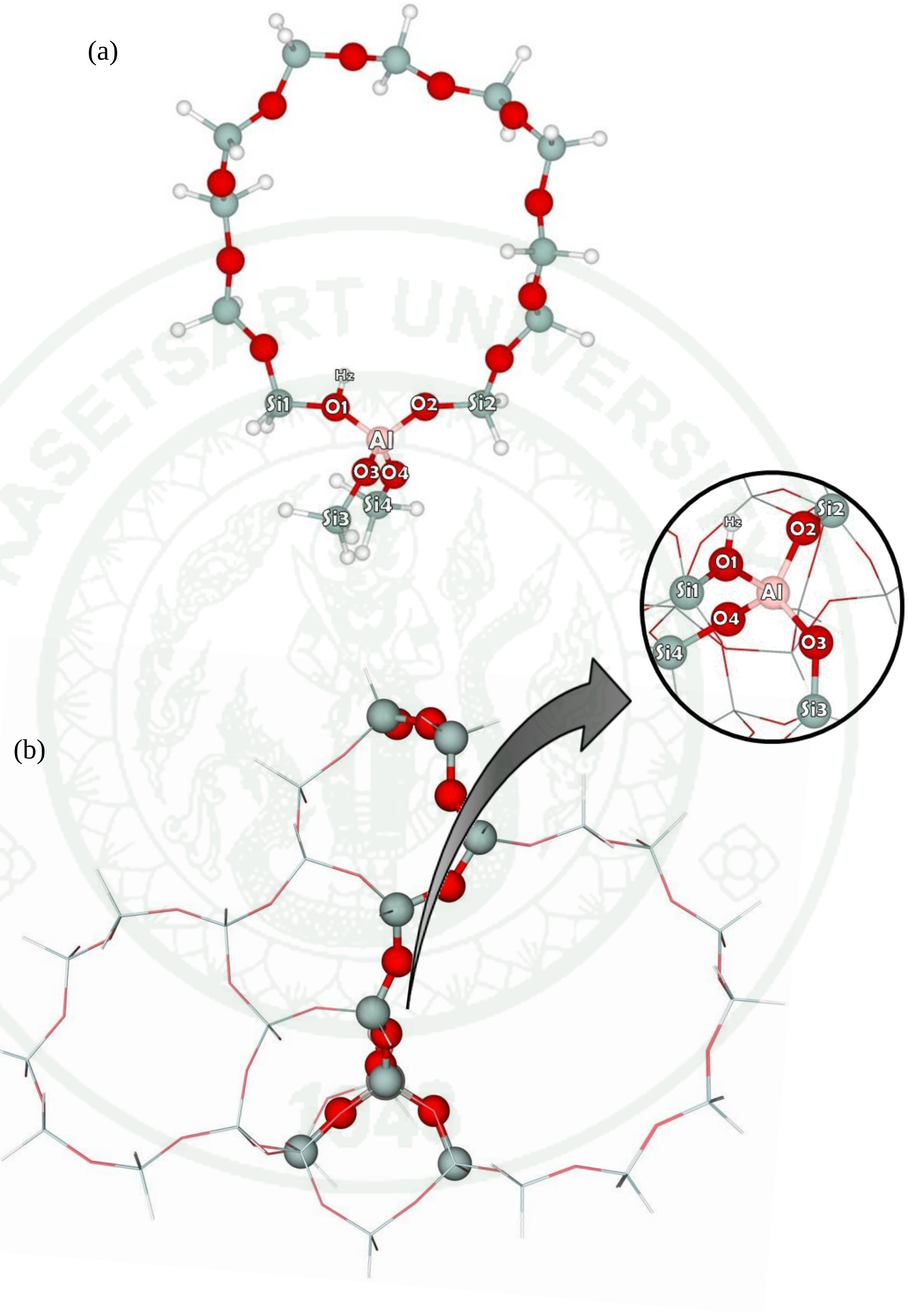

Figure 12 The optimized geometric parameters of (a) the 14T cluster of H-ITQ-22 zeolite, (b) the 58T cluster of H-ITQ-22 zeolite.

The adsorption complexes of the propene oxide, propanal and acetone, which are the reactant and products for the isomerization of propene oxide, on the Brønsted acid site of the ITQ-22 zeolite in the quantum cluster are depicted in Figure 13. These adsorbates interact on the acidic proton of zeolite via hydrogen bonding, and the geometric structures of all adsorption complexes are slightly deviated from those of isolated structures (Table 2).

The propene oxide adsorbed on the Brønsted acid site with the hydrogen bond at the intersection of ITQ-22 is shown in Figure 13. Two optimum adsorption configurations are found, namely ADS_A and ADS_B with comparable adsorption energies of -24.1 and -22.8 kcal/mol for the 14T cluster and adsorption energies of -29.0 and -31.3 kcal/mol for the 58T cluster, respectively. On both adsorption complexes, most of the geometric parameters are the same (see Table 2). Although the epoxide ring is asymmetric, the epoxide ring center aligns above the acidic site with almost equal distances of C1-O1 and C2-O1 and of C1-O2 and C2-O2. The Brønsted acid O1-Hz bond distance is significantly increased from 0.97 to 1.11 Å. Strong hydrogen bond interactions in both configurations are confirmed by high adsorption energy; a short intermolecular distance between the propene oxide and the Brønsted acid of zeolite Hz···Op (1.33 and 1.34 Å) and the nearly linear arrangement of O1-Hz-Op angle (172.16 and 175.75 degrees). The shorter Hz···Op distance of ADS_A refers to the higher interaction with the zeolite. Because of the decrease of the electron density on Op via the electron transfer from the Op to the Hz atom, the C1-Op and C2-Op bonds are elongated. The greater increase in the length of the C1-Op bond leads to the prediction that it would be broken more easily than the shorter C2-Op bond.

The propanal and acetone also adsorb on the acidic proton of zeolite via hydrogen bonding (see Figure 13b and 13c). Since the carbonyl C=Op bonds are strong double bonds, they are not changed significantly during the adsorption on the active site of zeolite. The C=Op bond of the acetone adsorption complex alters slightly from isolated acetone by 0.01-0.02 Å, and that of the propanal is changed by only 0.01 Å (cf. Table 2). The hydrogen bonding interaction lengthens the Brønsted acid O1-Hz bond distance by 1.14 and 1.12 Å for the adsorption of propanal and acetone, respectively. The adsorption energies of propanal and acetone are evaluated to be -43.2 and -46.4 kcal/mol for the 14T cluster and -47.9 and -57.3 kcal/mol for the 58T cluster, respectively. The van der Waals interactions between the adsorbates and the zeolite pore walls stabilize the adsorption complexes inside. Therefore, this 58T cluster should be suitable to use for investigation of the isomerization reaction for this system.

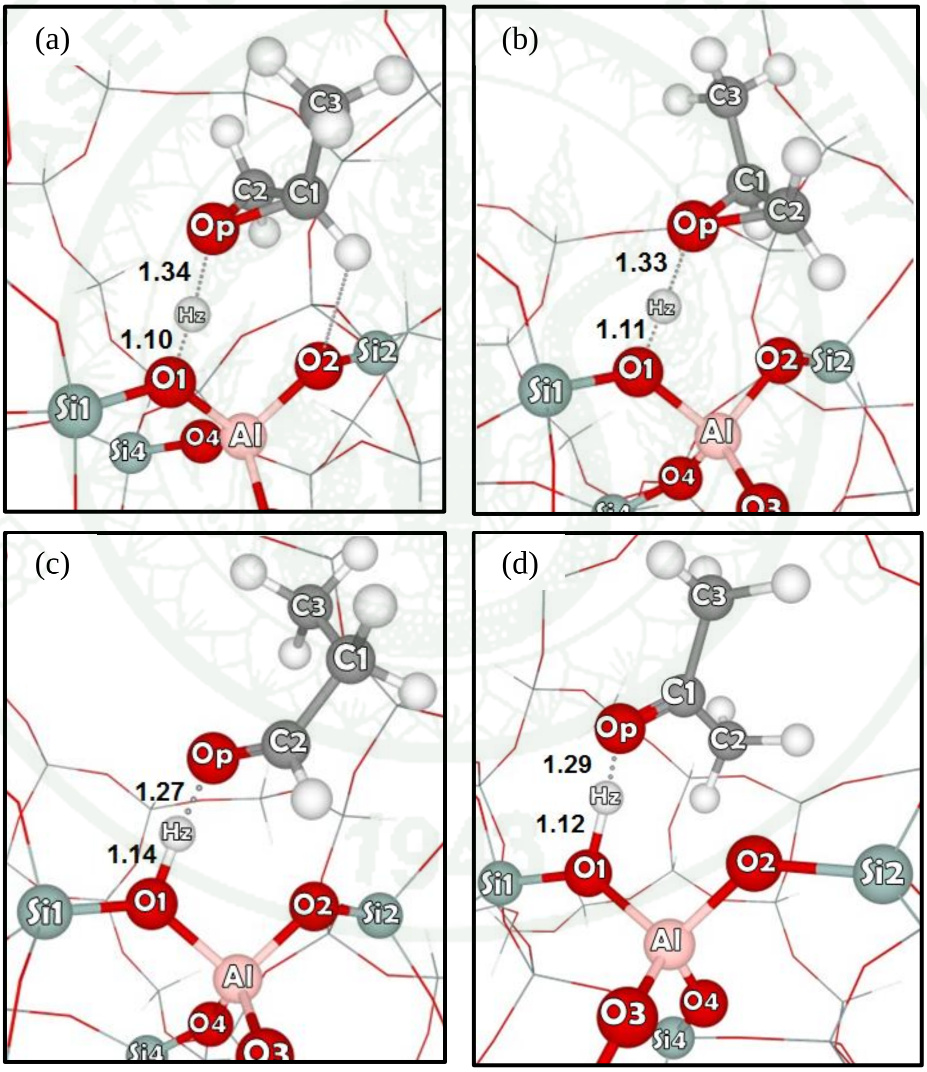

Figure 13 Optimized structure of propene oxide on H-ITQ-22 zeolite: a) ADS_A, b) ADS_B, c) propanal and d) acetone. Distances are in Ås.

Table 2 The Relevant Parameters for the Propene Oxide, Propanal, and Acetone Adsorbed on 14T and 58T H-ITQ-22 Zeolite Clusters

	Distances (Å)					Adsorption energies (kcal/mol)
	O1-Hz	Op-Hz	C2-Op	C1-C2	C1-Op	
isolated propene oxide A			1.419	1.469	1.418	
propene oxide A (ADA) on 14T	1.063	1.415	1.443	1.467	1.445	-24.09
propene oxide A (ADA) on 58T	1.108	1.326	1.448	1.467	1.452	-29.04
isolated propene oxide B			1.419	1.468	1.419	
propene oxide B (ADB) on 14T	1.061	1.415	1.449	1.468	1.440	-24.51
propene oxide B (ADB) on 58T	1.103	1.336	1.455	1.468	1.447	-31.32
isolated propanal			1.206	1.508	2.399	
propanal on 14T	1.082	1.378	1.226	1.487	2.392	-24.19
propanal on 58T	1.143	1.274	1.231	1.483	2.383	-28.92
isolated acetone			2.386	1.515	1.209	
acetone on 14T	1.082	1.371	2.393	1.497	1.229	-24.16
acetone on 58T	1.129	1.294	2.403	1.488	1.243	-31.90

[a] The propene oxide adsorption on H-ZSM-5 from previous experiment is -31.1 kcal/mol (Sepa *et al.*, 1996).

2. The Reaction Mechanism of Isomerization of Propene Oxide.

The isomerization mechanism of propene oxide to carbonyl compounds is considered to occur via the C-O bond breaking of the oxirane ring in the propene oxide molecule. The asymmetric structure of propene oxide has two different C-O bonds (more or less substituted carbon atom sides) that can be broken and, thus, has two possible products of the ringopening reaction: propanal and acetone. Propanal is formed via the C-O bond breaking at the tertiary carbon atom (C1- Op), while acetone is formed via the C-O bond breaking at the other carbon atom (C2-Op) in the oxirane ring. To elucidate the explanation and represent it in a more instructive format, the detailed mechanism will be separated into two subsections.

2.1 The Reaction Mechanism Leading to Propanal.

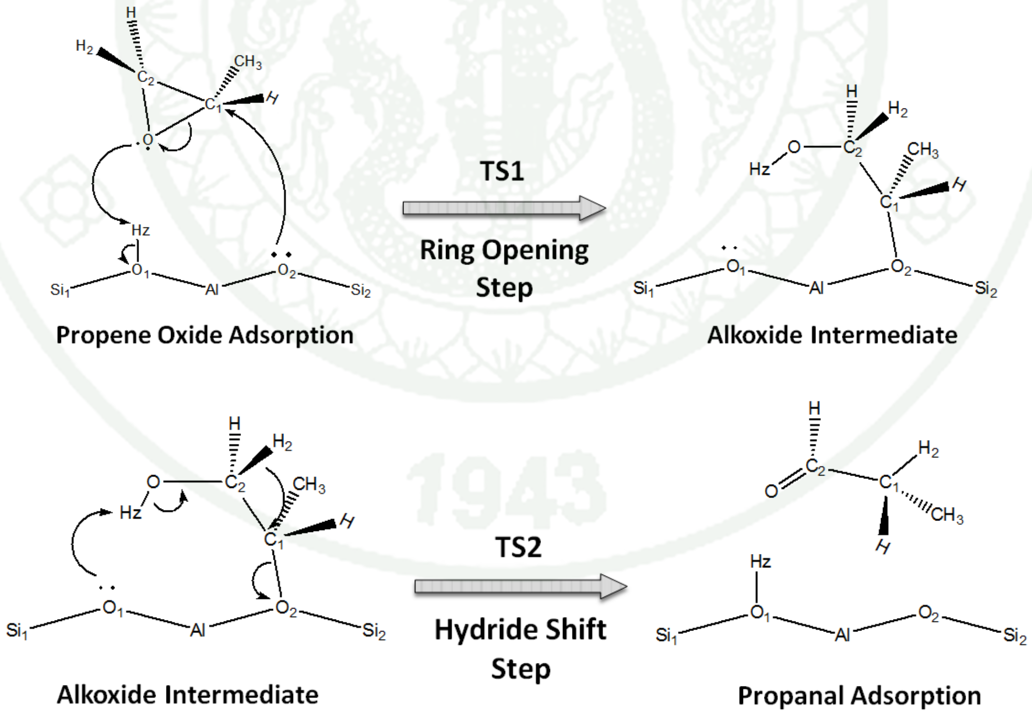

Figure 14 Proposed reaction mechanism of propene oxide isomerization to propanal in the stepwise mechanism; (1) Ring Opening step (2) Hydride Rearrangement Step

As mentioned above, the propene oxide to propanal is presumably initialized from the ring opening reaction. Based on the previous calculation study (Namuangruk *et al.*, 2006a), the isomerization mechanism of propene oxide to propanal has been proposed as a stepwise reaction processes. The calculated energy profile and activation energies for the isomerization of propene oxide to propanal are shown in Figure17 and optimized structural parameters are shown in Table3 and Table4. First, the propene oxide molecule diffuses into the pore of zeolite and then adsorbs on the acidic proton at the active site to form the propene oxide adsorption complex. Propene oxide adsorbs on the acidic proton via hydrogen bonding with the Op-Hz distance of 1.326 Å and the adsorption energy of -29.0 kcal/mol. In this adsorption complex, the C1-Op and C2-Op bond lengths are calculated to be 1.451 Å and 1.448 Å, respectively.

Then, the C1-Op bond is broken to produce the secondary alkoxide intermediate (INT_A) through the secondary carbenium ion transition state (TS1_A). At the TS1_A transition-state configuration, the acidic proton of the zeolite is protonated to the adsorbed propene oxide, the C1-Op bond is broken, and the hybridization of C1 is changed from tetrahedral (sp3) to planar (sp2). The transition state can be confirmed by the frequency calculation with one imaginary frequency at –497.41 cm^{-1}, which is related to the movement of the acidic proton of zeolite (Hz) to the propene oxide oxygen (Op) and the breaking of C1-Op bond. The calculated energy barrier for this ring-opening step is 24.37 kcal/mol and the apparent activation energy is -4.67 kcal/mol. The secondary alkoxide intermediate (INT_A) is attached to the oxygen atom (O2) of the zeolite and is stabilized by the zeolite framework.

The next step is the carbonyl-forming step, which involves the transformation of the INT_A intermediate to the adsorbed propanal (P_A) via the 1,2-hydride shift. At this transition-state configuration (TS2_A), the H2 atom is moving toward the carbon atom C2 placed with the C2-H2 and C1-H2 distances being 1.243 Å and 1.468 Å, respectively.

The Hz atom is located in-between the O1 and Op atoms. The vibrational motion that occurs at the TS2_A transition state possesses one imaginary frequency at –709.25 cm^{-1}. This movement corresponds to the H2 atom transfer from C1 to C2 simultaneously with the C1-O2 covalent bond breaking and the Hz transfer from Op back to O1 to restore the active site of the zeolite. The activation energy for this step is calculated to be 20.3 kcal/mol and the propanal product is adsorbed on the acidic site of the ITQ-22 zeolite with the adsorption energy of -47.9 kcal/mol. Finally, the adsorbed propanal is desorbed endothermically and requires an energy of 28.9 kcal/mol.

Although all geometric parameters calculated from the 14T cluster (written in parentheses in Figure 15,16 are quite similar to those obtained from the 58T cluster model, the calculated relative energies and energy barriers differ considerably from the 58T cluster results. However, for the energetic profile of the reaction, the 58T cluster approach that takes into account the zeolite framework effects should be more suitable. The cause of these differences between the two models is the van der Waals effect from the zeolite framework acting on the adsorbate species at each stationary point.

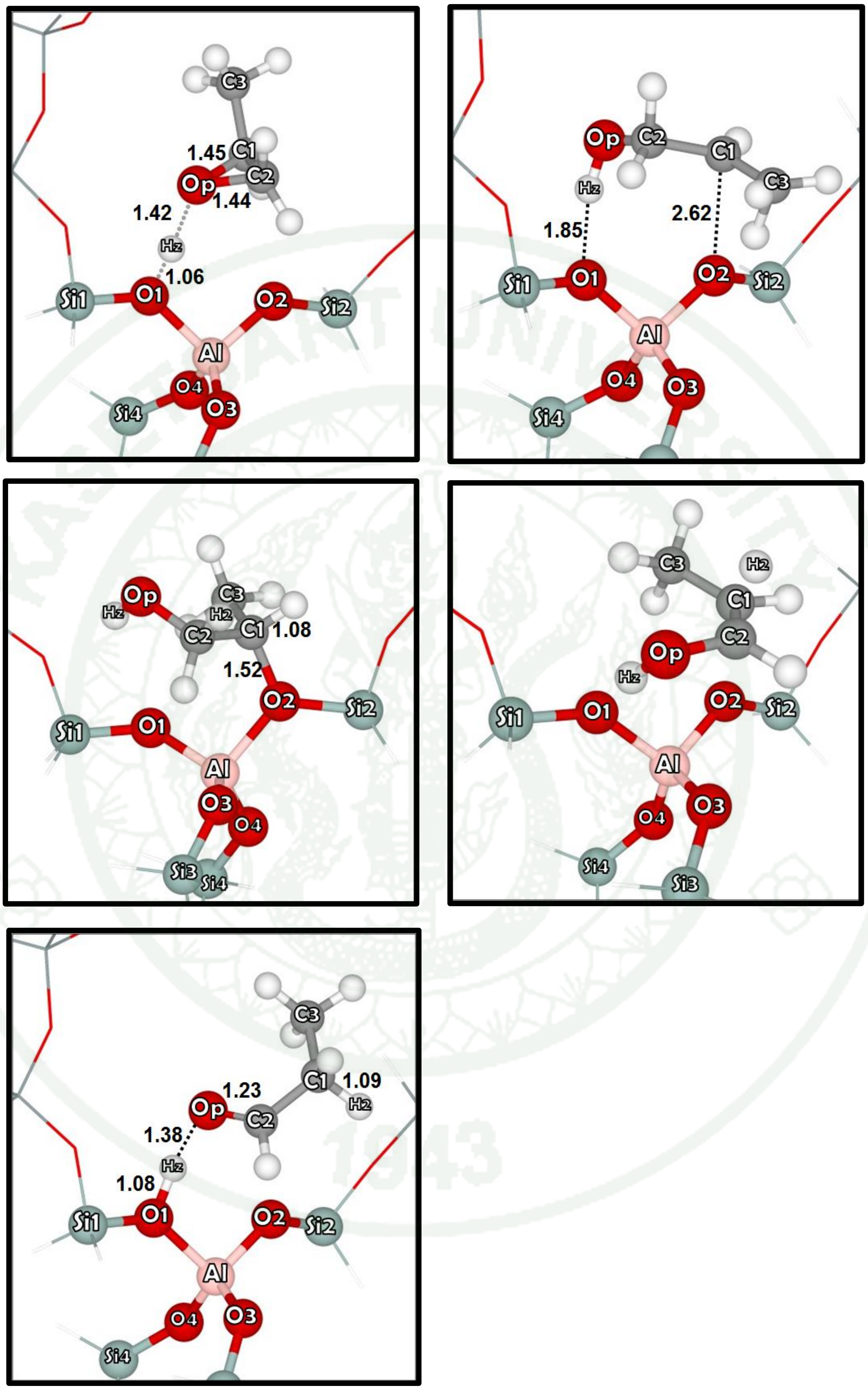

Figure 15 Optimized structures of the all structures involved in the reaction mechanism leading to propanal over 14T of H-ITQ-22 zeolite; (a) AD_A, (b) TS1_A, (c) INT_A, (d) TS2_A, (e) P_A

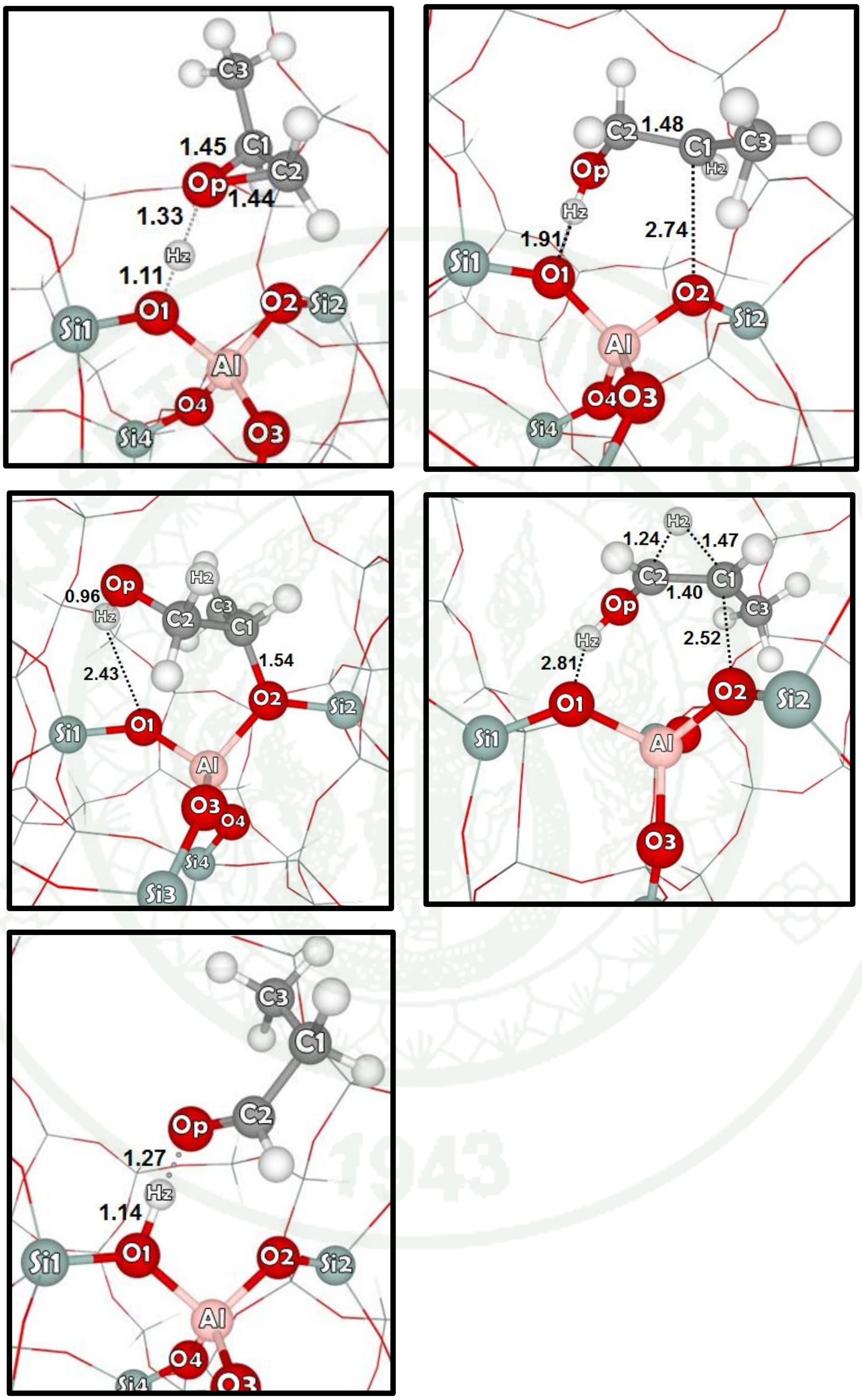

Figure 16 Optimized structures of the all structures involved in the reaction mechanism leading to propanal over 58T of H-ITQ-22 zeolite; (a) AD_A, (b) TS1_A, (c) INT_A, (d) TS2_A, (e) P_A

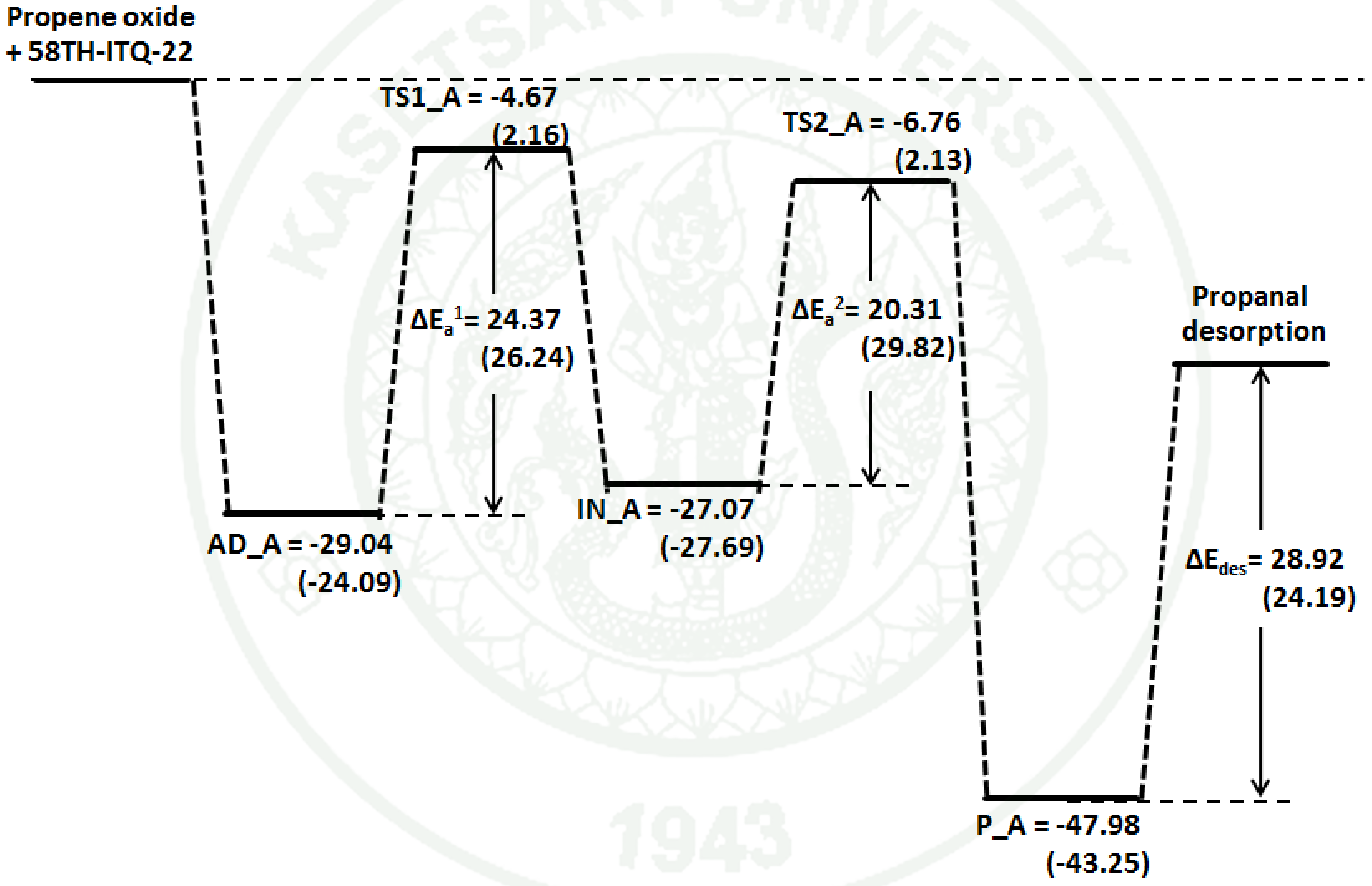

Figure 17 The calculated energy profile for the isomerization of propene oxide to acetone over 46T and 14T (in parentheses) clusters

Table 3 Optimized Structural Parameters of the Adsorption and Reaction Complexes of Propene oxide to Propanal on 14T Cluster of H-ITQ-22 Zeolite. Distances are in Å and Angles are in Degrees.

parameter	AD_A	TS1_A	INT_A	TS2_A	P_A
Distances					
O1-Hz	1.063	1.854	1.993	1.797	1.083
Al-Hz	2.409	3.044	3.791	2.672	2.432
Al-O1	1.834	1.741	1.708	1.749	1.837
Al-O2	1.707	1.756	1.851	1.738	1.706
O1-Si1	1.669	1.610	1.599	1.609	1.665
O2-Si2	1.609	1.619	1.705	1.609	1.607
Hz-Op	1.415	0.978	0.968	0.987	1.387
Op-C1	1.445	2.387	2.453	2.407	2.392
Op-C2	1.444	1.383	1.401	1.339	1.226
C1-C2	1.467	1.476	1.551	1.410	1.487
C1-H2	2.207	2.021	2.152	1.490	1.099
C2-H2	1.086	1.110	1.093	1.229	2.095
O2-C1	3.044	2.628	1.515	2.339	3.481
O2-C2	2.951	3.274	2.526	2.962	2.638
Angles					
Si1-O1-Al	133.89	135.70	138.06	140.20	133.76
Si1-O2-Al	126.71	126.58	121.95	127.45	127.41

Table 4 Optimized Structural Parameters of the Adsorption and Reaction Complexes of Propene oxide to Propanal on 58T Cluster of H-ITQ-22 Zeolite. Distances are in Å and Angles are in Degrees.

parameter	AD_A	TS1_A	INT_A	TS2_A	P_A
Distances					
O1-Hz	1.108	1.915	2.431	2.807	1.143
Al-Hz	2.409	3.091	3.681	2.959	2.456
Al-O1	1.818	1.736	1.706	1.761	1.814
Al-O2	1.702	1.743	1.835	1.723	1.703
O1-Si1	1.651	1.595	1.589	1.580	1.644
O2-Si2	1.590	1.598	1.682	1.585	1.589
Hz-Op	1.326	0.975	0.966	0.977	1.274
Op-C1	1.451	2.393	2.456	2.386	2.383
Op-C2	1.448	1.384	1.399	1.341	1.230
C1-C2	1.467	1.479	1.549	1.400	1.483
C1-H2	2.211	2.024	2.143	1.468	1.099
C2-H2	1.086	1.110	1.093	1.249	2.085
O2-C1	3.004	2.748	1.543	2.521	3.752
O2-C2	2.968	3.384	2.566	2.906	2.729
Angles					
Si1-O1-Al	134.76	136.51	137.42	140.47	134.77
Si1-O2-Al	127.99	127.44	123.63	129.28	128.14

2.2 The Reaction Mechanism Leading to Acetone.

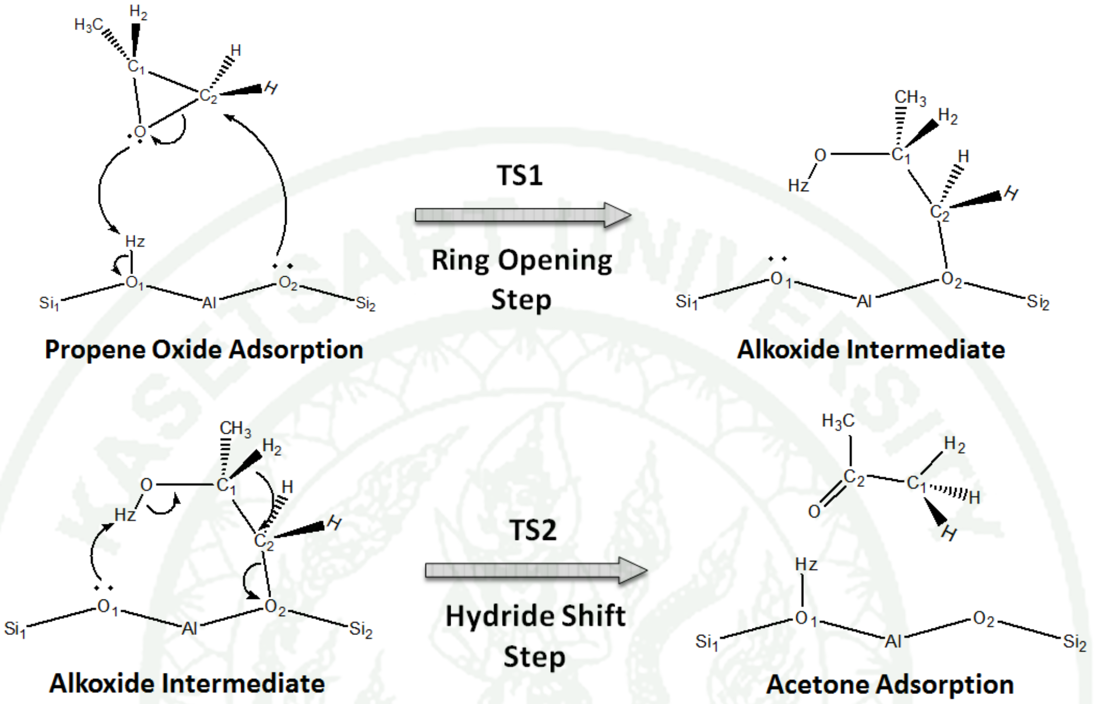

Figure 18 Proposed reaction mechanism of propene oxide isomerization to acetone in the stepwise mechanism; (1) Ring Opening step (2) Hydride rearrangement Step

The isomerization of propene oxide can also produce acetone by breaking the less substituted C-O bond at the ring-opening step. The calculated energy profile for this route is illustrated in Figure21. The reaction starts with the adsorbed propene oxide (AD_B) on the acidic proton of the zeolite. Subsequently, an adsorbed propene oxide is protonated at the Op atom and the less substituted C2-Op bond is broken leading to the formation of the primary alkoxide intermediate through the transition-state TS1_B, which possesses a primary carbenium ion configuration, which is less stable than the secondary carbenium ion (TS1_A) in the propanal route. This justification has been supported by the higher calculated energy barrier and apparent energy for the primary carbenium ion (TS1_B) which is evaluated to be 38.4 and 7.06 kcal/mol, respectively. The transition-state TS1_B has been verified by one imaginary frequency at -497 cm^{-1}. The acidic proton transfers from the zeolite framework to the oxygen atom of propene oxide and the C2-Op bond breaks simultaneously as the covalent bond between C2 and O2 forms. At the transition-state configuration, it is observed that a Hz atom moves from O1 close to Op with the Op-Hz distance of 0.985 Å and the O1-Hz distance of 1.778 Å.

The binding energy of the primary alkoxide intermediate (Int_B) is calculated to be 30.9 kcal/mol, which is more stable than that of the secondary alkoxide intermediate (Int_A) by 3.8 kcal/mol, resulting from the less steric disturbance effect from the substituted group on the alkoxide carbon atom. This less steric hindrance on the alkoxide carbon atom allows the adsorbate to move closer to the active site of the zeolite in comparison to the more steric one, C2-O2 = 1.482 Å for the primary alkoxide (Int_B) and C1-O2 = 1.543 Å for the secondary alkoxide (Int_A), respectively. Therefore, in the zeolite framework, the less steric alkoxide (Int_B) is more stable than the more steric alkoxide (Int_A). This observation is also in agreement with previous reports that the stability of the alkoxide intermediate formed in the zeolite structure is very sensitive to the local geometry of the active site and the nature of the alkoxide carbon atom (Boronat *et al.*, 1998; Boronat *et al.*, 2004; Boronat *et al.*, 2001). When the degree of substitution on alkoxide carbon increases, the covalent C-O bond distance is lengthened and the alkoxide is destabilized (Boronat *et al.*, 2001).

The primary alkoxide intermediate (Int_B) is transformed to the adsorbed acetone product (P_B) via the 1,2-hydride shift process through the transition state (TS2_B) which indicates that the distance of the breaking of the C1-H2 bond is 1.233 Å, the forming of the C2-H2 bond is 1.538 Å, while the breaking C2-O2 covalent bond is lengthened from 1.482 to 2.055 Å. Consequently, Hz moves back to the bridging oxygen atom by locating midway between Op and O1. The transition-state TS2_B has been verified by one imaginary frequency at -890 cm^{-1}. The energy barrier is calculated to be 23.7 kcal/mol, which is higher than that of the propanal route by 3.3 kcal/mol. Finally, the adsorbed acetone is desorbed endothermically, requiring a desorption energy of 31.9 kcal/mol.

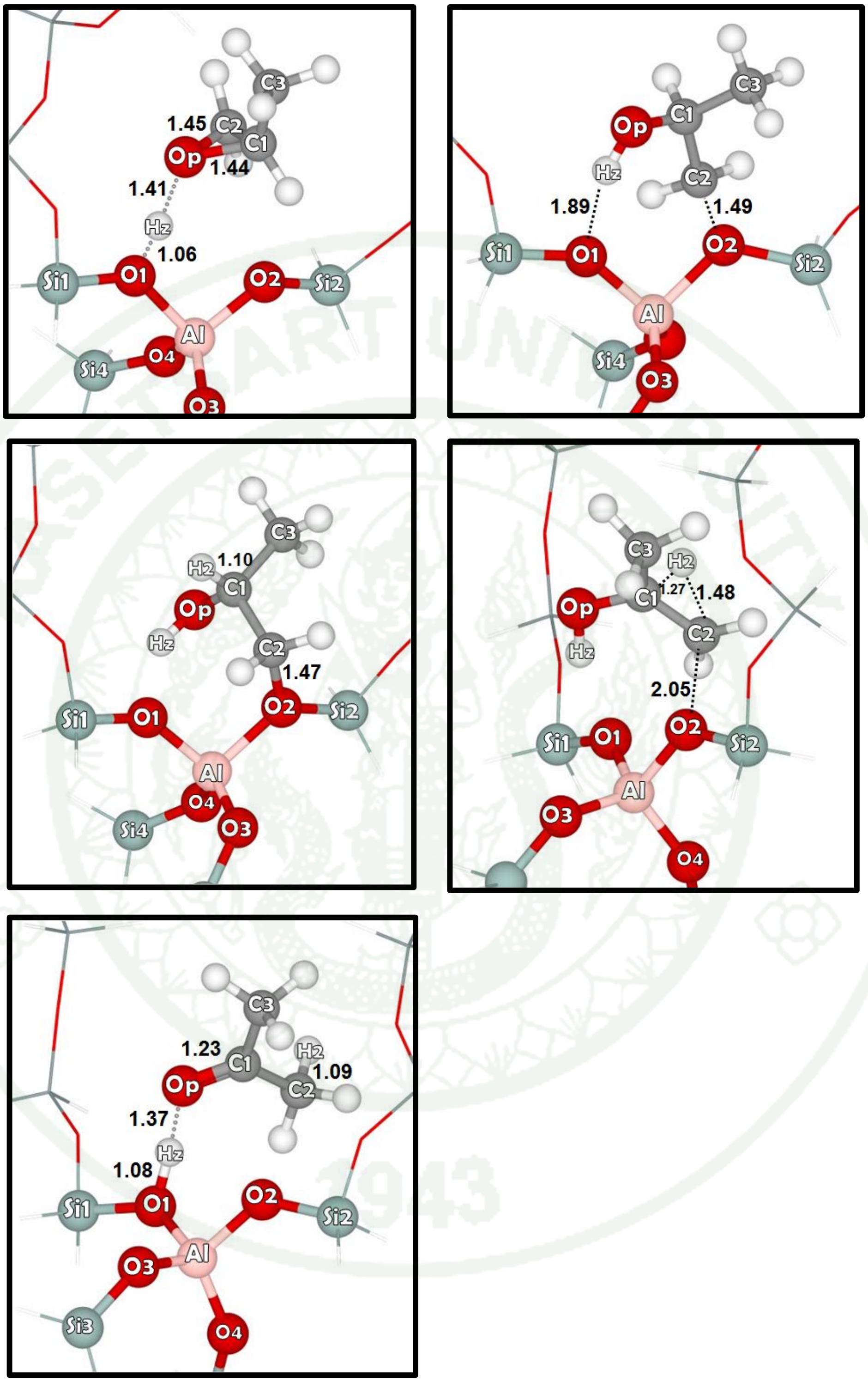

Figure 19 Optimized structures of the all structures involved in the reaction mechanism leading to acetone over 14T of H-ITQ-22 zeolite; (a) AD_B, (b) TS1_B, (c) INT_B, (d) TS2_B, (e) P_B

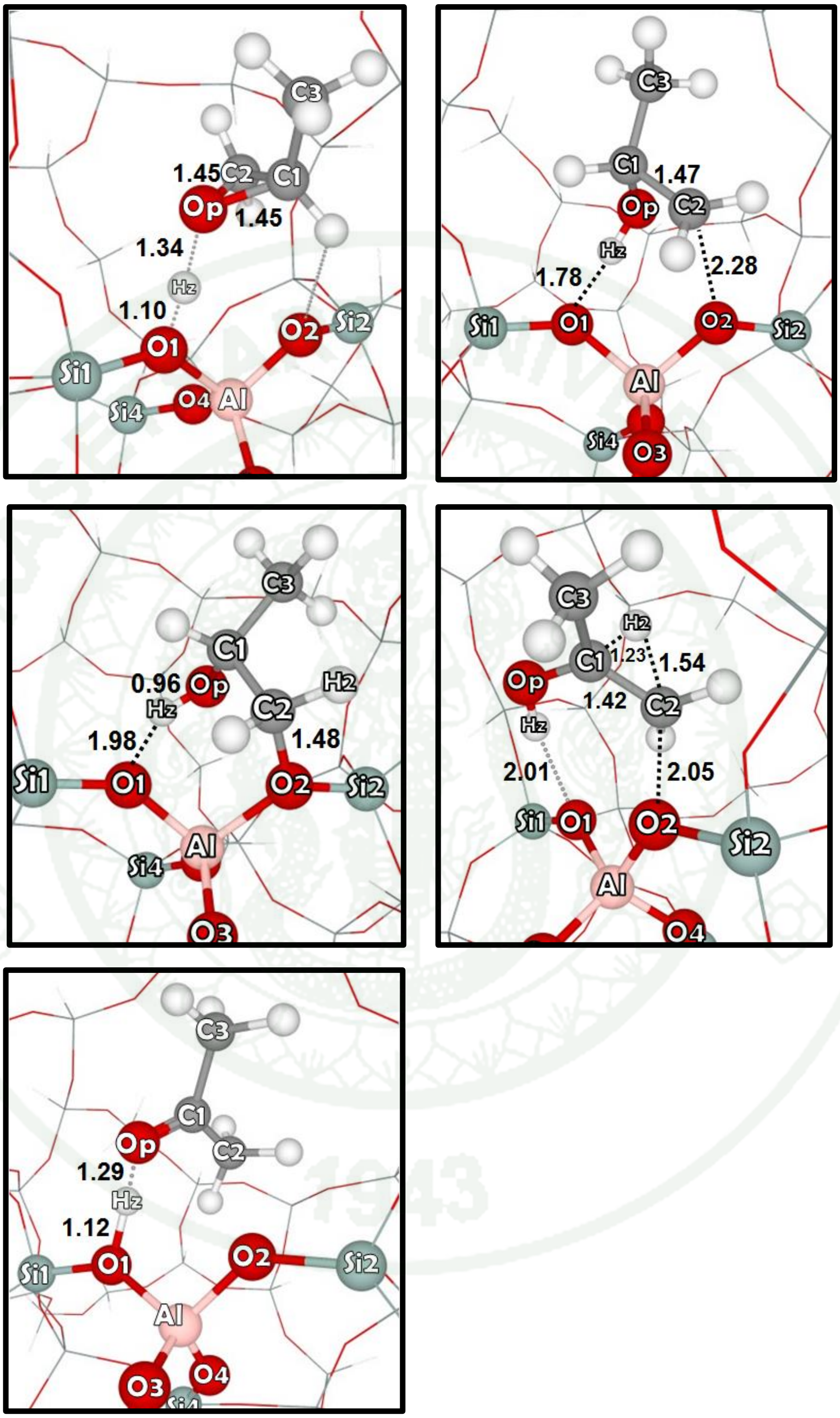

Figure 20 Optimized structures of the all structures involved in the reaction mechanism leading to acetone over 58T of H-ITQ-22 zeolite; (a) AD_B, (b) TS1_B, (c) INT_B, (d) TS2_B, (e) P_B

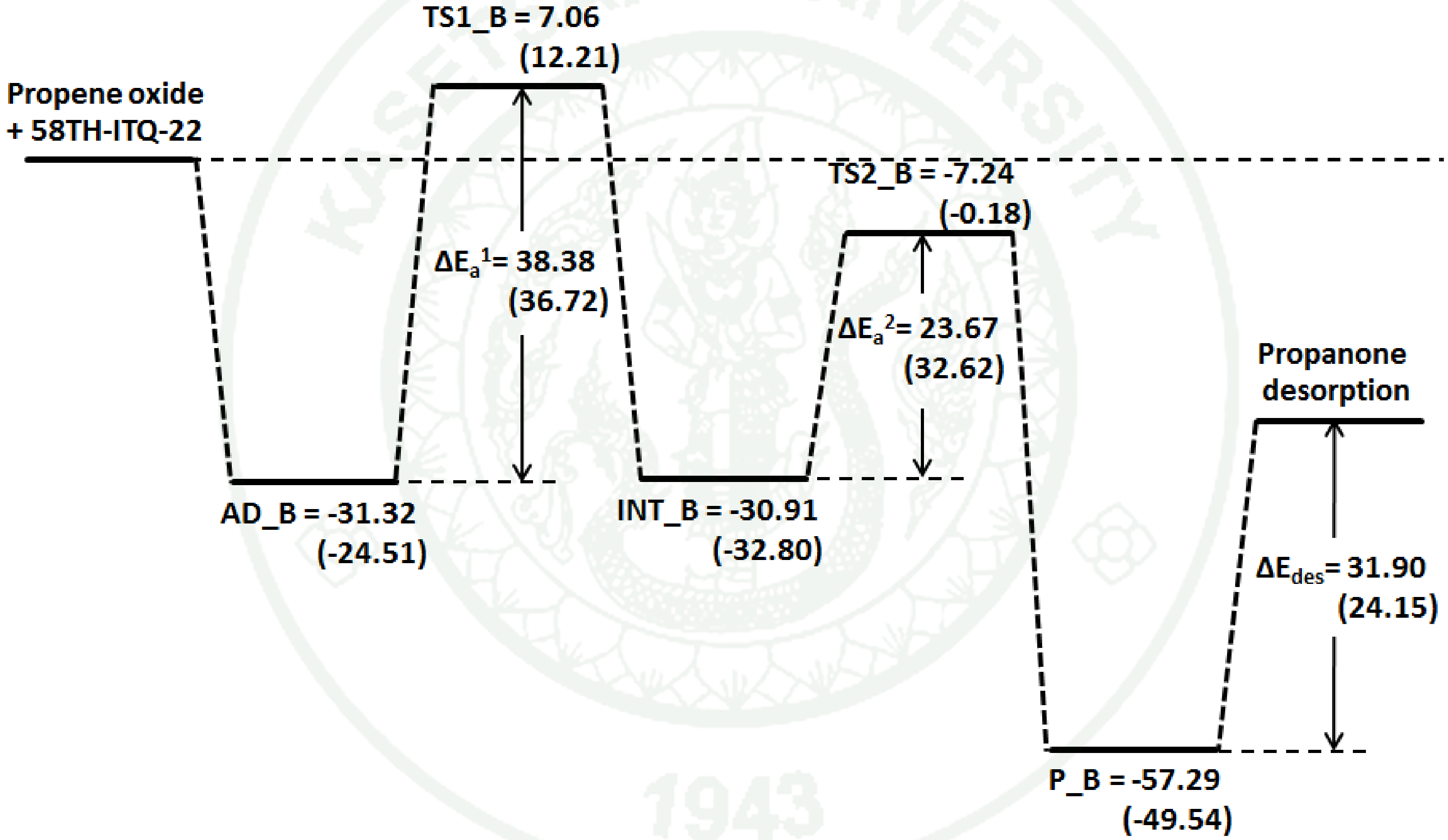

Figure 21 The calculated energy profile for the isomerization of propene oxide to acetone over 46T and 14T (in parentheses) clusters

Table 5 Optimized Structural Parameters of the Adsorption and Reaction Complexes of Propene oxide to Acetone on 14T Cluster of H-ITQ-22 Zeolite. Distances are in Å and Angles are in Degrees.

parameter	ADS_B	TS1_B	INT_B	TS2_B	P_B
Distances					
O1-Hz	1.062	1.890	1.844	1.834	1.082
Al-Hz	2.419	3.087	2.774	2.906	2.384
Al-O1	1.833	1.707	1.716	1.748	1.835
Al-O2	1.707	1.877	1.847	1.763	1.708
O1-Si1	1.667	1.606	1.608	1.614	1.665
O2-Si2	1.609	1.709	1.698	1.623	1.604
Hz-Op	1.415	0.967	0.971	0.984	1.371
Op-C1	1.449	1.396	1.404	1.345	1.229
Op-C2	1.440	2.472	2.460	2.381	2.393
C1-C2	1.468	1.524	1.548	1.409	1.497
C1-H2	1.087	1.109	1.102	1.269	2.108
C2-H2	2.174	2.040	2.119	1.484	1.096
O2-C1	2.981	2.557	2.501	2.755	2.801
O2-C2	3.029	1.499	1.473	2.054	2.912
Angles					
Si1-O1-Al	134.24	141.05	139.84	136.30	133.54
Si1-O2-Al	126.77	121.80	124.12	127.19	126.86

Table 6 Optimized Structural Parameters of the Adsorption and Reaction Complexes of Propene oxide to Propanal on 58T Cluster of H-ITQ-22 Zeolite. Distances are in Å and Angles are in Degrees.

parameter	AD_B	TS1_B	INT_B	TS2_B	P_B
Distances					
O1-Hz	1.103	1.778	1.977	2.005	1.129
Al-Hz	2.430	2.744	2.729	3.267	2.509
Al-O1	1.817	1.746	1.709	1.736	1.790
Al-O2	1.701	1.741	1.832	1.758	1.709
O1-Si1	1.651	1.600	1.588	1.595	1.628
O2-Si2	1.589	1.604	1.676	1.609	1.584
Hz-Op	1.336	0.985	0.965	0.975	1.294
Op-C1	1.448	1.426	1.410	1.344	1.243
Op-C2	1.455	2.094	2.469	2.405	2.403
C1-C2	1.469	1.473	1.558	1.416	1.489
C1-H2	1.087	1.093	1.098	1.233	2.105
C2-H2	2.179	2.152	2.139	1.538	1.096
O2-C1	3.004	3.271	2.507	2.842	2.980
O2-C2	3.066	2.283	1.482	2.055	2.980
Angles					
Si1-O1-Al	134.70	136.73	141.71	135.76	134.40
Si1-O2-Al	128.09	127.81	125.16	127.74	128.40

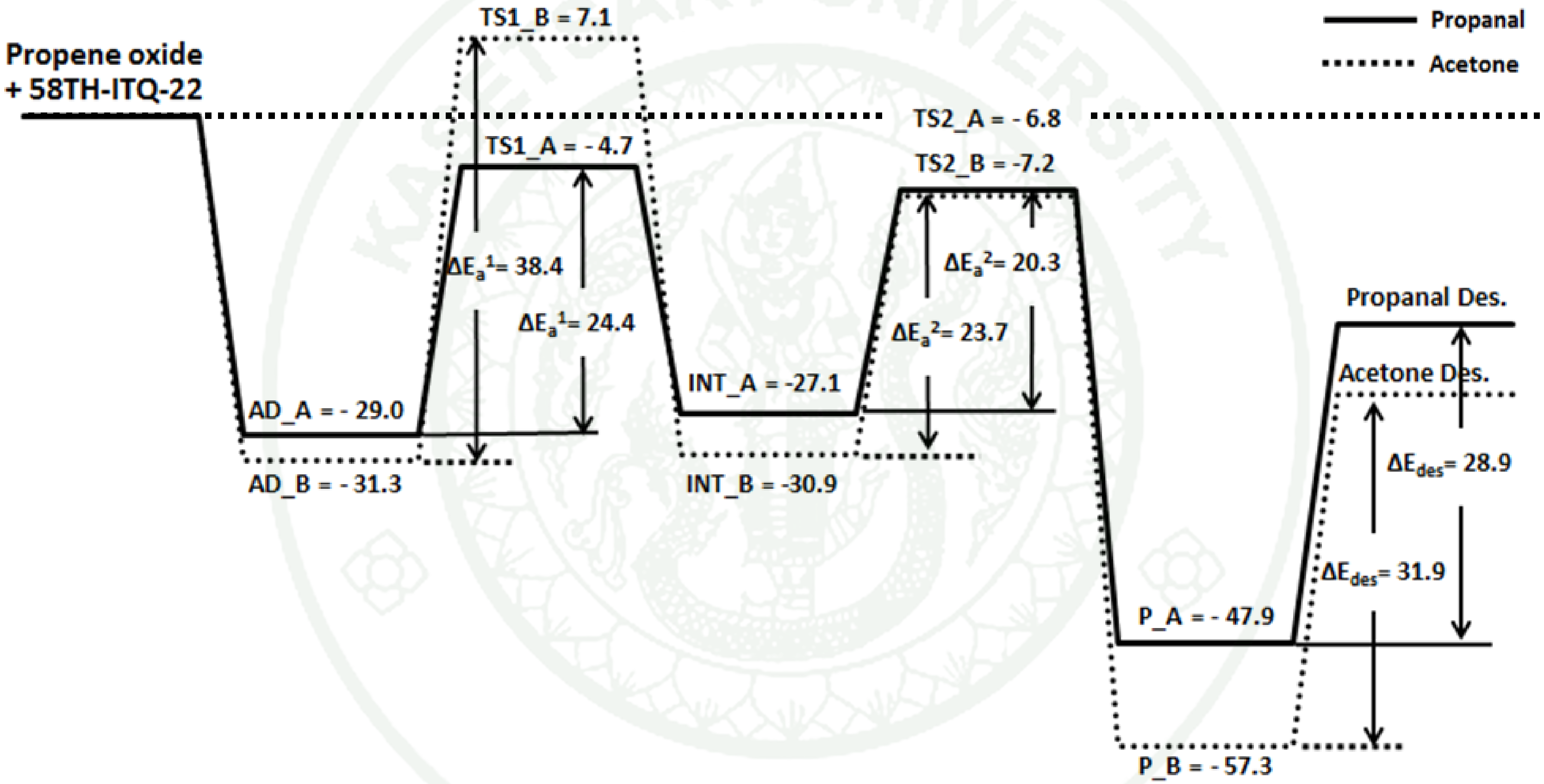

Figure 22 The calculated relative energies profile for the isomerization of propene oxide to acetone and acetone over 58T clusters of H-ITQ-22 zeolite Calculated at M06-2X/6-31G(d,p)

Table 7 The Calculated Relative Energies (kcal/mol) of Reactant, First-Transition State (TS1), Intermediate, Second-Transition State (TS2), Product, First Activation Energy Barrier ($\Delta E\text{a}_1$), and Second Activation Energy Barrier ($\Delta E\text{a}_2$) for the Isomerization Reaction of Propene Oxide over 14T and 58T Clusters of H-ITQ-22 Calculated at M06-2X/6-31G(d,p) Levels

	14T cluster		58T cluster	
	propanal	acetone	propanal	acetone
Reactant	-24.09	-24.51	-29.04	-31.32
TS1	2.16	12.21	-4.67	7.06
intermediate	-27.69	-32.80	-27.07	-30.91
TS2	2.13	-0.18	-6.76	-7.24
product	-43.25	-49.54	-47.98	-57.29
Product des.	24.19	24.15	28.92	31.90
$\Delta E\text{a}_1$	26.24	36.72	24.37	38.38
$\Delta E\text{a}_2$	29.82	32.62	20.31	23.67

For ease of comparison, the complete energetic profiles for all mechanisms are shown in the same diagram (Figure 22). This diagram shows the energies obtained from the 58T cluster models which include the zeolite framework effect. The ringopening step is considered to be the rate-determining step. The activation energies are 24.4 and 38.4 kcal/mol for propanal and acetone formation, respectively. The reaction intermediates and transition states are greatly stabilized by the zeolite framework. The step following is the energy barrier for carbonyl forming, which involves the 1,2-hydride shift on connecting the C-C bond, and is evaluated to be 20.3 and 23.7 kcal/mol for propanal and acetone, respectively.

Therefore, it can be concluded, by considering the relative reaction barrier and the transition-state stability, that the propanal is more favorably formed than the acetone. However, since the confinement effect of the H-ITQ-22 zeolite stabilizes the transition states and intermediates for both routes, the preference against the rupture of the more sterically hindered C-O bond is not very high. This finding corresponds well with the experimental results (Šepa *et al.*, 1996) that propanal was produced in a higher yield than that of acetone but the minor product, acetone, was also produced in a significant yield for the propene oxide isomerization in H-ITQ-22 zeolites.

CONCLUSION

The isomerization of propene oxide over 14T and 58T clusters of H-ITQ-22 zeolite has been investigated by using the M06-2X/6-31G(d,p) methods. The reaction mechanisms proceed through a ring-opening step followed by a 1,2-hydride shift to form two different carbonyl compounds, propanal and acetone. The ring-opening step of these mechanisms is found to be the rate-determining step and their transition states are in the carbenium ion form. The propanal route proceeds via the secondary carbenium ion while that of the acetone proceeds via the primary one. Because the sterically more hindered C-O bond can be broken more easily and the secondary carbenium ion transition state is more stable, the ring-opening activation barrier for the propanal of 24.4 kcal/mol is lower than that for the acetone of 38.4 kcal/mol. The main product from this reaction is, therefore, the propanal.

The computational results suggest that the 14T cluster is adequate to determine the geometrical characters of the transition state, the intermediate, the reactant, and the product of these small adsorbates. However, since the 14T cluster does not take into account the van der Waals from the zeolite framework, it cannot give reasonable results for the energetic profile of the reaction. The extended 58T model, which includes the zeolite cavity and those effects, can be used to calculate more reliable results.

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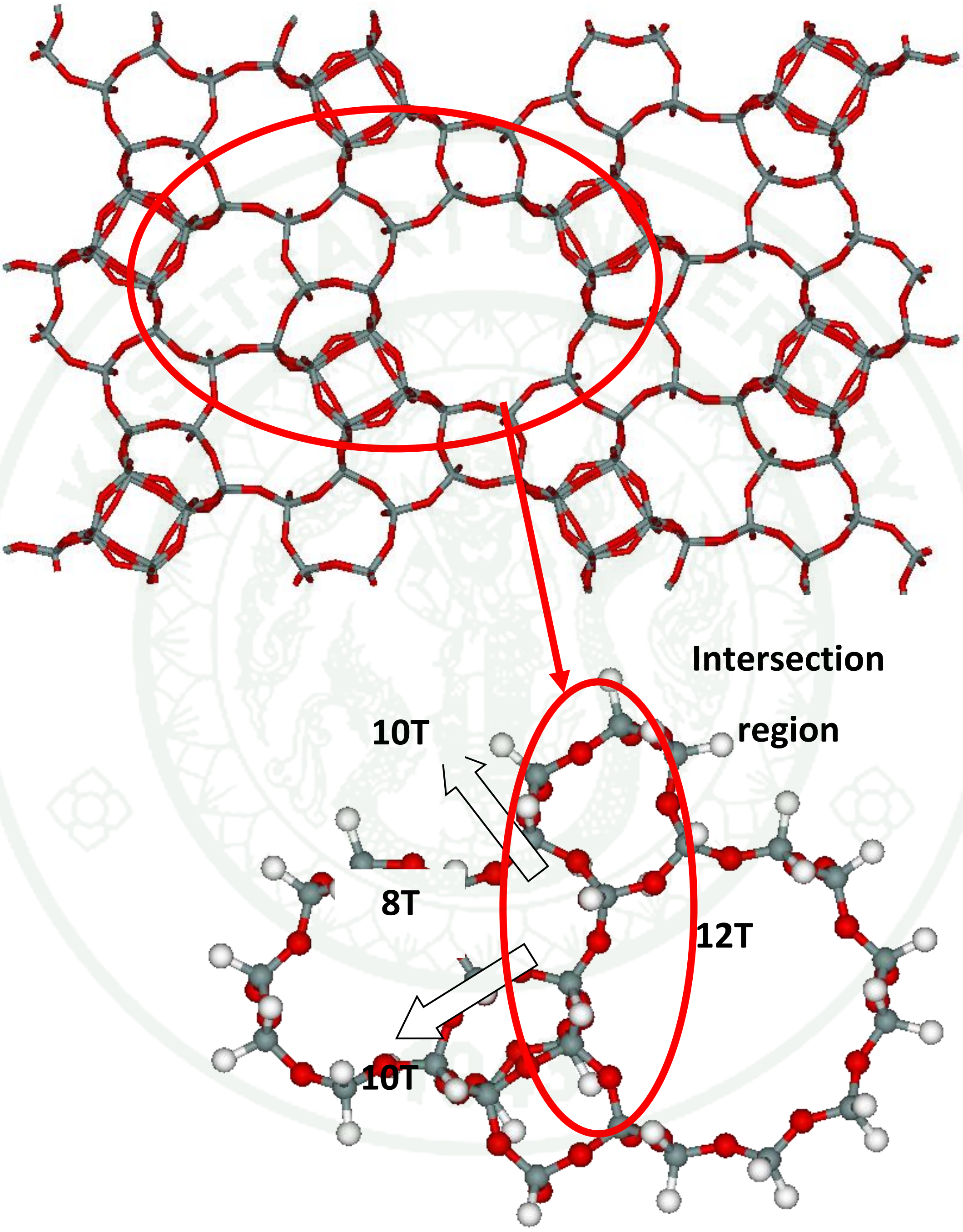
APPENDIX

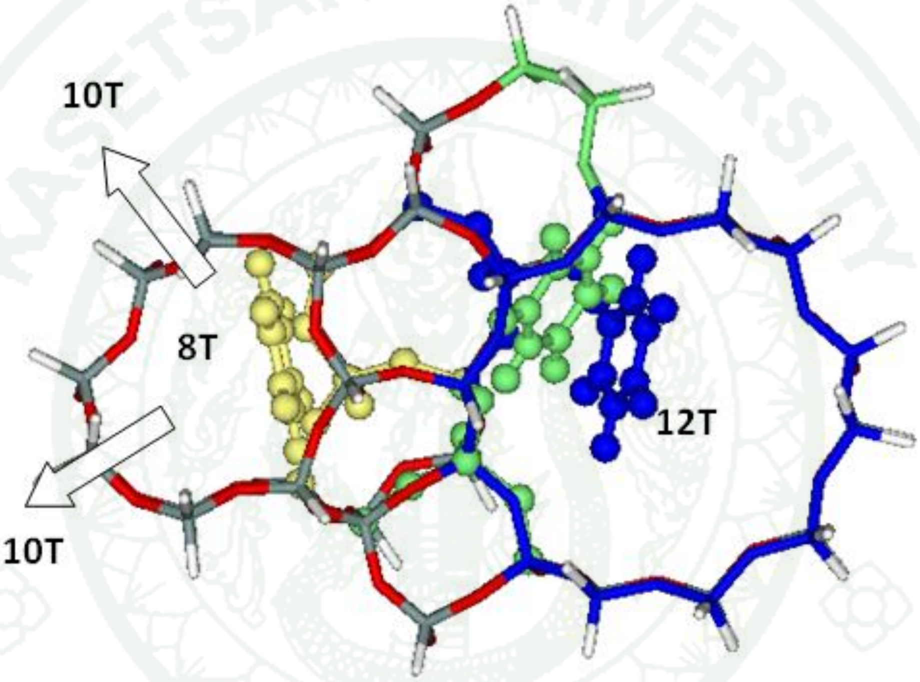
Structure of ITQ-22 zeolite (Framework Type IWW)



Appendix Figure 1 The framework structure of ITQ22

The acidity of different T site position of ITQ-22 zeolite

The adsorption of pyridine is used to study the acidity of different T site position. The models are expanded to 28T quantum cluster to cover the framework. The pyridine adsorption on different T site of H-ITQ-22 are shown in Figure24 and the adsorption energies are shown in table 2.



Appendix Figure 2 The pyridine molecules adsorb on H-ITQ-22 at 1) T1 position (Green color), 2) T14 position (Yellow color) and 3) T15 position (Blue color)

As shown in Table8, the adsorption energy of pyridine at T01O02 position is higher than another position. So T01O02 position is the most appropriate position for use to be an active region of H-ITQ-22 zeolite.

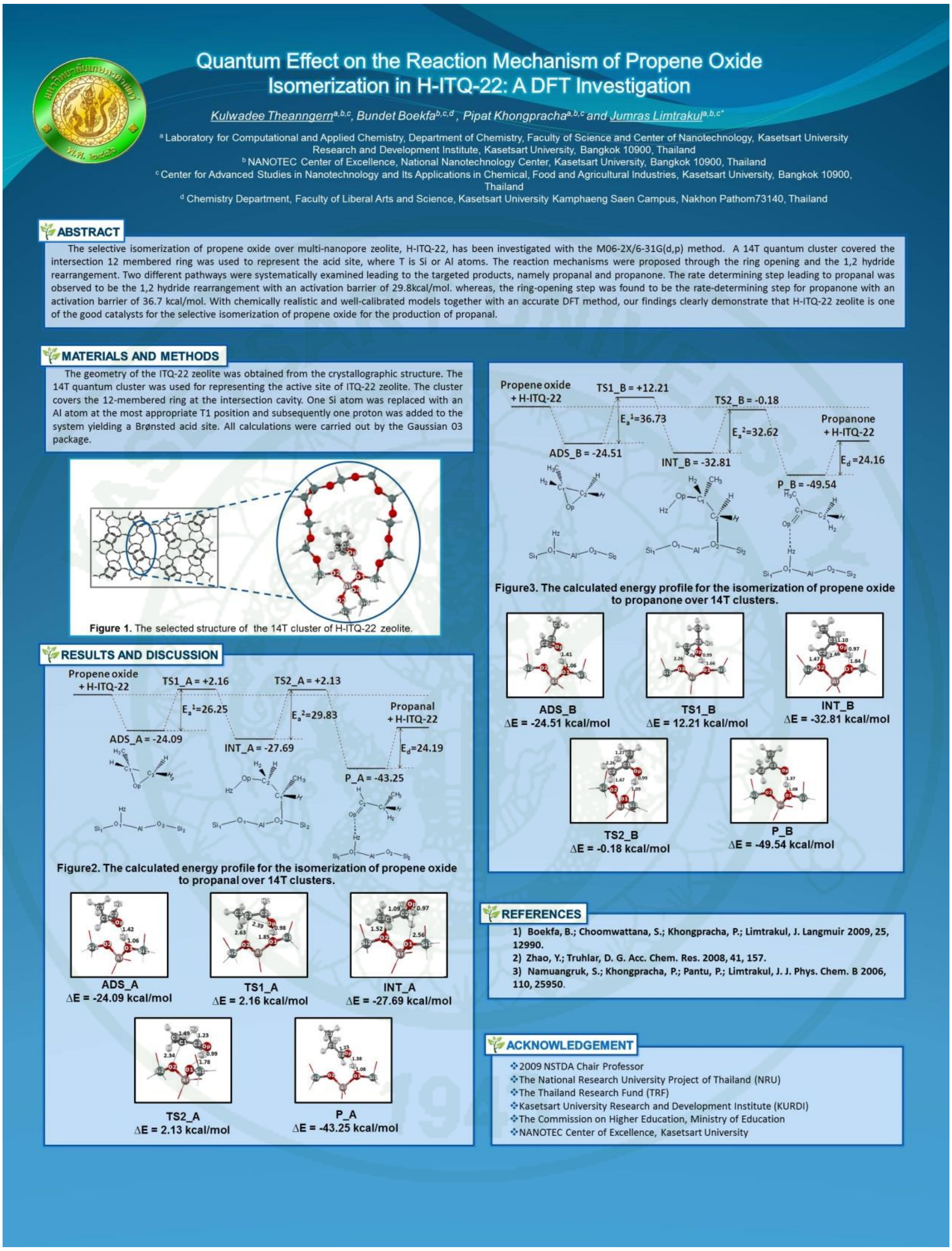
Appendix Table 1 The detailed framework structure and the adsorption energies (kcal/mol) of pyridine on H-ITQ-22 with M08-HX/6-31G(d,p) level of theory

Name	**Position**	**Adsorption energy (kcal/mol)**
T01O02	Pyridine locates at Intersection between 12T and 10T channel	-46.48
T14O30	Pyridine locates at cavity between zigzag 10T and 10T channel	-43.96
T15O33	Pyridine locates in the straight 12T channel	-44.71

*This data supported by Dr.Bundet Boekfa

POSTER PRESENTATION

1. Kulwadee Theanngern, Bundet Boekfa, Pipat Khongpracha and Jumras Limtrakul. **Quantum Effect on the Reaction Mechanism of Propene Oxide Isomerization in H-ITQ-22: A DFT Investigation.** The 241th American Chemical Society National Meeting & Exposition 2011, at the Anaheim Convention Center, Anaheim, California, U.S.A., 27-31 March 2011.



Quantum Effect on the Reaction Mechanism of Propene Oxide Isomerization in H-ITQ-22: A DFT Investigation

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ABSTRACT

The selective isomerization of propene oxide over multi-nanopore zeolite, H-ITQ-22, has been investigated with the M06-2X/6-31G(d,p) method. A 14T quantum cluster covered the intersection 12 membered ring was used to represent the acid site, where T is Si or Al atoms. The reaction mechanisms were proposed through the ring opening and the 1,2 hydride rearrangement. Two different pathways were systematically examined leading to the targeted products, namely propanal and propanone. The rate determining step leading to propanal was observed to be the 1,2 hydride rearrangement with an activation barrier of 29.8kcal/mol. whereas, the ring-opening step was found to be the rate-determining step for propanone with an activation barrier of 36.7 kcal/mol. With chemically realistic and well-calibrated models together with an accurate DFT method, our findings clearly demonstrate that H-ITQ-22 zeolite is one of the good catalysts for the selective isomerization of propene oxide for the production of propanal.

MATERIALS AND METHODS

The geometry of the ITQ-22 zeolite was obtained from the crystallographic structure. The 14T quantum cluster was used for representing the active site of ITQ-22 zeolite. The cluster covers the 12-membered ring at the intersection cavity. One Si atom was replaced with an Al atom at the most appropriate T1 position and subsequently one proton was added to the system yielding a Brønsted acid site. All calculations were carried out by the Gaussian 03 package.

Figure 1. The selected structure of the 14T cluster of H-ITQ-22 zeolite.

RESULTS AND DISCUSSION

Figure2. The calculated energy profile for the isomerization of propene oxide to propanal over 14T clusters.

Figure3. The calculated energy profile for the isomerization of propene oxide to propanone over 14T clusters.

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Quantum Effect on the Reaction Mechanism of Propene Oxide Isomerization in H-ITQ-22: A DFT Investigation

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Introduction

The reactive epoxide, driven from the constraint of the three-membered ring, makes it suitable to be a building block in the synthesis of organic compounds and polymers. The use of epoxide as a chemical starting material is of great current interest from both academic and industrial viewpoints. Propene oxide is one of the most important epoxides with a huge application in polymer industries[1-4]. The reaction of propene oxide that is attracting attention is the "ring-opening isomerization" to various oxygenated products, especially propanal and propanone[5-7]. This process can be catalyzed by either homogeneous or heterogeneous catalysts such as Al_2O_3, Al_2O_3-SiO_2, ZnO[8], Nafion-H, and zeolites[9-10]. The most current catalysts for this process are deficient in the versatility to be selective for the desired products. It is desirable to develop a catalytic process which is able to handle and give a beneficial selectivity.

Zeolite is an aluminosilicate porous material widely used in petroleum refineries and petrochemical industries[11-18]. Owing to its shape selectivity, intrinsic acidity and simple separation system, this material is one of the candidates for this process. Recently, Andras Fasi and co-workers studied the ring-opening isomerization of epoxide in various zeolites, including H-ZSM-5[9-10]. Their results showed that the reaction of epoxide in zeolite lead to the carbonyl compounds and propanal was the major product when H-ZSM-5 was employed as a catalyst. The comprehensive mechanistic study of this reaction in zeolite was initiated with the quantum chemical calculation[19]. Propene oxide isomerization over H-ZSM-5 zeolite was proposed in two mechanisms based on the reaction products, propanal and propanone. The ring-opening step was found to be the rate-determining step with activation barriers of 38.5 kcal/mol and 42.4 kcal/mol for propanal and propanone, respectively.

ITQ-22 (IWR) is the synthetic multipore zeolite with the dimension 8 x 10 x 12 membered ring pore structure[20]. Conventionally, this novel zeolite is applied for the isomerization of m-xylene, the disproportionation of m-xylene and the alkylation of benzene with isopropanol or propylene. The catalytic selectivity toward these reactions has proved to be better than ZSM-5 zeolite.

The exchange functional is required to realistically describe the interaction of ITQ-22 and the probing species. Therefore, the periodic calculation seems not to take into account some effects such as the van de Waals interaction, while the small quantum cluster is not able to represent the confinement effect of the zeolite framework.[21-23] The M06-2X functional recently developed by Zhao and Thrular[24-25] has been successfully applied to study the adsorption and reaction mechanisms of non-polar and aromatic molecules on zeolites.[26-29]

The aim of this work is to study the propene oxide isomerization over the multipore ITQ-22 zeolite using the density functional theory. The detailed reaction mechanism of propene oxide to propanal and propanone have been discussed.

Methods

The geometry of the ITQ-22 zeolite was obtained from the crystallographic structure[20]. The 14T quantum cluster where T means the tetrahedral unit of Si or Al atoms was used for representing the active site of ITQ-22 zeolite. The cluster covers the 12-membered ring at the intersection cavity. One Si atom was replaced with an Al atom at the most appropriate T1 position and subsequently one proton was added to the system yielding a Brønsted acid site. All geometries were optimized with the M06-2X functional using the 6-31G(d,p) basis set. Only the active region, $\equiv SiO(H)Al(OSi)_4\equiv$, and the probe molecule were allowed to relax while the rest was kept fixed with the crystallographic structure. Only one imaginary frequency with its vibration corresponding to the transition structure was confirmed by frequency calculation. In order to examine the effect of the extended framework, single point calculations were performed on a 58T quantum cluster covered intersection and 8-, 10- and 12-MR windows of ITQ-22 as shown in Fig 1. All calculations were carried out by the Gaussian 03 package[30] incorporated with the Minnesota Density Functionals module 3.1 by Zhao and Truhlar.

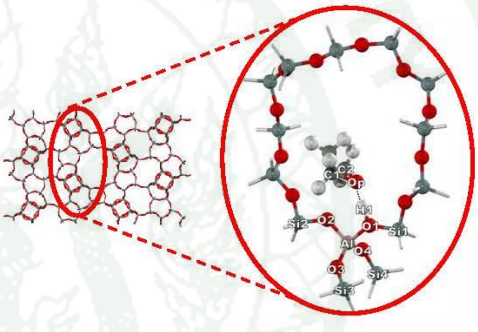
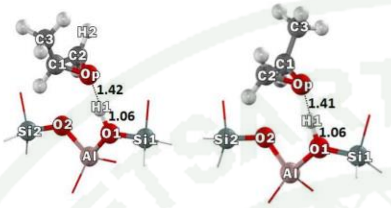


Figure 1. The selected structure of the 14T cluster of H-ITQ-22 zeolite.

Results and Discussion

The Zeolite Model and Adsorption Complexes. The active site of ITQ-22 zeolite calculated by the 14T quantum cluster is shown in Figure 1. The optimized geometric parameters from the 14T quantum cluster are tabulated in Table 1. The Brønsted acid O1-Hz bond distance is 0.97 Å. The Al···Hz distance is 2.35 Å, which compared well with the experimental value (2.38-2.48 Å).

The propene oxide adsorbed on the Brønsted acid site with the hydrogen bond at the intersection of ITQ-22 is shown in Figure 2. Two optimum adsorption configurations are found, namely ADS_A and ADS_B with comparable adsorption energies of -24.09 and -24.51 kcal/mol, respectively. On both adsorption complexes, most of the geometric parameters are the same (see Table 1 and Table 2). The Brønsted acid O1-Hz bond distance is significantly increased from 0.97 to 1.06 Å. Strong hydrogen bond interactions in both configurations are confirmed by high adsorption energy; a short intermolecular distance between the propene oxide and the Brønsted acid of zeolite H1···Op (1.42 and 1.41 Å) and the nearly linear arrangement of O1-H1-Op angle (174.69 and 175.49 degrees). The shorter H1···Op distance of ADS_B refers to the higher interaction with the zeolite. The calculated adsorption energies are in the range of the experimental data of acetone adsorbed on H-ZSM-5 zeolite (-31.1 kcal/mol).



a) ADS_A
ΔE = -24.09 kcal/mol

b) ADS_B
ΔE = -24.51 kcal/mol

Figure2. Optimized structure of propene oxide on H-ITQ-22 zeolite: a) ADS_A and b) ADS_B. Distances are in Ås.

The Reaction Mechanism of Isomerization of Propene Oxide. The isomerization reaction of propene oxide occur via the C-O bond breaking in the propene oxide. Two different types of products, propanal and propanone, are produced from the breaking of the C-O bond at the tertiary carbon (C1-Op) and the other carbon atom (C2-Op). The energy profiles of both competitive routes are shown in Figure 3 and Figure 5.

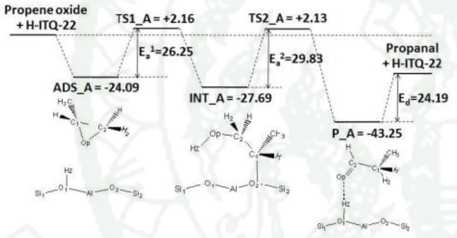
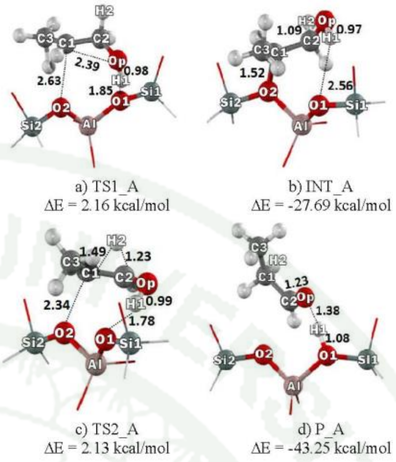


Figure3. The calculated energy profile for the isomerization of propene oxide to propanal over 14T clusters.

For a reaction that gives a propanal product, the reaction mechanism is proposed to be a stepwise mechanism. The optimized structures of all reaction intermediates are tabulated in Table 1. After the adsorption, ADS_A, the C1-Op bond is broken to produce a secondary alkoxide intermediate, INT_A. At the transition state structure, the C1-Op bond is broken and the coordination of C1 is changed from tetrahedral to the planar form. Only one imaginary frequency from the transition structure is observed at –497.41 cm^{-1} corresponding with the moving of O1-H1 bond and the breaking of the C1-Op bond. The calculated activation barrier is 26.25 kcal/mol. The intermediate, INT_A, is formed subsequently to this step and has a relative energy -27.69 kcal/mol with respect to the starting reagent.



a) TS1_A
ΔE = 2.16 kcal/mol

b) INT_A
ΔE = -27.69 kcal/mol

c) TS2_A
ΔE = 2.13 kcal/mol

d) P_A
ΔE = -43.25 kcal/mol

Figure 4. Optimized structure of propene oxide to propanal on H-ITQ-22 zeolite: a) TS1_A, b) INT_A, c) TS2_A and d) P_A. Distances are in Ås.

Table 1. Optimized Structural Parameters of the Adsorption and Reaction Complexes of Propene oxide to Propanal on H-ITQ-22 Zeolite. Distances are in Ås and Angles are in Degrees.

parameter	Bare	ADS_A	TS1_A	INT_A	TS2_A	P_A
Distances						
O1-H1	0.97	1.06	1.85	2.56	1.78	1.08
Al-H1	2.35	2.20	3.04	3.79	2.67	2.43
Al-O1	1.89	1.83	1.74	1.71	1.75	1.84
Al-O2	1.70	1.71	1.76	1.85	1.74	1.70
O1-Si1	1.69	1.67	1.61	1.60	1.61	1.66
O2-Si2	1.62	1.61	1.62	1.70	1.61	1.61
H1-Op		1.42	0.98	0.97	0.99	1.38
Op-C1	1.42	1.44	2.39	2.45	2.41	2.39
Op-C2	1.42	1.44	1.38	1.40	1.34	1.23
C1-C2	1.47	1.47	1.48	1.55	1.41	1.49
C1-H2	1.09	2.23	2.02	2.15	1.49	1.10
C2-H2	2.20	1.09	1.11	1.09	1.23	2.09
O2-C1		3.04	2.63	1.52	2.34	3.48
O2-C2		2.95	3.27	2.53	2.52	2.64
Angles						
Si1-O1-Al	135.8	133.8	135.7	138.1	140.2	133.8

The next step is the 1,2 hydride shift where H transfers from the C2 atom to the C1 atom and concurrently the proton H1 moves back to the zeolite. The transition state, TS2_A, is confirmed by one imaginary frequency at –709.25 cm^{-1} where the vibration shows consecutive movement between the intermediate INT_A and the product. The activation barrier is calculated to be 29.83 kcal/mol. Therefore, this step is the rate-determining step of this pathway. The propanal product, P_A has a relative energy of -43.25 kcal/mol. The desorption energy of propanol from the ITQ-22 is calculated to be 24.19 kcal/mol. The propene oxide isomerization to propanal is exothermic reaction with the heat of reaction -19.06 kcal/mol.

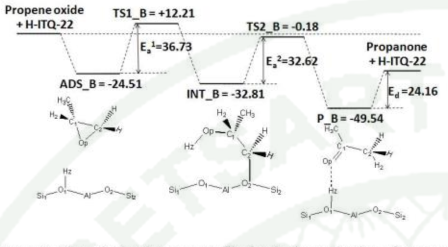
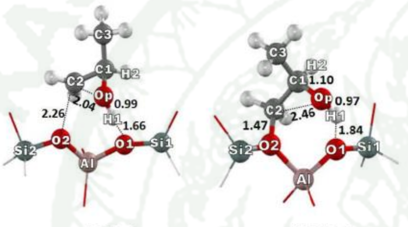
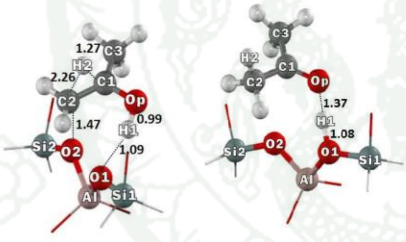


Figure5. The calculated energy profile for the isomerization of propene oxide to propanone over 14T clusters.



a) TS1_B
ΔE = 12.21 kcal/mol

b) INT_B
ΔE = -32.81 kcal/mol



c) TS2_B
ΔE = -0.18 kcal/mol

d) P_B
ΔE = -49.54 kcal/mol

Figure 6. Optimized structure of propene oxide to propanone on H-ITQ-22 zeolite: a) TS1_B, b) INT_B, c) TS2_B and d) P_B. Distances are in Ås.

For the propanone production route, the reaction mechanism is similar to with the propanal route. The reaction is proposed to be a stepwise mechanism as shown in Figure 5. The optimized geometric parameters of all reaction intermediates are tabulated in Table 2. First, propene oxide adsorbed on the ITQ-22 zeolite forms the adsorption complex ADS_B. The propene oxide molecule is then protonated at the Op atom and the C2-Op bond is broken yielding the carbenium ion activated complex. For the transition state, TS1_B, requires the energy barrier of 36.73 kcal/mol, which is higher than that in the propanal step. This is due to the fact that a carbenium ion in the TS1_B is considered to be a primary carbenium ion that is less stable than a secondary carbenium ion, as in the TS1_A transition structure. The reaction generates the primary alkoxide intermediate, INT_B, with a relative energy of -32.81 kcal/mol. Next, the reaction goes through the transition state, TS2_B, which is a 1,2 hydride shift transfer from the C1 atom to the C2 atom and the return of the acidic proton H1. This step requires the energy barrier of 32.62 kcal/mol. The propanone product has a relative energy of -49.54 kcal/mol. The desorption energy of propanone from ITQ-22 is 24.16 kcal/mol. The propene oxide isomerization to propanone is an exothermic reaction with the heat of reaction -25.38 kcal/mol.

The isomerization of propene oxide to propanal and propanone on H-ITQ-22 has been successfully studied with the M06-2X functional. The rate determining step requires activation energies 29.83 and 36.73 kcal/mol for propanal and propanone, respectively. This leads to the conclusion that propanal is the major product from the propene oxide isomerization reaction. Our findings are also confirmed by the experiment data that higher selectivity of propanal over propanone is observed in propene oxide isomerization using zeolite as a catalyst[9].

Table2. Optimized Structural Parameters of the Adsorption and Reaction Complexes of Propene Oxide to Propanone on H-ITQ-22 zeolite. Distances are in Ås and Angles are in Degrees.

parameter	Bare	ADS_B	TS1_B	INT_B	TS2_B	P_B
Distances						
O1-H1	0.97	1.06	1.66	1.84	1.83	1.08
Al-H1	2.35	2.42	2.70	2.77	2.91	2.38
Al-O1	1.89	1.83	1.75	1.72	1.75	1.83
Al-O2	1.70	1.71	1.74	1.85	1.76	1.71
O1-Si1	1.69	1.67	1.62	1.61	1.61	1.67
O2-Si2	1.62	1.61	1.62	1.70	1.62	1.60
H1-Op		1.41	0.99	0.97	0.98	1.37
Op-C1	1.42	1.44	1.42	1.40	1.33	1.23
Op-C2	1.42	1.44	2.04	2.46	2.38	2.39
C1-C2	1.47	1.47	1.47	1.55	1.41	1.50
C1-H2	2.21	1.09	1.09	1.10	1.27	2.11
C2-H2	1.09	2.17	2.16	2.12	1.48	1.10
O2-C1		2.98	3.25	2.50	3.24	2.80
O2-C2		3.03	2.26	1.47	2.05	2.91
Angles						
Si1-O1-Al	135.8	134.2	136.3	139.8	136.3	133.5

Conclusion

The selective isomerization of propene oxide over multi-nanopore zeolite, H-ITQ-22, has been investigated with the M06-2X/6-31G(d,p) method. A 14T quantum cluster covered the intersection 12 membered ring was used to represent the acid site, where T is Si or Al atoms. The reaction mechanisms were proposed through the ring opening and the 1,2 hydride rearrangement. Two different pathways were systematically examined leading to the targeted products, namely propanal and propanone. The rate determining step leading to propanal was observed to be the 1,2 hydride rearrangement with an activation barrier of 29.8 kcal/mol, whereas, the ring-opening step was found to be the rate-determining step for propanone with an activation barrier of 36.7 kcal/mol. With chemically realistic and well-calibrated models together with an accurate DFT method, our findings clearly demonstrate that H-ITQ-22 zeolite is one of the good catalysts for the selective isomerization of propene oxide for the production of propanal.

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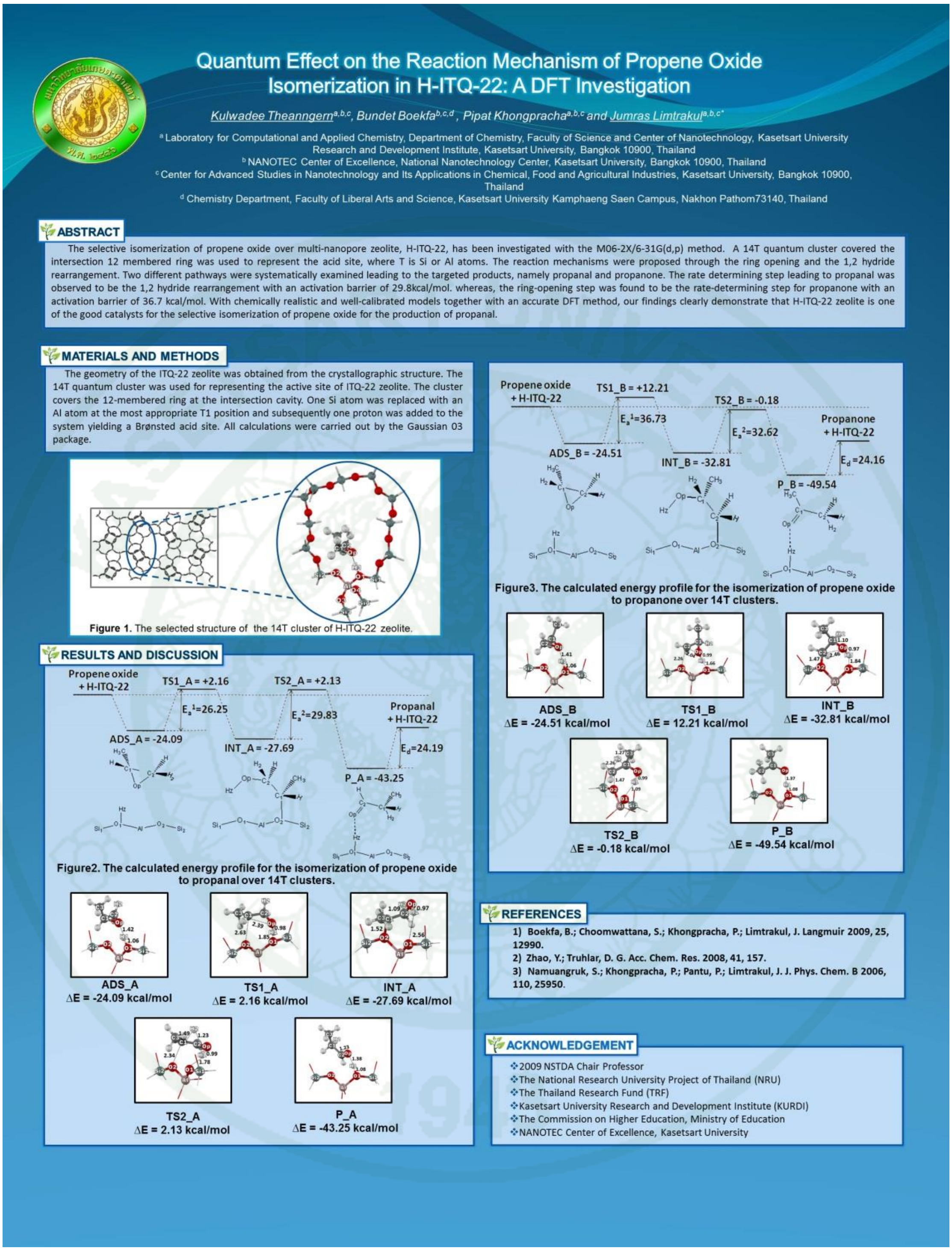
POSTER PRESENTATION

2. Kulwadee Theanngern, Bundet Boekfa, Pipat Khongpracha and Jumras Limtrakul. **Quantum Effect on the Reaction Mechanism of Propene Oxide Isomerization in H-ITQ-22: A DFT Investigation.** Department of Chemistry, Faculty of Science, Kasetsart University, 8 August 2012.



Quantum Effect on the Reaction Mechanism of Propene Oxide Isomerization in H-ITQ-22: A DFT Investigation

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ABSTRACT

The selective isomerization of propene oxide over multi-nanopore zeolite, H-ITQ-22, has been investigated with the M06-2X/6-31G(d,p) method. A 14T quantum cluster covered the intersection 12 membered ring was used to represent the acid site, where T is Si or Al atoms. The reaction mechanisms were proposed through the ring opening and the 1,2 hydride rearrangement. Two different pathways were systematically examined leading to the targeted products, namely propanal and propanone. The rate determining step leading to propanal was observed to be the 1,2 hydride rearrangement with an activation barrier of 29.8kcal/mol. whereas, the ring-opening step was found to be the rate-determining step for propanone with an activation barrier of 36.7 kcal/mol. With chemically realistic and well-calibrated models together with an accurate DFT method, our findings clearly demonstrate that H-ITQ-22 zeolite is one of the good catalysts for the selective isomerization of propene oxide for the production of propanal.

MATERIALS AND METHODS

The geometry of the ITQ-22 zeolite was obtained from the crystallographic structure. The 14T quantum cluster was used for representing the active site of ITQ-22 zeolite. The cluster covers the 12-membered ring at the intersection cavity. One Si atom was replaced with an Al atom at the most appropriate T1 position and subsequently one proton was added to the system yielding a Brønsted acid site. All calculations were carried out by the Gaussian 03 package.

Figure 1. The selected structure of the 14T cluster of H-ITQ-22 zeolite.

RESULTS AND DISCUSSION

Figure2. The calculated energy profile for the isomerization of propene oxide to propanal over 14T clusters.

ADS_A
ΔE = -24.09 kcal/mol

TS1_A
ΔE = 2.16 kcal/mol

INT_A
ΔE = -27.69 kcal/mol

TS2_A
ΔE = 2.13 kcal/mol

P_A
ΔE = -43.25 kcal/mol

Figure3. The calculated energy profile for the isomerization of propene oxide to propanone over 14T clusters.

ADS_B
ΔE = -24.51 kcal/mol

TS1_B
ΔE = 12.21 kcal/mol

INT_B
ΔE = -32.81 kcal/mol

TS2_B
ΔE = -0.18 kcal/mol

P_B
ΔE = -49.54 kcal/mol

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