การศึกษาเชิงทฤษฎีของไฮโดรดีซัลเฟอไรเซชันของไทโอฟีนโดยใช้กรดและซีโอไลต์เป็นตัวเร่งปฏิกิริยา

นางสาว ภาวนีย์ ผลเต็ม

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2550

THEORETICAL STUDY OF HYDRODESULFURIZATION OF THIOPHENE BY ACID AND ZEOLITE CATALYSTS

Miss Pawanee Pholtem

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2007

Thesis Title	THEORETICAL STUDY OF HYDRODESULFURIZATION OF THIOPHENE BY ACID AND ZEOLITE CATALYSTS
By	Miss Pawanee Pholtem
Field of study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Vithaya Ruangpornvisuti, Dr.rer.nat.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.... Dean of the Faculty of Science
(Professor Piamsak Menasveta, Ph.D.)

THESIS COMMITTEE

Sirirat Kokpol .... Chairman
(Associate Professor Sirirat Kokpol, Ph.D.)

.... Thesis Advisor
(Associate Professor Vithaya Ruangpornvisuti, Dr.rer.nat.)

Nuanphun Chantarasiri .... Member
(Associate Professor Nuanphun Chantarasiri, Ph.D.)

W. Trakarnpruk .... Member
(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

ภาวนีย์ ผลเต็ม: การศึกษาเชิงทฤษฎีของไฮโดรดีซัลเฟอไรเซชันของไทโอฟีนโดยใช้กรดและซีโอไลต์เป็นตัวเร่งปฏิกิริยา (THEORETICAL STUDY OF HYDRODESULFURIZATION OF THIOPHENE BY ACID AND ZEOLITE CATALYSTS) อ. ที่ปรึกษา : รศ. ดร. วิทยา เรืองพรวิสุทธิ์, 76 หน้า.

ศึกษากลไกการเกิดปฏิกิริยา พลังงาน และค่าทางเทอร์โมไดนามิกส์ ของปฏิกิริยาการเปลี่ยนไท-โอฟีนเป็น 1-บิวทีนในระบบที่มีกรดเป็นตัวเร่งปฏิกิริยา และระบบที่มีเอช-แซดเอสเอ็ม-5 เป็นตัวเร่งปฏิกิริยา โดยวิธีคำนวณทางเคมีควอนตัม ณ ระดับทฤษฎี MP2/6-311+G (d,p) และ B3LYP/6-31G (d) ตามลำดับ พบว่าในระบบที่มีกรดเป็นตัวเร่งปฏิกิริยา เกิดปฏิกิริยา 9 ขั้นตอน โดยเกิดปฏิกิริยาข้างเคียงเกิดขึ้นอีก 3 ขั้นตอน และในระบบที่มี เอช-แซดเอสเอ็ม-5 เป็นตัวเร่งปฏิกิริยา พบว่าเกิดปฏิกิริยา 11 ขั้นตอน โดยปฏิกิริยาไฮโดรจีเนชันขั้นตอนแรกในระบบที่มีกรด และปฏิกิริยาไฮโดรจีเนชันขั้นตอนที่สามในระบบที่มีเอช-แซดเอสเอ็ม-5 เป็นตัวเร่งปฏิกิริยา เป็นปฏิกิริยาขั้นตอนที่ช้าที่สุด

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต Pawanee Pholtem
ปีการศึกษา 2550 ลายมือชื่ออาจารย์ที่ปรึกษา

4773425923: PETROCHEMISTRY AND POLYMER SCIENCE PROGRAM

KEY WORD: THIOPHENE/ DEHYDROSULFURIZATION/ZEOLITE/MP2/DFT

PAWANEE PHOLTEM: THEORETICAL STUDY OF HYDRODESULFURIZATION OF THIOPHENE BY ACID AND ZEOLITE CATALYSTS THESIS ADVISOR: ASSOC. PROF. VITHAYA RUANGPORNVISUTI, Dr.rer.nat., 76 pp.

Reaction mechanisms, energetic and thermodynamic properties of thiophene conversion to 1-butene in acid catalyzed system and in H-ZSM-5 catalyst were investigated using quantum chemical calculations at the MP2/6-311+G (d,p) and B3LYP/6-31G (d) levels of theory, respectively. Nine reaction steps and three pathways of side reaction for acid-catalyzed system and eleven reaction steps for H-ZSM-5 catalytic system were found. At the first step for acid-catalyzed system and at the third step for the H-ZSM-5 catalytic reaction system are hydrogenation reaction and found to be the rate determining step.

Field of study Petrochemistry and Polymer Science Student's signature Pawanee Pholtem

Academic year 2007 Advisor's signature

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor Associate Professor Dr.Vithaya Ruangpornvisuti for his continuous attention and guidance thought the years of my study. I deeply appreciate suggestion and comments of my committee members, Associate Professor Dr. Sirirat Kokpol, Associate Professor Dr. Nuanphun Chantarasiri and Associate Professor Dr. Wimonrat Takarnpreuk.

The greatest thanks are extended to Mr. Banchob Wano who always assists intensive quantum and computational chemistry details. Moreover, I greatly appreciated the Petrochemistry and Polymer Science Program and Graduate School Chulalongkorn University for research grant.

Special thanks to all members in Associate Professor Dr. Vithaya Ruangpornvisuti's group for their worthy comments, valuable suggestions and encouragement I also would like to thanks all my friends at Chulalongkorn University for their friendship throughout my study.

Finally, I would like to dedicate this to my parents for their love, understanding and support for me is priceless. Without them, I would never be able to achieve this goal.

CONTENTS

CHAPTER V CONCLUSTION AND SUGGESTION

LIST OF FIGURES

Figure **Page**

LIST OF TABLES

CHAPTER I

INTRODUCTION

1.1 Background

As the global energy consumption rapidly increases and environmental legislation becomes stricter, the need to upgrade low-quality oil to clean transport fuels increases. To meet current environmental regulations, refiners must remove even the most refractory sulfur-containing species. This is generating increased interest in obtaining a detailed description of the catalytic hydrotreating reactions occurring during desulfurization. Hydrodesulfurization (HDS) has been investigated for many decades, leading to increased insight into the structure of the active catalyst particles, their interactions with the support, the effect of promoters, and the kinetics of the reactions. However, much less is known about the reaction mechanisms and the nature of the active sites, and many different views have been studied.*[1]*

Organosulfur compounds in fuels cause toxic emissions and inefficient performance of exhaust catalysts. *[2,3]* thus, processes for their removal have been widely explored. Selective adsorption and can be carried out at low temperatures; they avoid saturation of alkenes and arenes, which prevail during hydrodesulfurization catalysis, but available materials show limited adsorption capacities and selectivities. Thiophene, benzothiophene, and their alkyl derivatives shown in Figure 1.1 are the most abundant organosulfur compounds in gasoline; more reactive sulfides, disulfides, and mercaptans are present as minor components. *[4,5]* Thiophene is the simplest homologue of the family of sulfur-containing molecules that are refractory to classical HDS, is often used to perform a rapid evaluation of the catalytic performance. *[6]* It represents a particular challenge, because it resembles abundant arenes and alkenes in electron density and basicity, thus making chemical specificity difficult during adsorption and catalysis. The crystalline framework structure, high specific area, and structural and compositional flexibility make zeolites potential candidates for thiophene adsorption. Thiophene adsorbs on H-ZSM5 with modest selectivity. *[7,8]*

Thiophene or Hydrofuran is heterocyclic sulfur which was found since 1871. It's appearance are colorless, toxic, high reactive. Melting point is 38 ^{o}C and boiling point is 78 ^{o}C. Extraction of thiophene by basic attraction is very difficult so in the industry always transform its by desulfurization which can reduce sulfur compound before refining. *[9]*

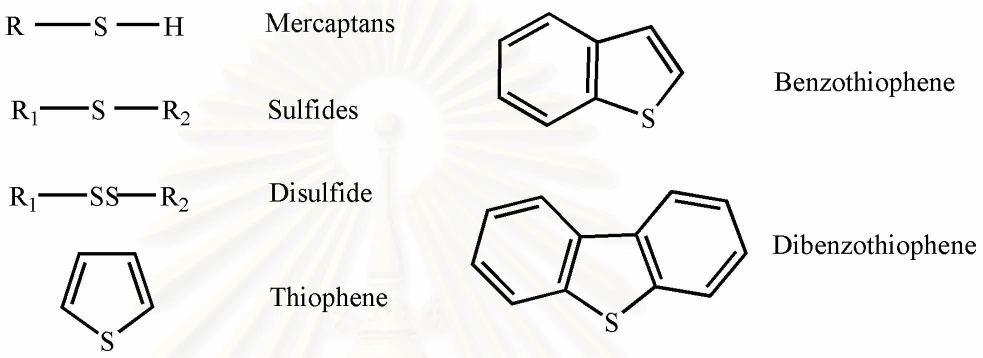

Figure 1.1 Typical organosulfur compounds in fuels

1.2 Zeolite and Catalytic Activity

Zeolites are aluminosilicates which have a very porous structure consisting of cavities and channels through which molecules of the right size and shape may readily diffuse. The unique and useful catalytic properties of zeolites result from the presence of Brønsted acid sites in the interior. Where an aluminum atom replaces a silicon atom in the zeolite framework, a charge-balancing cation is required to preserve overall charge neutrality. When the cation is a proton, the zeolite can be a proton donor, or Brønsted acid, and can catalyze a wide range of industrially useful chemical reactions. *[10,11]*

Interestingly, it has been found that zeolites alone can catalyze HDS. *[12]* Zeolites are microporous (alumino) silicate crystals. Because they are silicates, they show good thermal and mechanical properties, which make them appropriate catalysts or catalyst supports. Furthermore, their well-characterized microporous network is the reason they are commonly employed as molecular sieves. This property is also particularly useful in catalysis, whether zeolites are catalysts or catalyst-supports, as it induces shape selectivity reactions. Zeolites can act themselves as catalysts. A fraction of framework silicon atoms are naturally found to be substituted for +III (viz., Al)- or +IV (viz., P)-valent atoms. Cations or anions are introduced to neutralizethe framework charge. The catalytic activity of zeolites will depend upon the nature of these cations or anions. Lewis and/or Brønsted basic and/or acidic sites are then generated. The example reaction mechanism in the cracking of the thiophenic ring catalyzed by zeolite is shown in Figure 1.2. *[13]*

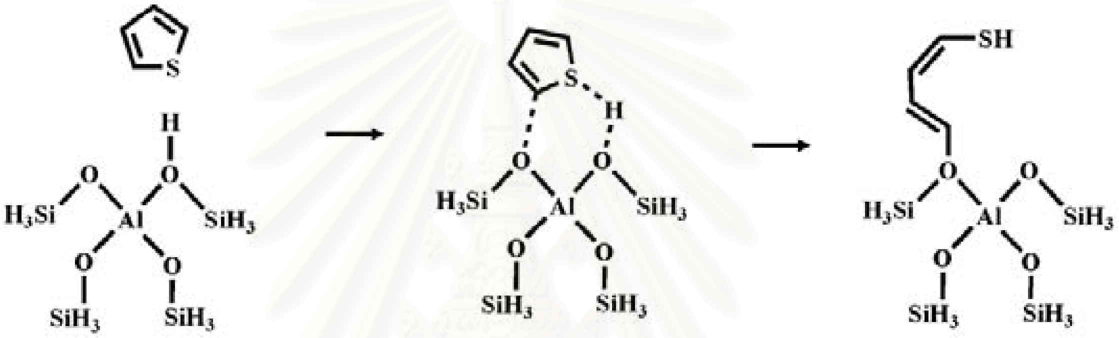

Figure 1.2 Reaction mechanisms in the cracking of the thiophinic rings catalyzed by zeolites.

1.3 H-ZSM-5

ZSM-5 (Zeolite Socony Mobil-5 is discovered by Mobil Oil Company) is a commercial name of Mobil Five (MFI) zeolite with high silica to alumina ratio, and H-ZSM-5 which is compensated negative charge by H^+. The dimension of pores and channels are of the order of a nanometer. In some cases, the channels of the internal surface from intersections that are considerably larger than their channels. For example, the diameter of the roughly cylindrical pores and channels of zeolite having the MFI topology as zsm-5 are about 5 Å, but the diameter of the roughly sphrecal intersection is about 9 Å which act as nanoscopic catalytic reactors. ZSM-5 has two types of channel, both form by 10 member oxygen rings. The first of these channel is straight channel and elliptical in cross section, the second pores is zigzag or sinusoidal and are circular in cross section. The intersection of both channels is called intersection channel. *[14]* The micro-porous molecular structure of ZSM-5 are shown in Figure 1.3.

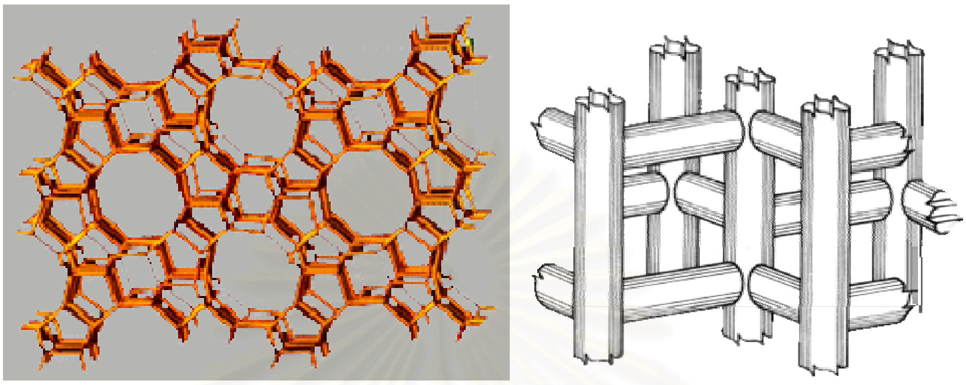

Figure 1.3 A view of the topology of ZSM-5, and a schematic representation of the tunnel system. (rotated by 90^o relative to the first Figure)

1.4 Literature Reviews

In 1999 Xavier *et al. [15]* studied desulfurization of thiophene upon contact with acidic zeolite using DFT-based method. Mechanism led from thiophene converted to butadiene. Two different mechanisms have been compared. One occurring in the absence of hydrogen and the other occurring with the participation of hydrogen. Hydrogen will not decrease activation barriers of the process but will change the intermediate involved and thus will dramatically change the intrinsic thermodynamic of the reactions. Desulfurization of thiophene is possible at severe condition. In 2001 they *[16]* investigated the mechanism involved in the cracking reaction of thiophene to buta-1,2-diene-thiol-alkoxy. To use the partner molecule H_2O and H_2S in order to favor the protonation, to allow an easier protonation of the product of the cracking reaction and to partly induce stronger Lewis basic behavior of catalytic oxygen atom has been demonstrated to successfully decrease the cracking activation energy.

In 2002 Rutger *et al. [17]* studied hydrodesulfurization reaction of dibenzothiophene (DBT) by an unpromoted acidic zeolite using density functional theory method. The elementary DBT cracking reaction, which leads to the formation of biphenylthiol, is the most difficult reaction in the DBT desulfurization reaction pathway. Once this step has been achieved, sulfur removal becomes favorable. The reverse reaction of desulfurization, which gives biphenylthiol from biphenyl and H_2S, appears to have the largest activation energies and is therefore not favorable.

In the 2002 Shan *et al.* *[18]* used MS transient response technique and fixed bed reaction apparatus in order to investigating the cracking of thiophene and alkyl-thiophene species. Thiophene cracks over the USY zeolite to propylene, butane, butene and H_2S. Furthermore, 2-methyl-thiophene, 3-methyl-thiophene, di-methyl-thiophene, tri-methyl-thiophene and benzothiophene are formed. Cracking and hydrogen transfer are two important elementary reaction steps for thiophene and alkyl-thiophene species desulfurization.

In 2006 Bonita *et al.* *[19]* investigated the transformation of thiophenic compounds over various kinds of acidic zeolite carried out in a fix bad reactor at 350 ^{o}C under atmospheric pressue. Main reactions were isomerization and disproportionation. HY zeolite is the most selective in disproportionation but HZSM-5 and Hβ are more active and more selective than HY for the isomerization. In 2007 they *[20]* used quantum chemical calculations to explain their previous study why 2-methyl thophne and 3-methyl thiophene presented the same reactivity and why the methylbenzothiophene isomer were reactive than the methylthiophene isomer. HY zeolite with Si/Al atomic ratio of 16 was selected because of most selective in disproportionation using B3LYP/6-31G(d,p) level of theory.

1.5 Objective

In objective of this work is investigated mechanism of all species involved in hydrodesulfurization (HDS) reaction of thiophene to 1-butene catalyzed by acid and zeolite using quantum calculation. Energetics and thermodynamic properties of their mechanistic have been determined by Second order Møller-Plesset perturbation theory (MP2) at basis set 6-311+G(d,p) in acid catalyzed and by density function theory (DFT) at basis set B3LYP/6-31G(d) in zeolite catalyzed.

CHAPTER II

THEORETICAL BACKGROUND

2.1 AB Initio Calculations

Ab Initio strictly means ‘from the beginning’ or ‘from the first principles’ which would imply that a calculation using such an approach would require as input only physical constants such as the speed of light Planck’s constant and so on. Ab Initio in fact usually refers to a calculation which uses the full Hartree-Fock/Roothaan-Hall equations, without ignoring or approximating any of the integrals or any of the terms in the Hamiltonian. The ab initio methods do rely upon calibration calculations and this has led some quantum chemists, notably Dewar (who has played a large part in the development of semi-empirical methods), to claim that any real difference between the ab initio and the semi-empirical methods is entirely pedagogical. By contrast, semi-empirical methods simplify the calculations, using parameters for some of the integrals and/or ignoring some of the terms in Hamiltonian. *[21]*

2.1.1 The Schrödinger Equation

The ultimate goal of most quantum chemical approaches is the approximate solution of the time-independent, non-relativistic Schrödinger equation:

$$\hat{H}\psi_i(\vec{x}_1,\vec{x}_2,...,\vec{x}_N,\vec{R}_1,\vec{R}_2,...,\vec{R}_M) = i\,\psi_i(\vec{x}_1,\vec{x}_2,...,\vec{x}_N,\vec{R}_1,\vec{R}_2,...,\vec{R}_M) \qquad (2.1)$$

where $\hat{H}$ is the Hamilton operator for a molecular system consisting of M nuclei and N electrons in the absence of magnetic or electric fields. $\hat{H}$ is a differential operator representing the total energy:

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \tag{2.2}$$

Here, A and B run over the M nuclei while i and j denote the N electrons in the system. The first two terms describe the kinetic energy of the electrons and nuclei respectively, where the Laplacian operator ∇_q^2 is definied as a sum of differential operators (in cartesian coordinates):

$$\nabla_q^2 = \frac{\partial^2}{\partial x_q^2} + \frac{\partial^2}{\partial y_q^2} + \frac{\partial^2}{\partial z_q^2} \tag{2.3}$$

M_A is the mass of nucleus A in multiples of the mass of an electron. The remaining three terms define the potential parts of the Hamiltonian and represent the attractive electrostatic interaction between the nuclei and the electrons and the repulsive potential due to electron-electron and nucleus-nucleus interactions, respectively. R_{pq} (and similarly R_{qp}) is the distance between the particles p and q, i.e., $r_{pq} = \left|\vec{r}_p - \vec{r}_q\right|$. $\psi_i(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N, \vec{R}_1, \vec{R}_2, ..., \vec{R}_M)$ stands for the wave function of the i'th state of the system, which depends on the 3N spatial coordinates $\{\vec{r}_i\}$, and the N spin coordinates $\{S_I\}$ of the electrons, which are collectively termed $\{\vec{x}_i\}$,and the 3M spatial coordinates of the nuclei, $\{\vec{R}_I\}$. The wave function ψ_i contains all information that can possibly be known about the quantum system at hand. Finally, E_I is the numerical value of the energy of the state described by ψ_i

All equations given in this text appear in a very compact form, without any fundamental physical constants. We achieve this by employing the so-called system of atomic units, which is particularly adapted for working with the atoms and molecules. In this system, physical quantities are expressed as multiples of fundamental constants and, if necessary, as combinations of such constants. The mass of an electron, m_e, the modulus of its charge, |e|, Planck's constant *h* divided by 2π, *ħ*, and $4\pi, \varepsilon_0$, the permittivity of the vacuum, are all set to unity. Mass, charge, action etc. are then expressed as multiples of these constants, which can therefore be dropped from all equations.

2.1.2 Born-Oppenheimer Approximation

The Schrödinger equation can be further simplified if we take advantage of the significant differences between the masses of nuclei and electrons. Even the lightest of all nuclei, the proton (^{1}H), weighs roughly 1800 times more than an electron. Thus, the nuclei move much slower than the electrons. The practical consequence is that we can at least to a good approximation take the extreme point of view and consider the electrons as moving in the field of fixed nuclei. This is the famous Born-Oppenheimer or clamped-nuclei approximation. If the nuclei and fixed in space and do not move, their kinetic energy is zero and the potential energy due to nucleus-nucleus repulsion is merely a constant. Thus, the complete Hamiltonian given in equation (2.4) reduces to the so-called electronic Hamiltonian:

$$\hat{H}_{elec} = \frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\sum_{A=1}^{K}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}} \qquad (2.4)$$

The solution of the Schrödinger equation with $\widehat{H}_{elec}$ is the electronic wave function ψ_{elec} and the electronic energy E_{elec}. ψ_{elec} depends on the electron coordinates, while the nuclear coordinates enter only parametrically and do not explicity appear in ψ_{elec}. The total energy E_{tot} is then the sum of E_{elec} and the constant nuclear repulsion term:

$$E_{nuc} = \sum_{A=1}^{K}\sum_{B>A}^{M}\frac{Z_A Z_B}{r_{AB}} \qquad (2.5)$$

$$\hat{H}_{elec}\,\psi_{elec} = E_{elec}\,\psi_{elec} \qquad (2.6)$$

and

$$E_{tot} = E_{elec} + E_{nuc} \tag{2.7}$$

The attractive potential exerted on the electrons due to the nuclei – the expectation value of the second operator $\widehat{V}_{Ne}$ in equation (2.4) is the often termed the external potential, V_{ext} , in density functional theory, even though the external potential is not necessarily limited to the nuclear field but may include external magnetic or electric fields etc. From now on we will only consider the electronic problem of equations (2.4)-(2.6) and the subscript “elec” will be dropped. *[22,23,24,25]*

2.1.3 The Hartree-Fock Calculations

The Hartree-Fock (HF) method seeks to approximately solve the electronic Schrödinger equation, and it assumes that the wave function can be approximated by a single Slater determinant made up of one spin orbital per electron. Since the energy expression is symmetric, the variation theorem holds, and so we know that the Slater determinant with the lowest energy is as close as we can get to the true wave function for the assumed functional form of a single Slater determinant. The Hartree-Fock method determines the set of spin orbitals which minimize the energy and give us this best single determinant. So, we need to minimize the Hartree-Fock energy expression with respect to changes in the orbitals:

$$\chi_i \rightarrow \chi_i + {}^{\delta}\chi_i \tag{2.8}$$

We have also been assuming that the orbitals are orthonormal, and we want to ensure that our variational procedure leaves them orthonormal. The Hartree-Fock equations can be solved numerically (exact Hartree-Fock), or they can be solved in the space spanned by a set of basis functions (Hartree-Fock-Roothan equations). In either case, note that the solutions depend on the orbitals. Hence, we need to guess some initial orbitals and then refine our guesses iteratively. For this reason, Hartree-Fock is called a self-consistent-field (SCF) approach.

The first term above in square brackets:

$$\sum_{j\neq i}\left[\int dx_{2}\left|x_{j}(x_{2})\right|^{2} r_{12}^{-1}\right]\chi_{i}(x_{1}) \tag{2.9}$$

gives the Coulomb interaction of an electron in spin orbital χ_i with the average charge distribution of the other electrons. Here we see in what sense Hartree-Fock is a mean field theory. This is called the *Coulomb term,* and it is convenient to define a Coulomb operator as:

$$J_{j}(x_{1}) = \int dx_{2}\left|\ \chi_{j}(x_{2})\right|^{2} r_{12}^{-1} \tag{2.10}$$

which gives the average local potential at point x_1 due to the charge distribution from the electron in orbital χ_j.

We can define an exchange operator in terms of its action on an arbitrary spin obital χ_i :

$$K_{j}(x_{1})\chi_{1}(x)_{1} = \left[\int dx_{2}\chi_{j}^{*}(x_{2}) r_{12}^{-1}\chi_{i}(x_{2})\right]\chi_{j}(x_{1}) \tag{2.11}$$

Introducing a basis set transforms the Hartree-Fock equations into the Roothaan equations. Denoting the atomic orbital basis functions as $\overline{\chi}$, we have the expansion:

$$\chi_{i} = \sum_{\mu=1}^{K} C_{\mu i}\overline{\chi}_{\mu} \tag{2.12}$$

for each spin orbital i. This leads to:

$$. \qquad f(x_{1}) \sum_{v} C_{vi}\tilde{\chi}_{v}(\mathrm{X}_{1}) = \in_{i} \sum_{v} C_{vi}\tilde{\chi}_{v}(\mathrm{X}_{1}) \tag{2.13}$$

This can be simplified by introducing the matrix element notation :

$$S_{\mu v} = \int dx_{1}\overline{\chi}_{\mu}^{*}(x_{1})\overline{\chi}_{v}(x_{1}), \tag{2.14}$$

$$F_{\mu\nu} = \int dx_1 \overline{\chi}^*_{\mu}(x_1)\overline{\chi}_{\nu}(x_1). \qquad (2.15)$$

Now the Hartree-Fock-Roothaan equations can be written in matrix form as:

$$\sum_{\nu} F_{\mu\nu}C_{\nu i} = \in_i \sum_{\nu} S_{\mu\nu}C_{\nu i} \qquad (2.16)$$

where $\in$ is a diagonal matrix of the orbital energies $\in_i$. This is like an eigenvalue equation except for the overlap matrix S. One performs a transformation of basis to go to an orthogonal basis to make S vanish. Then it's just a matter of solving an eigenvalue equation Well, not quite. Since F depends on it's own solution (through the orbitals), the process must be done iteratively. This is why the solution of the Hartree-Fock-Roothaan equations are often called the self-consistent-field procedure. *[26]*

2.2 Density Functional Calculation (DFT)

Density Functional Theory (DFT) is based not on the wave function but rather on the electron probability density function or electron density function, commonly called simply the electron density or charge density, designated by $\rho(x, y, z)$. This is a *probability per unit to volume; the probability of finding an electron in a volume element dx dy dz* centered on point with coordinates x, y, z is $\rho(x, y, z)$ *dx dy dz* is a pure number, a probability. However if we regard the charge on the electron as our unit of charge then ρ has units of electronic charge volume $^{-1}$ and $\rho(x, y, z)$ *dx dy dz* units of electronic charge. If we think of electronic charge as being smeared out in a fog around the molecule, then the variation of ρ from point to point (ρ is a function of x, y, z) corresponds to the varying density of the fog and $\rho(x, y, z)$ *dx dy dz* centered on a point P(x, y, z) corresponds to the amount of fog in the volume element *dx dy dz*. In a scatterplot of electron density in a molecule, the variation of ρ with position can be indicated by the density of the points. The electron density function is the basic not only of DFT, but of a whole suite of method of regarding and studying atom and molecules, and, unlike the wavefunction, is measurable e.g. by X-ray diffraction or electron diffraction. Apart from being and experimental observable and being rapidly grasped intuitively, the electron density has another property particularly suitable for any method with claim to being an improvement on, or at least a valuable alternative to, wavefunction method: It is a function of position only, that is, of just three valuables (x,y,z), while the wavefunction of an n-electron molecule is a functional of an n-electron molecule is a function of 4n variables, three spatial coordinates and one spin coordinate, for each electron. No matter how big the molecule may be, the electron density remains a function of three variables, (x, y, z), while the complexity of the wavefunction increase with the number of electrons. The main advantage of DFT is that in about the same time needed for HF calculation one can often obtain results of about the same quality as from MP2 calculation. Chemical applications of DFT are but one aspect of an ambitious project to recast conventional quantum mechanics.

A question sometimes asked is whether DFT should be regarded as a special kind of ab initio method. The case against this view is that the correct mathematical form of the DFT functional is not know, in contrast to conventional ab initio theory where the correct mathematic from of the fundamental equation, the Schrödinger equation is known. In conventional ab initio theory, the wavefunction can be improve systematically by going to bigger basis set and higher correlation levels, which take of closer and closer to an exact solution of the Schrödinger equation but in DFT there is so far no known way to systematically improve the functional; one must feel one's way toward with the aid of intuition and comparison of the results with experiment and of high level conventional ab initio equation calculation. In this sense current DFT is semiempirical, but the limit use of empirical parameters (typically from zero to about), and the possible of one day finding the exact functional makes if ab initio in spirit. Where the exact functional known, DFT might indeed give chemically accurate results a priori.

In the born interpretation the square of a one electron wavefunction ψ at any point X is the probability density (with unit of volume^{-1}) for the wavefunction at the point, and $|\psi|^2 dx\, dy\, dz$ is the probability (a pure number) at any moment of finding the electron in an infinitesimal volume *dx dy dz* around the point (the probability of finding the electron at a mathematic point is zero). For a multielectron wavefunction Ψ the relationship between the wavefunction Ψ and the electron density ρ is more complicated (involving the summation over all spin states of all electrons of n-field integrals of the square of the wavefunction), but it can be shown that $\rho(x, y, z)$ is related to the component one electron spatial wavefunction ψ_i of a single determinant wavefunction Ψ by

$$\rho = \sum_{i=1}^{n} n_i \left|\psi_i\right|^2 \tag{2.17}$$

The sum is over n the occupied MOs ψ_i and for a closed-shell molecule each n_i = 2, for a total of 2n electrons. Equation 2.17 applies stricky only to a single-determinant wavefunction Ψ but for multideterminant wavefunctions arising from configuration interaction treatments ther are similar equations. A short hand for $\rho(x, y, z)\, dx\ dy\ dz$ is $\rho(r)dr$, where r is the position vector of the point with coordinate (x, y, z).

If the electron density ρ rather than the wavefunction could be used to calculate molecular geometries, energies, etc., this might be an improvement over the wavefunction approach because as mentioned above, the electron density in an n- electron molecular is a function of only the three spatial coordinates x, y, z but the wavefunction is a function of 4n coordinates. Density function theory seeks to calculate all the properties of atoms and molecules from the electron density. *[27]*

2.3 Møller-Plesset perturbation theory

A Perturbation theory is developed for treating a system of n electrons in which the Hatree-Fock solution appears as the zero-order approximation. It is shown by this development that the first order correction the energy and the charge density of the system is zero. The expression for the second-order correction for the energy greatly simplifies because of the special property of the zero order solution. It is pointed out that the development of the higher order approximation involves only calculations based on a definite one-body problem.

Some method of describing electron correlation are compared from the point of view of requirements for theoretical chemical models. The perturbation approach originally introduced by Moller and Plessent, terminated at finite order, is found to satisfy most of these requirements, It is size consistent, that is applicable to an ensemble of isolated system s in an additive manner. On the other hand, it does not provide an upper bound for the electronic energy.

Equilibrium geometries, dissociation energies, and energy separations between electronic states of different spin multiplicities are described substantially better by Moller-Plesset theory the second or third order than by Hatree-Fock theory.

Møller-Plesset perturbation theory (MP) is one of several quantum chemistry post-Hartree-Fock ab initio methods in the field of computational chemistry. It improves on the Hartree-Fock method by adding electron correlation effects by means of Rayleigh-Schrödinger perturbation theory (RS-PT), usually to second (MP2), third (MP3) or fourth (MP4) order. Its main idea was published as early as 1934.

Second (MP2), third (MP3), and fourth (MP4) order Møller-Plesset calculations are standard levels used in calculating small systems and are implemented in many computational chemistry codes. Higher level MP calculations, generally only MP5, are possible in some codes. However, they are rarely used because of their costs.

Systematic studies of MP perturbation theory have shown that it is not necessarily a convergent theory at high orders. The convergence properties can be slow, rapid, oscillatory, regular, highly erratic or simply non-existent, depending on the precise chemical system or basis set.*[28]* Additionally, various important molecular properties calculated at MP3 and MP4 level are in no way better than their MP2 counterparts, even for small molecules.*[29]*

For open shell molecules, MPn-theory can directly be applied only to unrestricted Hartree-Fock reference functions (since RHF states are not in general eigenvectors of the Fock operator). However, the resulting energies often suffer from severe spin contamination, leading to very wrong results. A much better alternative is to use one of the MP2-like methods based on restricted Hartree-Fock references.

These methods, Hartree-Fock, unrestricted Hartree-Fock and restricted Hartree-Fock use a single determinant wave function. Multi-configurational self-consistent field methods use several determinants and can be used for the unperturbed operator, although not in a unique way so many methods, such as Complete Active Space Perturbation Theory (CASPT2) have been developed.

Original formulation of the MP-energy corrections are obtained from Rayleigh-Schrödinger (RS) perturbation theory with the perturbation (correlation potential):

$$\hat{V} = H - F - (\Phi_0 | H - F | \Phi_0) \tag{2.18}$$

here the normalized Slater determinant Φ_0 is the lowest eigenfunction of the Fock operator

$$F\Phi_0 = (\sum_{k=1}^{N} f(k))\Phi_0 = 2(\sum_{i=1}^{N/2} \varepsilon_i)\Phi_0 \tag{2.19}$$

Here N is the number of electrons of the molecule under consideration, H is the usual electronic Hamiltonian, $f(1)$ is the one-electron Fock operator, and ε_i is the orbital energy belonging to the doubly occupied spatial orbital φ_i. The shifted Fock operator

$$\hat{H}_0 = F + (\Phi_0 | H - F | \Phi_0) \tag{2.20}$$

Serves as the unperturbed (zeroth-order) operator.

The Slater determinant Φ_0 being an eigenfunction of F, it follows readily that

$$F\Phi_0 - (\Phi_0 | F | \Phi_0)\Phi_0 = 0 \Rightarrow \hat{H}_0\Phi_0 = (\Phi_0 | H | \Phi_0)\Phi_0 \tag{2.21}$$

So that the zeroth-order energy is the expectation value of H with respect to Φ_0, *i.e.*, the Hartree-Fock energy:

$$E_{MP0} = E_{HF} = (\Phi_0 | H | \Phi_0) \tag{2.22}$$

Since the first-order MP energy

$$E_{MP1} = (\Phi_0 | \hat{V} | \Phi_0) = 0 \tag{2.23}$$

is obviously zero, the lowest-order MP correlation energy appears in second order. This result is the Møller-Plesset theorem. The correlation potential does not contribute in first-order to the exact electronic energy.

In order to obtain the MP2 formula for a closed-shell molecule, thae second order RS-PT formula is written on basis of doubly-excited Slater determinants. (Singly-excited Slater determinants do not contribute because of the Brillouin theorem). After application of the Slater-Condon rules for the simplification of *N*-electron matrix elements with Slater determinants in bra and ket and integrating out spin, it becomes

$$E_{MP2} = \sum_{i,j,a,b} (\varphi_i(1)\varphi_j(2)) \left| r_{12}^{-1} \right| \varphi_a(1)\varphi_b(2) x \frac{(\varphi_a(1)\varphi_b(2)) \left| r_{12}^{-1} \right| \varphi_j(1)\varphi_i(2)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \qquad (2.24)$$

where φ_i and φ_j are canonical occupied orbitals and φ_a and φ_b are canonical virtual orbitals. The quantities ε_i, ε_j, ε_a, and ε_b are the corresponding orbital energies. Clearly, through second-order in the correlation potential, the total electronic energy is given by the Hartree-Fock energy plus second-order MP correction: $E \approx E_{\mathrm{HF}} + E_{\mathrm{MP2}}$. The solution of the zeroth-order MP equation (which by definition is the Hartree-Fock equation) gives the Hartree-Fock energy. The first non-vanishing perturbation correction beyond the Hartree-Fock treatment is the second-order energy.

Alternative formulation as equivalent expressions are obtained by a slightly different partitioning of the Hamiltonian, which results in a different division of energy terms over zeroth- and first-order contributions, while for second- and higher-order energy corrections the two partitionings give identical results. The formulation is commonly used by chemists, who are now large users of these methods. This difference is due to the fact, well-known in Hartree-Fock theory, that

$$(\Phi_0 | H - F | \Phi_0) \neq 0 \Leftrightarrow E_{HF} \neq 2\sum_{i=1}^{N/2} \varepsilon_i \qquad (2.25)$$

(The Hartree-Fock energy is not equal to the sum of occupied-orbital energies). In the alternative partitioning one defines,

$$\hat{H}_0 = F, \qquad \hat{V} = H - F \tag{2.26}$$

Clearly in this portioning,

$$E_{MP0} = 2\sum_{i=1}^{N/2} \varepsilon_i, \qquad E_{MP1} = E_{HF} - 2\sum_{i=1}^{N/2} \varepsilon_i \tag{2.27}$$

Obviously, the Møller-Plesset theorem does not hold in the sense that $E_{\mathrm{MP1}} \neq 0$. The solution of the zeroth-order MP equation is the sum of orbital energies. The zeroth plus first order correction yields the Hartree-Fock energy. As with the original formulation, the first non-vanishing perturbation correction beyond the Hartree-Fock treatment is the second-order energy. We reiterate that the second- and higher-order corrections are the same in both formulations.

Use of Møller-Plesset perturbation methods, Second (MP2), third (MP3), and fourth (MP4) order Møller-Plesset calculations are standard levels used in calculating small systems and are implemented in many computational chemistry codes. Higher level MP calculations, generally only MP5, are possible in some codes. However, they are rarely used because of their costs.

Systematic studies of MP perturbation theory have shown that it is not necessarily a convergent theory at high orders. The convergence properties can be slow, rapid, oscillatory, regular, highly erratic or simply non-existent, depending on the precise chemical system or basis set. Additionally, various important molecular properties calculated at MP3 and MP4 level are in no way better than their MP2 counterparts, even for small molecules.

For open shell molecules, MPn-theory can directly be applied only to unrestricted Hartree-Fock reference functions (since RHF states are not in general eigenvectors of the Fock operator). However, the resulting energies often suffer from severe spin contamination, leading to very wrong results. A much better alternative is to use one of the MP2-like methods based on restricted Hartree-Fock references. *[30]*

2.4 Basis Sets

A basis set in chemistry is a set of functions used to create the molecular orbitals, which are expanded as a linear combination of such functions with the weights or coefficients to be determined. Usually these functions are atomic orbitals, in that they are centered on atoms, but functions centered in bonds or lone pairs have been used as have pairs of functions centered in the two lobes of a p orbital. Additionally, basis sets composed of sets of plane waves up to a cutoff wavelength are often used, especially in calculations involving systems with periodic boundary conditions. *[25]*

The approximate treatment of electron-electron distribution and motion assigns individual electrons to one-electron function, termed *spin orbital*. These consist of a product of spatial functions, termed molecular orbitals *(MO)*, $\psi_1(x,y,z)$, $\psi_2(x,y,z)$, $\psi_3(x,y,z)$, ..., and either α or β spin components. The spin orbitals are allowed complete freedom to spread throughout the molecule. Their exact forms are determined to minimize the total energy. In the simplest level of theory, a single assignment of electron to orbital is made by used ψ as atomic orbital wavefunction based on the Schrödinger equation for the hydrogen atom. This is not a suitable approach for molecular calculation. This problem can be solved by representing MO as linear combination of basis functions.

In practical calculation, the molecular orbitals $\psi 1$, $\psi 2$, ..., are further restricted to be linear combinations of a set of N known one-electron function $\phi_1(x,y,z)$, $\phi_2(x,y,z)$, ..., $\phi_N(x,y,z)$:

$$\psi_i = \sum_{\mu=1}^{N} c_{\mu i}\phi_\mu \qquad (2.28)$$

The functions ϕ_1, ϕ_2, ..., ϕ_N, which are defined in the specification of the model, are known as one-electron basis function called basis function. The set of basis functions is called basis set. If the basis functions are the atomic orbitals for the atoms making up the molecule, function in equation 2.18 is often described as the linear combination of atomic orbitals (LCAO). There are two types of basis function which commonly used in the electronic structure calculations, Slater type orbitals (STO) and Gaussian type orbitals (GTO).

The Slater orbitals are primarily used for atomic and diatomic systems where high accuracy is required and semiempirical calculations where all three- and four-center integrals are neglected. The Slater type orbitals have the function form:

$$b = Ae^{-\zeta r} r^{n^{*}-1} Y_{lm}(\theta,\phi) \tag{2.29}$$

where parameter n^{*} and ξ are chosen to make the larger part of the orbitals look like atomic Hartree-Fock orbitals. There are a lot like hydrogen orbitals, but without the complicated nodal structure.

The Gaussian type orbitals can be written in terms of polar or cartesian coordinates:

$$g = x^{a} y^{b} z^{c} e^{-\alpha r^{2}} Y_{lm}(\theta,\phi) \tag{2.30}$$

in which a, b, and c are integers and α is a parameter that is usually fixed. Primitive Gaussian function is shown in equation 2.20. Normally, several of these Gaussian functions are summed to define more realistic atomic orbitals basis functions, as shown below:

$$b_{\mu} = \sum_{p} k_{\mu p} g_{p} \tag{2.31}$$

The coefficients $k_{\mu p}$ in this expansion are chosen to make the basis functions look as much like Slater orbitals as possible. Slater functions are good approximation to atomic wavefunctions but required excessive computer time more than Gaussian functions, while single-Gaussian functions are a poor approximation to the nearly ideal description of an atomic wavefunction that Slater function provides. The solution to the problem of this poor functional behavior is to use several Gaussians to approximate a Slater function. In the simplest version of this basis, n Gaussian functions are superimposed with fixed coefficients to form one-Slater type orbital. Such a basis is denoted STO-nG, and n = 3, 4.

The limit of quantum mechanics involves an infinite set of basis function. This is clearly impractical since the computational expanse of molecular orbital calculations is proportional to the power of the total number of basis functions. Therefore, ultimate choice of basis set size demands on a compromise between accuracy and efficiency. The classification of basis sets is given below.

2.4.1 Minimal Basis Sets

The minimum basis set is a selected basis function for every atomic orbital that is required to describe the free atom. For hydrogen atom, the minimum basis set is just one *1s* orbital. But for carbon atom, the minimum basis set consisted of a *1s* orbital, a *2s* orbital and the full set of three *2p* orbitals. For example, the minimum basis set for the methane molecule consists of 4 *1s* orbitals, one per hydrogen atom, and the set of *1s*, *2s* and *2p* orbitals described above for carbon. Thus, total basis set comprises of 9 basis functions.

Several minimum basis sets are used as common basis sets especially the STO-nG basis sets because they are available for almost all elements in the periodic table. The most common of minimum basis sets is STO-3G, where a linear combination of three Gaussian type orbitals (GTOs) is fitted to a Slater-type orbital (STO). The individual GTOs are called primitive orbitals, while the combined functions are called contracted functions. For example, the STO-3G basis set for methane consists of a total of 9 contracted functions built from 27 primitive functions. Other commonly uses of STO-nG basis sets are STO-4G and STO-6G where each STO is fitted to 4 and 6 GTOs, respectively.

2.4.2 Scaled Orbital by Splitting the Minimum Basis Sets

In the early calculation on the hydrogen molecule, it is discovered that the STO *1s* orbitals do not give the best result in the molecular environment when the Schrödinger equation is solved, because electron is attracted to both nuclei rather than just one nucleus. In each molecular orbital, both large and small sets of orbital appear and they are mixed in the ratio that gives the lowest energy. The combination of a large orbital and a small orbital is essentially equivalent to an orbital of intermediate size. The result orbital is a size that best fit for the molecular environment since it is obtained from minimizing the energy. The advantage of this procedure is that the mixing coefficients in the molecular orbitals appear in a linear function. This simple dodge is equivalent to scaling the single minimal basis set orbitals. The minimum basis set can scaled not only the valence orbitals of the minimal basis set (split valence basis set), but also all the orbitals of the minimal basis set (double zeta basis sets).

2.4.2.1 Split the Valence Orbitals (Split Valence Basis Sets)

The split valence basis sets mean that each valence orbital is spited into two parts, an inner shell and an outer shell. For example, the 3-21G basis set is referred to basis function of the inner shell represented by two Gaussian functions and that of the outer shell represented by one Gaussian function. The core orbitals are represented by one basis function and each function composes of three Gaussian functions. The purpose of splitting the valence shell is to give the SCF algorithm more flexibility in adjusting the contributions of the basis function to the molecular orbitals, achieving a more realistic simulated electron distribution.

2.4.2.2 Split all Orbitals (Double Zeta Basis Sets)

Double zeta basis set is a member of minimum basis set replaced by two functions. In this way both core and valence orbitals are scaled in size. For some heavier atoms, double zeta basis sets may have slightly less than double the number of minimum basis set orbitals. For example, some double zeta basis sets for the atoms Ga-Br have 7 rather than 8 *s* basis functions, and 5 rather than 6 *p* basis functions.

The term “double zeta” arises from the fact that the exponent in a STO is often referred by the Greek letter “*zeta*”. Since it takes two orbitals with different exponents, it is called “double zeta”. The minimum basis set is “single zeta”. The normal abbreviation for a double zeta basis set is DZ. It is also quite common to use split valence basis sets where the valence orbitals are spitted into three functions. Basis sets where this is done for all functions are called triple zeta functions and referred to as TZ, TZP, TZ2P etc.

2.4.3 Polarized Basis Sets

In the discussion on the scaling of the hydrogen orbitals in the H_2 molecule, it is argued that the orbital on one atom in the molecule becomes smaller because of the attraction of the other nucleus. However, it is also clear that the influence of the other nucleus may distort or polarize the electron density near the nucleus. This problem desires orbitals that have more flexible shapes in a molecule than the *s, p, d,* etc., shapes in the free atoms. This is best accomplished by add basis functions of higher angular momentum quantum number. Thus, the spherical *1s* orbital on hydrogen is distorted by mixing in an orbital with *p* symmetry. The positive lobe at one side increases the value of the orbital while the negative lobe at the other side decreases the orbital. The orbital has overall “moved” sideways. It has been polarized. Similarly, the *p* orbital can polarize if it mixes in an orbital of *d* symmetry. These additional basis functions are called polarization functions. The polarization functions are added to the 6-31G basis set as follows:

6-31G* added a set of d orbitals to the atoms in the first and second rows .

6-31G** added a set of d orbitals to the atoms in the first and second rows and a set of *p* functions to hydrogen.

The nomenclature above is slowly being replaced. The 6-31G* is called 6-31G(d), while the 6-31G** is called 6-31G(d,p). This new nomenclature allows the possibility of adding several polarization functions. Thus 6-31G (3df,pd) added 3 *d*-type GTOs and 1 *f*-type GTO and added 1 *p*-type and 1 *d*-type function to H.

2.4.4 Diffuse Function Basis Sets

In some cases the normal basis functions are not adequate. This is particular the case in excited states and in anions where the electronic density is spread out more over the molecule. This model has correctly by using some basis functions which themselves are more spread out. This means that small exponents are added to GTOs. These additional basis functions are called diffuse functions. The diffuse functions added to the 6-31G basis set as follows:

6-31+G added a set of diffuse *s* and *p* orbitals to the atoms in the first and second rows.

Diffuse functions can be added along with polarization functions also. Some examples of these functions are 6-31+G*, 6-31++G*, 6-31+G** and 6-31++G** basis sets. *[25,31,32]*

2.5 Transition State Theory and Statistical Mechanics

Transition state theory (TST) assumes that a reaction proceeded from one energy minimum to another *via* an intermediate maximum. The *transition state* is the configuration which divides the reactant and product parts of surface. For example, a molecule which has reached the transition state is continuing to product. The geometrical configuration of the energy maximum is called the transition structure. Within standard TST, the transition state and transition structure are identical, but this is not necessarily for more refined models. The direction of reaction coordinate is started from the reactant to product along a path where the energies are as low as possible and the TS is the point where the energy has a maximum. In the multidimensional case, TS is a first-order point on the potential energy surface as a maximum in the reaction coordinate direction and a minimum along all other coordinates, shown in Figure 2.1. *[25]*

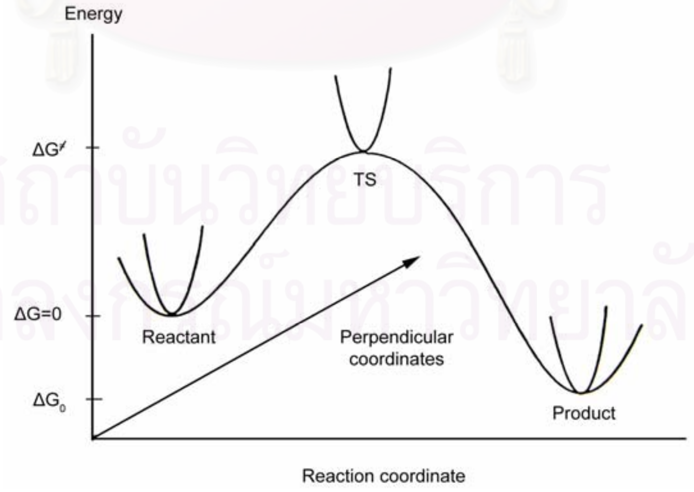

Figure 2.1 Schematic illustration of reaction path.

Transition state theory assumes equilibrium energy distribution among all possible quantum states at all points along the reaction coordinates. The probability of finding a molecule in a given quantum state is proportional to $e^{-\Delta E/k_BT}$, which is Boltzman distribution. Assuming that the molecule at the TS is in equilibrium with the reactant, the macroscopic rate constant can be expressed as:

$$k(T) = \frac{k_B T}{hc^o}\exp(-\Delta^{\ddagger}G/RT) \qquad (2.32)$$

in which $\Delta G^{\neq}$ is the Gibbs free energy difference between the TS and reactant, T is absolute temperature, c^o of unity is used, h is Plank's constant, R is gas constant and k_B is Boltzmann's constant. It is clear that if the free energy of the reactant and TS can be calculated, the reactant rate follows trivially. The equilibrium constant for a reaction can be calculated from the free energy difference between the reactant and product.

$$K(T) = \exp(-\Delta G^0/RT) \qquad (2.33)$$

The Gibbs free energy is given in terms of the enthalpy and entropy, $G = H - TS$. The enthalpy and entropy for a macroscopic ensemble of particles may be calculated from properties of the individual molecules by means of statistical mechanics. The difference between rate constant and equilibrium constant are shown as Figure 2.2. *[26]*

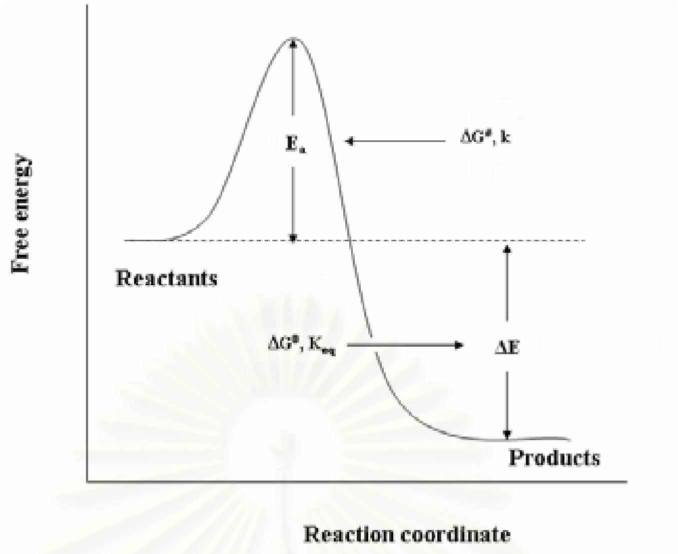

Figure 2.2 The difference between rate constant (*k*) and equilibrium constant (*K*).

CHAPTER III

DETAILS OF THE CALCULATIONS

3.1 Quantum Chemical Methods

Full geometry optimizations of all involved molecules of thiophene conversion to 1-butene in acid-catalyzed system were computed by second-order Møller-Plesset *[33]* (frozen core), MP2(fc) method and in H-ZSM-5 catalyst were computed by density function theory. Geometry optimization calculations have been carried out to a minimum for reactants, complexes and products and to a saddle point for transition state. Zero point energy (ZPE) corrections have been calculated for all optimized structures. Details of the MP2 and DFT methods employed in acid-catalyzed system and H-ZSM-5 catalyst are as follows references. *[27,28]*

3.1.1 Second-Order Møller-Plesset (MP2)

Structure optimizations of all involved species of thiophene conversion to 1-butene in acid-catalyzed system have been carried out at the MP2(fc)/6-311+G(d,p) level of theory. Energetics and thermodynamic properties of the acid-catalyzed reaction have been derived from the zero-point vibration energy calculation.

3.1.2 Density Function Theory (DFT)

The zeolite catalyst using H-ZSM-5 of 5T [$(H_3SiO)_4Al$] cluster and its adsorption states were optimized by density function theory using the hybrid density functional of Lee-Yang-Parr correlation (B3LP) *[34]* method. Optimization energy and zero-point vibration energy which obtained from single point calculation were also performed.

3.2 Models of Reactions

The mechanistic study of thiophene conversion to 1-butene by acid catalysts are modeled as (a) in acid-catalyzed system and (b) in H-ZSM-5 zeolite catalyst. Acid catalyzed and H-ZSM-5 models applied in this work are represented using proton (H^+) and 5T cluster of H-ZSM-5, respectively.

3.2.1 Acid-Catalyzed System

Overall reaction of thiophene conversion to 1-butene in acid-catalyzed system is shown in Figure 3.1. The hydrogen molecule used in the conversion of a molecule of thiophene to a molecule of 1-butene are chemical relevance of this reaction.

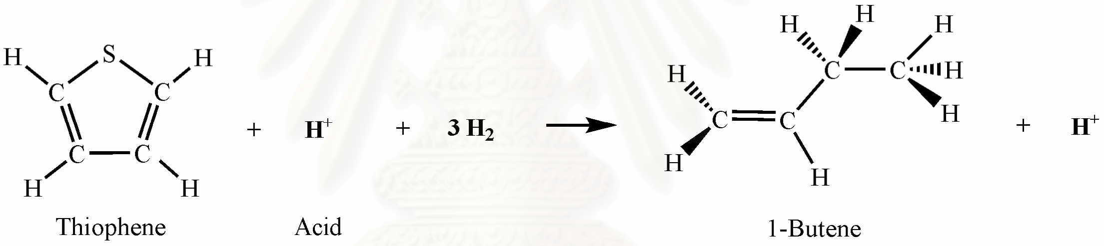

Figure 3.1 Overall reaction of thiophene conversion to 1-butene in acid-catalyzed system.

3.2.2 ZSM-5 Catalytic System

Overall reaction of thiophene conversion to 1-butene in ZSM-5 catalyst as 5T cluster is shown in Figure 3.2. The reaction steps of thiophene conversion reaction have been investigated on the experimental based on the experimental result of reference. *[15]* It shows three hydrogen molecules in the reaction are in chemical relevance of the reaction.

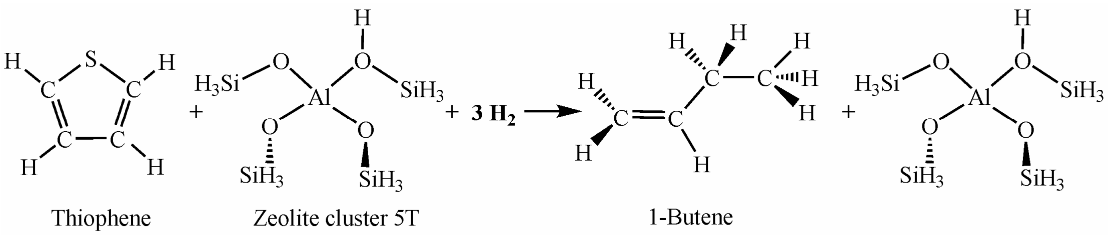

Figure 3.2 Overall reaction of thiophene conversion to 1-butene in zeolite-catalyzed system.

3.3 Reaction Rate and Thermodynamic Property

The standard enthalpy ΔH^0 and Gibbs free energy changes ΔG^0 of conversion reactions of this system have been derived from the frequency calculations. The rate constant $k(T)$ and equilibrium constant K derived from transition state theory was computed from activation free energy, $\Delta^{\ddagger}G$ by

$$k(T) \;=\; \frac{k_B T}{hc^o}\exp(-\Delta^{\ddagger}G/RT) \qquad (3.1)$$

and

$$K(T) = \exp(-\Delta G^0 / RT) \qquad (3.2)$$

Where concentration factor, c^o of unity is used, k_B is Boltzmann's constant, h is Plank's constant, T is the absolute temperature and R is gas constant. The above formula was employed to compute the reaction rate constants for corresponding activation free energies.

Calculations are performed to determine structures of transition state (TS), confirmed by additional calculations of the intrinsic reaction path. The corresponding frequencies were computed at the same level in order to check the obtained stationary points to be ground states (minimum structures) with only real frequencies, or to be transition states (maximum structures or saddle points) with only one imaginary frequency which displays the desired displacement orientation and connection. Zero-point energies (ZPE) from the frequency calculations were added to the total energies of each species in the catalytic cycle.

3.4 Programs Used in Calculations

All calculations have been performed with the GAUSSIAN 03 program. *[35]* The MOLDEN 4.2 program *[36]* was utilized to display the molecular structure, monitor the geometrical parameters and observe the molecular geometry convergence via the Gaussian output files. The molecular graphics of all related species were generated with the MOLEKEL 4.3 program. *[37]*

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Acid-Catalyzed system

In the acid-catalyzed system, the 9 reaction steps were found in the thiophene conversion reaction. It also shows three pathways of side reactions namely, (i) two steps of interconversions of protonated thiophene isomers, (ii) one step of isomerization of thio-di-butene isomers (**3** ↔ **3'**) via transition state **TS3_3'** and (iii) one step of deprotonation of species **5**. Of the 9 reaction, the first step is the protonation of thiophene **1** to form protonated thiophene **2** and the second is the ring opening step of **2** to afford the thio-di-butene **3**. The third and forth are proton transfer and desulfurization reactions to form species **4** and **5,** respectively. The fifth and sixth steps are hydrogenation reaction (**5** ↔ **6**) and (**6** ↔**7**). The seventh and eight steps are the proton transfer reaction to form species **8** and hydrogenation reaction to form species **9**, respectively. The ninth is the last step which is the deprotonation reaction to release final product 1-butene, **10**. All structures including transition states in the thiophene conversion to 1-butene are shown in Figure 4.1 and their selected geometrical data are listed in Table 4.1. Table 4.1 shows the changes of bond C1-C2, C2-C3, C3-C4, C1-S and C4-S of all involved species. Cartesian coordinates of all involved species are list in Tables A1 to A24 (Appendix A). The bonds C1-C2, C2-C3 and C3-C4 of 1-butene, product **10** are 1.34, 1.51 and 1.53 angstrom which correspond to double, single and single bonds, respectively. All reaction steps in terms of the relative energetic profile based are shown in Figure 4.2. The rate constants, activation energies, Gibbs free energies, equilibrium constants and thermodynamic properties of all the reaction steps are shown in Table 4.2. It show that the last step (**9** → **10**) is barrierless reaction step of which the energy is the highest value (~188 kcal/mol). All computed rate and equilibrium constants of thiophene conversion to 1-butene in acid-catalyzed system are shown in Table B1 (Appendix B).

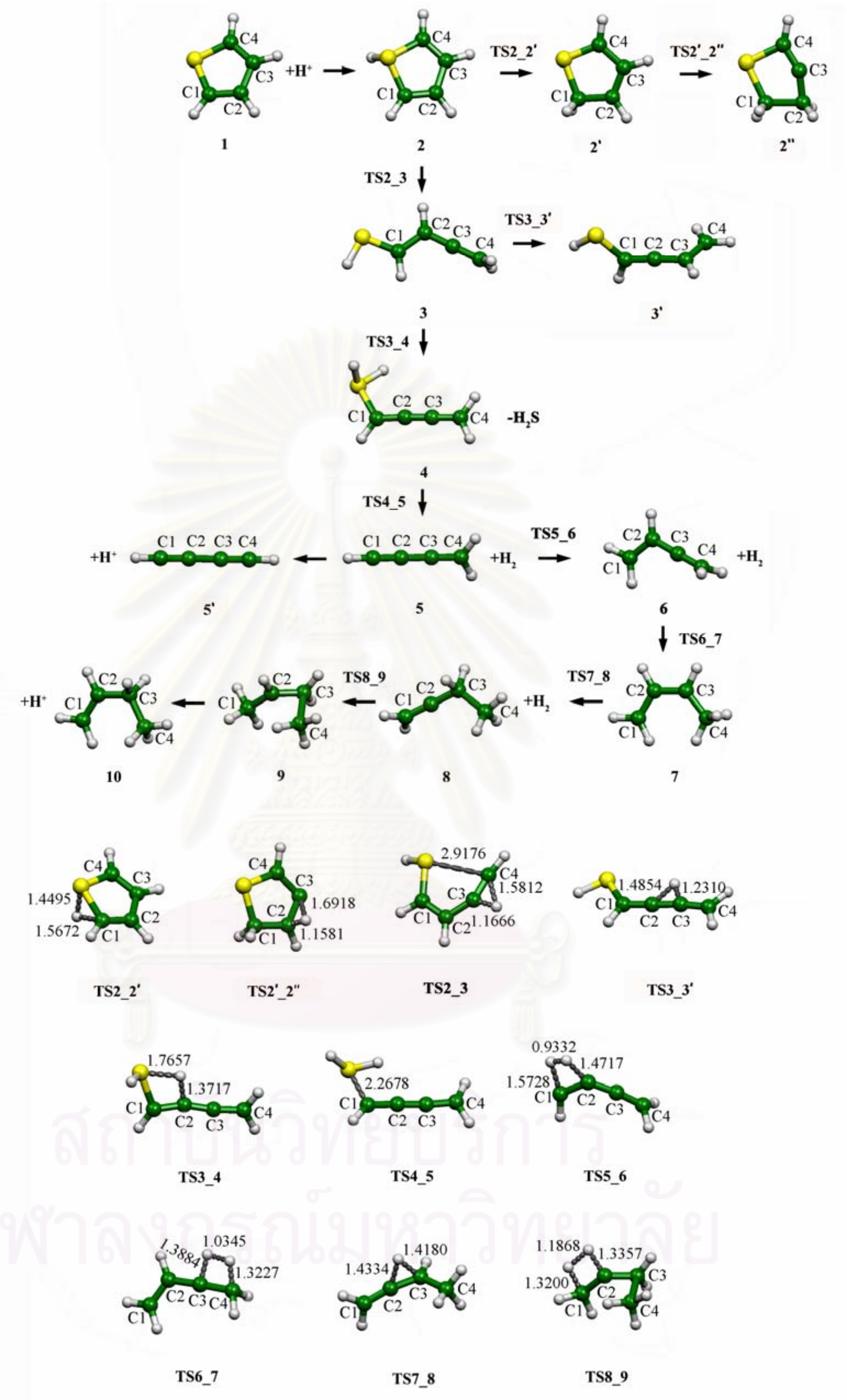

Figure 4.1 Model structure of thiophene conversion to 1-butene and corresponding transition state in acid-catalyzed system. Bond length of transition state is in angstrom.

Table 4.1 Selected geometrical data of involved species in acid-catalyzed system. (bonds in angstrom and angles in degree)

Species	Bond distances					Bong angles		Dihedral angles
	C1-C2	C2-C3	C3-C4	C1-S	C4-S	C1-C2-C3	C2-C3-C4	C1-C2-C3-C4
1	1.38	1.42	1.38	1.71	1.71	112.22	112.22	-
2	1.35	1.45	1.35	1.77	1.77	114.07	114.07	-
2'	1.47	1.37	1.43	1.80	1.65	113.91	111.33	0.01
2"	1.61	1.41	1.29	1.99	1.78	83.40	150.79	-30.49
3	1.41	1.34	1.30	1.66	-	118.06	179.51	179.84
3'	1.30	1.38	1.38	1.75	-	176.70	117.62	152.71
4	1.31	1.26	1.31	1.82	-	177.32	179.51	-4.70
5	1.23	1.33	1.29	-	-	180.00	180.00	-19.70
5'	1.22	1.37	1.22	-	-	180.00	180.00	180.00
6	1.37	1.38	1.29	-	-	177.35	179.55	-179.62
7	1.37	1.41	1.46	-	-	121.56	128.73	-0.01
8	1.28	1.40	1.54	-	-	176.33	118.13	99.53
9	1.66	1.41	1.48	-	-	76.22	124.10	-96.48
10	1.34	1.51	1.53	-	-	125.96	115.14	-

Table 4.2 Rate and equilibrium constants, energetics and thermodynamic properties of thiophene conversion to 1-butene in acid-catalyzed system, computed at the MP2(fc)/6-311+G(d,p) level

Reactions	$\Delta^{\ddagger}E$ [a]	$\Delta^{\ddagger}G$ [a]	k_{298} [b]	ΔE [a, c]	ΔH [a, c]	ΔG [a, c]	K_{298}
1+H^{+} → **2**	-	-	-	-169.68	-169.87	-169.43	-[d]
2 → TS2_2'→ 2'	10.39	10.52	1.21 x 10^{5}	-20.69	-20.69	-20.82	1.67 x 10^{15}
2' → TS2'_2'' → 2''	94.00	93.85	-[e]	74.6	73.79	75.28	5.22 x 10^{-55}
.**2 → TS2_3 → 3**	58.02	57.31	6.02 x 10^{-30}	17.15	16.04	17.99	1.58 x 10^{-12}
3 → TS3_3'→ 3'	51.84	50.95	2.79 x 10^{-25}	23.88	23.18	24.23	8.84 x 10^{-18}
3 → TS3_4 → 4	60.44	60.52	2.69 x 10^{-32}	29.69	29.27	30.06	2.93 x 10^{-22}
4 → TS4_5 → 5+H$_2$S	18.89	18.25	2.58 x 10^{-1}	15.04	14.08	17.38	1.63 x 10^{-13}
5 → 5' + H^{+}	-	-	-	124.44	123.85	131.29	-[e]
5+H$_2$ → **TS5 _6 → 6**	122.97	130.24	-[e]	-31.57	-33.72	-24.50	1.06 x 10^{18}
6+H$_2$ → **TS6 _7 → 7**	102.94	109.16	5.84 x 10^{-68}	-40.76	-34.09	-42.58	1.19 x 10^{25}
7 → TS7_8 → 8	27.49	27.86	2.36 x 10^{-8}	19.83	19.73	20.10	3.06 x 10^{-15}
8+H$_2$ → **TS8_9 → 9**	82.04	89.40	-[e]	-44.04	-36.79	-46.20	1.17 x 10^{27}
9 → 10+H^{+}	-	-	-	188.88	181.64	181.99	-[e]

[a] In kcal mol^{-1}.

[b] In s^{-1}.

[c] Frequency calculations at the MP2(fc)/6-311+G(d,p) level.

[d] Very small values.

[e] Small values

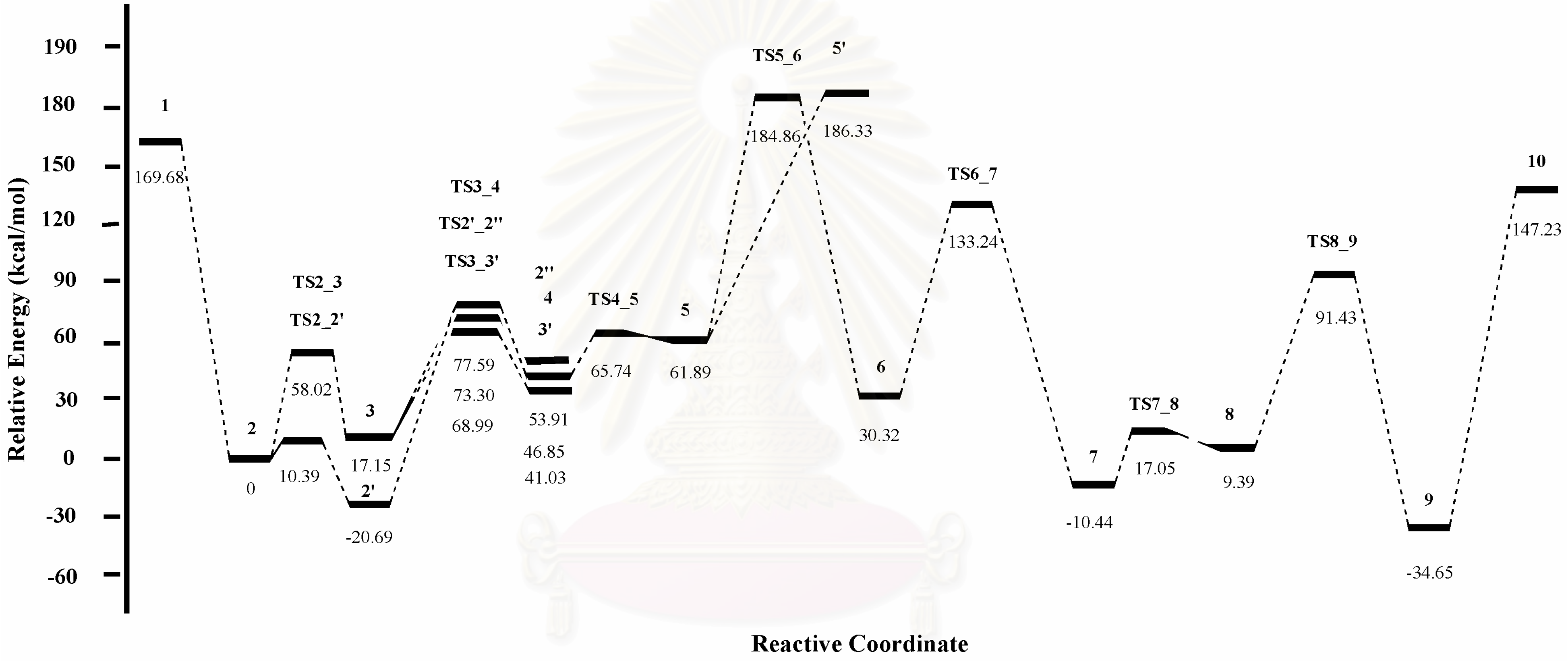

Figure 4.2 Relative energetic profile based on the MP2(fc)/6-311+G(d,p) calculations of thiophene convert to 1- butane in acid-catalyzed system.

4.2 H-ZSM-5 Catalytic system

Reaction in H-ZSM-5 zeolite modeled as 5T cluster, the 11 reaction steps were found as shown in Table 4.4. The reaction mechanism is shown in Figure 4.3 and their optimized structures of all involved species in reaction are shown Figure 4.4. Figure 4.3 shows adsorption state of thiophene **1** adsorbed on the H-ZSM-5 (**H**Z) as the first step and form the **FS** via transition state **TS1** as the second step. The third reaction step is the rearrangement of the **FS** as the **SS** in order to form the intermediate **THS_1** via transition state **TS2** for the forth step. The fifth and sixth steps are the molecular rearrangement steps of adsorption reactions (**THS_1 ↔THS_2**) and (**THS_2↔THS_3**), respectively. The seventh step is desulfurization reaction (**THS_3↔FOS_1**) via transition state **TS3** and released a molecule of hydrogensulfide. The eighth, ninth and tenth steps are hydrogenations (**FOS_1↔FOS_2**), (**FOS_2↔FOS_3**) and (**FOS_3↔FOS_4**) via transition state s **TS4, TS5** and **TS6**, respectively. As the rate constants for these hydrogenations are very small as indicated in Table 4.4, their reaction rates are therefore strongly depend on the pressures of the **FOS_1, FOS_2** and **FOS_3** as reactants for reactions (**FOS_1↔FOS_2**), (**FOS_2↔FOS_3**) and (**FOS_3↔FOS_4**), respectively. The final (eleventh) step is desorption reaction in which the 1-butene product is released.

All structures including transition states in the thiophene conversion to 1-butene in H-ZSM-5 are shown in Figure 4.4 and their selected geometrical data are listed in Table 4.3. Table 4.3 shows the changes of bond C1-C2, C2-C3 and C3-C4 of all species in H-ZSM-5. Cartesian coordinates of all involved species are list in Tables C1 to C19 (Appendix C).The bonds C1-C2, C2-C3 and C3-C4 of 1-butene product are 1.33, 1.50 and 1.54 angstrom which correspond to double, single and single bonds, respectively.

The rate constants, activation energies, Gibbs free energies, equilibrium constants and thermodynamic properties of all the reaction steps are shown in Table 4.4 and all reaction steps in terms of the relative energetic profile based are shown in Figure 4.5. The ninth reaction step (**FOS_3↔FOS_4**) is rate determining step of which the rate constant is very small. All computed rate and equilibrium constants of thiophene conversion to 1-butene in H-ZSM-5 catalytic system are shown in Table D1 (Appendix D).

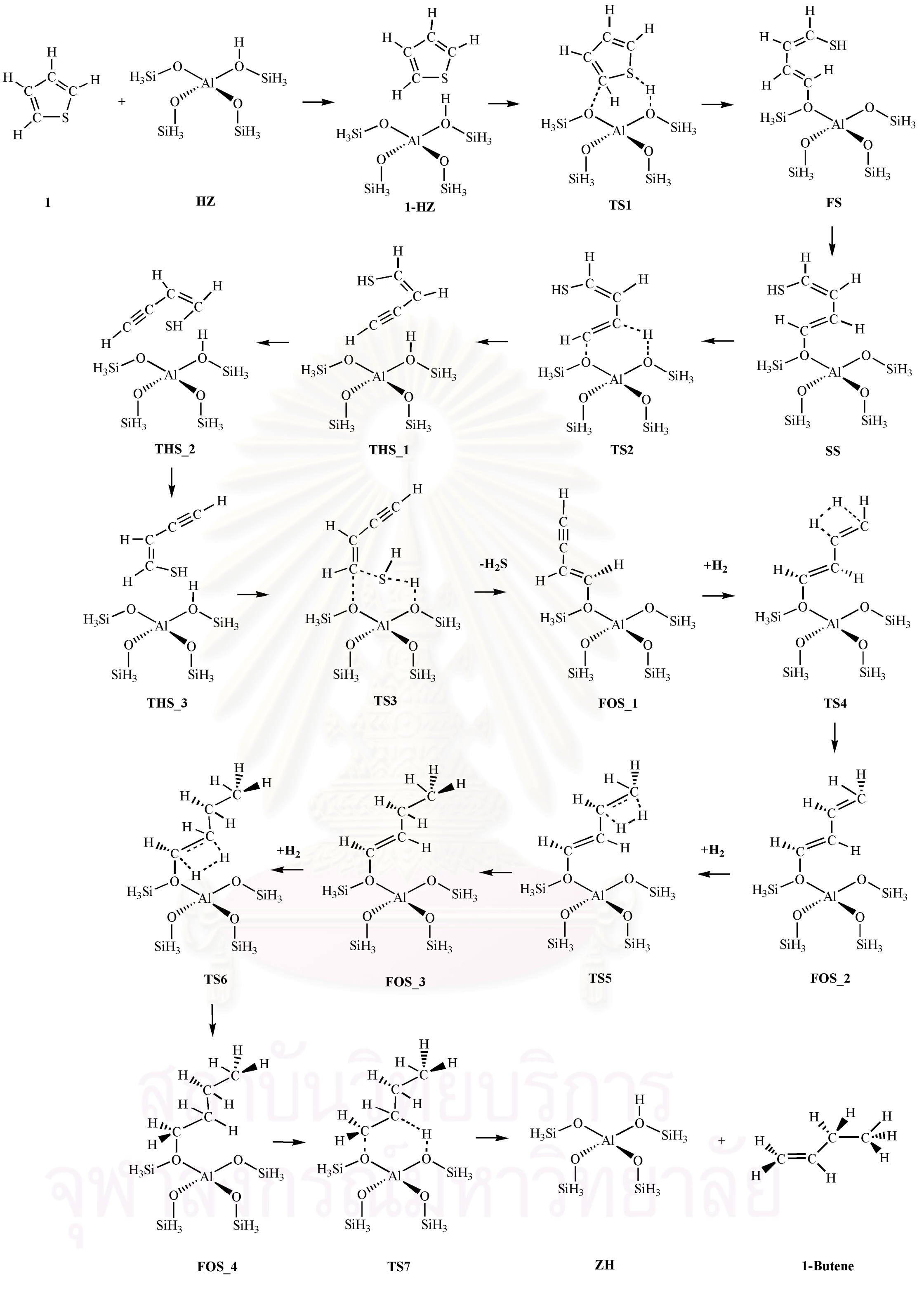

Figure 4.3 Reaction mechanism of thiophene conversion to1-butene in H-ZSM-5 catalyst.

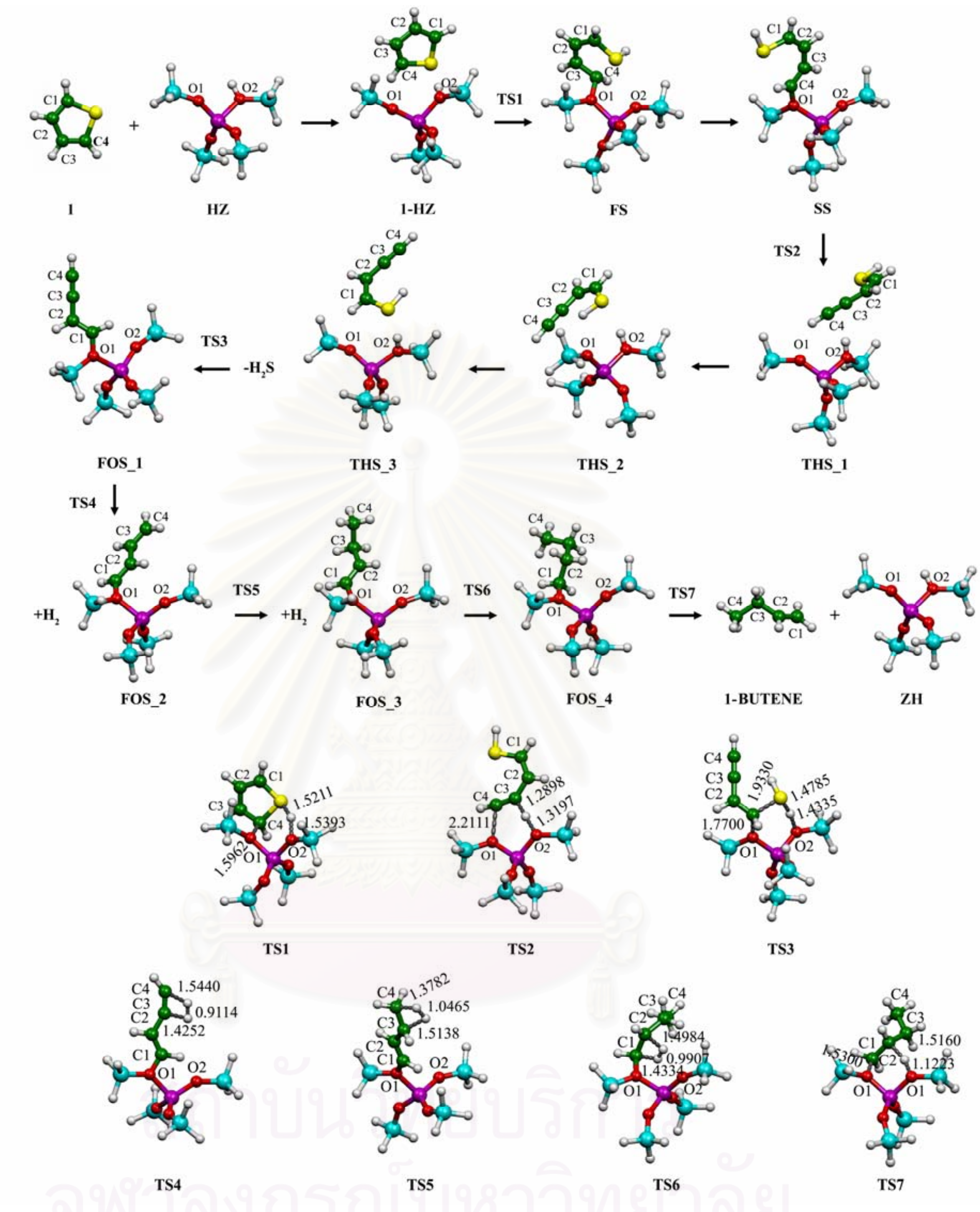

Figure 4.4 Model structure of thiophene conversion to 1-butene and corresponding transition state by zeolite catalyst. Bond length of transition state is in angstrom.

Table 4.3 Selected geometrical data of involved species in ZHM-5-catalyzed system. (bonds in angstrom and angles in degree)

Species	1	1-HZ	FS	SS	THS_1	THS_2	THS_3	FOS_1	FOS_2	FOS_3	FOS_4	1-BUTENE
Bond distances												
C1-C2	1.37	1.36	1.40	1.35	1.35	1.35	1.35	1.34	1.34	1.33	1.52	1.33
C2-C3	1.43	1.43	1.38	1.46	1.42	1.42	1.42	1.42	1.46	1.50	1.54	1.50
C3-C4	1.37	1.36	1.47	1.33	1.22	1.21	1.21	1.21	1.34	1.54	1.53	1.54
C1-S	1.74	1.74	1.71	1.77	1.76	1.77	1.77	-	-	-	-	-
C4-S	1.74	1.75	1.94	3.25	3.89	3.98	3.97	-	-	-	-	-
C1-O1	-	-	-	-	-	-	3.48	1.39	1.41	1.42	1.47	-
C4-O1	-	3.74	1.47	1.42	3.23	4.14	-	-	-	-	-	-
S-O2	-	3.33	3.41	-	-	-	3.23	-	-	-	-	-
Bond angles												
C1-C2-C3	112.76	113.02	118.39	130.44	124.21	124.64	124.81	121.80	122.75	123.38	112.88	125.39
C2-C3-C4	112.76	113.00	115.29	127.87	179.16	179.62	179.68	178.27	123.49	112.45	114.67	112.75
O1-C4-C3	-	104.43	113.46	119.85	150.70	101.00	-	-	-	-	-	-
O1-C1-C2	-	-	-	-	-	-	124.20	124.33	121.33	121.54	110.90	-
Dihedral angles												-
C1-C2-C3-C4	-	-0.30	4.50	-13.63	-148.05	-70.18	88.02	-177.94	-179.57	121.21	66.07	119.57
C2-C3-C4-O1	-	117.27	111.90	-178.32	-117.19	56.57	-	-	-	-	-	-
C3-C2-C1-O1	-	-	-	-	-	-	-134.84	179.33	177.69	177.92	174.65	-
S-C1-C2-C3	-	0.73	4.57	0.90	0.31	-1.58	0.14	-	-	-	-	-

Table 4.4 Rate, equilibrium constants, energetics and thermodynamic properties of thiophene convert to 1-butene in ZHM-5-catalyzed system, computed at the B3LYP/ 6-31G(d) level

Reactions	$\Delta^{\ddagger}E$ [a]	$\Delta^{\ddagger}G$ [a]	k_{298} [b]	ΔE [a, c]	ΔH [a, c]	ΔG [a, c]	K_{298}
1 + **HZ** → **1-HZ**	-	-	-	-5.27	-5.59	5.24	-[d]
1-HZ →**TS1** → **FS**	99.21	110.10	-[d]	65.51	65.40	67.68	-[e]
FS → **SS**	-	-	-	-40.44	-39.79	-42.95	3.98×10^{31}
SS→ **TS2**→ **THS_1**	93.14	103.37	-[d]	18.05	19.40	16.00	1.70×10^{-12}
THS_1→ **THS_2**	-	-	-	-0.07	-0.22	0.89	2.21×10^{-1}
THS_2→ **THS_3**	-	-	-	0.21	-0.21	0.46	4.58×10^{-1}
THS_3→ **TS3** → **FOS_1**+H_2S	65.77	72.34	-[e]	13.93	14.49	4.83	2.79×10^{-4}
FOS_1+H_2 → **TS4**→ **FOS_2**	111.02	127.13	-[d]	-45.18	169.02	161.8	9.00×10^{27}
FOS_2+H_2 → **TS5**→ **FOS_3**	87.33	100.34	-[d]	-26.07	-28.32	-18.21	2.48×10^{13}
FOS_3+H_2 → **TS6**→ **FOS_4**	158.86	173.24	-[d]	-27.45	-29.35	-20.44	1.08×10^{15}
FOS_4→ **TS7**→**1-butene+ ZH**	65.69	73.01	-[e]	15.05	16.14	1.54	7.33×10^{-2}

[a] In kcal mol^{-1}.

[b] In s^{-1}.

[c] Frequency calculations at the B3LYP/6-31G(d) level.

[d] Very small values.

[e] Small values.

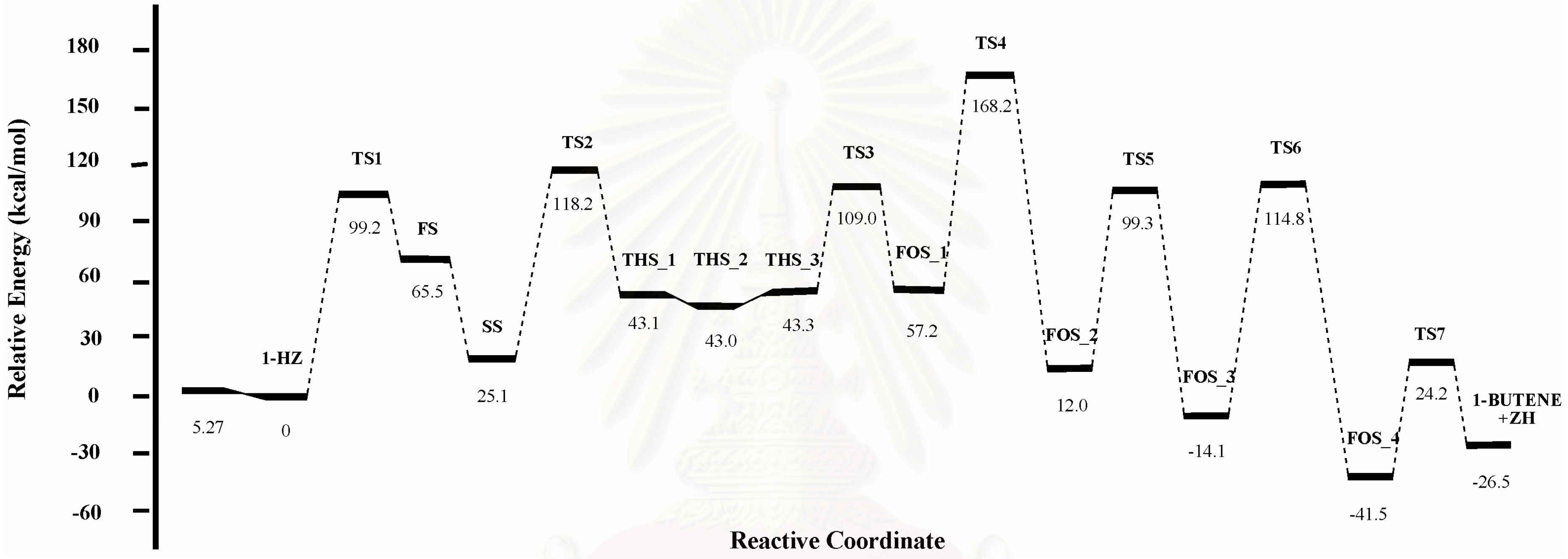

Figure 4.5 Relative energetic profile based on the B3LYP/6-31G(d) calculations of thiophene conversion to1- butene in ZHM-5 catalyst.

CHAPTER V

CONCLUSION AND SUGGESTION

Reaction mechanism of hydrodesulfurization of thiophene to 1-butene in acid-catalyzed system and in H-ZSM-5 catalyst were studied using quantum chemical calculations at the MP2(fc)/6-311+G(d,p) and B3LYP/6-31G(d) levels of theory, respectively. The hydrodesulfurization of thiophene to 1-butene in acid-catalyzed system, the 9 reaction steps and 3 pathways of side reactions were found and the reaction depends on the last step which is the barrierless deprotonation reaction and its reaction energy is ~ 188 kcal/mol. For the hydrodesulfurization of thiophene to 1-butene in H-ZSM-5 catalyst, the 11 reaction steps were found and the activation energy of rate determining step is ~ 159 kcal/mol. Therefore, the hydrodesulfurization of thiophene to 1-butene in H-ZSM-5 catalyst is more energetically favorite than that in acid-catalyzed system. We can conclude that in the hydrodesulfurization of thiophene to 1-butene, the H-ZSM-5 catalyst is a higher efficiency compared to the acid-catalyzed system and the reaction in H-ZSM-5 catalyst is more advantage as the following remarks.

(1) No side reaction found,
(2) Low energetic required and
(3) Easy to handle.

As H-ZSM-5 zeolite is easy-to-handle heterogeneous catalyst, It is concluded that the H-ZSM-5 is more appropriate catalyst in the hydrodesulfurization of thiophene to 1-butene.

Suggestion for Further Work

Further studies will aim to extend or change the scope of hydrodesulfurization:

1. Investigation of various kind of catalysts and/or compare each catalyst in term of activation energy, thermodynamic properties and step of mechanisms.

2. Investigation of organosulfur compounds convertion to other olefins such as propene, butadiene etc.

REFERENCES

[1] Poul, G. M.; Berit, H.; Henrik, T.; Jens, K. N. The hydrogenation and direct desulfurization reaction pathway in thiophene hydrodesulfurization over MOS_2 catalysts at realistic conditions. *J. Catal.* 248 (2007): 188-203.

[2] Song, C.; Ma, X. New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization. *Appl. Catal.* 41 (2003): 207-238.

[3] Shorey, S.W.; Lomas, D.A.; Keesdom, W.H. Use FCC feed pretreating methods to remove sulfur. *Hydrocarb. Process.* 73 (1999): 43-68.

[4] Babich, I. V.; Moulijn, J.A. Science and technology of novel processes for deep desulfurization of oil refinery streams: a review. *Fuel* 82 (2003): 607-631.

[5] Kim, G. K.; Barry, H. C.; Henrik, T. Catalyst and process technologies for ultra low sulfur diesel. *Appl. Catal. A-Gen.* 183 (1999): 205-215.

[6] Sylvain, C.; Jean, F. P.; Christian, S.; Edouard, V.; Edmond, P. DFT study of thiophene adsorption on molybdenum sulfide. *J. Catal.* 239 (2006): 145-153.

[7] Jens, W.; Manfred, S.; Stefan, E. Removal of thiophene impurities from benzene by selective adsorption in zeolite ZSM-5**.** *J. Chem. Soc.* (1991): 1133-1148.

[8] Antonio, C.; Karl, G.S.; Enrique, I. Effects of zeolite structure and aluminum content on thiophene adsorption, desorption, and surface reactions. *Appl. Catal. B-Environ.* 60 (2005): 223-232.

[9] Mittendorfer, F.; Hafner, J. Initial step in the desulfurization of thiophene/Ni-DFT study. *J. Catal.* 214 (1992): 234-241.

[10] Zygmunt, S. A.; Mueller, R. M.**;** Curtiss, L. A.; Iton, L. E. An Assessment of Density Functional Methods for Studying Molecular Adsorption in Cluster Models of Zeolites. *J. Mol. Struct.* ***(****Theochem*) 430 (1998): 9-16.

[11] Zygmunt, S. A.; Curtiss, L. A.; Iton, L. E.; Erhardt, M. K. Computational Studies of Water Adsorption in the Zeolite H-ZSM-5, *J. Phys. Chem*. 100 (1996): 6663-6679.

[12] Xavier, R.; Rutger, A.; Van, S. A periodic density function theory study of thiophenic derivative cracking catalyzed by mordenite. *J. Catal.* 215 (2003): 20-29.

[13] Chen, N.Y.; Degnan, T.F.; Smith, C.M., *Molecular Transport and Reaction in Zeolites, Design and Applications of Shape Selective Catalysts*: Weinheim, (1994).

[14] Breck, D. W. *Zeolite molecular sieves*. Union Carbide Corporation. New York: (1984).

[15] Xavier, R.; Rutger, A.; Van, S. A theoretical study of the solid acid catalyzed desulfurization of thiophene. *J. Catal.* 183, (1999): 107-118.

[16] Xavier, R.; Rutger, A.; Van, S. A DFT study of the cracking reaction of thiophene activated by small zeolitic clusters. *J. Catal.* 200, (2001): 79-90.

[17] Xavier, R.; Xavier, S.; Rutger A.; Van, S. A Theoretical Study of Hydrodesulfurization and Hydrogenation of Dibenzothiophene Catalyzed by Small Zeolitic Cluster. *J. Catal.* 208, (2002): 89-99.

[18] Shan, H. H.; Li, C. Y.; Yang C. H.; Zhao, H.; Zhao B. Y.; Zhang, J. F. Mechanistic studies on thiophene species cracking over USY zeolite. *Cat. Today*. 77 (2002): 117-1126.

[19] Boita, T.; Moreau, M.; Richard, F.; Perot, G. Transformation of Thiophenic Compounds over Acidic Zeolites. *Appl. Catal. A-Gen. 305*, (2006): 90-101.

[20] Boita, T.; Moreau, M.; Richard, F.; Perot, G. Transformation of Thiophenic Compounds over HY Zeolite Study of the Acid-Catalyzed Isomerization and Disproportionation Mechanisms by Quantum Chemical Calculations. *J. Mol. Catal. A-Chem.* 273, (2007): 48-54.

[21] Andew, R. L. *Molecular Modelling*. University of Southampton,UK: Longman, (1996).

[22] Errol, L. *Computational Chemistry Introduction to the Theory and Applications of Molecular and Quantum Mechanics*. USA: Kluwer Academic Publisher, (2003).

[23] Elaine, M. *Molecular Modelling and Bonding.* The Open University, UK: (2002)

[24] Koch, W.; Holthausen, C. M. *A Chemist's Guide to Density Functional Theory*. Chichester: John Wiley & Sons, (2000).

[25] Jensen, F. *Introduction to computational chemistry*. Chichester: John Wiley & Sons, (2007).

[26] Lewars, E. *Computational chemistry: Introduction to the theory and applications of molecular and quantum mechanics*. Trent University, Peter-borough, Ontario: (2003).

[27] Alan, H. *Modelling Molecular Structures*. John Wiley & Sons, (2001).

[28] Leininger, M.L.; Allen, W.D.; Schaefer, H.F.; Sherrill, C.D. Is Moller-Plesset perturbation theory a convergent ab initio method? *J. Chem. Phys.* 112 (2000): 9213-9222.

[29] Helgaker, T.; Poul, J.; Jeppe, O. *Molecular Electronic Structure Theory*. Wiley & Sons, (2000).

[30] Devid, C. Y. *Computational Chemistry*. New York: Wiley Interscience, (2001).

[31] Alan, H. Molecular *Modeling for Beginner*. Wiley & Sons, (2003).

[32] Ira, N. L. *Quantum Chemistry*. Prentice-Hall, (2000).

[33] Moller, C., Plesset, M. S. *Phys. Rev.* 46 (1934): 618.

[34] Lee, C.; Yang, W.; Parr, R.G. Development of the Colle-Salvetti correlation energy formula into a functional of the electron density. *Phys. Rev. B* 37 (1988): 785.

[35] Frisch, M. J. et al. *Gaussian 03*. Revision B.03: Gaussian, Inc. Pittsburgh PA, (2003).

[36] Schaftenaar, G. *MOLDEN 4.2 CAOS/CAMM*. Netherlands: Center Nijmegen, Toernooiveld, (1991).

[37] Flükiger, P.; Lüthi, P. H.; Portmann, S.; Weber, J. *MOLEKEL 4.3*. Switzerland: Swiss Center for Scientific Computing, (2000).

APPENDICES

APPENDIX A

Table A1 Cartesian coordinates of **1**

Atom	Coordinate (Å)		
	X	Y	Z
C	-1.27728800	0.71061000	0.00000000
C	-1.27728800	-0.71061000	0.00000000
C	0.00215000	-1.23326600	0.00000000
C	0.00215000	1.23326600	0.00000000
S	1.19021800	0.00000000	0.00000000
H	-2.17018400	1.32550600	0.00000000
H	-2.17018400	-1.32550600	0.00000000
H	0.29927100	-2.27366400	0.00000000
H	0.29927100	2.27366400	0.00000000

Table A2 Cartesian coordinates of **2**

Atom	Coordinate (Å)		
	X	Y	Z
C	-0.05989000	-1.28161700	0.03110500
C	-1.29551500	-0.72942300	0.00349000
C	-1.29551500	0.72942300	0.00349000
C	-0.05989000	1.28161700	0.03110500
S	1.15782700	0.00000000	-0.09939300
H	0.25503500	-2.31692100	0.00722200
H	-2.20017700	-1.32815100	-0.00291800
H	-2.20017700	1.32815100	-0.00291800
H	0.25503500	2.31692100	0.00722100
H	1.62991700	-0.00000100	1.16654000

Table A3 Cartesian coordinates of **2'**

Atom	Coordinate (Å)		
	X	Y	Z
C	-0.10008300	1.21598700	0.00054700
C	1.26704000	0.79979600	-0.00019700
C	1.37179700	-0.56185400	-0.00020800
C	0.06973100	-1.26311500	0.00038000
S	-1.21811100	0.00113600	-0.00026600
H	-0.43531300	2.25102300	0.00055600
H	2.09364500	1.50054200	-0.00042200
H	-0.06252700	-1.89866200	0.88792700
H	-0.06280400	-1.89940600	-0.88658500
H	2.30587700	-1.11656000	-0.00036500

Table A4 Cartesian coordinates of **2''**

Atom	Coordinate (Å)		
	X	Y	Z
C	-0.62561000	1.24721700	0.04172700
C	0.63949200	0.98095900	0.10041000
C	1.72848900	0.10803500	-0.12468700
C	0.62239100	-1.03615500	0.12467400
S	-1.19043600	-0.43398300	-0.05752500
H	-1.23677700	2.13971200	0.04168500
H	0.72623800	-1.37973600	1.15060000
H	0.76130200	-1.80405900	-0.63397200
H	2.48860800	0.06805500	0.65352800
H	2.11904100	0.11941800	-1.14418200

Table A5 Cartesian coordinates of **3**

Atom	Coordinate (Å)		
	X	Y	Z
C	0.50083300	-0.36845900	0.00000200
C	-0.52798100	0.60018500	-0.00002200
C	-1.80157200	0.16985700	-0.00001900
C	-3.03487100	-0.23525400	0.00001500
S	2.11142700	0.04813500	0.00000400
H	0.22544500	-1.42260000	0.00002700
H	-3.56095400	-0.40393100	0.93845400
H	-3.56090000	-0.40428200	-0.93839000
H	2.59624500	-1.20222200	0.00004500
H	-0.30113200	1.66489200	-0.00005400

Table A6 Cartesian coordinates of **3'**

Atom	Coordinate (Å)		
	X	Y	Z
C	-0.62798700	0.54131100	0.39681500
C	0.60605500	0.40894500	0.01790600
C	1.91239200	0.34397700	-0.40783300
C	2.74435300	-0.55428500	0.22061600
S	-2.03957200	-0.31295400	-0.19107700
H	-0.76280600	1.29979400	1.17756600
H	2.25885100	0.97370900	-1.22421800
H	3.78263000	-0.66614500	-0.08504000
H	2.37601400	-1.17380300	1.03510700
H	-2.83041300	0.13401600	0.78879600

Table A7 Cartesian coordinates of **4**

Atom	Coordinate (Å)		
	X	Y	Z
C	0.59892800	0.84685700	0.00012800
C	-0.63339500	0.40306200	0.00580100
C	-1.84127500	0.03059900	0.00468200
C	-3.09719600	-0.34497700	0.00319000
S	2.04195800	-0.26837100	-0.03714200
H	0.92270100	1.87924200	-0.02383900
H	-3.89647900	0.39105200	-0.00163600
H	-3.37504100	-1.39497800	0.00702900
H	2.00144400	-0.84579500	1.19586800
H	1.51366500	-1.34883500	-0.66596800

Table A8 Cartesian coordinates of **5**

Atom	Coordinate (Å)		
	X	Y	Z
C	1.98267900	0.00001700	0.00000600
C	0.75410600	-0.00003200	-0.00000900
C	-0.57680400	-0.00002700	-0.00001300
C	-1.86452300	0.00001500	0.00000600
H	-2.41558200	0.94534700	0.00001700
H	-2.41571100	-0.94523600	0.00001700
H	3.05854400	0.00005200	0.00002200

Table A9 Cartesian coordinates of **5'**

Atom	Coordinate (Å)		
	X	Y	Z
C	-3.40919000	0.30663800	0.00000000
C	-2.20029900	0.11175600	0.00000000
C	-0.84475100	-0.10679300	0.00000000
C	0.36397700	-0.30167300	0.00000000
H	-4.46092900	0.47619300	0.00000000
H	1.41570100	-0.47124600	0.00000000

Table A10 Cartesian coordinates of **6**

Atom	Coordinate (Å)		
	X	Y	Z
C	1.84004300	-0.17952100	0.00001100
C	0.60206900	0.17302500	-0.00003100
C	-0.71780000	0.56011700	-0.00000400
C	-1.66760500	-0.43385900	0.00004400
H	2.37021800	-0.32959700	0.94263900
H	2.37028000	-0.32965400	-0.94257300
H	-0.97559800	1.61568000	-0.00002200
H	-2.72841600	-0.19310400	-0.00005100
H	-1.37673100	-1.48189700	-0.00011100

Table A11 Cartesian coordinates of **7**

Atom	Coordinate (Å)		
	X	Y	Z
C	1.52496500	-0.46554300	0.00001000
C	0.57209300	0.64582200	-0.00003400
C	-0.83334400	0.59965100	0.00003100
C	-1.51360500	-0.59424000	-0.00001600
H	2.18708200	-0.33215100	-0.86911900
H	1.09381000	-1.46327700	0.00000300
H	-1.38280800	1.53543100	0.00006600
H	-2.60061900	-0.61231900	0.00000700
H	-1.00258000	-1.55271600	-0.00006900
H	2.18692200	-0.33212900	0.86926700
H	1.01753800	1.64301800	-0.00010800

Table A12 Cartesian coordinates of **8**

Atom	Coordinate (Å)		
	X	Y	Z
C	-1.95138900	-0.24385000	0.02464000
C	-0.73508000	0.14757900	-0.06293600
C	0.59420800	0.59956600	-0.07198300
C	1.71630400	-0.44556200	0.04784500
H	-2.37222900	-0.82199100	-0.80448400
H	-2.57329700	-0.01213900	0.89177700
H	0.48367200	1.16856800	0.89804900
H	2.65308500	0.07194900	0.25606900
H	1.50663600	-1.15124200	0.85243500
H	0.74442200	1.38334200	-0.82406100
H	1.81344700	-0.98488300	-0.89517800

Table A13 Cartesian coordinates of **9**

Atom	Coordinate (Å)		
	X	Y	Z
C	1.58264600	-0.18201000	0.17674500
C	0.33513000	0.27477500	-0.48531700
C	-0.75369500	0.85381800	0.19544600
C	-1.17994700	-0.74454800	0.05510300
H	1.99233800	-1.08370500	-0.28167700
H	1.45874800	-0.30609900	1.25389900
H	-1.45424600	1.46380100	-0.36375300
H	-2.14699700	-0.71618300	-0.44404100
H	-0.55666800	-1.42028300	-0.55865600
H	2.30450800	0.63014200	0.00486000
H	0.29726400	0.26379400	-1.57489100
H	-0.63133800	1.09900700	1.24563000
H	-1.16841300	-1.14268100	1.06676400

Table A14 Cartesian coordinates of **10**

Atom	Coordinate (Å)		
	X	Y	Z
C	0.64748400	0.72628000	0.00001800
C	1.43550800	-0.58131400	-0.00001300
H	1.20304800	-1.18011500	0.88543200
H	1.20305400	-1.18006500	-0.88549300
H	2.51008200	-0.37982700	-0.00000100
H	0.93026600	1.32692300	-0.87451300
H	0.93023100	1.32685900	0.87460500
C	-0.85029800	0.57047100	-0.00001500
C	-1.52165500	-0.59158300	0.00000800
H	-2.60683100	-0.60510000	-0.00001400
H	-1.01419800	-1.55081400	0.00004300
H	-1.42188700	1.49901300	-0.00005200

Table A15 Cartesian coordinates of **TS2_2'**

Atom	Coordinate (Å)		
	X	Y	Z
C	1.58057000	-1.14083000	0.09154900
C	1.49479600	0.10984400	-0.02725000
C	0.67815600	1.28466000	-0.01594900
C	-0.65887200	1.03281600	0.04198400
S	-1.27787400	-0.58094600	-0.07599300
H	1.87343900	-2.17968200	0.07443900
H	2.65045600	-0.00037700	-0.14239900
H	1.11263300	2.27470900	-0.01904000
H	-1.36368900	1.85542800	0.13053200
H	-2.39475400	-0.37388600	0.63035200

Table A16 Cartesian coordinates of **TS2'_2''**

Atom	Coordinate (Å)		
	X	Y	Z
C	-0.30613600	1.22550800	0.02373900
C	1.18379700	1.09790900	-0.15110300
C	1.44634400	-0.29827500	0.03416500
C	0.24896800	-1.24086600	-0.02513200
S	-1.19177500	-0.15669100	0.00150000
H	-0.83157900	2.17717400	0.08959900
H	0.14569500	-1.96953400	0.78645400
H	0.24794000	-1.78136800	-0.97978600
H	1.67099100	0.07665100	1.10661100
H	2.39751000	-0.70152700	-0.31689700

Table A17 Cartesian coordinates of **TS2_3**

Atom	Coordinate (Å)		
	X	Y	Z
C	0.01879900	1.25511700	0.01725100
C	-1.26566400	0.76007400	-0.01235700
C	-1.33347600	-0.66034100	-0.00929600
C	-0.09830200	-1.26684900	-0.03906200
S	1.19524000	0.00269500	-0.05399600
H	0.35220900	2.28452900	0.07054600
H	-2.13640800	1.40670000	0.01611700
H	0.19940000	-2.30726200	-0.10543800
H	0.78864000	-0.72302100	1.13304500
H	-2.25581600	-1.23206800	0.01044200

Table A18 Cartesian coordinates of **TS3_3'**

Atom	Coordinate (Å)		
	X	Y	Z
C	-0.70671200	0.68920700	0.00001200
C	0.57171100	0.34748300	-0.00010600
C	1.82523100	-0.01152400	0.00000000
C	3.12626700	-0.21078600	0.00003700
S	-2.08589200	-0.36047700	0.00001000
H	-0.87340200	1.76564300	0.00006700
H	1.00195400	-0.97129700	-0.00010000
H	3.78200500	0.65419600	0.00008600
H	3.56262000	-1.20102800	0.00004400
H	-2.99788800	0.63384400	0.00008800

Table A19 Cartesian coordinates of **TS3_4**

Atom	Coordinate (Å)		
	X	Y	Z
C	0.98498800	0.98498800	0.05720900
C	0.47577600	0.47577600	-0.00659700
C	0.14256600	0.14256600	-0.00914100
C	-0.37639600	-0.37639600	0.00740200
S	-0.43985300	-0.43985300	-0.09592300
H	2.01446300	2.01446300	-0.01607500
H	0.25749600	0.25749600	-0.18135500
H	-1.42245600	-1.42245600	0.26259900
H	-0.42624300	-0.42624300	1.12722500
H	-0.74721500	-0.74721500	0.04913500

Table A20 Cartesian coordinates of **TS4_5**

Atom	Coordinate (Å)		
	X	Y	Z
C	0.56834500	1.01272900	0.05474300
C	-0.55256100	0.38582100	-0.01323700
C	-1.77777500	0.01708300	-0.04440800
C	-3.03530700	-0.34507300	0.01639300
S	1.95346600	-0.38540900	-0.10954100
H	0.95686800	2.02304900	0.11949500
H	-3.88832000	0.30464400	-0.16843300
H	-3.32274900	-1.39865200	0.24338600
H	2.85615600	-0.27487800	0.87523500
H	0.92638200	-0.91097600	0.60202600

Table A21 Cartesian coordinates of **TS5_6**

Atom	Coordinate (Å)		
	X	Y	Z
C	-0.68596500	-0.47220000	-0.06833500
C	-1.66504900	0.59421100	0.03480300
C	0.62879600	-0.26812500	-0.00581200
C	1.88514800	0.06728700	0.03218100
H	2.32546500	0.43881500	-0.90324700
H	2.39879000	0.48420900	0.90305900
H	-1.38603000	1.64219000	-0.17031000
H	-2.44919200	-0.74172700	0.30723000
H	-1.86660800	-1.35052600	-0.09375700

Table A22 Cartesian coordinates of **TS6_7**

Atom	Coordinate (Å)		
	X	Y	Z
C	-1.88705300	-0.28654100	-0.02831200
C	-0.52618000	0.13380100	-0.17647300
C	0.85955300	0.51719900	-0.05805000
C	1.80393800	-0.44963300	0.06028800
H	-1.92876300	-1.33139500	-0.34823800
H	1.10135600	1.57195500	-0.00773800
H	2.82581700	-0.17718100	0.31168100
H	1.58214000	-1.50812700	-0.04589100
H	-2.32953500	-0.48711300	0.95089200
H	-1.85309600	1.01978900	0.17625700
H	-0.89946700	1.42311900	0.17831700

Table A23 Cartesian coordinates of **TS7_8**

Atom	Coordinate (Å)		
	X	Y	Z
C	1.71924600	-0.40775100	0.04892700
C	0.60546600	0.54825700	-0.13914500
C	-0.71147000	0.18693000	0.03211000
C	-1.93176900	-0.25007600	-0.02550000
H	2.57093600	0.05381200	0.57148000
H	2.08634100	-0.71253900	-0.94674200
H	-2.66612200	-0.16469000	0.77859700
H	-2.30750600	-0.74562400	-0.92673200
H	1.44302800	-1.32336300	0.59025800
H	-0.04011000	0.91377700	1.06928100
H	0.82458800	1.51446700	-0.63449500

Table A24 Cartesian coordinates of **TS8_9**

Atom	Coordinate (Å)		
	X	Y	Z
C	1.57445800	-0.21414400	0.28809400
C	0.31330200	0.32627500	-0.39988800
C	-0.82825600	0.75012900	0.31275800
C	-1.15927000	-0.72295700	-0.13926600
H	2.24603800	-0.85508700	-0.29602900
H	1.41316700	-0.66550900	1.27091200
H	-1.53927000	1.40555400	-0.18024000
H	-2.12135700	-0.64431600	-0.64921500
H	-0.50661900	-1.23442900	-0.86532000
H	-0.77743000	0.81258400	1.39654100
H	-1.15891400	-1.33530600	0.76201200
H	1.96149300	0.46333400	-0.77652600
H	1.08148900	1.21736000	-1.03232300

APPENDIX B

Table B1 Rate and equilibrium constants, energetics and thermodynamic properties of thiophene conversion to 1-butene in acid-catalyzed system, computed at the MP2(fc)/6-311+G(d,p) level

Reactions	$\Delta^{\ddagger}E$ [a]	$\Delta^{\ddagger}G$ [a]	k_{298} [b]	ΔE [a, c]	ΔH [a, c]	ΔG [a, c]	K_{298}
1+H^{+} → **2**	-	-	-	-169.68	-169.87	-169.43	9.3 x 10^{124}
2 → **TS2_2'**→ **2'**	10.39	10.52	1.21 x 10^{5}	-20.69	-20.69	-20.82	1.67 x 10^{15}
2' → **TS2'_2''** → **2''**	94.00	93.85	9.93 x 10^{-57}	74.6	73.79	75.28	5.22 x 10^{-55}
.**2** → **TS2_3** → **3**	58.02	57.31	6.02 x 10^{-30}	17.15	16.04	17.99	1.58 x 10^{-12}
3 → **TS3_3'**→ **3'**	51.84	50.95	2.79 x 10^{-25}	23.88	23.18	24.23	8.84 x 10^{-18}
3 → **TS3_4** → **4**	60.44	60.52	2.69 x 10^{-32}	29.69	29.27	30.06	2.93 x 10^{-22}
4 → **TS4_5** → **5**+H_2S	18.89	18.25	2.58 x 10^{-1}	15.04	14.08	17.38	1.63 x 10^{-13}
5 → **5' +** H^{+}	-	-	-	124.44	123.85	131.29	7.35 x 10^{-139}
5+H_2 → **TS5 _6** → **6**	122.97	130.24	2.06 x 10^{-83}	-31.57	-33.72	-24.50	1.06 x 10^{18}
6+H_2 → **TS6 _7** → **7**	102.94	109.16	5.84 x 10^{-68}	-40.76	-34.09	-42.58	1.19 x 10^{25}
7 → **TS7_8** → **8**	27.49	27.86	2.36 x 10^{-8}	19.83	19.73	20.10	3.06 x 10^{-15}
8+H_2 → **TS8_9** → **9**	82.04	89.40	1.79 x 10^{-53}	-44.04	-36.79	-46.20	1.17 x 10^{27}
9 → **10**+H^{+}	-	-	-	188.88	181.64	181.99	1.31 x 10^{-134}

[a] In kcal mol^{-1}.

[b] In s^{-1}.

[c] Frequency calculations at the MP2(fc)/6-311+G(d,p) level.

APPENDIX C

Table C1 Cartesian coordinates of **HZ**

Atom	Coordinate (Å)		
	X	Y	Z
Al	0.20172500	-0.02987300	-0.04641500
O	-0.73636200	-0.32501800	-1.72776800
O	-1.18892500	-0.19053700	0.96652100
O	0.92364900	1.51672600	-0.12347700
O	1.23830900	-1.39680500	-0.24828900
Si	-1.89913000	-0.09272500	2.44122800
H	-3.32504800	-0.51494500	2.33421100
H	-1.23107500	-0.97882500	3.43721800
H	-1.87499800	1.29760800	2.98014000
Si	1.59486100	3.00272100	-0.12986700
H	2.89983400	3.00190400	-0.85186800
H	0.70542100	3.98809300	-0.81174200
H	1.84117600	3.49494500	1.25570800
Si	2.52260000	-2.32995000	0.15618600
H	2.26862200	-3.10706900	1.40311200
H	2.79753100	-3.30335500	-0.93985700
H	3.75738300	-1.52131700	0.36878600
Si	-2.46407100	-0.34757500	-1.86203900
H	-2.72661000	-0.49112500	-3.31473500
H	-3.02892000	-1.49709100	-1.12765900
H	-2.91195000	0.95895500	-1.35400200
H	-0.24678500	-1.02895900	-2.18892000

Table C2 Cartesian coordinates of **1-HZ**

Atom	Coordinate (Å)		
	X	Y	Z
Al	-1.21183100	0.19366500	0.17084900
O	-0.51108000	0.11779800	1.73692300
O	-2.46703000	-0.94514000	-0.20104500
O	0.03707000	-0.69077300	-0.99099700
O	-1.33198500	1.77305500	-0.49034200
Si	-0.05353300	-0.29756500	3.24235500
H	-1.17243400	-0.17407700	4.22007800
H	0.44725300	-1.70352600	3.30540700
Si	-0.35423700	-2.11602600	-1.88438000
H	-1.43566200	-1.83152700	-2.84540500
H	0.90666100	-2.41252400	-2.61193500
H	-0.67327400	-3.21241500	-0.95215400
Si	-4.03764000	-1.37850200	-0.01251800
Si	-1.72233600	3.31663400	-0.83782300
H	-0.89552600	3.82029700	-1.97388000
H	-3.15596800	3.45212200	-1.22759100
H	-4.78026300	-0.42205400	0.85885700
H	-1.48455300	4.22342200	0.32341500
H	-4.73320700	-1.43021900	-1.33060600
H	-4.14089400	-2.73226900	0.60429800
C	2.97663000	0.83533000	0.59772100
S	3.04243400	0.72629100	-1.14343000
C	4.09276800	-0.66479600	-1.06185300
C	3.73229700	-0.13764900	1.18273200
C	4.37537100	-0.99565300	0.23099300
H	5.02041300	-1.82334600	0.50527800
H	4.44739600	-1.12927000	-1.97196400
H	3.82670600	-0.24662700	2.25736400
H	2.37837700	1.60262000	1.06986100
H	0.93261600	-0.30674400	-1.11505700
H	1.05744700	0.58137100	3.71713100

Table C3 Cartesian coordinates of **FS**

Atom	Coordinate (Å)		
	X	Y	Z
A	1.06402100	0.12848400	0.03577600
O	-0.60662100	-0.80180400	-0.36950400
O	2.25029100	-0.75391200	-0.83170900
O	1.09627200	0.00154800	1.75100700
O	0.63259300	1.68756300	-0.59567200
S	-0.90633400	-2.42184600	0.21396500
H	-1.99688800	-2.39030200	1.20894800
H	-1.17370700	-3.35328700	-0.90225600
H	0.38739800	-2.75343400	0.83864500
S	1.69786800	0.02436300	3.26882800
H	3.07614300	0.59293000	3.32295000
H	0.83383200	0.84580100	4.16552000
H	1.75112400	-1.35265100	3.84179000
S	3.39029200	-1.48290000	-1.73915900
S	1.14793400	3.18732600	-1.01160700
H	1.70516500	3.93360200	0.15296400
H	2.19211600	3.15140300	-2.07492400
H	3.83164900	-0.61551600	-2.86958400
H	-0.00906500	3.97068900	-1.53845900
H	4.59583600	-1.82242300	-0.93039600
H	2.86860300	-2.75317600	-2.32603000
C	-1.72594300	-0.02550900	-0.93016800
S	-2.58781300	1.12203700	0.37523900
C	-4.04764600	0.21751500	0.39278600
C	-2.85395800	-0.86178600	-1.37746000
C	-4.01327800	-0.73761200	-0.63316300
H	-4.86178000	-1.39856600	-0.79698400
H	-4.69582500	0.26776900	1.25368300
H	-2.70441900	-1.58823800	-2.16689200
H	-1.24486400	0.68201100	-1.59741800
H	-2.73452600	2.04047400	-0.64379800

Table C4 Cartesian coordinates of **SS**

Atom	Coordinate (Å)		
	X	Y	Z
A	1.25964700	0.20542800	0.11816900
O	-0.21072100	-0.97629200	-0.34272100
O	2.38906800	-1.08946300	-0.14015700
O	0.95905500	0.67443800	1.73580600
O	1.23462000	1.43954900	-1.07674800
S	0.18011500	-2.62229900	-0.78493700
H	0.97710100	-2.62739900	-2.02435600
S	0.73659700	1.29047900	3.22831900
H	2.03019700	1.43736500	3.95546800
H	0.09007200	2.63397300	3.17685100
H	-0.14280300	0.40105900	4.04226000
S	1.53403700	2.86172900	-1.81992600
S	3.95814900	-1.57752900	-0.14083300
H	4.82886400	-0.64917300	-0.91669000
H	4.04660100	-2.92743500	-0.76733400
H	0.32008200	3.31791500	-2.56084500
H	2.64285300	2.73712300	-2.80872500
H	1.90458000	3.93661200	-0.85447400
H	4.50831000	-1.67542000	1.24081000
H	-1.16412900	-3.19289700	-1.04909000
H	0.79938500	-3.33027000	0.34991400
C	-1.55756700	-0.55400600	-0.23578900
C	-2.00446000	0.44902700	-1.00242200
C	-3.33446900	1.04201000	-1.01279600
C	-4.48958800	0.60832800	-0.46926900
S	-4.71066900	-0.87013000	0.47392700
H	-6.05266000	-0.79006900	0.56763600
H	-1.28296700	0.89348000	-1.68373100
H	-3.40360900	1.97427800	-1.56835500
H	-5.38808500	1.20229500	-0.59917300
H	-2.10273900	-1.08126100	0.53629300

Table C5 Cartesian coordinates of **THS_1**

Atom	Coordinate (Å)		
	X	Y	Z
Al	-1.47544300	-0.13155300	0.01620400
O	-1.06510500	-0.57316500	1.64526000
O	-2.22875800	1.41033000	-0.21805100
O	-1.99275000	-1.42285500	-0.98278000
O	0.22681700	0.43691500	-0.66238900
Si	-1.63702600	-0.71502700	3.17663500
H	-1.88091700	0.61438000	3.80741800
Si	-2.54947800	-2.67311200	-1.86561900
H	-1.61860600	-2.98991100	-2.98912300
H	-2.68979900	-3.90774000	-1.03981100
H	-3.88461200	-2.37239200	-2.45840200
Si	0.53255300	2.05359400	-1.19076800
Si	-3.56216900	2.36167300	-0.25746000
H	-3.15755400	3.77563000	-0.50358900
H	-4.31249000	2.31916600	1.03123500
H	1.96386700	2.03267300	-1.57961800
H	0.31933700	3.01319200	-0.08983600
H	-0.32188700	2.31742200	-2.36225200
H	-4.50397200	1.96306700	-1.34290000
H	-0.62850700	-1.43292100	4.00924300
H	-2.91327000	-1.48461100	3.23617400
C	1.98719700	-1.34887900	0.94697500
C	2.93483000	-1.34416700	0.18493800
C	4.03981400	-1.35941100	-0.70488700
C	5.03608000	-0.44987200	-0.69267400
S	5.12538100	0.89889400	0.43845500
H	4.08164400	-2.16200200	-1.43762100
H	5.84868500	-0.53500000	-1.40677600
H	1.14134200	-1.35272500	1.60648500
H	6.24117400	1.44580200	-0.08446900
H	1.00675600	-0.09176400	-0.36355400

Table C6 Cartesian coordinates of **THS_2**

Atom	Coordinate (Å)		
	X	Y	Z
A	-1.02906900	0.22702400	0.04057400
O	-0.27408000	-1.27216800	-0.89139400
O	-2.65684800	-0.36124300	-0.03456400
O	-0.68313500	1.63178500	-0.87759100
O	-0.18904900	0.09570800	1.55264100
S	-4.25890900	-0.09152000	0.18366600
H	-4.98543100	-1.39252600	0.23177200
H	-4.53184900	0.63230200	1.45967600
H	-4.84437100	0.71318100	-0.92727100
S	-0.30109900	3.01553500	-1.64439300
H	0.53586200	3.90661400	-0.78523000
H	0.47001100	2.74879100	-2.89306800
H	-1.52262500	3.78412800	-2.01968200
S	-0.22254100	0.44702700	3.15362200
H	-1.29660000	-0.30017100	3.86946400
H	1.08262100	0.06809100	3.76861500
H	-0.43926700	1.90149500	3.40745800
S	-1.23994800	-2.53096000	-1.57482300
H	-0.24728200	-3.43779400	-2.20457100
H	-1.98831900	-3.25510700	-0.52857800
H	-2.10969400	-1.91702200	-2.59312500
H	0.63479500	-1.52606500	-0.58724800
C	3.88998000	-1.32971700	-0.53043700
C	4.33222200	-0.08471700	-0.79474000
C	3.76994900	1.10106600	-0.25810500
C	3.28276000	2.11369000	0.19613700
S	2.56433600	-1.78003800	0.54974000
H	4.36634700	-2.19104800	-0.98781800
H	5.17810700	0.02087800	-1.47132900
H	2.83672800	3.00317500	0.58160200
H	2.29987300	-0.54535500	1.03314400

Table C7 Cartesian coordinates of **THS_3**

Atom	Coordinate (Å)		
	X	Y	Z
Al	1.29175100	0.13734000	0.13745400
O	0.32679100	0.03034500	1.56968700
O	0.05144300	-0.30325400	-1.25664700
O	2.32664800	-1.20601700	-0.22414200
O	1.85505200	1.71195100	-0.23303200
Si	0.14843800	-0.50778100	3.10311800
H	-1.21874900	-0.15483500	3.59283300
Si	3.74162500	-2.00168000	0.00526400
H	4.11720200	-2.06203500	1.44794900
H	3.61531200	-3.40101900	-0.49356900
H	4.86759500	-1.35760600	-0.73018700
Si	2.54811900	3.16532200	-0.48067500
Si	0.22277100	-1.69888300	-2.25734400
H	-0.98516600	-1.64750000	-3.12077800
H	0.20638600	-2.92475200	-1.43740800
H	2.16370600	4.14073800	0.58062900
H	2.12308200	3.74011500	-1.79105200
H	4.03678100	3.07127100	-0.49093400
H	1.44159700	-1.56160700	-3.07484900
H	1.13362100	0.10484700	4.03955100
H	0.28648600	-1.99013700	3.20397900
C	-2.99030100	0.61864500	0.69499100
C	-4.01443800	-0.19351200	1.01988600
H	-4.05359700	-0.57178900	2.03931500
C	-5.04179000	-0.59778800	0.12855500
C	-5.91558900	-0.94840000	-0.63483900
H	-6.69379400	-1.25785600	-1.29544600
S	-2.69113800	1.36052200	-0.88372900
H	-3.69509200	0.73648100	-1.54126600
H	-0.81441900	0.17491200	-1.28095700
H	-2.22560300	0.87143700	1.42137900

Table C8 Cartesian coordinates of **FOS_1**

Atom	Coordinate (Å)		
	X	Y	Z
Al	0.82134100	0.20886800	0.01147200
O	-0.86388300	-0.83432400	0.24043400
O	0.17553000	1.77984000	-0.23608600
O	1.38222300	-0.68348200	-1.35110800
O	1.61964900	-0.09932700	1.49448800
Si	-0.71279600	-2.57095400	0.13491400
H	-1.12155000	-2.99611700	-1.21998400
Si	2.34378300	-0.93176900	-2.65401500
H	1.65619700	-0.53224300	-3.91503300
H	3.61752600	-0.16136900	-2.56421600
H	2.68734000	-2.37858400	-2.76530100
Si	2.48285000	-0.00266100	2.87724000
Si	0.18290000	3.36068900	-0.66407900
H	-1.19692600	3.91471000	-0.56084500
H	0.65092500	3.54886800	-2.06722900
H	2.19976800	-1.18289100	3.74482500
H	2.14252600	1.22304300	3.65564800
H	3.94853000	0.02227200	2.60578200
H	1.06950300	4.16567100	0.22359300
H	-1.63393000	-3.11469100	1.15727000
H	0.69427700	-2.85149400	0.44666000
C	-2.08467200	-0.15997300	0.27078000
C	-3.27395800	-0.74076000	0.06334600
C	-4.48658200	-0.00414500	0.12059400
C	-5.53824200	0.59250600	0.16305500
H	-6.45599500	1.13438100	0.20039600
H	-3.35235900	-1.80297900	-0.16185900
H	-1.94500100	0.89442800	0.46583400

Table C9 Cartesian coordinates of **FOS_2**

Atom	Coordinate (Å)		
	X	Y	Z
Al	0.64367800	-0.33875500	-0.01748400
O	-0.28692600	1.33000300	0.33221200
O	-0.14864000	-1.02216100	-1.37790200
O	0.55928000	-1.20273300	1.45645700
O	2.10247200	0.54938500	-0.34111000
Si	0.63477400	2.80988000	0.19196000
H	-0.38180700	3.82805600	0.56020300
Si	0.52260800	-2.16131900	2.77417500
H	1.87596900	-2.69757100	3.09699600
H	0.04035500	-1.40187800	3.96552100
H	-0.39310200	-3.32265700	2.58222600
Si	3.68110300	0.49509400	-0.79730600
Si	-0.66197300	-2.09044700	-2.49983300
H	-2.04137700	-1.73511900	-2.94942700
H	-0.70405400	-3.48476500	-1.97277000
H	4.23920300	1.87714400	-0.76873100
H	3.84198900	-0.03867400	-2.17943600
H	4.49397500	-0.35208000	0.12032300
H	0.21876500	-2.08435600	-3.70259900
H	1.05052900	3.01044800	-1.20733700
H	1.73038800	2.83588600	1.17694600
C	-1.63344400	1.34900900	0.75536700
C	-2.61100500	0.86712100	-0.01681800
C	-4.00219700	0.82636300	0.40799600
C	-4.99316000	0.33863500	-0.35105200
H	-6.02124900	0.32515800	-0.00313800
H	-2.35958300	0.47383400	-0.99894800
H	-1.76713000	1.75011600	1.75455900
H	-4.80554800	-0.06645800	-1.34245800
H	-4.22696500	1.21909700	1.39921500

Table C10 Cartesian coordinates of **FOS_3**

Atom	Coordinate (Å)		
	X	Y	Z
Al	-0.78773900	-0.28296300	0.04917600
O	0.44062000	1.10068700	-0.51693400
O	-0.08798900	-0.98256200	1.45393300
O	-0.98421200	-1.30178900	-1.31158900
O	-2.00894000	0.92500100	0.32913200
Si	-0.14981000	2.74494600	-0.53008000
H	-1.28437400	2.88548200	-1.45932000
H	-0.41174200	3.20286400	0.84655700
Si	-1.17118300	-2.27152000	-2.60675600
H	-2.60695400	-2.40179400	-2.98748200
H	-0.43687800	-1.73185300	-3.79033400
H	-0.64386800	-3.64183600	-2.34260600
H	1.02253800	3.47659200	-1.07553500
C	1.77089000	0.80591100	-0.91301500
C	2.65193500	0.29509300	-0.06135500
C	4.05715100	-0.07485800	-0.44741400
C	5.11167400	0.68159600	0.37814700
H	6.12194800	0.36603100	0.09675400
H	5.03515100	1.76271700	0.21912800
H	4.19055400	-1.15500700	-0.29563400
H	4.98648600	0.49027300	1.45005600
H	4.21357900	0.11067300	-1.51730900
H	2.34470400	0.12540400	0.96869200
H	1.95479700	1.00711600	-1.96307500
Si	0.26012900	-2.10695300	2.58538800
Si	-3.50181100	1.23225200	0.94611100
H	-0.65093500	-1.99898600	3.76053600
H	1.65777100	-1.92324700	3.07842900
H	0.15053300	-3.49582300	2.05185700
H	-3.93753700	2.59127100	0.51568600
H	-3.50150000	1.20321700	2.43638500
H	-4.51194500	0.24612700	0.46814700

Table C11 Cartesian coordinates of **FOS_4**

Atom	Coordinate (Å)		
	X	Y	Z
Al	-0.83300900	-0.23421900	-0.01665400
O	0.63606700	0.96766500	-0.31431000
O	-0.44429900	-1.07942700	1.42851400
O	-0.85444600	-1.18317600	-1.44883000
O	-1.96608400	1.07348000	0.11474200
Si	0.32500600	2.66919000	-0.24034600
H	-0.56421400	3.08467800	-1.34158000
H	-0.16252100	3.04816400	1.09828300
Si	-1.24641300	-2.22898100	-2.63778000
H	-0.07441200	-2.45417100	-3.53446200
H	-1.66308300	-3.55592300	-2.09865300
H	-2.36432600	-1.71215500	-3.47909700
H	1.67605700	3.25040100	-0.45892800
C	1.96252800	0.42347100	-0.64568700
C	2.79765900	0.22657500	0.61076800
C	4.14538200	-0.46289800	0.33153900
C	5.12205900	0.36045000	-0.51804600
H	6.08390800	-0.15482700	-0.61348700
H	2.42568200	1.11045400	-1.35794100
H	4.74606500	0.53374500	-1.53321900
H	4.61266400	-0.68846500	1.29775400
H	5.31373300	1.33977800	-0.06238100
H	3.96298600	-1.43400700	-0.14898600
H	2.21139600	-0.37485600	1.31401700
H	2.97316100	1.20166200	1.08661500
H	1.76444300	-0.52164400	-1.15738000
Si	-0.54180600	-2.00268000	2.77017700
Si	-3.50537000	1.59414900	0.34848000
H	-1.41383300	-1.38030200	3.80806000
H	0.81387500	-2.18091600	3.36936600
H	-1.08725100	-3.35936800	2.47587900
H	-4.38806000	1.24662200	-0.80133300
H	-3.50347000	3.07785100	0.49375500
H	-4.10919700	1.01071700	1.58040600

Table C12 Cartesian coordinates of **1-butene**

Atom	Coordinate (Å)		
	X	Y	Z
C	1.86158800	0.01768500	-0.27956800
C	0.72339800	-0.29593000	0.34035500
C	-0.54018200	0.52077800	0.30814600
C	-1.72924500	-0.24662500	-0.29468700
H	-2.64077200	0.36138200	-0.27484100
H	2.74069700	-0.61894900	-0.22342200
H	-1.52778300	-0.52621200	-1.33465700
H	-0.80070900	0.82637000	1.33265900
H	-1.93041300	-1.16845100	0.26449600
H	-0.36623900	1.44432800	-0.25846900
H	0.67247500	-1.22280500	0.91574000
H	1.95938700	0.92889300	-0.86698500

Table C13 Cartesian coordinates of **TS1**

Atom	Coordinate (Å)		
	X	Y	Z
Al	-1.02930000	0.29398000	-0.14318900
O	0.46269200	-0.59766600	-0.76333000
O	-2.19082700	0.52010100	-1.42776100
O	-0.13073800	1.83840200	0.15487200
O	-1.55888900	-0.22635500	1.43931100
Si	1.39290400	-0.70872000	-2.20740200
H	2.71617300	0.00184900	-2.17786900
H	1.59149400	-2.10198400	-2.73223600
H	0.55383700	0.00787500	-3.23314100
Si	-0.31784100	3.50752700	0.09846000
H	-1.72085200	3.95986500	-0.18494700
H	0.09888500	4.11301900	1.41270400
H	0.57944500	4.10104600	-0.95430900
Si	-3.01009600	-0.92592100	-1.57509900
Si	-2.18525100	-1.42691200	2.40510200
H	-2.29082200	-0.91995000	3.82090300
H	-3.55680800	-1.89712300	1.99936600
H	-2.46899500	-1.93003300	-0.58525000
H	-1.29433400	-2.64452600	2.45193500
H	-4.48890900	-0.78951900	-1.32550500
H	-2.87374500	-1.52397200	-2.95131200
C	1.23967400	-0.96703200	0.58118000
S	2.21406300	0.40382900	1.29533200
C	3.62931900	-0.01455700	0.37853000
C	2.22678200	-1.89278700	0.15100400
C	3.51942700	-1.31295200	-0.05696600
H	1.16076500	1.41972200	0.88030300
H	4.35221500	-1.86903700	-0.48853000
H	4.50025500	0.62308700	0.27704600
H	2.06235000	-2.96551300	0.06567500
H	0.36981200	-1.26333700	1.21925100

Table C14 Cartesian coordinates of **TS2**

Atom	Coordinate (Å)		
	X	Y	Z
A	1.25765100	-0.02660400	0.02008700
O	0.11129100	1.30248600	0.40566100
O	1.87215500	-0.81589400	1.42494100
O	2.43228700	0.51129500	-1.11557500
O	0.08332600	-1.19631700	-0.75803200
S	0.46429400	2.91661900	0.57105000
H	1.69046700	3.12601000	1.38449400
S	3.58259800	1.06504400	-2.12412100
H	4.76247400	0.15251200	-2.16981800
H	3.06664800	1.19519300	-3.51923100
H	4.07296800	2.41165100	-1.70476500
S	0.24822700	-2.84443300	-1.03226100
S	2.80992300	-1.21281800	2.69646100
H	2.59116700	-2.63703200	3.08635300
H	2.50029000	-0.37241400	3.89165000
H	-0.67545100	-3.21553900	-2.13881200
H	-0.12114600	-3.63483100	0.17053800
H	1.64675300	-3.13955100	-1.42447000
H	4.26424000	-1.04901200	2.40152900
H	-0.68909300	3.54313200	1.28752800
H	0.61489000	3.61023800	-0.73580500
C	-2.06087500	0.89477000	0.33730300
C	-2.27210300	-0.18915700	-0.27136600
C	-3.37158600	-1.00840400	-0.74057600
C	-4.66876000	-0.72076100	-0.51250700
S	-5.19135700	0.67646800	0.41642500
H	-6.51300400	0.52439900	0.19915800
H	-3.12495300	-1.89716400	-1.31193900
H	-5.44893600	-1.36878200	-0.89899800
H	-2.04153100	1.74686500	0.98192300
H	-1.10667100	-0.68632200	-0.51214900

Table C15 Cartesian coordinates of **TS3**

Atom	Coordinate (Å)		
	X	Y	Z
Al	1.03843800	-0.04448000	0.04376600
O	-0.54035500	-1.00256600	-0.09305800
O	0.50029600	1.49860100	-0.73567800
O	2.31488800	-0.75832400	-0.86356300
O	1.32816600	0.26409700	1.72804800
Si	-0.23179500	-2.49422500	-0.88892300
H	-1.42236300	-3.36887200	-0.97712300
Si	3.93179200	-0.99374700	-1.04724100
H	4.52224700	-1.79221500	0.06821400
H	4.18488600	-1.73637800	-2.31709100
H	4.68360900	0.29568500	-1.12317500
Si	0.92350200	0.10216700	3.30579800
Si	1.07772400	2.98581500	-1.23053900
H	0.40716600	4.05749500	-0.43831900
H	0.74490400	3.20515300	-2.66604800
H	1.09239700	-1.29635000	3.80413600
H	-0.51287500	0.46817800	3.54305500
H	1.75754100	0.99506000	4.16033400
H	2.54854600	3.09826100	-1.05100100
H	0.78168800	-3.23546900	-0.09488900
H	0.25317700	-2.26134500	-2.27157400
C	-2.10920400	-0.49438100	0.54987200
C	-3.21095500	-1.20297600	0.10018300
H	-3.21522700	-2.27848400	0.23590000
C	-4.34636400	-0.62890300	-0.50091300
C	-5.34531400	-0.15824500	-1.01171200
H	-6.22323600	0.25359600	-1.45269300
S	-2.25330300	1.39177500	0.16705400
H	-2.98826000	1.32695100	-0.95840000
H	-0.87674800	1.56674900	-0.34319600
H	-1.75435400	-0.49574400	

Table C16 Cartesian coordinates of **TS4**

Atom	Coordinate (Å)		
	X	Y	Z
A	-0.98283500	-0.01184500	0.00312900
O	0.70087900	-0.97993700	0.00316400
O	-0.44838700	1.66047900	-0.01222200
O	-1.62487000	-0.70057600	1.45919600
O	-1.63941700	-0.72243600	-1.43579000
S	1.16020600	-2.65233200	0.01258100
H	1.96646600	-2.98683000	1.22906500
S	-2.01326900	-0.50555400	3.06304400
H	-0.89408300	0.06956000	3.89312900
H	-3.21434000	0.37762100	3.27988600
H	-2.34612100	-1.84741000	3.66494900
S	-2.03824100	-0.55571700	-3.04023400
S	-0.87234800	3.27037800	-0.02768600
H	0.38437500	4.10428400	-0.03445000
H	-1.66833600	3.69398100	1.17853200
H	-2.39099000	-1.90560800	-3.61207600
H	-0.91881300	-0.01070400	-3.89010400
H	-3.23065400	0.33680800	-3.26630700
H	-1.66619300	3.67122700	-1.24307100
H	1.96220000	-3.00125300	-1.20266500
H	-0.10379900	-3.45153400	0.01954800
C	1.66485700	-0.01687400	-0.00436300
C	2.98326300	-0.29405200	-0.00414900
C	3.99538000	0.71713800	-0.01205200
C	5.23983800	1.04921400	-0.01520100
H	6.20784100	0.58857000	-0.01243500
H	3.39247800	-1.31694000	0.00217000
H	1.23288000	1.02841700	-0.01099200
H	4.21930800	2.20788700	-0.02295100
H	3.33008800	2.00826600	-0.02099100

Table C17 Cartesian coordinates of **TS5**

Atom	Coordinate (Å)		
	X	Y	Z
Al	-0.96874500	0.24179700	-0.06464400
O	0.55882400	-0.99328800	0.01676700
O	-0.81642400	1.15294800	-1.51444100
O	-0.85715800	1.07180200	1.43028000
O	-2.08938900	-1.11006500	-0.16134000
Si	0.19959100	-2.69385700	0.22025900
H	-0.63695600	-2.89881700	1.41190300
H	-0.34779100	-3.24840400	-1.03103500
Si	-1.21570000	2.30791500	2.44773800
H	-0.98706700	3.63368200	1.80374500
H	-2.64044800	2.25799800	2.88301800
H	-0.35703400	2.23230300	3.66161400
H	1.50833800	-3.33249200	0.46737000
C	1.81307300	-0.38172200	-0.17395100
C	3.03301800	-0.84267200	0.13644500
C	4.24630900	-0.05354500	-0.08278900
C	5.58292300	-0.49232300	0.40393900
H	5.85326100	0.84436400	0.20495300
H	5.80921700	-0.28403000	1.44630100
H	4.23647800	0.51752600	-1.00451000
H	5.94527100	-1.49863700	0.13367200
H	4.89677600	1.23925800	0.36123600
H	3.16629100	-1.80506200	0.61986800
H	1.68306100	0.60284200	-0.61026200
Si	-0.06935000	2.38967600	-2.29509400
Si	-3.63673300	-1.62477300	-0.39601400
H	-0.58248500	3.71758300	-1.85812300
H	-0.27282000	2.26597200	-3.76310900
H	1.40455600	2.37476200	-2.03912200
H	-3.85666400	-2.88090700	0.37492400
H	-3.90198700	-1.91923700	-1.83190200
H	-4.63437700	-0.61713300	0.06140500

Table C18 Cartesian coordinates of **TS6**

Atom	Coordinate (Å)		
	X	Y	Z
Al	-0.53286900	-0.40671600	0.06856100
O	-0.12769900	1.33030700	-0.48523000
O	0.31961600	-0.66615400	1.55556100
O	-0.00150600	-1.42297600	-1.23860300
O	-2.18525100	0.14878000	0.10584100
Si	-1.18343200	2.69698800	-0.65797400
H	-2.21516800	2.45282400	-1.71642500
H	-1.82862200	3.04836900	0.64703400
Si	0.22776100	-2.74484100	-2.20634300
H	1.33660200	-2.47133600	-3.19319100
H	0.62556800	-3.98265600	-1.44348100
H	-0.99467600	-3.10101000	-3.01270000
H	-0.36199900	3.88073700	-1.09293200
C	1.20559300	1.46901000	-0.86150300
C	2.22145000	1.74084900	0.24871100
C	3.49591700	0.99049500	0.44122900
C	4.00470100	0.41084000	-0.88089600
H	4.96217200	-0.10754700	-0.75403200
H	3.25705500	-0.30264500	-1.30185700
H	4.36661900	1.54178700	0.84151100
H	4.14126200	1.19306200	-1.63704600
H	3.22410300	0.21717300	1.19290400
Si	0.77623400	-1.31615900	3.00659200
Si	-3.81032100	-0.07573400	0.36705600
H	-0.26006600	-1.14249200	4.08725900
H	2.03632000	-0.64205200	3.49478400
H	1.08112300	-2.79061200	2.92607500
H	-4.45182600	-0.97784500	-0.65554300
H	-4.52867400	1.24836700	0.28558800
H	-4.12777900	-0.65718000	1.72025900
H	2.06612700	2.61763800	0.87931300
H	1.26264400	2.33273400	-1.56367000
H	1.60432200	0.03507500	-0.87295800
H	1.98156600	0.26452300	-0.03861600

Table C19 Cartesian coordinates of **TS7**

Atom	Coordinate (Å)		
	X	Y	Z
Al	-0.67870000	-0.03441700	-0.19708800
O	0.35948500	1.40659900	-0.64182300
O	0.25252100	-0.30986700	1.36676200
O	-0.56457400	-1.33758700	-1.32683200
O	-2.24375800	0.67791800	0.04034100
Si	0.24091800	3.10455500	-0.84668600
H	-0.74284100	3.42158100	-1.93230800
H	-0.19755500	3.74842600	0.43331900
Si	-0.83142000	-2.80296600	-2.04972300
H	0.22433200	-3.06418500	-3.09498400
H	-0.78249400	-3.95864400	-1.08319900
H	-2.16511300	-2.87194000	-2.74834100
H	1.55790100	3.71472600	-1.23863000
C	1.72587800	0.77811000	-0.92287600
C	2.44793600	0.63872500	0.34722400
C	3.32421300	-0.57327200	0.50127000
C	4.67380700	-0.40455500	-0.17255700
H	5.38904800	-1.17077300	0.15399700
H	2.10564700	1.52501300	-1.64989500
H	4.59404000	-0.47850000	-1.26491400
H	3.48216900	-0.76872800	1.58203800
H	5.11746400	0.57395300	0.05329600
H	2.82307000	-1.47601600	0.09711000
H	2.86442800	1.55330600	0.78966700
H	1.51810700	-0.18872000	-1.41699000
Si	0.07581800	-1.17183000	2.82756900
Si	-3.82239700	0.60080000	0.54733100
H	-1.04503300	-0.62202200	3.66001100
H	1.34269000	-1.06409300	3.62580000
H	-0.19617300	-2.62924400	2.59518400
H	-4.68297300	-0.28673800	-0.31468300
H	-4.43879100	1.97615300	0.50226000
H	-3.97407300	0.10634200	1.96339900
H	1.28798500	0.04915400	1.12519600

APPENDIX D

Table D1 Rate, equilibrium constants, energetics and thermodynamic properties of thiophene convert to 1-butene in ZHM-5-catalyzed system, computed at the B3LYP/ 6-31G(d) level

Reactions	$\Delta^{\ddagger}E$ [a]	$\Delta^{\ddagger}G$ [a]	k_{298} [b]	ΔE [a, c]	ΔH [a, c]	ΔG [a, c]	K_{298}
1 + HZ → 1-HZ	-	-	-	-5.27	-5.59	5.24	3.04×10^{-133}
1-HZ →TS1 → FS	99.21	110.10	1.21×10^{-68}	65.51	65.40	67.68	1.61×10^{-50}
FS → SS	-	-	-	-40.44	-39.79	-42.95	3.98×10^{31}
SS→ TS2→ THS_1	93.14	103.37	1.04×10^{-63}	18.05	19.40	16.00	1.70×10^{-12}
THS_1→ THS_2	-	-	-	-0.07	-0.22	0.89	2.21×10^{-1}
THS_2→ THS_3	-	-	-	0.21	-0.21	0.46	4.58×10^{-1}
THS_3→ TS3 → FOS_1+H_2S	65.77	72.34	5.80×10^{-41}	13.93	14.49	4.83	2.79×10^{-4}
FOS_1+H_2 **→ TS4→ FOS_2**	111.02	127.13	3.92×10^{-81}	-45.18	169.02	161.8	9.00×10^{27}
FOS_2+H_2 **→ TS5→ FOS_3**	87.33	100.34	1.72×10^{-61}	-26.07	-28.32	-18.21	2.48×10^{13}
FOS_3+H_2 **→ TS6→ FOS_4**	158.86	173.24	6.27×10^{-115}	-27.45	-29.35	-20.44	1.08×10^{15}
FOS_4→ TS7→1-butene+ ZH	65.69	73.01	1.88×10^{-41}	15.05	16.14	1.54	7.33×10^{-2}

[a] In kcal mol^{-1}.

[b] In s^{-1}.

[c] Frequency calculations at the MP2(fc)/6-311+G(d,p) level.

VITA

NAME: Miss Pawanee Pholtem

BIRTH DATE: July 28th, 1981

BIRTH PLACE: Bangkok, Thailand

EDUCATION:

YEAR	**INSTITUTION**	**DEGREE/DIPLOMA**
1998	Sainumpeung School	High School
2001	Chulalongkorn Univ.	B.S. (Material Science)
2007	Chulalongkorn Univ.	M.S. (Petrochemistry and Polymer Science)

WORK EXPERIENCE: 2002 Technician

Intertek Testing Services (Thailand) Co., Ltd.

2003 Sales Representative

Thaikaseihin Co., Ltd.

ADDRESS: 13/150 Moo Navamin Road, Klongkum, Beungkum,
Bangkok, 10240, Thailand. Tel. 08-9202-2656.

E-MAIL: pawanee_p@hotmail.com