



CHAPTER I

INTRODUCTION

1.1 Research Rational

Catalytic cracking is an important process in petrochemical industry. It involves 3 reactions *i.e.* proton exchange, cracking, and dehydrogenation. Competitions between these reactions give rise to different ratio of petrochemical products. Thus, the knowledge and the predictability of these reactions are valuable, since it helps us to reduce cost and produce petrochemicals more effectively. ZSM-5, a type of zeolitic compounds, has been used as the commercial catalyst for this process since with pore diameters of ZSM-5 more hydrocarbons could be adsorbed and it yields high selectivity [1]. In general, experimental geometries of ZSM-5 are not available since positions of Si and Al atoms of zeolite are not distinguishable from the diffraction analysis. Computational chemistry is therefore a valuable tool for obtaining structures and properties of zeolites. The combination between structural details and experimentally observed properties has fulfilled the missing information. There have been numerous theoretical and experimental works on thermodynamics and kinetics aspects of the catalytic cracking reactions [2-11]. However, the mechanistic details of hydrocarbon conversion in ZSM-5 are rather complex and not yet fully understood. In previous studies, theoretical calculations often used limited-size cluster models, 1T, 2T, 3T, and 5T, with methodologies and basis sets at the intermediate level of accuracy. Small clusters of the zeolite catalyst did not represent a unique zeolite framework, especially the long-range stabilization of zeolite lattice. Recently, embedded and periodic models has been used to improve the long-range stabilization effect [12].

In this dissertation, we focused on the proton exchange, the dehydrogenation, and the C-C bond cleavage reactions of small- to medium-sized alkanes (C₂-C₄), *i.e.* ethane, propane, iso-butane (i-butane), and normal-butane (n-butane).

1.2 Zeolites

Zeolites are crystalline microporous materials [13, 14]. Zeolite framework structures are aluminosilicates, which are made of aluminate (AlO_4^{5-}) and silicate (SiO_4^{4-}) tetrahedral and linked to each other by sharing oxygen atoms at the corner of each tetrahedron that based on an infinitely extending three-dimensional network as shown in Figure 1.1.

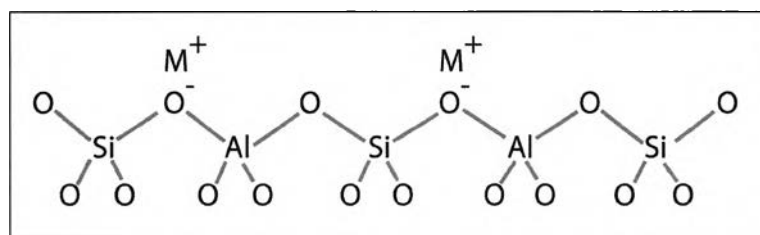
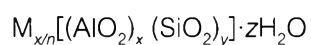


Figure 1.1 The general framework structure of zeolites [13]

The framework negative charges are determined by the number of AlO_2^- tetrahedral sites in the structure. The negative charges are balanced by cations that occupy nonframework positions. The general formula for the composition of zeolites is



where M is the cation of valency n , generally from the group I or II ions such as sodium, potassium, magnesium, calcium, strontium and barium. Moreover, the cation of other metals, nonmetals, and organic compounds are also possible to balance the charges. The symbols x and y are the number of tetrahedral aluminate and silicate, respectively. z is the number of water molecules in the channels and cavities of zeolites. The number of acid sites can be determined from the x value. It is worth noting that each zeolite has a specific number of tetrahedra ($x+y$). For example, the tetrahedral number of ZSM-5 equals to 96.

The variety of zeolite materials is commonly a result of three factors. First, the difference in sizes of channels and cavities is caused by many ways of the connection of the tetrahedra. Secondly, the different types of the cations present in the structure to balance the negative charge of the zeolitic framework. Finally, there is the difference in the composition of aluminate and silicate in the tetrahedral framework. The structure types, nomenclature and, their characteristic of zeolites are collected in the 'Atlas of the Zeolite Structure Types' which is currently updated and also available on the internet [15, 16].

1.3 Structures of Zeolites

A primary building unit is a silicate or aluminate tetrahedron which is the smallest unit of all zeolite structures [13, 14, 17]. Two primary building units are connected by sharing oxygen as shown in Figure 1.2.

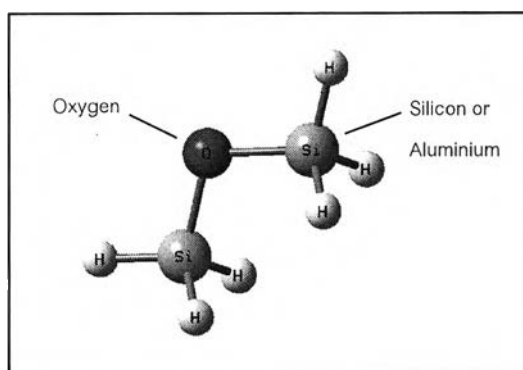


Figure 1.2 Zeolites are constructed from two primary building units (SiO_4 or AlO_4^-) by linked corner-sharing [17]

Secondary building units [13] (SBU) consist of selected geometric groups of tetrahedral. There are 9 secondary building units, that are 4, 6, and 8-membered single rings, 4-4, 6-6, and 8-8 membered double rings, and 4-1, 5-1, and 4-4-1 branched rings as illustrated in Figure 1.3. SBU can be used to describe all of known zeolite structures.

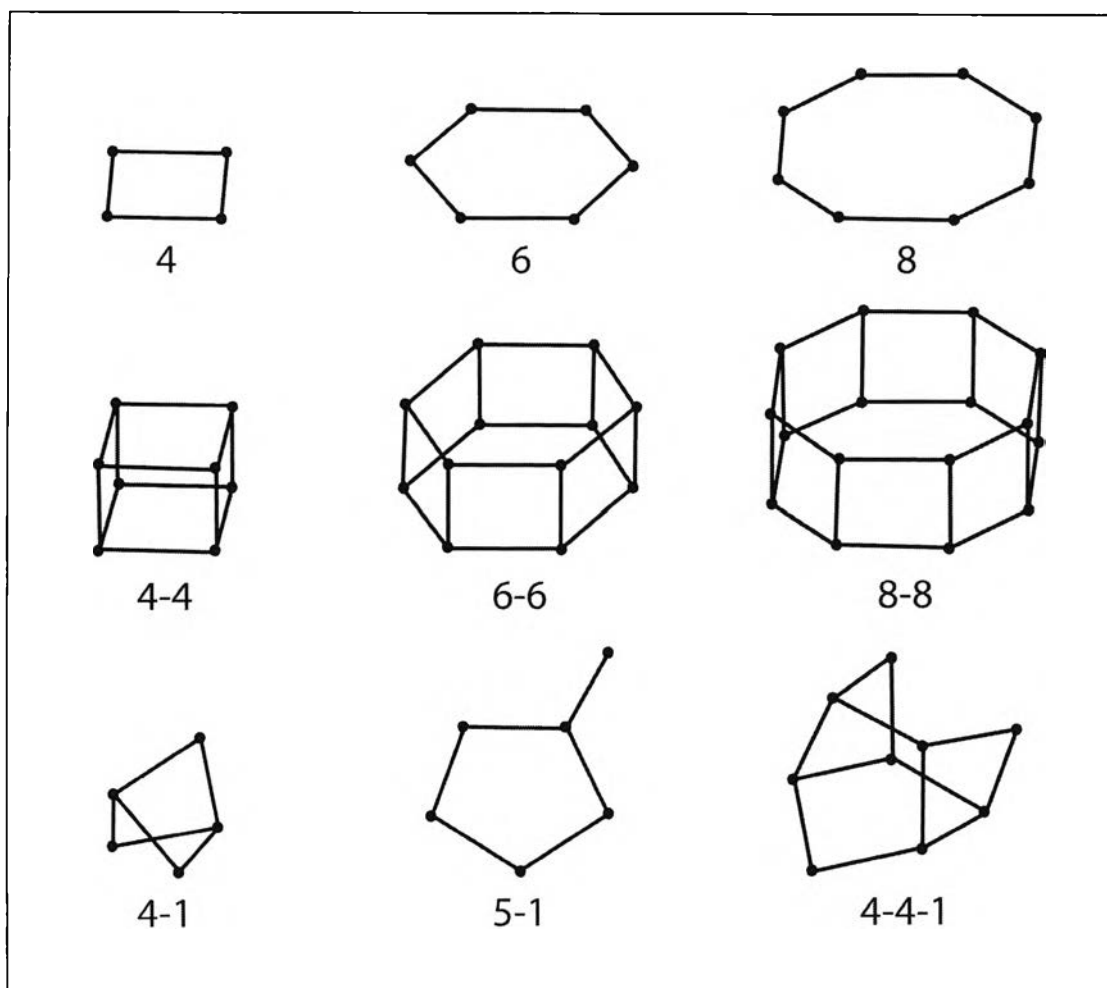


Figure 1.3 Secondary building units found in zeolite structures [13]

For the structure of ZSM-5, the SBU are linked to form the framework consisting of five tetrahedral units (pentasil). The framework appears in a chain-type building block of the intergrowth ZSM-5 as shown in Figure 1.4. The arrangements of these secondary building units are mainly factors for describing structural differences and similarities. For example, the difference between the structures of ZSM-5 and ZSM-11 in Figure 1.4 is the connecting point of two framework sheets. The sheets of ZSM-5 are linked through a center of inversion (i), whereas the sheets of ZSM-11 are related through a mirror plane (σ) [18].

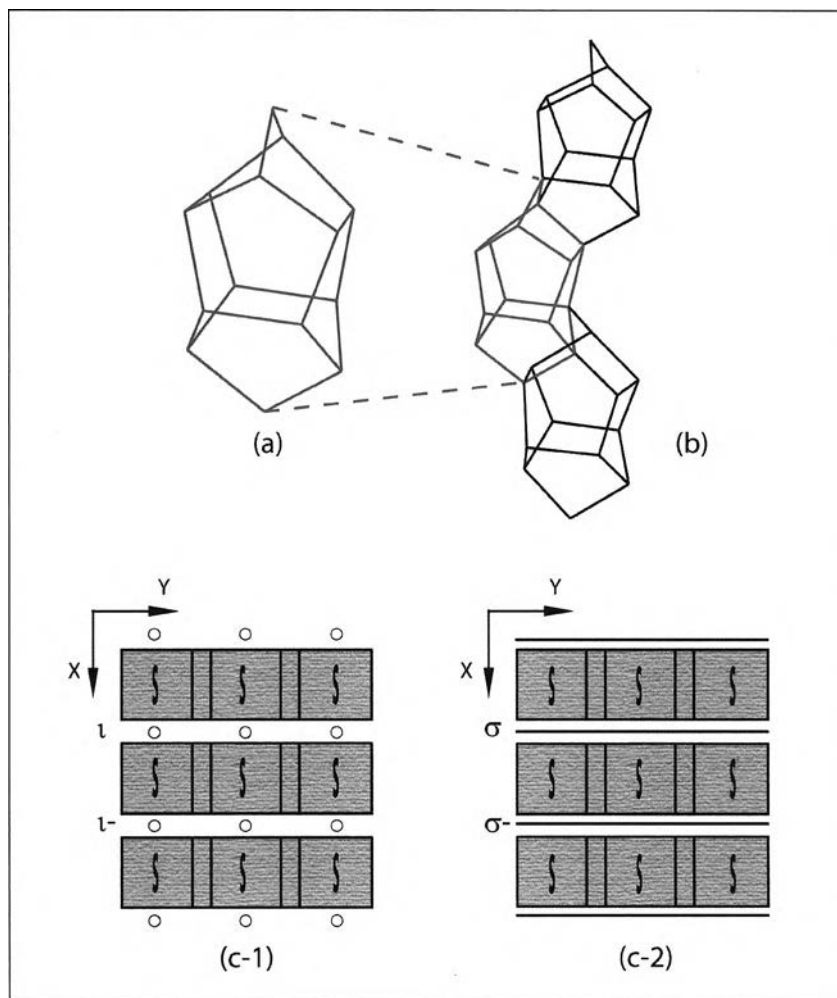


Figure 1.4 The 5-1 secondary building unit (a) to form the chain units (b) and stacking sequences of layers found in the ZSM-5 (c-1) and ZSM-11(c-2) structures [18]

1.4 ZSM-5 Zeolite

In 1972 Zeolite Socony Mobil-five (ZSM-5), with structure code 'MFI', was first synthesized by the oil company 'Mobil' [19]. The synthetic ZSM-5 zeolite was obtained from the proportion of silicon sites are occupied by Al^{3+} . The ZSM-5 zeolite has the same framework structure as silicalite. The purely siliceous zeolite, silicalite, consists of two phases depend on temperature. The first is the orthorhombic phase that contains 12 independent T sites. The second is monoclinic phase that contains 24 independent T

sites [20], (which is ascribed to a shift of neighboring (010) pentasil layers), as shown in **Figure 1.5** [18, 20, 21]. The crystal of structure ZSM-5 has the orthorhombic space group symmetry with (Pnma) lattice parameters, $a=20.022\text{\AA}$, $b=19.899\text{\AA}$ and $c=13.383\text{\AA}$, that contains 96 silicon and 192 oxygen atoms (SiO_2), resulting in a framework density of 17.9 T sites/1000 \AA [18].

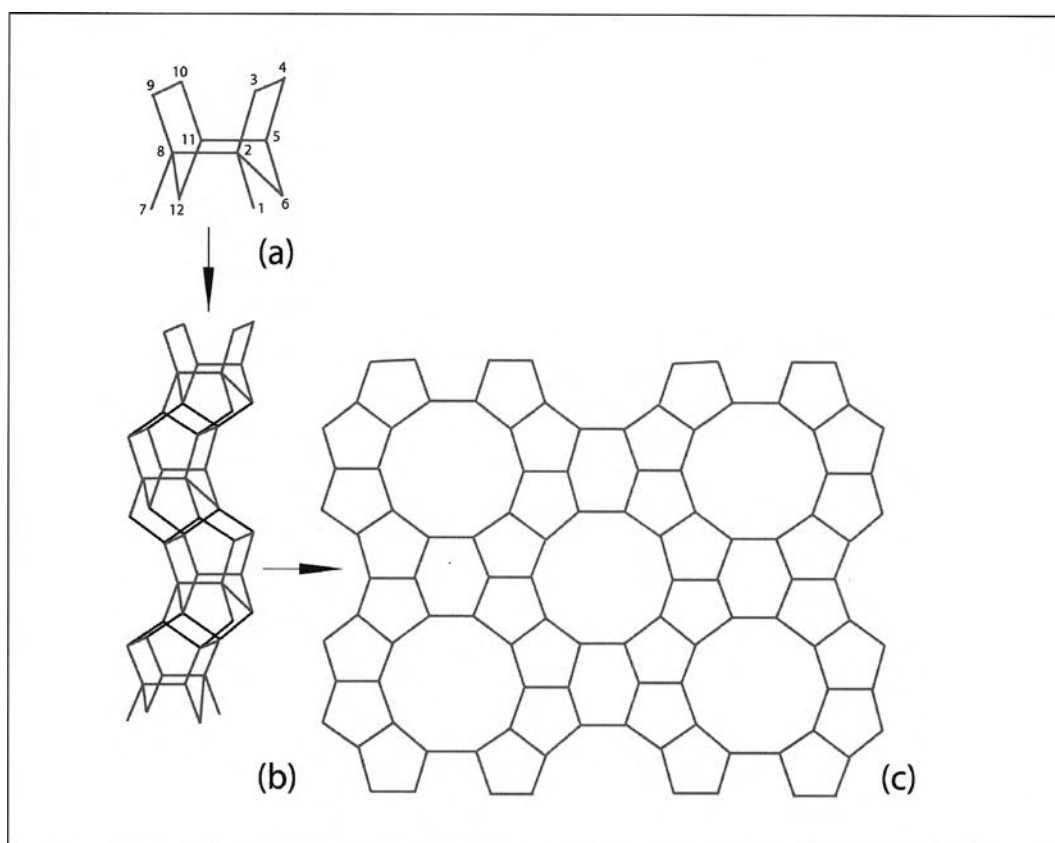


Figure 1.5 Diagrammatic representation of the ZSM-5 structure. Secondary building blocks (pentasil layers) illustrating the 12 T sites (a) which combine to form chain-type building blocks (b). These pentasil layers can combine to form the channel system of the ZSM-5 structure (c). A displacement of these pentasil layers along the (010) direction results in the monoclinic phase of the zeolite, and the subsequent reduction in symmetry allows for 24 independent T sites [18]

The ZSM-5 structure shows a medium-pore opening that composes of a 10-member ring. The ZSM-5 framework contains two types of channels. One is straight that

runs parallel to the b-axis of the orthorhombic unit cell, and has elliptical ($5.1 \times 5.5 \text{ \AA}$) openings, while the another is sinusoidal (zigzag) and directed along the a-axis that has near-circular ($5.4 \times 5.6 \text{ \AA}$) openings [18]. Figure 1.6 exhibits structure of ZSM-5 and schematic of three-dimensional channel.

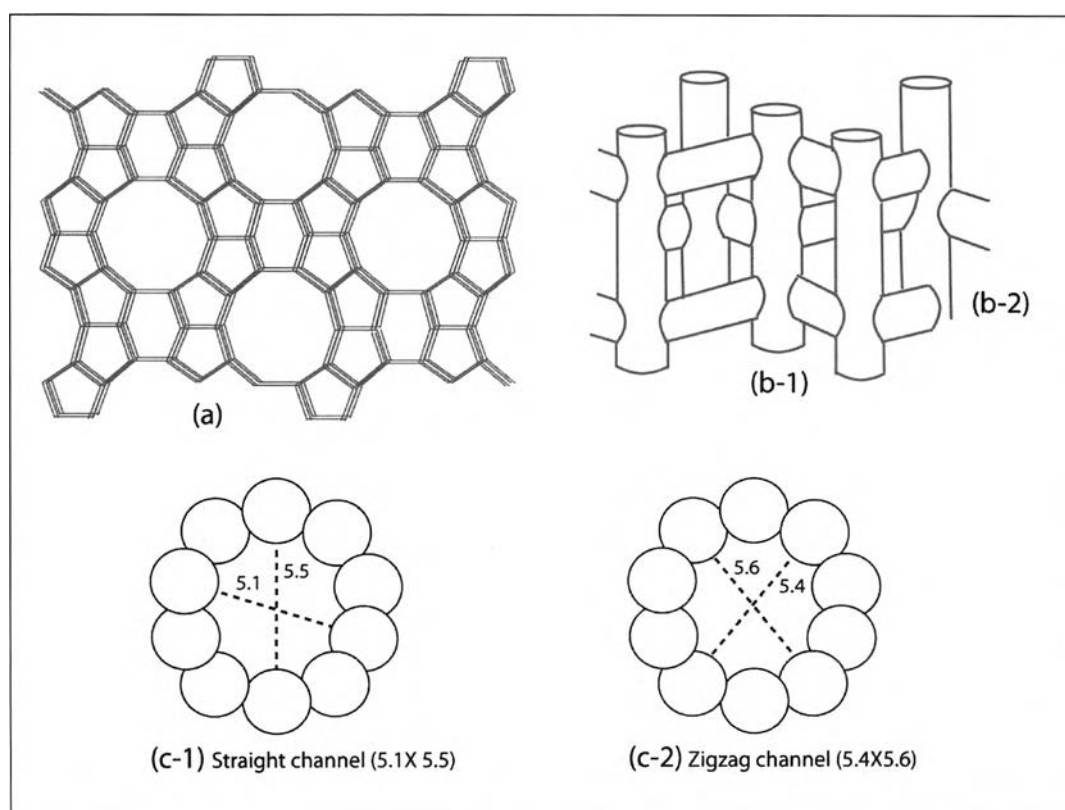


Figure 1.6 Structure of ZSM-5 (MFI) (a); Schematic illustration of the three-dimensional channels; (b) consist of the sinusoidal channels (b-2); run perpendicular to the straight channels (b-1); and pore opening straight channel (c-1); and pore opening zigzag (c-2) [13, 17, 18].

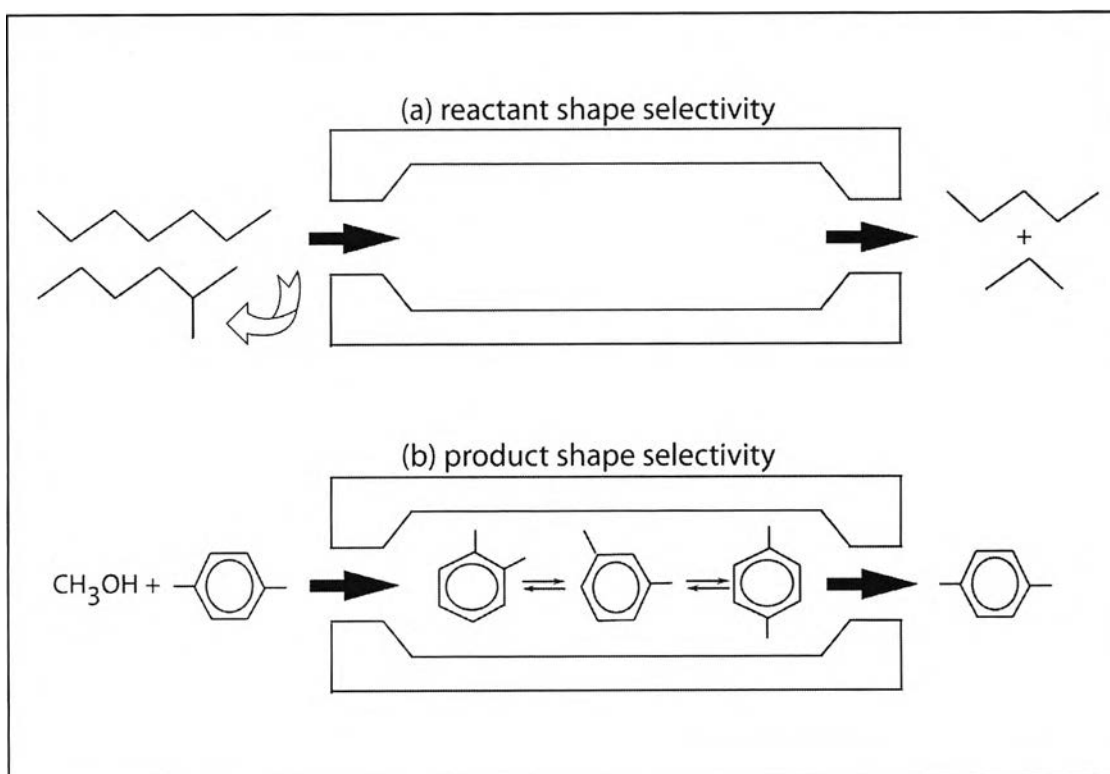
1.4.1 Chemical Composition of Zeolite ZSM-5

The chemical formula of a typical unit cell of hydrated Na-ZSM-5 is $\text{Na}_n[\text{Al}_n\text{Si}_{96-n}\text{O}_{192} \cdot 16\text{H}_2\text{O}]$, $n < 27$. The lowest Si/Al ratio known in the ZSM-5 lattice is 10. The limit on Si/Al ratio cannot be lower than 1 in the framework. The Löwenstein's rule controls pairs of AlO_4^- tetrahedra by forbids Al–O–Al bridges [18].

1.4.2 Shape Selectivity Properties of ZSM-5 Zeolite

ZSM-5 is known as molecular sieves that possess shape selectivity. ZSM-5 plays a very important role as a catalyst; they can adsorb molecules of certain dimensions while rejecting those of larger dimensions [13, 17, 19]. Shape selectivity is separated into 3 types: reactant, product, and transition-state shape selectivity, as shown in Figure 1.7 [13].

Reactant shape selectivity represents effectively enter and diffuse inside the crystal between linear and branched in Figure 1.7 (a). Product shape selectivity, Figure 1.7 (b), for example o- and m-xylene, cannot rapidly escape from the crystal, and undergo secondary reactions to p-xylene that occurs to be the diffusing product molecules. Restricted transition-state shape selectivity, Figure 1.7 (c), in case of bulky transition state for a certain reaction mechanism that controls the rate constant of reaction.



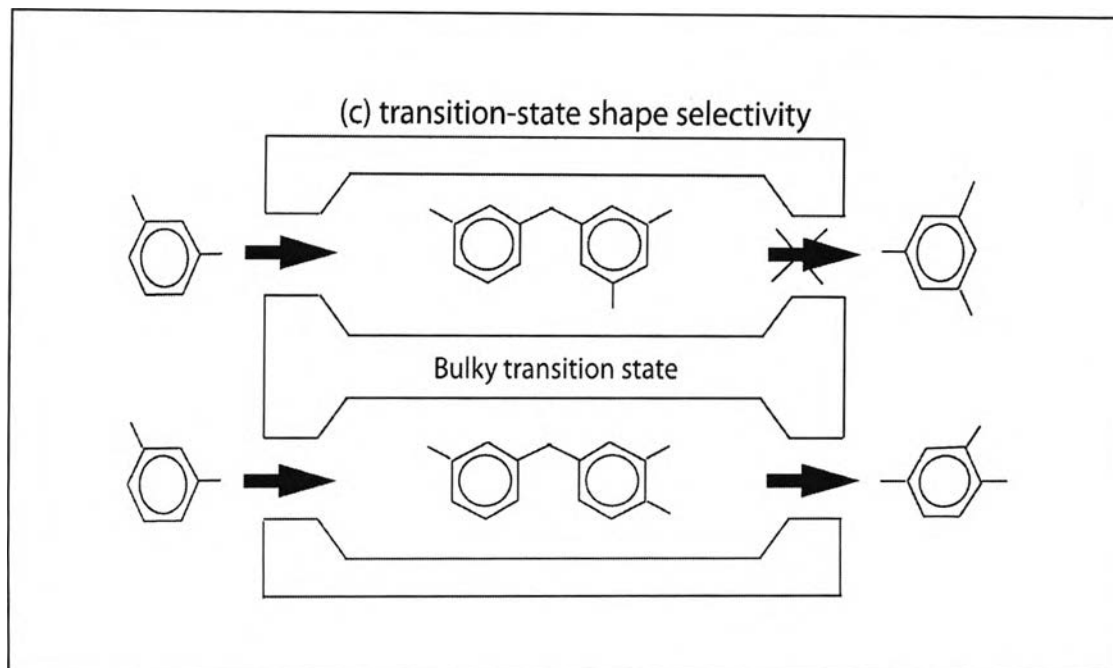
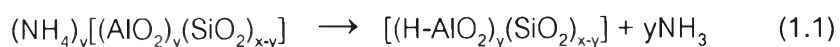


Figure 1.7 Three types of shape selectivity in zeolites: reactant (a), product (b), and transition-state shape selectivity (c) [13]

1.4.3 Acid Sites of Zeolite ZSM-5

The zeolite acid catalyst is produced by combustion in air called calcinations to remove large organic quaternary amine cations occluded during synthesis. The obtained material contains alkali cations (e.g. Na^+) and some protons as shown in Figure 1.8 (a). Direct exchange with acid of alkali cations is also possible, but has to be done very carefully otherwise Al atoms will be extracted from the zeolite lattice [13]. Ammonium exchange is performed, following by subsequent deammoniation *i.e.*, thermal treatment releasing ammonia gas and leaving proton, results in the structure shown in Equation 1.1 and Figure 1.8 (b).



Hydroxyl protons (-OH groups) in Figure 1.8 (b) are located on oxygen bridges connecting a silicon and aluminum tetrahedral acting as Brønsted acid site for

charge-compensating cations to the framework anionic charge of zeolites. Simultaneously, Brønsted acid sites are in equilibrium with Lewis acid both types are usually present in zeolites. Brønsted acid sites are transformed to Lewis acid sites by dehydration upon heating at high temperature, as shown in Figure 1.8 (c). This process is reversible.

The acid sites on zeolites which act as catalytic sites can be classified according to the ability to be proton-donor (Brønsted acidity) or electron acceptor (Lewis acidity) [13]. In zeolite Brønsted acidity is generally believed to be weaker than Lewis acidity [13, 16]. The acid strength of the Brønsted acid depends on type of the substituting metal atoms in zeolites, (Si-OH-T, T = Al, Ga, Fe, etc.). Brønsted acid site on ZSM-5 zeolites is used in many industrially catalytic processes and had been the subject of extensive research e.g., for hydrocarbon conversion in the petroleum industry.

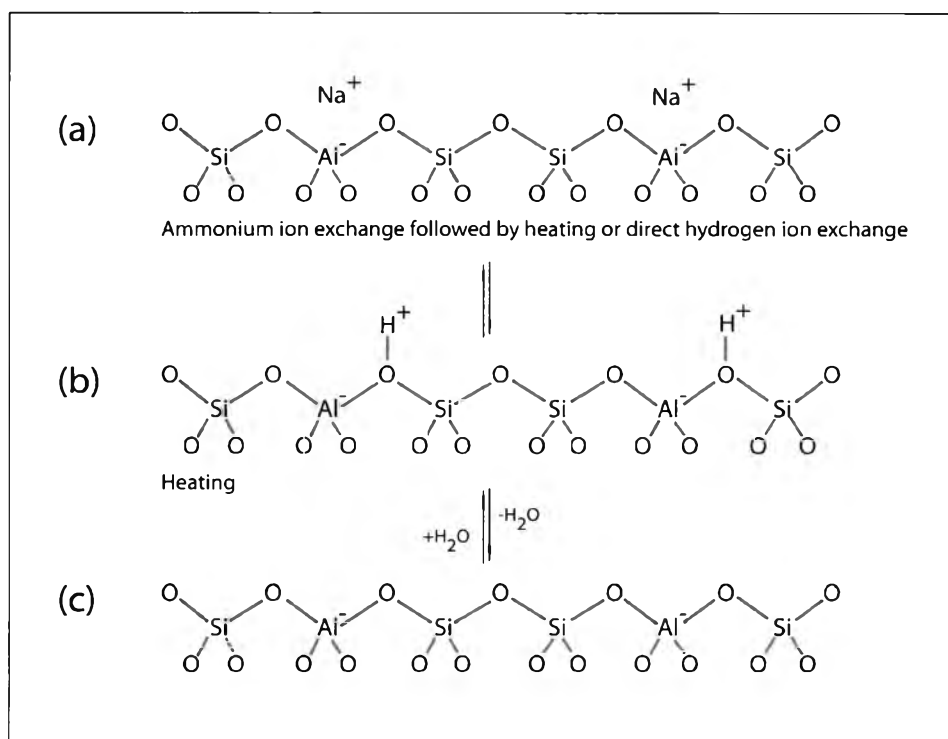


Figure 1.8 Schematic representations of acidities in zeolites. Calcined zeolite (a), Brønsted acid (b), and Lewis acid (c).

1.5 Literature Review

Polyolefins are produced from oil components that are the fastest growing industrial polymers, and 66.9% of plastics in household waste are polyolefins. However, polyolefins are suitable for feedstock recycling to produce valuable hydrocarbon products because they consist only of carbon and hydrogen [22]. Hydrocarbon cracking is the process that higher-molecular-weight hydrocarbons are converted to lower molecular-weight hydrocarbons through carbon-carbon bond breaking [23]. Hydrocarbons cracking occurs following three general mechanisms: thermal cracking, catalytic cracking, and hydrocracking [23]. Ethylene and propylene are the main products from thermal cracking (or pyrolysis) of either single or multicomponent reactants based on a hydrocarbon complex mixture called petroleum that is major industrial starting material [23-25]. In 2010, around 130 million tones of the production of polyethylene and polypropylene are expected [26]. The main problem of pyrolysis is the requirement of high energy (750-900°C) to break down long chain hydrocarbons into smaller ones via free radical mechanism. This process needs high cost of fuel and generates excessive coke in reactors [23-25]. One of the solutions for the above problem is that the use of a catalyst for the cracking process. Zeolites are the most popular hydrocarbon catalytic cracking in the petrochemical industry [27]. The usage of catalytic cracking process decreases the requirement of energy (low costs), enhances the efficiency in prohibition of coke generation, and increases yields of valuable products.

Zeolites are aluminosilicate compounds with various pore structures and Si/Al ratios. Famous zeolites such as HZSM-5, mordenite, and HY have been proven to be particularly effective in catalytic cracking reactions [28-33]. It was reported that the zeolite pore size and Brønsted acidity are important factors for indicating the catalytic efficiency. In general, the catalytic reactions in zeolites occur via four consecutive physical processes. First, the reactant molecules diffuse through the zeolite pores and channels and reach to the active sites. Second, the reactants in a gas phase are adsorbed on the interior surface of the catalyst. Next, the catalytic reaction occurs and

gives products. Finally, the product molecules desorb from the interior surface and diffuse from the zeolite pores.

It is necessary to note that many hydrocarbon transformations on zeolites proceed with the formation of the same intermediate species, although, the products are different depending on the nature of the catalyst and conditions of the process. Further transformations of these intermediates lead to either olefins (dehydrogenation) or branched alkanes (cracking and condensation) as well as of other reactions, e.g., isomerization. Examples of these processes are depicted in Figure 1.9 [34].

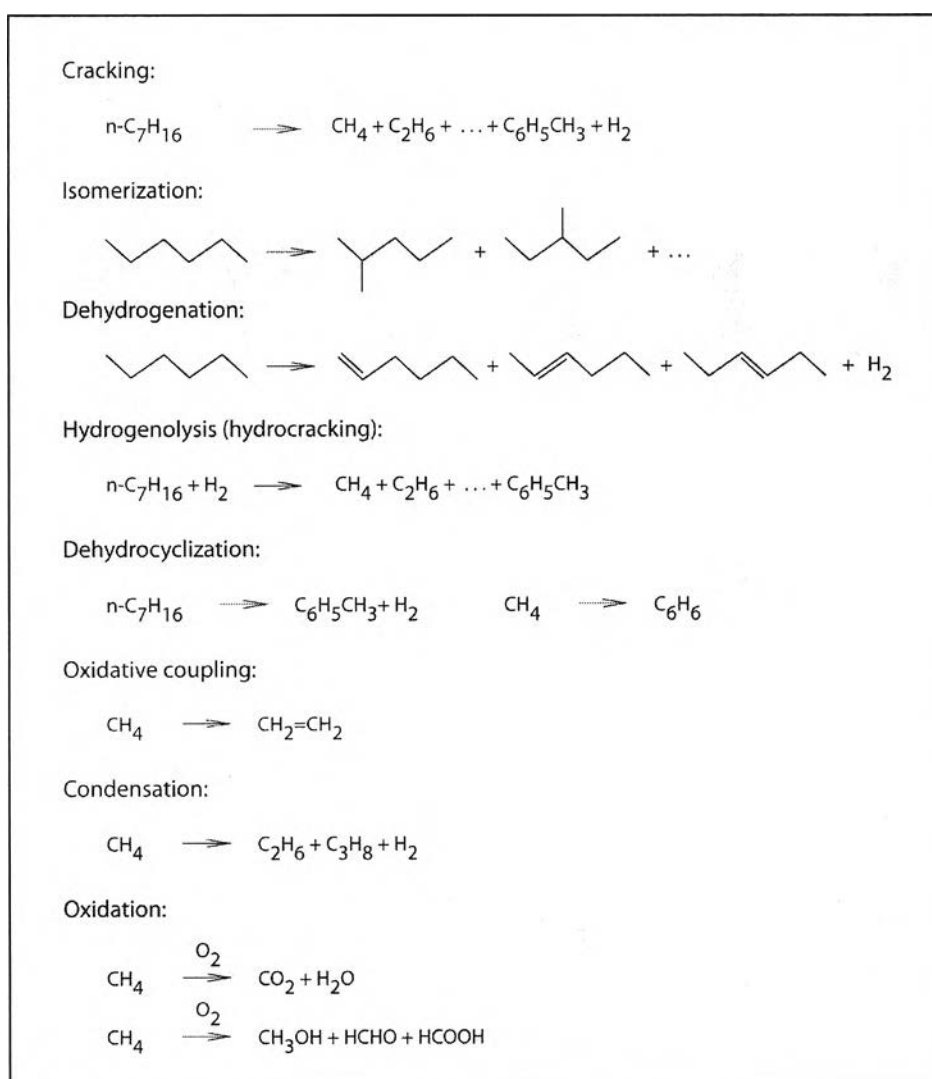


Figure 1.9 Examples of hydrocarbon transformation processes catalyzed by zeolites

It has been widely accepted that the transformation of hydrocarbons over acid zeolites proceeds through a chain mechanism where carbenium ions acted as chain carriers [35]. Carbenium ions may undergo several reactions: deprotonation, hydride transfer, isomerization, β -scission, and oligomerization. The stability of the carbenium ions increases with the increase of degree of substitution: tertiary > secondary > primary > methyl [35]. Until 1994, Kazansky and Senchenya proposed that the actual intermediates are not carbenium ions, but covalent alkoxide species instead (Figure 1.10) [36]. These results were based on *ab initio* quantum calculations with cluster models of zeolites, and they were confirmed by other research groups [8, 36-42]. The positively charged carbenium ions was proposed to be transition states of the cracking reaction originated from the elongation of the alkoxides C-O bonds. The classical carbenium ion theory successfully explains the cracking product distribution, although it is not totally complete.

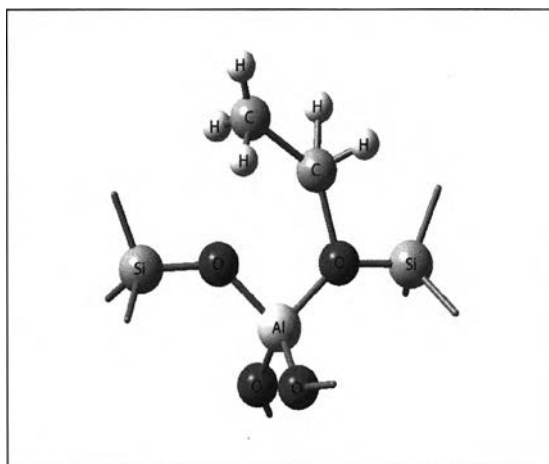


Figure 1.10 The cluster model of zeolite showing the covalently bonded ethoxy group [41]

According to the Haag and Dessau [43] monomolecular protolytic mechanism and Olah's superacid chemistry [44, 45], zeolites protonate alkanes at high temperatures giving unstable transition states known as carbonium ions. These carbonium ions can easily decompose (Figure 1.11) to produce H_2 (pathway 1) for smaller alkanes and carbenium ions (alkoxides) in pathway 2. The different between two

pathways, protolytic cracking or dehydrogenation, is the position where the proton attacks (C-C or C-H bond of the reacting alkane).

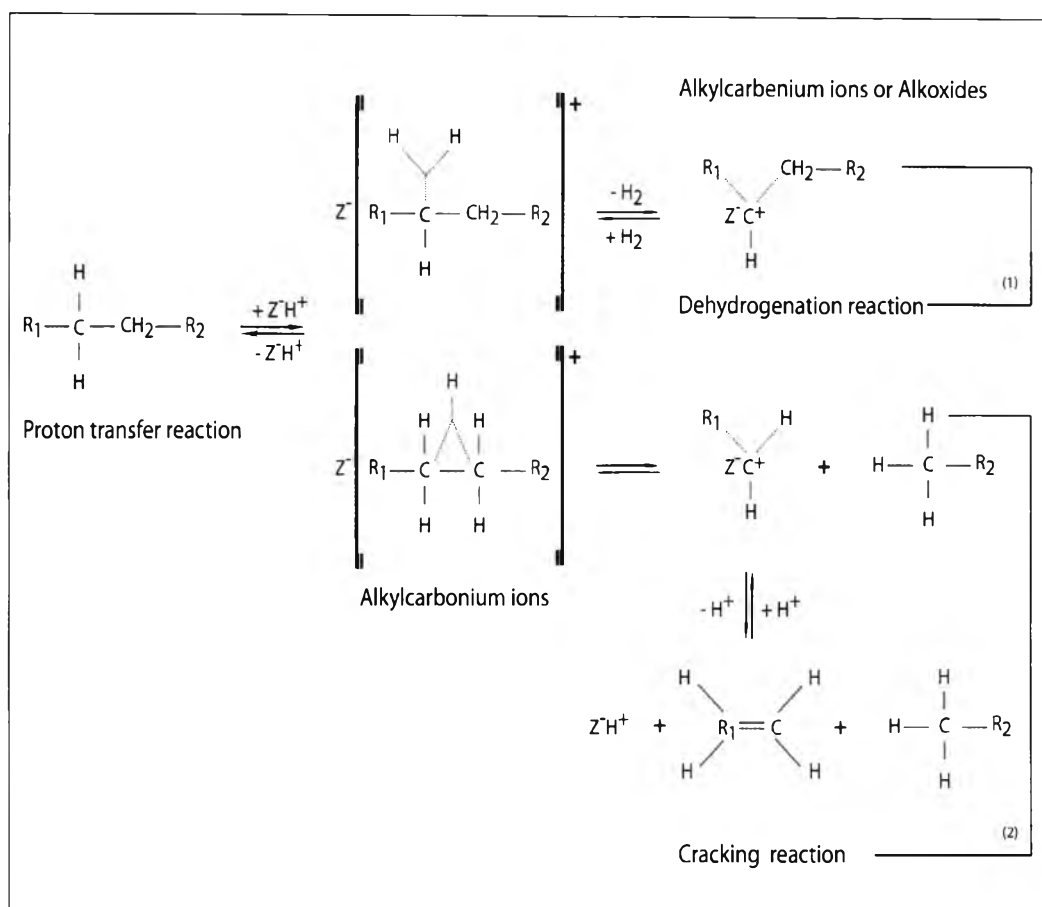


Figure 1.11 The carbonium ions transition state structure of protolytic cracking and dehydrogenation of alkanes [46]

Another mechanism was introduced by Collins and O'Malley from a similar computational study of protolytic cracking of n-butane with an $H_3SiOAl(OH)SiH_3$ (3T) zeolite cluster model [3]. With the BLYP/3-21G* DFT method, they predicted that the transition state (TS) formed by the protonation of one of the C-C bonds in butane ($C_4H_{11}^+$). In the TS, the zeolitic proton was located almost in the middle between the C-C bond. The location of the proton in this pathway is different from the pathway proposed by Kazansky [36]. In addition, after the C-C bond have been cleaved a shorter alkane have been formed, an acid site of the zeolitic framework is regenerated by a proton from

the alkene production. Therefore, the reaction in this mechanism occurs without the formation of a surface alkoxide species.

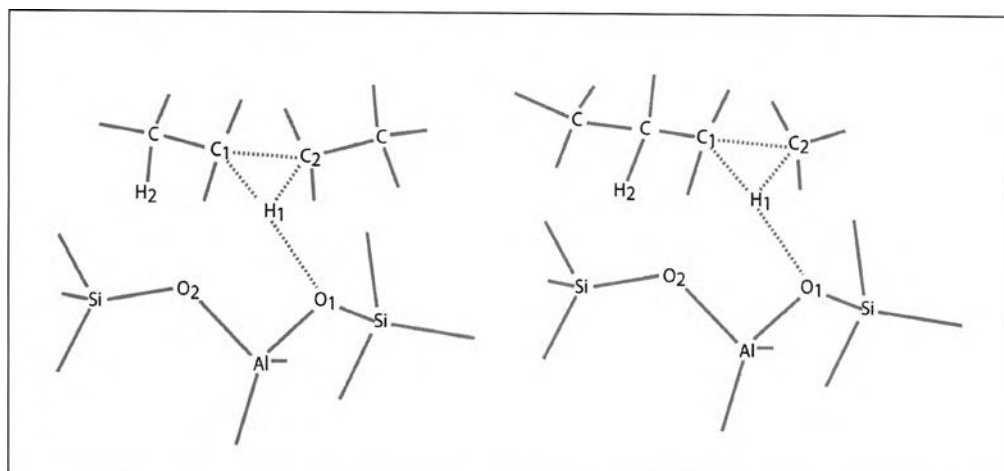


Figure 1.12 Schematic BLYP/3-21G* transition states for secondary and primary protolytic cracking of n-butane using a 3T cluster model for zeolite acid site [3]

Several theoretical calculations were carried out either by using a small cluster model, but with high level of methods and basis set, or by using large cluster models or periodic model but with intermediate level of methods and basis set to represent a particular zeolite framework. For example, the study on the protolytic cracking reactions of alkanes which was reported by Rigby *et al.* were performed using MP2/6-31G(d)//HF/3-21G with a 3T cluster model [8]. The authors calculated activation energies (relative to the adsorbed reactant rather than the gas phase species) for ethane, propane, and n-butane and reported values of 78, 68, and 67 kcal/mol, respectively. They concluded that the activation energy for n-alkane cracking is independent of chain length [2]. To study the long range effect of the zeolite lattice Zygmunt *et al.* performed single-point calculations on 18T, 28T, 38T, 46T, and 58T cluster models by using optimized geometries of the adsorbed and TS complexes in the 5T cluster obtained from HF/6-31G(d) [9]. In addition, the correction of apparent activation energy of ethane cracking was obtained by calculated the electron correlation and extended basis set effects at the B3LYP/6-311+G(3df,2p) and MP2-(FC)/6-311+G(3df,2p) level. This study identified the long-range stabilizing effect of the zeolite

lattice as the most important reason for the large discrepancies between earlier theoretical and experimental activation energies.

1.6 Research Objective

Theoretical studies were performed to describe the mechanisms of proton exchange and the degradation reactions (cracking and dehydrogenation reactions) of light alkanes such as ethane, propane, n-butane, and i-butane in ZSM-5. The result could be used as a model for larger alkanes.

In this dissertation, we focused on protonated intermediates that are possible to convert to the transition state of proton exchange, cracking or dehydrogenation reactions. The relationship between reaction barriers and transition state structures in each reaction are studied. The cluster models and periodic structure are employed for the calculations. Cluster models consist of 5T, 20T, 28T, 38T, and 96T that are taken from the crystal lattice of ZSM-5. The cluster-size effect to adsorption energies and apparent reaction barriers was studied and explained by the density functional calculations using DMol3 program mounted on MS Modeling 5.0 package of Accelrys Inc. The relative between the chain length of the hydrocarbon and carbon atom position of alkanes (primary, secondary and tertiary carbon) with the reaction barrier was considered.