CHAPTER I

INTRODUCTION

1.1 Research Rationale

Zeolite is one of the most important molecular sieves and widely used as acid catalysts in industrial processes. The catalytically activated center in zeolite is Brønsted acid sites: Si-OH-Al. Progress in steering such reactions would be fueled by enhanced understanding of the mechanisms of those reactions in framework of zeolite, which can be provided by molecular modeling. Valuable information about energetic, structural, and spectroscopic properties of the Brønsted acid site can be obtained from quantum chemical modeling of hydroxyl groups in zeolite. Due to zeolite has several hundred atoms per unit cell, so that the use of this complicated method is computationally very expensive. For that reason, an important issue in modeling zeolite electronic structures is how to represent the extend nature of zeolite with tractable calculations. Modeling active site of zeolite with relatively small cluster makes it possible to calculate the properties of zeolite framework. The cluster models that used in numerous computational researches of zeolite are 3T and 5T cluster models.

Industrially, pinacol rearrangement reaction in large-scale process uses strong acid catalysts such as H_2SO_4, H_3PO_4 or $AlCl_3$. The reaction would be much cleaner and more environmentally friendly if the corrosive acids are replaced by solid catalyst. The study of pinacol rearrangement reactions in metal-substituted molecular sieves has been reported by Hsu and Cheng [1] who found that among the first row transition metal elements substituted in aluminophosphate crystal structure, Fe, Cu and Ni was the three that gave the highest pinacol conversion and pinacolone selectivity. Few years later Cheng et al. [2] studied on Fe-substituted in the framework of several molecular sieves such as aluminophosphate, zeolite ZSM-5 and zeolite of mesopores and found that Fe-substituted was the active center for pinacol rearrangement reaction. Therefore in the present study, the catalytic behavior of pinacol rearrangement using acid-catalyzed system, ZSM-5 and metal substituted in framework of ZSM-5 have been theoretically investigated by using density functional method.

1.2 Pinacol Rearrangement

Carbon skeletal rearrangement reactions are very powerful synthetic tools to construct new carbon frames, and many reactions have been developed so far. Among them, pinacol rearrangement is one of the oldest known transformations of the carbon skeleton. The pinacol rearrangement is a typical 1,2-rearrangement reaction of vicinal diols under acidic condition. The pinacol (2,3-dimethyl-2,3-butanediol) is symmetrical diol, therefore each hydroxyl group of pinacol can be protonated with equal probability. When pinacol is lost the protonated hydroxyl group, 1,2-methyl shift would generate to form more stable carbocation. The new cation is simply the conjugate acid of the ketone pinacolone (3,3-dimethyl-2-butanone), which is product of the rearrangement catalyzed by proton transfer, as shown in Figure 1.1. Each step in this rearrangement is potentially reversible. Similar reactions, include different leaving groups and substitutents, are generally called pinacol rearrangement. The pinacol rearrangement is still interesting and important reaction in organic synthesis because it is a valuable process for preparing aldehydes and ketones.
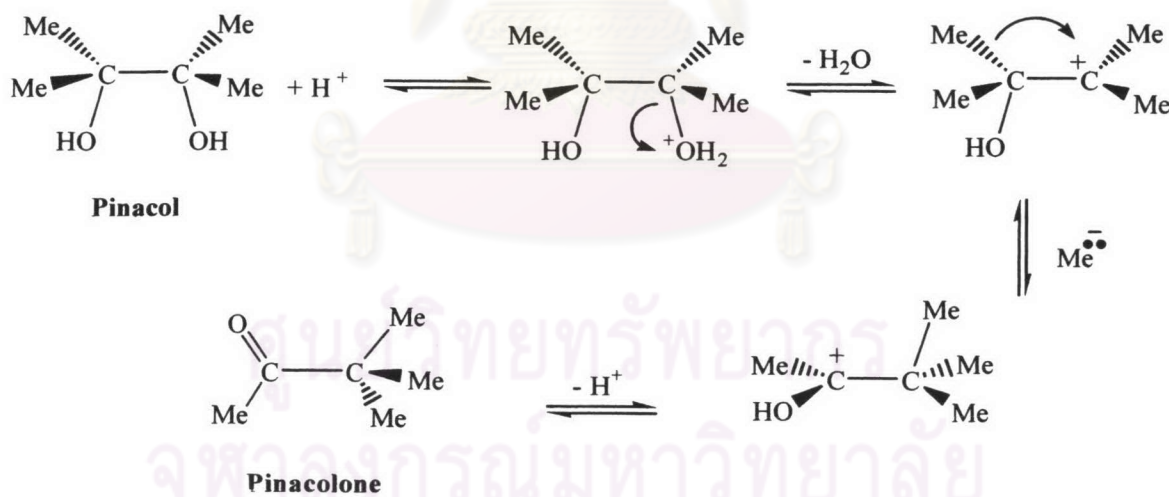

Figure 1.1 Pinacol rearrangement of pinacol to pinacolone.

There are two possible reaction pathways for the pinacol rearrangement. One is the stepwise mechanism via a carbonium ion intermediate, and the other is the concerted mechanism where migration and elimination occur simultaneously, as shown in Figure 1.2.
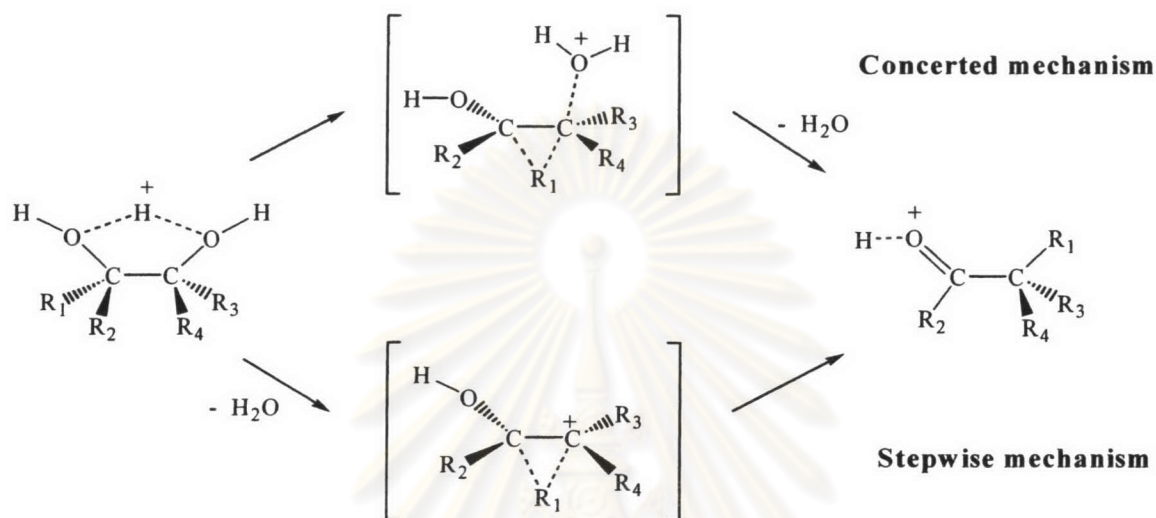

Figure 1.2 Pinacol rearrangement mechanism and 1, 2-elimination mechanism *[3]*.

The rearrangements of many reactions involve not only the stepwise but also the concerted mechanism. Nakamura and Osamura *[3]*, who studied the reaction mechanism and migratory aptitude of the pinacol rearrangement in the gas-phase calculation, stated that overall activation energy for the stepwise mechanism was higher than that of the concerted mechanism. This signifies that concerted mechanism is more favorable mechanism. Their results were in good agreement with experimental results for pinacol reactions in gas-phase and nonpolar solution. The effect of various acids at different concentrations on the pinacol rearrangement was investigated by Lezaeta *et al.* *[4]*. They presented that the pinacolone was the principle product and its relative yield decreased when the acid concentration was lowered. The pinacol rearrangement process was also carried out using different acid catalysts such as silica-alumina, zeolite, silicoaluminophosphates and perfluorinate resinsulfonic acids *[5-7]*.

The pinacol rearrangement of asymmetric diol is given more than one product because each protonated hydroxyl groups are not identical. For example, when propylene glycol is protonated, two possible geometries of protonated propylene glycol are found. The first geometry generates the primary carbocation and the other geometry generates the secondary carbocation, as shown in Figure 1.3.
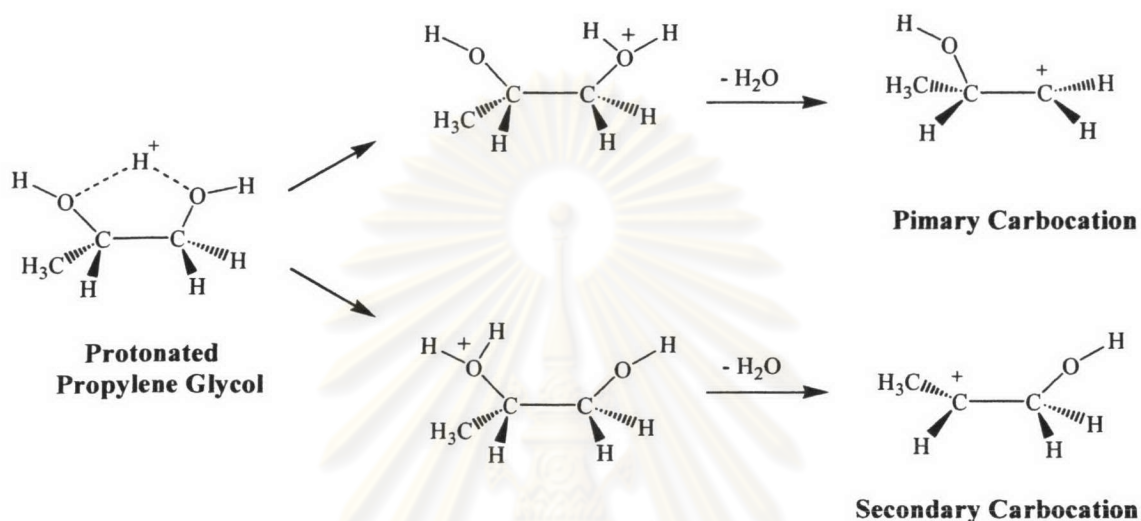

Figure 1.3 Dehydration pathways of protonated propylene glycol.

The dehydration is favored on the substituted carbon because the produced carbocation is stabilized by electron delocalization from the substitute group. The pinacol rearrangements of asymmetric diol have been studied in several conditions such as sulfuric acid, $AlCl_3$ and heteropoly acid [8-10]. The reaction mechanism and migratory aptitude of the pinacol rearrangement were theoretically examined for monosubstituted protonated 1, 2-ethanediols using RHF/6-31G method by Nakamura and Osamura [3]. They found that there were three possible reaction pathways for the concerted 1, 2-shift reactions of monosubstituted 1, 2-ethanediol. The three possible reaction pathways for pinacol rearrangement of propylene glycol are shown in Figure 1.4. In present work, the pinacol rearrangements of pinacol and propylene glycol at acid catalyzed models have been theoretically investigated by density functional method. The product compositions of various acid-catalyzed models have been evaluated in order to get more understanding of the effect of the hydration water on the reaction products.
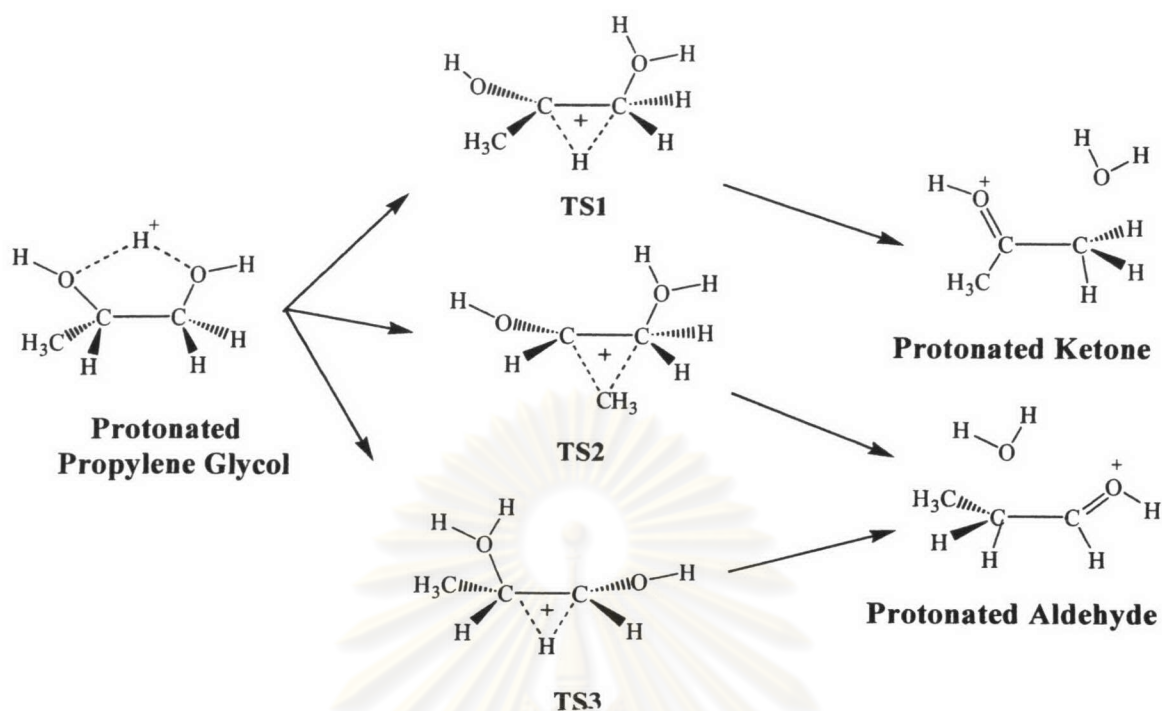
Figure 1.4 Three possible reaction pathways for pinacol rearrangement of propylene glycol.

1.3 Metal Substituted Molecular Sieve

A molecular sieve is a material with selective adsorption properties capable of separating components of a mixture on the basis of a difference in molecular size and shape. The main application of molecular sieve catalysts in the fields of chemical synthesis is based on the shape selective catalytic properties introduced by their structure *[11]*. It is widely recognized that intermediate chemical interaction of the reactants with certain groups of atoms of a catalyst plays a key role in the mechanism of chemical catalysis. Such groups of atoms are usually referred to as active sites. Detection of active sites, study of their formation, structure and chemical properties become one of the main objectives for fundamental research in catalysis. In this work, the study of metal substituted molecular sieve is focused on active site of metal substituted in zeolite framework. A brief introduction to zeolite is given in the following.

1.3.1 Zeolite

Zeolites are crystalline, hydrated aluminosilicates. Structurally, zeolites are framework of aluminosilicates, which are based on an infinitely extending three-dimensional network of tetrahedral aluminate (AlO_4^{5-}) and silicate (SiO_4^{4-}) linked to each other by sharing oxygen atoms at corner of each tetrahedral as shown in Figure 1.5.
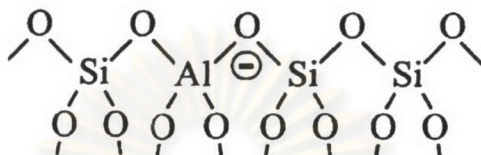
Figure 1.5 The general structure of zeolite *[12]*.

It is evident from this building principle that the net formulas of the tetrahedral are SiO_2 and AlO_2^- which mean that one negative charge resides at each tetrahedron in the framework that has aluminum in its center. The framework of a zeolite contains channels, channel intersections and /or cages with dimensions from 0.2 to 1 mm. The chemical composition of a zeolite can hence be represented by a formula of the type

$$A_{y/m}^{m+}[(SiO_2)_x \cdot (AlO_2^-)_y] \cdot zH_2O \qquad (1.1)$$

where A is a cation with the charge m, symbols x and y are the number of tetrahedral silicate and aluminate, respectively, and the last one, z is the number of water molecules in the channels and cavities of zeolites. The number of tetrahedral per crystallographic unit cell equals $x+y$ and x/y is the so-called framework silicon/aluminum ration, n_{Si}/n_{Ai} of simply Si/Al. Silicon and aluminum in aluminosilicate zeolites are referred to as the T-atoms. All zeolites are constructed from a common subunit of structure so call primary building unit of silicate or aluminate tetrahedral. These tetrahedra are linked together by corner sharing of Si or Al atoms in various ways, forming a secondary building unit. There are nine such building units, which can be used to describe all of the known zeolite structures. There consist of 4,6 and 8 member single rings, 4-4, 6-6 and 8-8 member double rings, and 4-1, 5-1 and 4-4=1 branched rings. Some topologies of these units are shown in Figure 1.6.
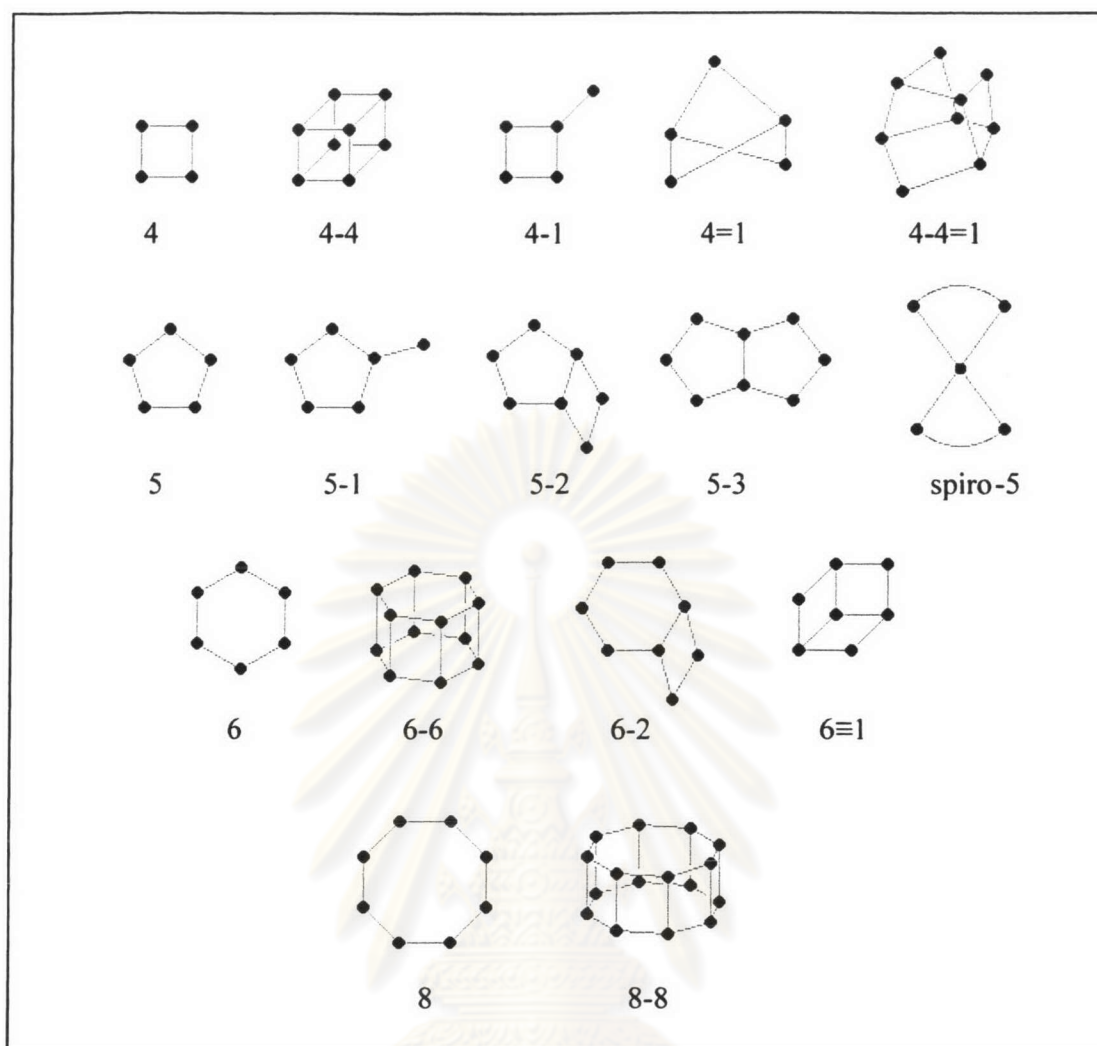
Figure 1.6 Secondary building units in zeolites. The corners of the polyhedra represent tetrahedral atoms (Si or Al) and the oxygen atoms are located towards the mid-points of the lines joining each tetrahedral atom (the oxygen atoms are not shown to aid clarity).

The T-O-T linkages form pores of uniform diameter and enclose regular internal cavities and channels of different size and shapes, depending on the chemical composition and the crystal structure of the specific zeolite involved. The structures of four selected zeolites along with their respective void systems and pore dimensions are shown in Figure 1.7. In these representations, the T-atoms are located at the vertices, and the lines connecting them stand for T-O-T bonds. For example, if 24 tetrahedra are linked together as the cubo-octahedron, they would refer as a sodalite unit or β-cage, shown in the top of Figure 1.7. If the sodalite units are connected via

their hexagonal faces, the structure of the mineral faujasite is resulted. It is identical with the structures of the synthetic zeolites X and Y. An example of a zeolite with unidimensional, 12-membered-ring pores is zeolite ZSM-12. Its pores are slightly elliptical with dimensions of 0.57x 0.61 nm. Zeolite ZSM-5 and its all silica analogue silivalite-1 are built from the pentasil unit. They contain intersecting systems of ten-member-ring pores, one being straight and one sinusoidal. ZSM-5 is an example of a zeolite which has gained huge important in heterogeneous catalysis. It is used in petrochemical industry for the catalytic cracking of hydrocarbons and it is often looked upon as the prototype of shape selective catalysts. Several zeolites with unidimensional, ten-member-ring pores exist as well, one example being Theta-1 which is isostructural to zeolite ZSM-22.
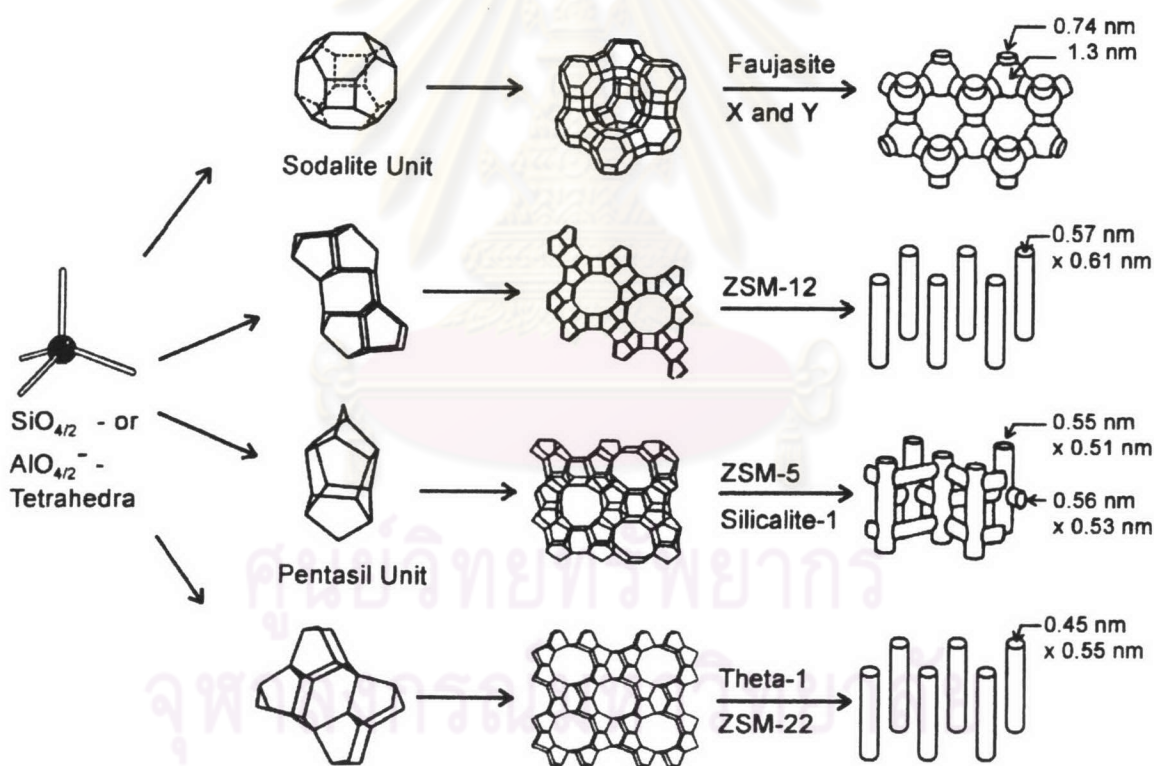

Figure 1.7 Structures of four selected zeolites (from top to bottom: faujasite or zeolites X, Y; zeolite ZSM-12; zeolite ZSM-5 or silicalite-1; zeolite Theta-1 or ZSM-22) and their micropore systems and dimensions *[13].*

1.3.2 Zeolite ZSM-5

The ZSM-5 is first synthesized by the oil company 'Mobil', which is abbreviated from Zeolite Socony Mobil-Five, in 1972 with the structure code 'MFI'. The tetrahedra of ZSM-5 are linked to form the pentasil unit which consists of five oxygen atoms in its structure. The name pentasil is therefore used for describing this unit type. The ZSM-5 is a medium pore zeolite and has two types of intersection channel which both formed by 10-membered oxygen rings. The first channel is straight and elliptical channel (0.51 x 0.56 nm), in cross section. The second channel is sinusoidal (zigzag) and circular channel (0.54x 0.56 nm), in cross section. The chemical formula of a typical unit of hydrated Na-ZSM-5 is

$$Na_n[Al_nSi_{96-n}O_{192} \cdot 16H_2O], \; n < 27 \qquad (1.2)$$
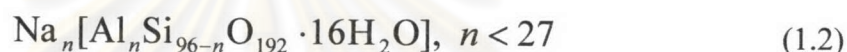
There seem to be a limit on the Al incorporation in the ZSM-5 framework. The lowest Si/Al ratio known in the ZSM-5 framework is 10. Pairs of AlO_4^- tetrahedra are forbidden by the Löewenstein's rule which precludes that two contiguous tetrahedra contain aluminum on tetrahedral positions are forbidden [13].

Elliptical channels
(0.51 x 0.56 nm.)

Near circular channels
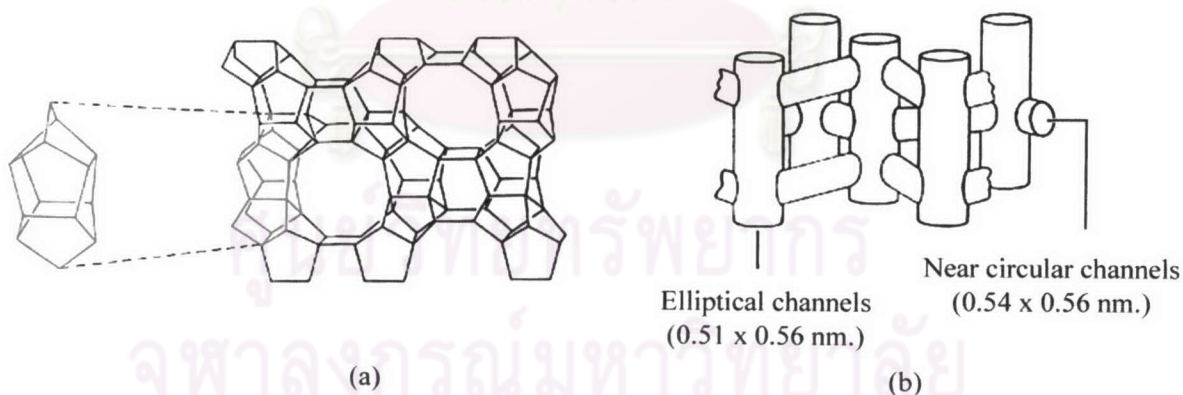(0.54 x 0.56 nm.)

(a)   (b)

Figure 1.8 Schematic illustration of the three-dimension channels in ZSM-5: (a) A pentasil unit (in colour) together with a slice of a structure of ZSM-5 and (b) the interconnecting channel systems in ZSM-5.

Zeolite ZSM-5 is one of the most efficient molecular sieve catalysts in a number of chemical processes *[14-17]*. The catalytic activity of ZSM-5 is associated with different active sites such as: Brønsted acid sites, Lewis acid sites, metal ions in cationic positions, transition metal ions in zeolite lattice positions, extra-lattice transition metal compounds in channels and cavities of a zeolite and metal particles in zeolite cavities *[18]*. The comprehensive application of ZSM-5 regarding to their basis properties can be categorized in three groups.

A. Shape Selectivity Properties of Zeolite ZSM-5

The shape selectivity of the zeolite means that both the pore dimension and catalytic sites residing inside the channels are used to control the selectivity of the product. The ZSM-5 is known as molecular sieve, a very important role in zeolite catalyst, since it allows the adsorption molecular of certain dimensions while refuses those of larger dimensions. Based on the observations of the reactions, three types of shape selectivity models have been proposed to rationalize the observed phenomena in reactions catalyzed by zeolite catalysts: reactant-shape selectivity, product-shape selectivity and transition state-shape selectivity.

i) Reactant Shape Selectivity

Reactant-shape selectivity refers to the selectivity occurring because of the different sizes of the reactants; when a mixture of at least two reactants with different sizes is fed into the zeolite molecular dimensions. The larger reactants cannot enter the zeolite pores and reach most of the active sites in the channel. Those banned bulkier reactants may contact external active sites to finish the conversion or leave the zeolite molecular dimensions without being converted to the products.

ii) Product Shape Selectivity

In product shape selectivity, all reactants are so small that they all can enter into the channels of the zeolite, where they may form isomers with different sizes inside the channels because the dimensions at the intersections are often larger than the pore openings. But only those species that are smaller than pore openings can escape from the channels of the zeolite and join the reaction mixture; the bulkier species are unable to escape from the channel and are excluded from the reaction

mixture. The product-shape selectivity model was always used to explain the product distributions in the reaction of toluene alkylation with methanol over zeolite ZSM-5, the slimmer *p*-xylene, the main product, diffuses out of the channel 100-1000 times faster than the other two bulkier *o*–, and *m*–isomers.

iii) Transition State Shape Selectivity

Transition state shape selectivity is based on the intrinsic shape of the channels in the zeolite, not on the path length. The transition state selectivity depends on neither the reactant nor the product, but the certain reaction mechanism of transition state that occurs in the zeolite crystal size. For example there are two (parallel or consecutive) reactions. One reaction is going via a bulky transition state or intermediate which cannot be accommodated inside the zeolite pores, thus this reaction is entirely suppressed.
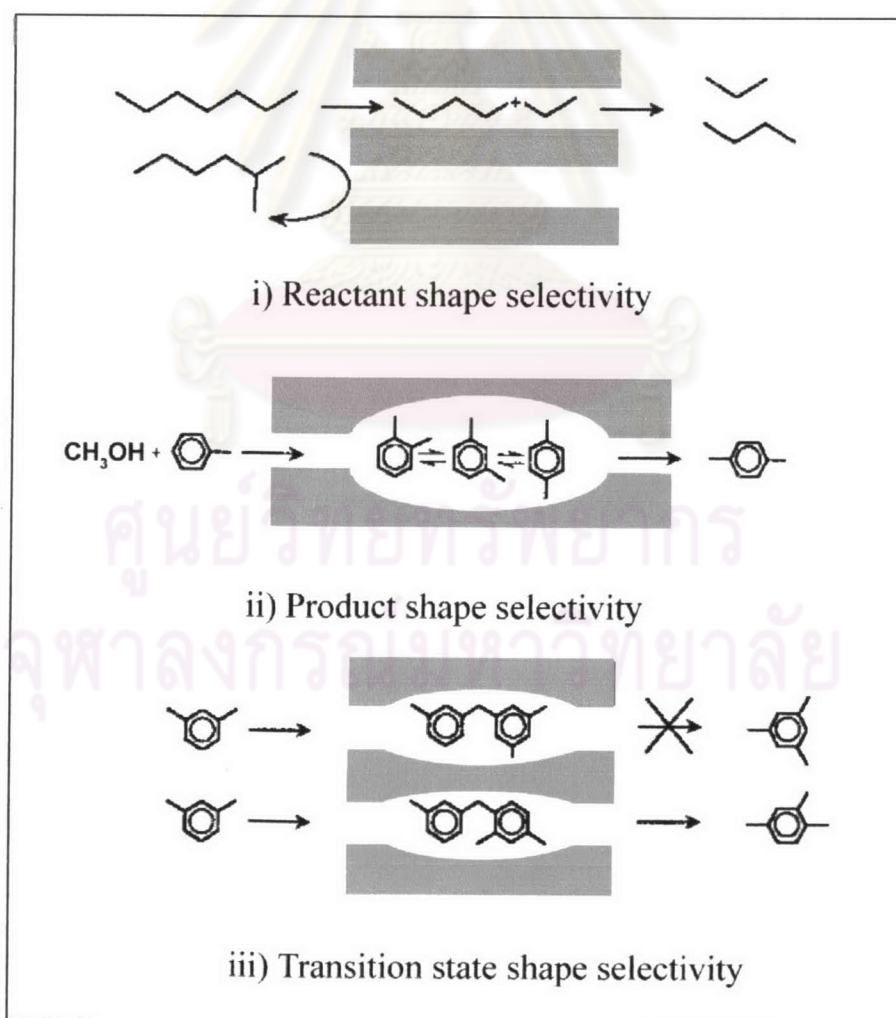

i) Reactant shape selectivity

ii) Product shape selectivity

iii) Transition state shape selectivity

Figure 1.9 Three types of shape selectivity in zeolite *[19]*.

B. Ion Exchange Properties of Zeolite ZSM-5

With their negatively charged porous framework and the small and mobile cations sitting in the pores, zeolites are typical ion exchangers. In fact, zeolites are widely used as builders in laundry detergents where their roles are to take up calcium and magnesium ions in exchange for sodium ions, thereby softening the washing water. The cation exchange behavior of zeolite depends upon several factors such as the nature of the cation species, the cation size, and cation charge, the concentration of the cation in solution, the anion species associated with the cation in solution, and the structural characteristic of the particular zeolite. Zeolite structures have unique feature that lead to unusual type of cation selectivity and sieving.

C. Acid Sites of Zeolite ZSM-5

Acidic zeolites catalyze a wide variety of chemical reactions making them very valuable in a variety of industrial processes. The acidic catalytic activity, which often associated with Brønsted acid sites, comes from the fact that zeolite systems in their protonic form have a hydroxyl group bridge in between an aluminum and a silicon atom, the -Al(OH)Si- group [20-22]. The cluster of the Brønsted acid sites in ZSM-5 model by using $H_3SiOAlH_2OSiH_3^-$, referred as Z^-, and the protonated form $H_3SiOAlH_2O(H)SiH_3$, referred as ZH. These are designated in the literature as 3T cluster because of the presence of three tetrahedral (Si and Al) atoms, as shown in Figure 1.10.
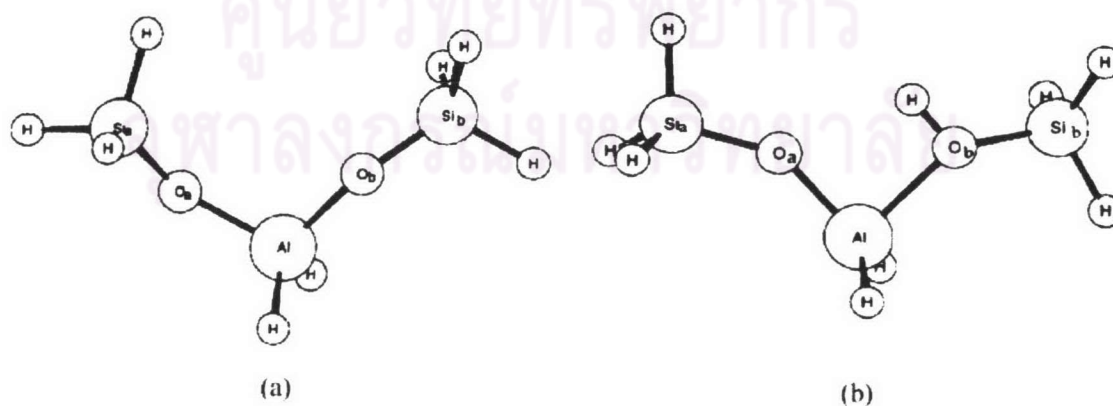

(a)   (b)

Figure 1.10 Structure of (a) Z^- and (b) ZH [23].

Lewis acidity is defined as electron acceptor acidity. An example is trigonally coordinated aluminum atom. If aluminum hydroxide has an unsaturated coordinate (fewer bonds than aluminum would like to have), the aluminum would readily accept electrons from other molecules in order to increase its coordination to tetrahedral or octahedral resulting in a Lewis acid site.
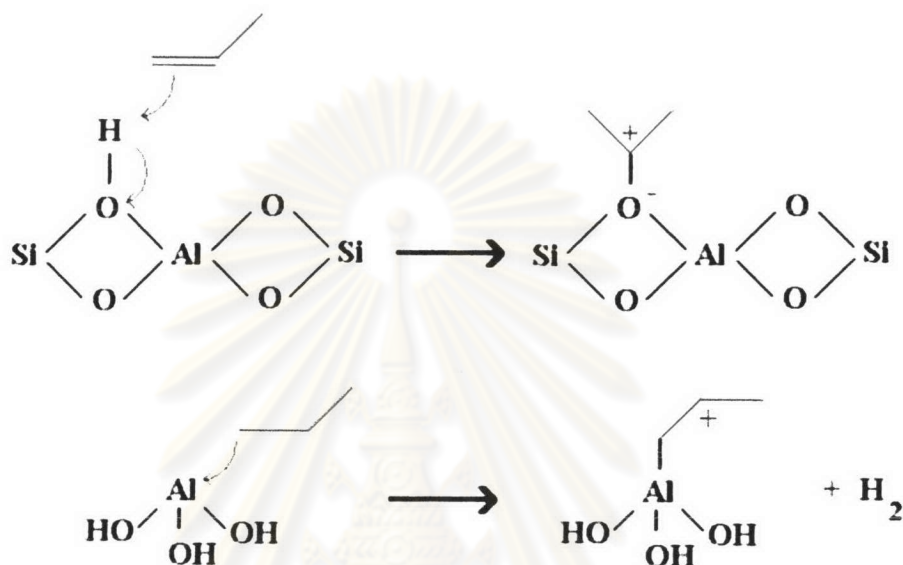

Figure 1.11 Schematic of Brønsted and Lewis acidities in a zeolite. The top reaction illustrates the adsorption of propylene on a Brønsted acid site, while the bottom reaction shows the adsorption of propane on an extraframework Lewis acid site *[24]*.

1.3.3 Metal Substituted in Zeolite ZSM-5

Although ZSM-5 catalysts are most commonly discussed in the context of chemical technologies, there is increasing interest in using zeolites for the synthesis of fine chemicals. Proton-exchanged zeolites present high acidity, so they are commonly used in acid-catalyzed reactions such as double bond migration, aldol condensation or pinacol rearrangement *[25-26]*. Many efforts have devoted to the synthesis, characterization and application of the isomorphously substituted zeolite with elements in their framework other than Si and Al, such as B, Ga, Fe, Ti or Zn *[27-30]*. Incorporation of heteroatoms can change the acidity and pore structure of zeolites and the modified zeolites have altered catalytic activity, selectivity and stability *[31]*.

This offers the potential to design zeolites for novel applications. Among the transition metal elements, Fe and Cu are two most interested metals that are substituted into the framework of zeolite especially zeolite ZSM-5. For example, Fe-ZSM-5 is an active catalyst for the oxidations of methane to methanol [32] and benzene to phenol [33-35], reduction of NO_x [36], nitrous oxide decomposition [37], oxidative dehydration [38], and phenol hydroxylation [39]. Copper substituted in the framework of zeolite ZSM-5, namely Cu-ZSM-5, has been recognized as highly efficient catalyst in selective reduction nitrogen oxides [40-41]. The density functional study of the interactions of Cu-ZSM-5 with NO_x, H_2O and SO_2 [42-43] is reported by using Cu-3T model which is a structure that has one tetragonal Al, two tetrahedral Si atoms and Cu atom is set on bridge between two oxygen atoms as shown in Figure 1.12a. The 3T model is also used in the theoretical study of methane and benzene hydroxylation in Fe-ZSM-5 zeolite [32, 34, 44]. The reaction intermediate structure for the direct methane hydroxylation on α-oxygen model of Fe-ZSM-5 zeolite is shown in Figure 1.12b.
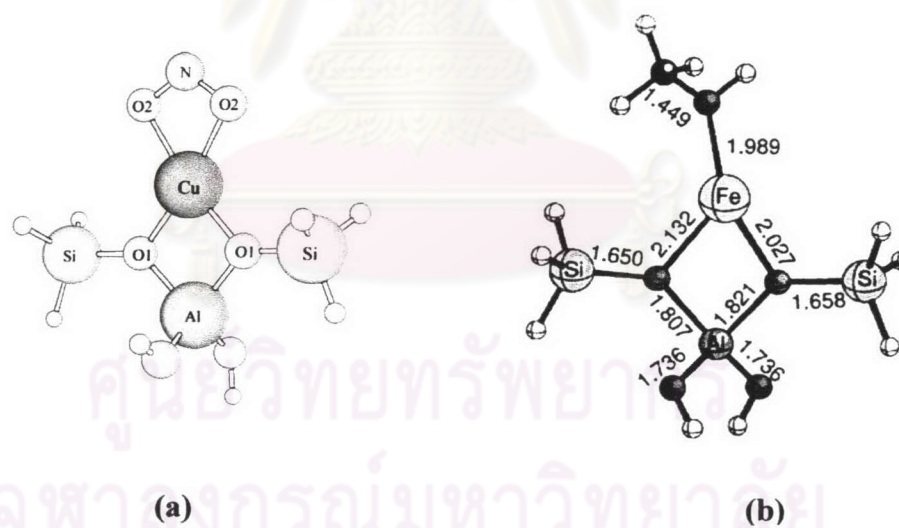

(a)   (b)

Figure 1.12 Representation of (a) the NO_2-Cu-3T molecular structures [42], and (b) the CH_3CH-Fe-3T [32]. Bond lengths are in angstroms.

1.4 Literature Review

Nakamura *et al.* (1993) *[3]* examined the reaction pathways of the pinacol rearrangement for some monosubstituted protonated 1,2-ethanediols by means of ab initio SCF MO methods. The relative activation energies were evaluated for both stepwise and concerted pathways. Gas-phase calculations were shown that the concerted mechanism dominated over the traditionally supported stepwise mechanism via a carbonium ion intermediate. These results agreed well with experiments in the gas phase and in aprotic solvents.

Hsu and cheng (1998) *[1]* found that pinacol rearrangement proceeds at relatively mild temperature over metal-substituted aluminophosphate molecular sieves. The conversion of pinacol and the selectivity of the product were found to influence by the metal species. Fe(III), Cu(II) and Ni(II) in order were the three which gave the highest pinacol conversion and pinacolone selectivity. The catalytic activity was found to have no direct correlation with the acid strength and amount of the acid site on the catalysts. The mechanism involving the redox ability of Fe(III) and its stabilization of the carbonium ion intermediates is proposed.

Kita *et al.* (1998) *[45]* publicized an efficient pinacol rearrangement by trialkyl orthoformate. The reactions of various types of diols with a catalytic amount of a Lewis acid in the presence of an ortho ester afforded the rearranged product in good yields via a cyclic ortho ester intermediate. The combined system was applicable not only to cyclic and acyclic tri- and tetra-substituted diols but also to the diols having acid-sensitive acetals.

Cheng *et al.* (2002) *[2]* studied on pinacol-type rearrangement reactions in toluene which were catalyzed by iron-substituted molecular sieves of different porous structures, including AlPO4-5, ZSM-5 of micropores and MCM-41 of mesopores. Iron(III)-substituted in the framework of the molecular sieves was found to be the active center for pinacol rearrangement reaction and catalytic activity was found to have no correlation with the acidity. Ten vicinal diol reactants with various alkyl or aryl substitutions were examined. The migrating preference of the substitution groups was dependent on the catalysts and the migration attitude was different from that observed on acid-catalyzed reactions.

Smith (2002) *[46]* proposed two possible mechanisms for rearrangement of ethylene glycol to acetaldehyde. Density functional theory at the 6-31G(d) level had been applied to answer the question of whether the pinacol rearrangement of ethylene glycol proceeds through a dehydration to enol the forming acetaldehyde or by a concerted migration of hydride with loss of water. The result was shown that the latter process had activation energy lower than the route through the enol intermediate.

Dai *et al.* (2004) *[47]* carried out the dehydration of propylene glycol in near-critical water to study the reactivity of diol under high temperature and pressure. The investigation of reaction mechanism indicated that there were two mechanisms, pinacol rearrangement and elimination mechanisms, to be possible in the dehydration of propylene glycol.

Pachuau *et al.* (2004) *[48]* used the semi- empirical PM3 SCF-MO method to investigate the Wagner–Meerwein migration of various groups during the pinacol-pinacolone rearrangement of some acyclic systems. The 1,2-migration was found to involve a three-centered moiety in the cationic transition state. The structures of the migratory groups in the transition state and migratory aptitude were reported.

Yoshizawa *et al.* (2000) *[32]* analyzed reaction pathways and energies for the direct methane-methanol and benzene-phenol conversions that occurred on the surface of Fe-ZSM-5 zeolite by using DFT computations. Reasonable model for "α-oxygen", a surface oxygen species responsible for the catalytic reactivities of Fe-ZSM-5 zeolite was proposed. The concerted reaction pathway for the methane (benzene) hydroxylation involved an H atom abstraction and a methyl (phenyl) migration at the iron active center.

Sierraalta *et al.* (2005) *[42]* reported theoretical calculations of the interaction of H_2O, SO_2, O_2, NO_2 and NO with copper-exchanged zeolite (Cu-ZSM-5) using ab initio density functional theory. The active site of the Cu-ZSM-5 catalyst was modeled by a Cu–3T site of zeolite.

1.5 Overall Objective

The aim of this study is to investigate mechanism of pinacol rearrangement of the propylene glycol and the pinacol conversions in acid-catalyst system, zeolite HZSM-5 and its metal-substituted catalysts using density functional theory at B3LYP/6-31G(d) level of theory. The energetic barriers and thermodynamic quantities of all related reactions have been computed at the same level of theory. All mechanisms of the pinacol rearrangements of the propylene glycol and pinacol conversions in different catalytic systems have been proposed.