CHAPTER III

DETAIL OF THE CALCULATION

All calculations were performed with the Gaussian 03 program. The Molden 4.2 program was utilized to display molecular structures and observe the geometry convergence via the Gaussian output files. The molecular graphics of all species were generated with the Molekel 4.3 program.

The standard enthalpy ΔH^O and Gibbs free energy changes ΔG^O of conversion reactions of this system have been derived from the frequency calculations. Each reaction entropy ΔS^O was calculated using a thermodynamic relation of $\Delta S^O = (\Delta H^O - \Delta G^O)/T$. The rate constant $k(T)$ derived from transition state theory was computed from activation free energy, $\Delta^{\ddagger}G^O$ by

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

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.

The multi-transition-state system introduced by Adam *et al.* [53] was extended for the Curtin-Hammett principle which is the two competitive transition states. The reaction scheme of Pinacol rearrangement of propylene glycol, which is a tri-transition-state system, is shown in Figure 3.1. According to transition state theory, the rate constant for each individual reaction i is given in equation 3.1.

$$k_i(T) = \frac{k_B T}{hc^o} \exp(-\Delta^{\ddagger}G_i^O/RT) \qquad (3.2)$$

where $\Delta^{\ddagger}G_i^O = G_i^{TS,O} - G_o^O$, i is the rank of reaction paths (i = 1, 2 and 3) and $G_i^{TS,O}$ and G_o^O are Gibbs free energies of transition state and corresponding reactant, respectively.

As transition states TS1 and TS2 step forward to product protonated propanal (HPPNL$^+$) and TS3 to product protonated propanone (HPPNE$^+$), the product ratio of [HPPNL$^+$] to [HPPNE$^+$] is therefore equivalent to the ratio of the sums of all ground-state population of reactants P_o and its corresponding rate constants forward to product [HPPNL$^+$] to sum for [HPPNE$^+$]. Therefore, the [HPPNL$^+$] to [HPPNE$^+$] ratio can be given by equation 3.3.

$$\frac{[\text{HPPNL}^+]}{[\text{HPPNE}^+]} = \frac{P_o k_1 + P_o k_2}{P_o k_3} = \frac{k_1 + k_2}{k_3}$$

$$= \frac{\sum_{i=1}^{2} \exp(-\Delta^{\ddagger} G_i^O / RT)}{\exp(-\Delta^{\ddagger} G_3^O / RT)} = \frac{\exp(-\Delta^{\ddagger} G_1^O / RT) + \exp(-\Delta^{\ddagger} G_2^O / RT)}{\exp(-\Delta^{\ddagger} G_3^O / RT)} \quad (3.3)$$

Where k_1, k_2 and k_3 are forward rate constants of reaction pathways 1, 2 and 3, respectively as shown in Figure 3.1.
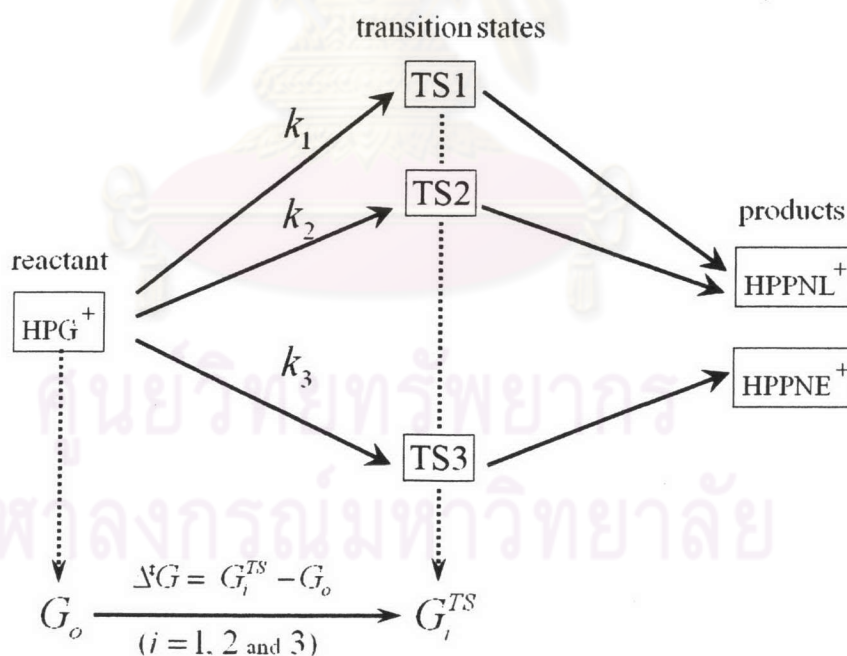

Figure 3.1 Tri-transition-state reaction for the formation of the two products of HPPNL$^+$ and HPPNE$^+$.

As mentioned in chapter I, this work is centered on the density functional theory study of pinacol rearrangement reaction which catalyzed by several catalysts. Thus in this work, the study is divided into three sections for acid catalyst, zeolite catalyst and metal-substituted molecular sieves.

3.1 Acid Catalyzed Reaction

For pinacol rearrangement of pinacol and propylene glycol in acid catalyst, full geometry optimizations were computed by density functional theory. Density functional calculations have been performed with the Becke's three parameters hybrid density function using the Lee, Yang and Parr correlation functional (B3LYP). All geometry optimizations have been carried out used the hybrid density functional B3LYP with the 6-31G(d) basis set. The energies of the B3LYP/6-31G(d) optimized-geometries have been calculated with the zero-point energy corrections. The B3LYP/6-31G(d,p) and B3LYP/6-311G(d,p) levels of theory were employed for the single point calculations of the B3LYP/6-31G(d) optimized-geometries of involved species in acid catalyst. The transition states were confirmed by one imaginary frequency. The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding minimum.

Figure 3.2 Structure of (a) propylene glycol and (b) pinacol.

In this section two reactants were investigated, pinacol and propylene glycol, see Figure 3.2. For pinacol rearrangement of propylene glycol, four acid-catalyzed models with respect to the increased numbers of hydration water were investigated for the effect of hydration water to product compositions. Model I is an acid-catalyzed model of a gas-phase system which is composed of one proton as acid catalytic atom without hydration water except dehydration water which is released from the reaction. Model II is an acid-catalyzed model of which the reactant is protonated by a single

proton of which the molecule is hydrated by one water molecule. Models III and IV are acid-catalyzed models of which protonated species are hydrated by two and three water molecules, respectively. The product ratios of these two products are calculated by equation 3.3.

For pinacol rearrangement of pinacol in acid catalyst, the structure geometries were calculated only in nohydration system, because the reaction has only one reaction pathway, while pinacol rearrangement of propylene glycol has three reaction pathways.

3.2 Zeolite HZSM-5 Catalyst

In this study, the zeolite models are represented by 3T and 5T cluster models. The simplest one, 3T cluster model [$H_3SiOAl(OH)_2OSiH_3$] consists of a three tetrahedral centers (3T = Al + 2Si). The other one is pentatetrahedral cluster [$(H_3SiO)_4Al$] [9]. The structures of 3T and 5T cluster models are shown in Figure 3.3.
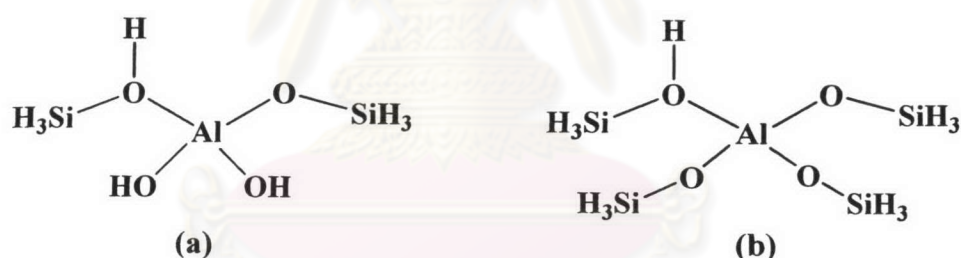

Figure 3.3 Cluster model of zeolite HZSM-5: (a) 3T and (b) 5T.

The structures and properties of pinacol rearrangement of both pinacol and propylene glycol over zeolite catalyst systems were calculated by density functional theory using 3T and 5T cluster models. Geometric optimizations and harmonic vibrational frequencies have been computed using the hybrid three-parameter B3LYP density functional approach and the 6-31G(d). The standard enthalpy, ΔH^o, and Gibbs free energy changes, ΔG^o, of conversion reactions of this system have been derived from the frequency calculations. The rate constants $k(T)$ derived from transition state theory were computed from activation free energy for each transition state, as the same as the acid catalyst.

3.3 Metal Substituted Molecular Sieve

In this section only pinacol in pinacol rearrangement was investigated. The structures and properties of pinacol rearrangement of pinacol to pinacolone over metal substituted molecular sieve catalyst systems, Fe- and Cu–ZSM-5 catalysts, were calculated by density functional theory. Geometry optimizations and harmonic vibrational frequencies have been computed using the 6-31G(d) basis set. The standard enthalpy ΔH^o and Gibbs free energy changes ΔG^o of conversion reactions of this system have been derived from the frequency calculations. The rate constants k(T) derived from transition state theory were computed from activation free energies.

Fe and Cu substituted in zeolite framework have been modeled by using 3T zeolite model because this model has been used widely in many research topics and given the good result for the theoretical calculation *[32, 34, 44]*. The Fe- and Cu- 3T models were consisted of an Al atom coupled through oxygen atoms to two Si atoms. The cluster model was terminated by two OH groups attached to the Al atom and three hydrogen atoms attach to each of the Si atoms. The Fe and Cu atoms were set on bridge between two oxygen atoms of 3T zeolite models, as shown in Figure 3.4.
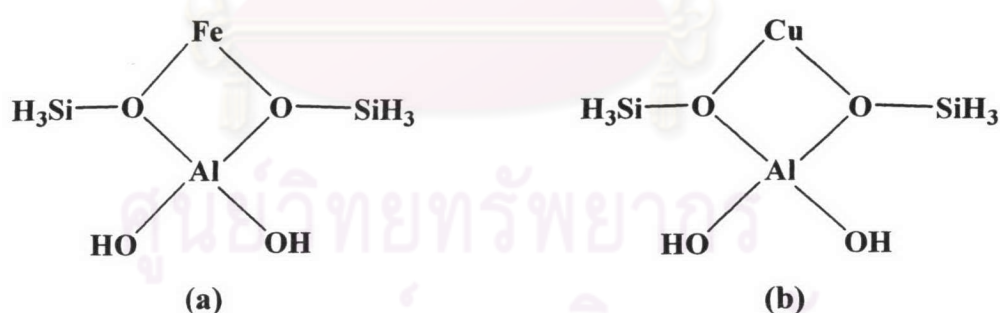

Figure 3.4 Fe- and Cu-ZSM-5 catalysts modeled by 3T zeolite model: (a) Fe-3T and (b) Cu-3T.

This study is considered the quintet spin state for Fe(II) substituted in zeolite ZSM-5 and doublet spin state for Cu(II), see details below
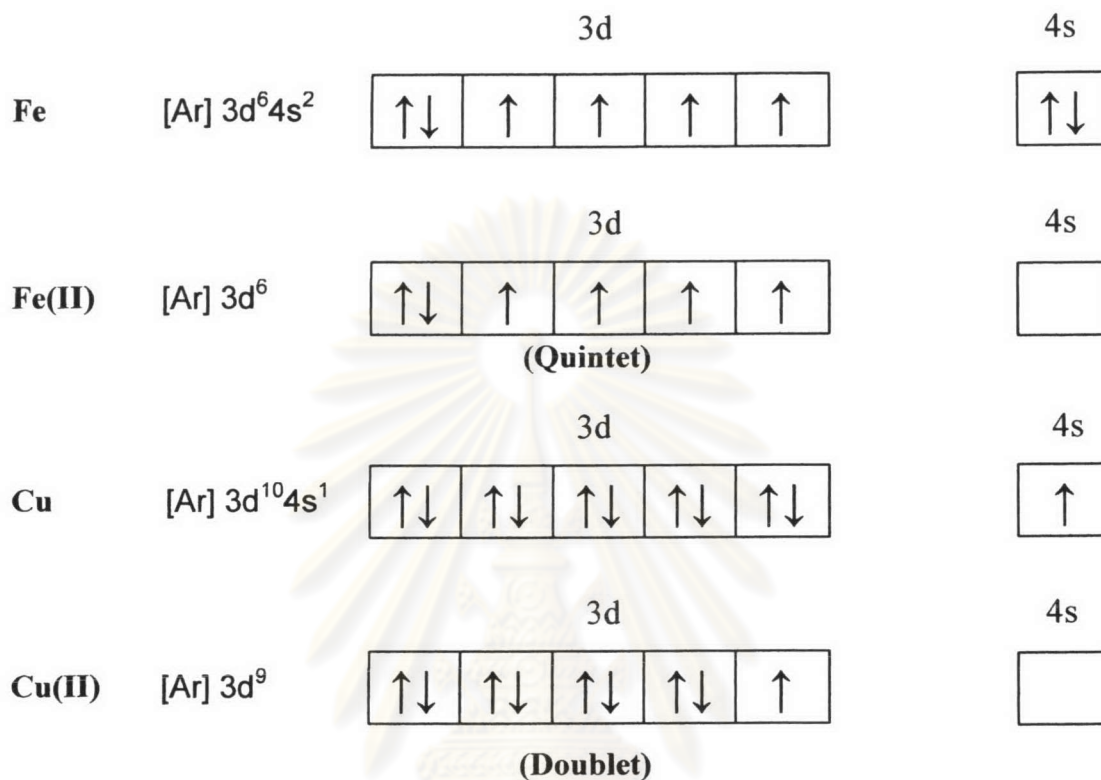

Figure 3.5 Spin orbital arrangement diagram of Fe(II) and Cu(II).