

CHAPTER V

CONCLUSION AND SUGGESTION

FOR FUTURE WORK

5.1 Propylene Glycol Conversion

5.1.1 Propylene Glycol: Acid Catalyzed Reaction

Reaction mechanisms of propylene glycol (PG) conversion to propanal (PPNL) and propanone (PPNE) of various acid-catalyzed water-addition models of three concerted pathways are investigated using the protonated forms of propylene glycol (HPG^+), propanal (HPPNL^+) and propanone (HPPNE^+). The zero point energies and thermodynamic quantities of activation steps are obtained at B3LYP/6-31G(d) level of theory. The three concerted pathways C2H, C1Me and C1H via transition states TS1 and TS2, and TS3 have produced the products HPPNL^+ and HPPNE^+ , respectively. The percent ratios of product HPPNL^+ to HPPNE^+ based on models I, II, III and IV are [99.88]:[0.12], [99.81]:[0.19], [89.01]:[10.99] and [46.59]:[53.41], respectively.

5.1.2 Propylene Glycol: Zeolite HZSM-5 Catalyst

Reaction mechanism of propylene glycol in pinacol rearrangement over zeolite catalyst is investigated using DFT method at B3LYP/6-31G(d) level of theory and modeling the zeolite with 3T and 5T cluster models. The relative energies of all involved species in the rearrangement reaction and their thermodynamic quantities are obtained. The three concerted pathways C2H, C1Me and C1H via transition states TS1 and TS2, and TS3 have produced the products PPNL^+ and HPPNE^+ , respectively. The orders of activation energy of pinacol rearrangement of propylene glycol over zeolite models are as $\text{TS2 (C1Me)} > \text{TS1 (C2H)} > \text{TS3 (C1H)}$. The percent ratios of product HPPNL^+ to HPPNE^+ based on 3T and 5T cluster models are [2.36]:[97.64] and [2.56]:[97.44], respectively. Thus, the main product of the pinacol rearrangement of propylene glycol over 3T and 5T cluster models is PPNE.

5.2 Pinacol Rearrangement

5.2.1 Pinacol: Acid Catalyzed Reaction

Reaction mechanism of pinacol (PC) conversion to pinacolone (PCL) in acid catalyzed is investigated using the protonated form of propylene glycol (HPC⁺), propanal (HPCL⁺). All structures of pinacol rearrangement reaction in acid catalyst are optimized using DFT at B3LYP/6-31G(d) level of theory. The zero point energies and thermodynamic quantities of activation steps are obtained and result that activation energy of pinacol rearrangement in acid catalyst is 14.13 kcal/mol.

5.2.2 Pinacol: Zeolite HZSM-5 Catalyst

The conversions of pinacol to pinacolone catalyzed by zeolite using 3T and 5T cluster model have been investigated using DFT method at B3LYP/6-31G(d) level of theory. The results with 3T and 5T cluster models are very similar. The overall activation thermodynamic quantities and rate constants of pinacol rearrangement are calculated and result that the activation energies of pinacol rearrangement over 3T and 5T cluster models are 31.31 and 31.99 kcal/mol, respectively.

5.2.3 Pinacol: Metal Substituted Molecular Sieve Catalyst

The reaction pathway and energies for the pinacol rearrangement over metal substituted molecular sieve catalysts, Fe- and Cu-ZSM-5, have been computed using DFT method at B3LYP/6-31G(d) level of theory. The Fe(II) and Cu(II) substituted in zeolite framework are modeled by using Fe-3T and Cu-3T cluster models. Reaction mechanism of pinacol rearrangement over Fe and Cu substituted in zeolite framework is different from the reaction over normal zeolite because it does not involve the acid of zeolite proton, but it involves in the positive charge of metals. The activation energy of pinacol rearrangement over Fe-3T and Cu-3T are 29.63 and 37.11 kcal/mol, respectively. Thus, Fe substituted in framework of zeolite presents higher catalytic activity for pinacol arrangement than Cu substituted in zeolite framework.

5.3 Suggestion for Future Work

The pinacol rearrangement over other metals substituted over zeolite framework could be explored. Moreover, framework of zeolite could be modeled by using larger cluster models such as 50T, 63T and 72T and may be included the theoretical model such as the ONIOM calculation in order to improve the geometrical and energetical optimization of relevant systems.



ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย