

Sudarat Yadnum 2009: Structures and Mechanisms of the Metal Organic Frameworks-505 and Cu-ZSM-5 Promoted Mukaiyama Aldol Reactions: An ONIOM Study. Master of Science (Chemistry), Major Field: Chemistry, Department of Chemistry. Thesis Advisor: Mr. Pipat Khongpracha, Ph.D. 53 pages.

The reaction mechanism and catalytic efficiency of metal-organic framework (MOF-505) and Cu-exchange ZSM-5 zeolite promoted Mukaiyama Aldol reaction were studied theoretically by density functional theory (B3LYP/6-31G(d,p)) and ONIOM (B3LYP/6-31G(d,p):UFF) methods. The Mukaiyama aldol reaction of encapsulated formaldehyde and silyl enol ether was studied on three model systems: (1) gas phase uncatalyzed system: $\text{O}=\text{CH}_2/\text{H}_3\text{SiOHC}=\text{CH}_2$; (2) MOF-505: $\text{MOF505}/\text{O}=\text{CH}_2/\text{H}_3\text{SiOHC}=\text{CH}_2$; and (3) Cu-exchanged zeolite: $\text{Cu-ZSM-5}/\text{O}=\text{CH}_2/\text{H}_3\text{SiOHC}=\text{CH}_2$. The reaction is proposed to take place in a single concerted step. It was found that both catalysts make the carbon atom in formaldehyde more electrophilic which leads to a lower energy barrier of the reaction as compared to the gas phase uncatalyzed system. For the comparison of the catalytic efficiency, it was found that Cu-ZSM-5 reduces the activation energy (6.3 kcal/mol) to be lower than that for MOF-505 (11.0 kcal/mol). Moreover, it was found that the charge distributions of reacting species in transition state over Cu-ZSM-5 system (0.192) was more positive than that of ones over MOF-505 system (0.035e). Therefore, Cu-ZSM-5 was also found to be more efficient catalyst than MOF-505 facilitating the electron transfer during the reaction.

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