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THESIS

STRUCTURES AND MECHANISMS OF THE METAL ORGANIC FRAMEWORKS-505 AND Cu-ZSM-5 PROMOTED MUKAIYAMA ALDOL REACTIONS: AN ONIOM STUDY

SUDARAT YADNUM

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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: $O=CH_2/H_3SiOHC=CH_2$; (2) MOF-505: $MOF505/O=CH_2/H_3SiOHC=CH_2$; and (3) Cu-exchanged zeolite: $Cu\text{-}ZSM\text{-}5/O=CH_2/H_3SiOHC=CH_2$. 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). Morover, 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.

Student’s signature Thesis Advisor’s signature ___ / ___ / ___

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Sudarat Yadnum
April 2009

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LIST OF ABBREVIATIONS

Ads = Adsorption structure

B3LYP = Becke's three parameters hybrid functional using the Lee-Yang-Parr correlation functional

BEA = Beta zeolite

Cf = Carbon atom of formaldehyde

DFT = Density functional theory

E_{act} = Activation energy

E_{des} = Desorption energy

FAU = Faujasite zeolite

FMO = Frontier Molecular Orbital

HOMO = Highest Occupied Molecular Orbital

Int = Intermediate structure

ITQ24 = Instituto de Tecnologia Quimica Valencia 24

kcal = Kilocalories

kJ = Kilojoules

LA = Lewis acid Catalyst

LUMO = Lowest Unoccupied Molecular Orbital

MM = Molecular Mechanics

MO = Molecular Orbital

MOFs = Metal-Organic Frameworks

MOF-11 = Metal-Organic Framework-11

MOF-505 = Metal-Organic Framework-505

MOR = Mordenite zeolite

MP2 = The second-order Møller-Plesset perturbation theory

NPA = Natural population analysis

Of = Oxygen atom of formaldehde

ONIOM = Our own N-layered Integrated molecular Orbital and molecular Mechanics

Prod = Product structure

LIST OF ABBREVIATIONS (Continued)

QM = Quantum Mechanics
QM/MM = Quantum Mechanics/Molecular Mechanics
TS = Transition state structure
TS_c = Concerted transition state structure
TS_s = Stepwise transition state structure
UFF = Universal Force Fields
XRD = X-Ray diffraction
ZPE = Zero point energy
ZSM-5 = Zeolite Socony Mobil 5

STRUCTURES AND MECHANISMS OF THE METAL ORGANIC FRAMEWORKS-505 AND Cu-ZSM-5 PROMOTED MUKAIYAMA ALDOL REACTIONS: AN ONIOM STUDY

INTRODUCTION

The Mukaiyama aldol reaction, the acid-catalyzed aldol reaction between a silyl enol ether and a carbonyl compound, is an important and versatile tool in organic and biochemical domains. This choice of reactants allows a crossed aldol reaction between an aldehyde and a ketone or a different aldehyde without self-condensation of the aldehyde. For this reason, the reaction is used extensively in organic synthesis, since it provides a synthetic route for β-hydroxylcarbonyl compounds via carbon-carbon bond formation (Chung *et al*., 2004 and Chancharunee *et al*., 2003). Takasu *et al*. (2004) studied the reaction on a [2+2] cycloaddition over the Mukaiyama aldol reaction of the Lewis acid catalyzed and uncatalyzed reactions between silyl enol ethers and α,β-unsaturated ether. Both experimental and theoretical investigations have been carried out to elucidate the mechanism of the silicon-direct aldol reaction (Denmark *et al*., 1994).

In the aspect of organic chemistry, formaldehyde is well known as one of the most versatile carbon electrophiles. However, its application is often limited by its intractability due to a low boiling point of -19.5 ºC. Moreover, it tends to rapidly polymerize to solid paraformaldehyde and trioxane. Therefore, in order to obtain formaldehyde monomer, thermal or Lewis acid pretreatment is used to depolymerize paraformaldehyde or trioxane. Environmentally friendly porous materials such as zeolite were found to be candidates for the storage of molecular formaldehyde. Zeolites are microporous molecular sieves which typically consist of interconnected tetrahedral of silicon and oxygen atoms arranged into a complex 3-dimensional arrangement of inter-connecting channels and cavities. In zeolites structures, some of the quadri-charged silicon is replaced by triple-charged aluminum, giving rise to a deficiency of positive charge. The charge is balanced by the presence of singly- or doubly-charged atoms, such as alkaline and transition metal, elsewhere in the structure (Chui *et al.*, 1999 and Rowsell *et al.*, 2004). The question about the source of a very high activity of metal sites produced by cation exchange in a silicalite environment of framework oxygens is the important area of the research in zeolite community. One of the main points of interest is the Cu^+ cation center in ZSM-5 zeolite catalyst for Mukaiyama aldol reaction. The first Cu species bonds symmetrically to two framework oxygen atoms, and the other bonds asymmetrically to three framework oxygen atoms (shown in Figure 1). Those results agree with XAFS, IR, and UV-vis spectroscopy studies, which showed that the average coordination number of Cu is 2.5.

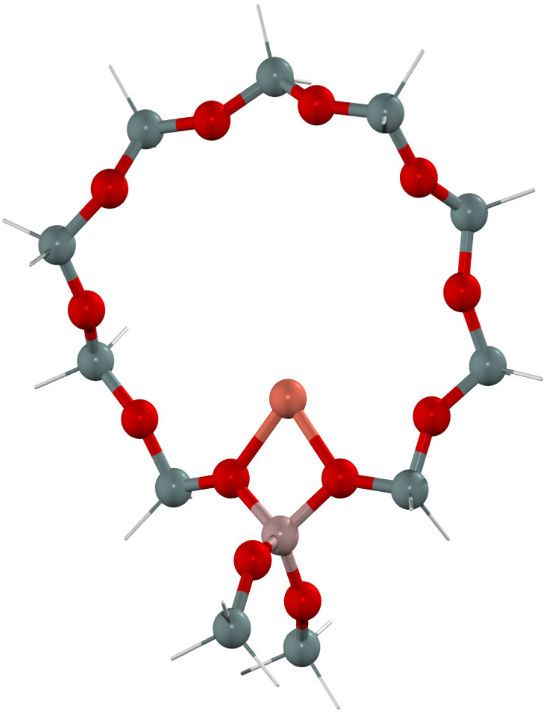
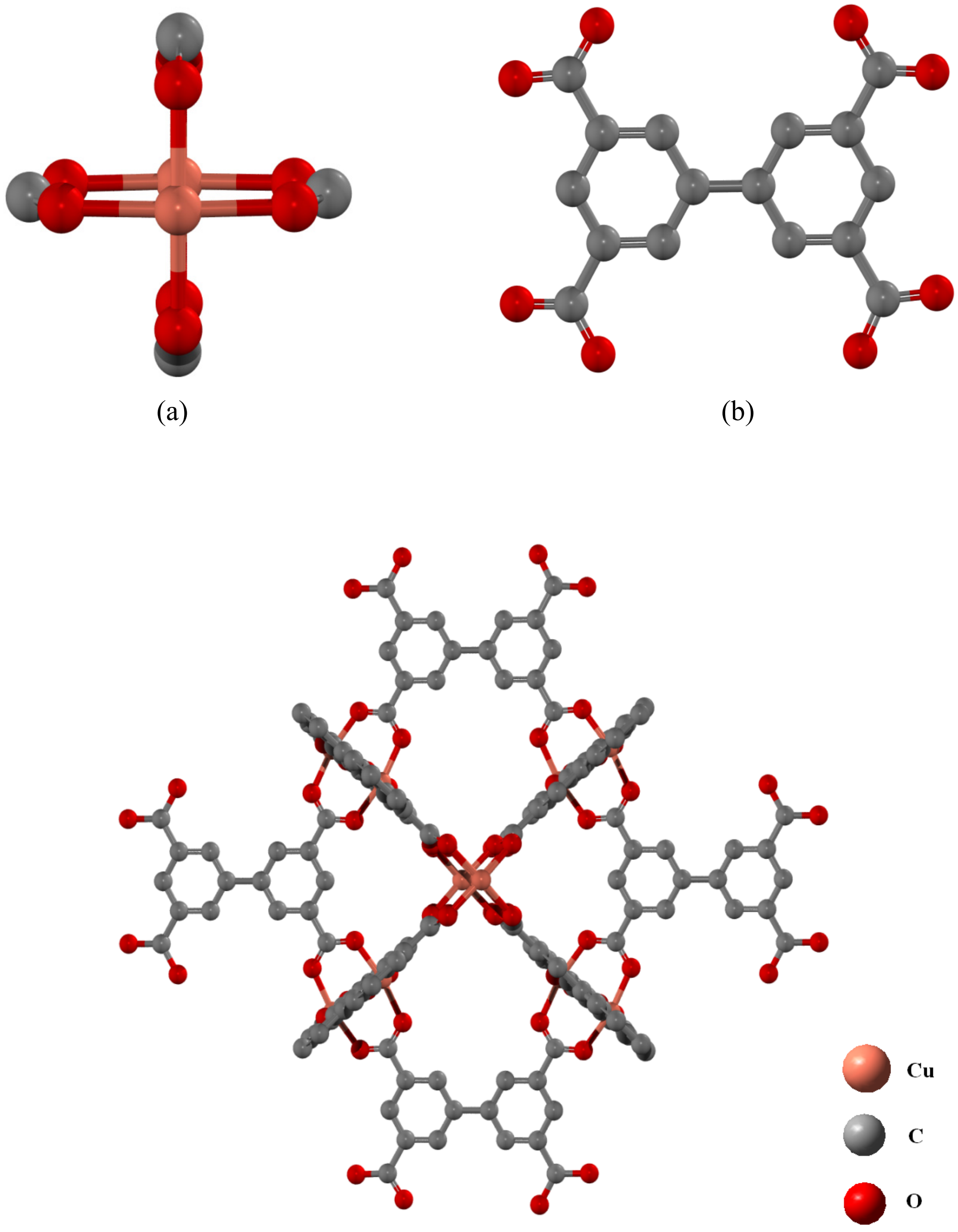


Figure 1 Cu^+ site in ZSM-5 zeolite structure

For the reaction with larger molecules, porous materials such as metal-organic frameworks (MOFs) which their lattices are constructed from a cluster of transition-metal ions held in position by ligation to organic molecules become more advantageous because of the accessible variation of pore dimension and chemistry inside the cavity. Microporous metal-organic frameworks are crystalline materials assembles by the bonding of metal ions with polyfunctional organic ligands. They have attracted great attention to chemists, material scientists, and physical scientists since 1990s in creation of nano-sized spaces and potential application in gas storage, adsorption and separation, molecular sensing, photonics, as well as magnetic materials. As porous materials which transition metal ions, MOFs also find applications in catalysis (Alaerts *et al.*, 2006 and Xiao *et al.*, 2007).

Chen *et al.* (2005) synthesized MOFs with $Cu_2(CO_2)_4$“paddle-wheel” units, and illustrated their use in the design of 0-periodic discrete and 3-periodic extended structures. MOF-505 was synthesized under analogous conditions: the solvothermal reaction of 3,3’,5,5’-biphenyltetracarboxylic acid and $Cu(NO_3)_2{\cdot}(H_2O)_{2.5}$ in N,N-dimethylformamide (DMF)/ethanol /H_2O(3:3:2 v/v/v) at 65 °C for 24 hours gave block-shaped crystal. The compound was formulated as $[Cu_2(bptc)(H_2O)_2(DMF)_3(H_2O)]$ by elemental microanalysis and single-crystal X-ray diffraction studies. The $Cu_2(CO_2)_4$ unit is a paddlewheel unit (shown in Figure 2a) that is defined by the carboxylate carbon atoms, and the $bptc^{-4}$ unit is a organic linker that is defined by the 3, 3’, 5, and 5’ carbon atoms (shown in Figure 2b). The carboxylate functionalities of the $bptc^{4-}$ ligand are nearly coplanar with the biphenyl rings (the dihedral angle between the carboxylate group and the phenyl ring is 7.4°). Thus, when the square SBUs are linked to the biphenyl rings, they must be mutually orthogonal, an aspect that is the hallmark of the NbO topology. The crystal structure of MOF-505 (shown in Figures 2c) clearly shows that the link has predisposed the inorganic unit at nearly 90 angles (94.4°) to the organic unit.



(a)

(b)

(c)

Figure 2 The single-crystal X-Ray structure of MOF-505 showing (a) $Cu_2(CO_2)_4$ unit, (b) bptc^{4-} unit, and (c) MOF-505 framework

In this work, we investigated the mechanism of the Mukaiyama aldol reaction between MOF-505 and zeolite encapsulating formaldehyde and silyl enol ether. In the type of reaction, a concerted mechanism was proposed in which the bond between the carbon atom of formaldehyde (Cf) and the silyl enol ether (C1) and the silyl group transferred. We suggest the fundamental steps of the reaction as follows:

$$CH_2{=}O + LA \longrightarrow CH_2{=}O@LA \qquad (1)$$

$$SiH_3O\text{-}CH{=}CH_2 + CH_2{=}O@LA \longrightarrow O{=}CHCH_2CH_2OSiH_3@LA \qquad (2)$$

$$O{=}CHCH_2CH_2OSiH_3@LA \longrightarrow O{=}CHCH_2CH_2OSiH_3 + LA \qquad (3)$$

where LA (Lewis Acid) = metal-organic framework 505 and Cu-ZSM-5 zeolite

OBJECTIVES

1. To investigate the structures and reaction mechanisms of the Mukaiyama aldol reaction or carbon-carbon formation over MOF-505 and Cu-ZSM-5 zeolite by using the ONIOM2 (B3LYP/6-31G(d,p):UFF) method for calculation.

2. To compare the catalytic efficiency between Metal organic framework (MOF-505) and zeolite structure (Cu-ZSM-5) on the Mukaiyama aldol reaction of formaldehyde and silyl enol ether.

3. To compare the energy barrier between uncatalyzed and catalyzed of the Mukaiyama aldol reaction.

LITERATURE REVIEW

Among organic reactions, the Mukaiyama aldol reaction is an aldol reaction between a silyl enol ether and aldehyde catalyzed by a Lewis acid. In its original scope, titanium tetrachloride ($TiCl_4$) was used as Lewis acid in stochiometric amounts, but truly catalytic systems exist as well. The reaction published by Mukaiyama in 1973 is that of the silyl enol ether of cyclohexanone with benzadehyde with one equivalent of titanium tetrachloride in dichloromethane. In the presence of $TiCl_4$, trimethylsilyl enol ethers of ketone react smoothly with ketones or aldehydes at room temperature to give the aldol type addition products, β-hydroxyketones, in good yields (Mukaiyama *at el*., 1973). A subsequent paper in 1974 dealt with the reaction between isopropenyl acetate and benzaldehyde with various Lewis acids such as aluminium chloride ($AlCl_3$), tin tetrachloride ($SnCl_4$) and boron trifluoride (BCl_3). Another paper of Mukaiyama *at el.* (1974), returning to silyl enol ethers, the reaction temperature is reduced to -78 °C. It was found that titanium tetrachloride powerfully activates the carbonyl carbon for nucleophilic reaction as shown in Figure 3. Myers *et al*. (1990), Denmark *et al.* (1994) and Miura *et al.* (1998) have independently shown that the Mukaiyama aldol reactions can proceed without a catalyst by increasing the acidity of silicon on the silyl enol ether. Lubineau *et al.* (1988) reported the uncatalyzed reactions under high pressure. Both experimental and theoretical investigations have been carried out to elucidate the mechanism of the uncatalyzed silicon-directed aldol reactions (Myers *et al*., 1990). Based on an elegant double-label crossover experiment, Gung *et al.* (1995) have reported the transition state, which has a boat like six-membered ring geometry with pentavalent trigonal bipyramid silicon for the concerted mechanism. From the calculated structural changes, they deduced that the silicon-directed aldol reaction is mainly driven by the nucleophilicity of the enol double bond. Akakura *et al* (2007) recently developed a new use of the super silyl group in organic reactions, and showed that it has unique reactivity. One of the reactions using this reagent is diastereoselective Mukaiyama aldehyde cross-aldol reaction catalyzed by a highly active Brønsted acid. This reaction produces syn-1,3-diol derivatives with high yield and high stereoselectivity. Certain features and outcomes of the reaction were not clear, so they decided to investigate the reaction mechanism through a theoretical study.

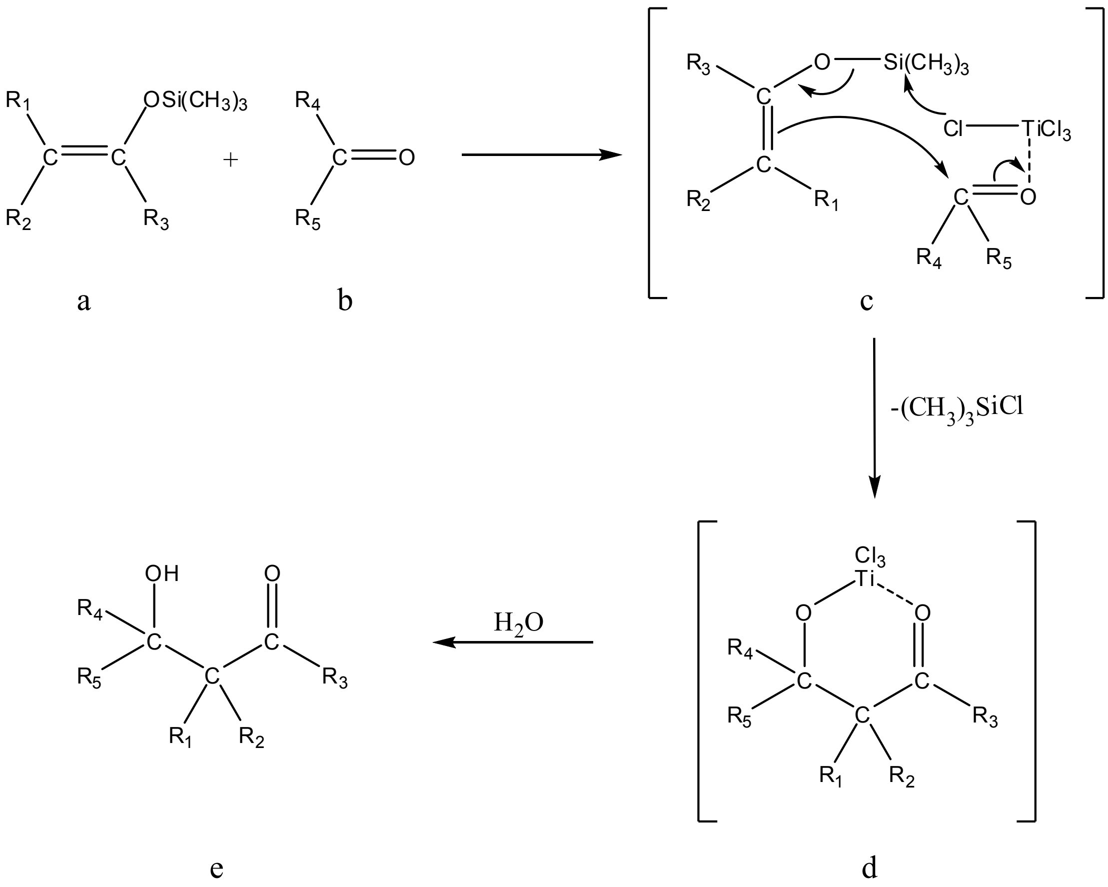


Figure 3 Schematic diagram the mechanism of Mukaiyama aldol reaction: (a) silyl enol ether, (b) carbonyl compound, (c) transition state, (d) intermediate chelate, and (e) product.

Source: Mukaiyama *et al.* (1974)

Wong *et al.* (2005) confirmed that the uncatalyzed Mukaiyama aldol reaction between trihydrosilyl enol ether and formaldehyde proceeds via a single concerted mechanism. The study of the effects of substituents on silyl enol ether and aldehyde reveals the following factors that influence the reactivity of the silicon-directed aldol reactions: (1) reaction exothermicity, (2) nucleophilicity of enol silane, (3) electrophilicity of aldehyde, (4) frontier molecular orbital interactions, and (5) electrostatic interactions. Substitution on both reactants is found to have a cooperative influence on the activation barrier. The aldol reaction is found to be more favorable with electron-donating substituents on trihydrosilyl enol ether and electron-withdrawing substituents on formaldehyde. They predicted that the reactions between NH_2 substituted trihydrosilyl enol ether and $CHOCOOCH_3$, and CF_3 substituted aldehydes will proceed readily without a catalyst at temperature below 0 ^{o}C. Later on, Wong *et al.* (2007) investigated the mechanism of metal chloride-promoted Mukaiyama aldol reaction calculated with *ab initio* (MP2/6-311+G(d,p)//B3LYP/6-31G(d)). The metal chlorides considered include $TiCl_4$, BCl_3, $AlCl_3$, and $GaCl_3$. In contrast to the concerted pathway of the uncatalyzed aldol reaction, the Lewis acid-promoted reactions favor a stepwise mechanism. Three possible stepwise pathways were located. The lowest energy pathway corresponds to a simultaneous C-C bond formation and a chlorine atom shift in the first (rate-determining) step. This process is calculated to have a low activation barrier of 12 kJ mol^{-1} for the $TiCl_4$-promoted reaction. The alternative [2+2] cycloaddition and direct carbon-carbon bond formation pathways are energetically competitive. BCl_3, $AlCl_3$ and $GaCl_3$ were revealed to be more effective Lewis acid catalysts for the Mukaiyama aldol reaction, with smaller activation barrier, than the $TiCl_4$ catalyst. Formation of a stable pretransition state intermolecular π-π complex between enol silane and the activated formaldehyde ($CH_2{=}O{\cdots}MCl_n$) is a key driving force for the facile metal chloride-promoted reactions.

Wong *et al.* (2008) investigated halogen-catalyzed (I_2, Br_2, and Cl_2) Mukaiyama aldol reactions between a trihydrosilyl enol ether and formaldehyde. Five reaction pathways, three concertd and two stepwise reaction modes were considered. These halogen-catalyzed reactions with simple substituents prefer a concerted pathway. In a distinct contrast, the I_2-catalyzed Mukaiyama aldol reaction between 1-phenyl-1-(trimethylsilyloxy)-ethylene and benz-aldehyde prefers a stepwise mechanism. Hence, it is suspected that the nature of substituent may have a strong influence on the reaction mechanism involved.

Armor *et al.* (1998) reported that the transition metal-exchanged zeolite offers the means to enhance a variety of chemical reactions. In many cases, a substantial enhancement in the rate of conversion and/or selectivity is observed. These enhancements are probably related to a combination of the zeolite host offering a distribution of highly dispersed exchange sites and the ligating effect of the zeolite upon the metal ion. Each zeolite could exert unique ligand field effects upon a cation. Shape selectivity by the zeolite is not a dominant feature in the above reactions, although the tortuosity of the zeolite could play a role in some of these reactions. Zeolites are microporous molecular sieves which typically consist of an interconnected tetrahedral of silicon and (an oxygen atom) arranged into a complex 3-dimensional arrangement of interconnecting channels and cavities. This gives rise to the unique catalytic characteristic of the unique catalytic characteristic of the zeolite, a function of their Brønsted acidity, their local pore structure and the long-range stabilization provided by the zeolite framework. Itoh *et al.* (1983) investigated the zeolite catalytic system and found it to be difficult to obtain direct evidence of carbanions, but their presence can reasonably be inferred from the reaction chemistry. Several metal-exchanged zeolites such as Rb and Cs have been effectively used for side-chain alkylation of toluene with methanol or formaldehyde. This type of chemistry can also be presumed for the aldol-type condensation reaction involving carbonyl compounds at high temperature in the vapor phase. Since oxygen is more electronegative than carbon, the compounds show a dipole moment ($C^{\delta+}=O^{\delta-}$), which can be attacked by other carbon nucleophiles on the carbon atom to give a new C-C bond. Komatsu *et al.* (1994), Iwamoto *et al.* (1991), chen et al. (1997), and Anderson et al. (2004) reported that ZSM-5 zeolite exchanged with Cu^+ cations [Cu(I)-ZSM-5] is an active catalyst for a number of reactions, including NO decomposition, the synthesis of methanol the oxidation of methanol to dimethoxymethane and the oxidative carbonylation of methanol to dimethyl carbonate. Zheng *et al.* (2007) investigated the coordination of Cu^+ in Cu(I)-ZSM-5 and the properties of CO adsorbed on such cations using the density functional theory. The influences of the structure of the cation–exchange site, the location of the Al in the site, and the number of Al atoms associated with the sites were explored. Cu^+ was found to have 2-fold coordination to framework O atoms when present at the intersections of the straight and sinusoidal exchange site. Kukulska *et al.* (2007) reported the ability of the Cu^+ ion in Cu-ZSM-5 to activate the molecules of the formaldehyde and the transformation of formaldehyde sorbed in zeolite. IR studies showed that the interaction of formaldehyde with Cu^+ ions in zeolite Cu-ZSM-5 results in an activation and weakening of the C=O bond, which results from the π-back-donation of the *d*-electrons of Cu^+ to π^* orbitals of formaldehyde. The experiments of coadsorption of formaldehyde and CO on the same Cu^+ proved that formaldehyde acts as an electron donor to the Cu* + CO system, which results in stronger π back-donation to antibonding orbitals of CO. Sasidharan *et al.* (2003) reported a detailed study on the activity with respect to various isomorphously substituted metallosilicates and rare-earth-modified zeolites, and the effect of various substrates and the effect of various substrates and solvents and reaction time on the Mukaiyama aldol reaction. The titanium silicates such as TS-1 and Ti-β can be used as efficient heterogeneous catalysts for carbon-carbon bond formation reactions such as Mukaiyama-type aldol condensation and Michael addition under liquid-phase condition. They show the activity of large-pore metallosilicates and Ti-β realized only marginally higher conversion than that of TS-1, but the turnover number of Ti-β (11.6) is higher than that of TS-1 (9.2) and reveals that large pore size still favors increased activity. However, the overall difference in activity between large-pore Ti-β and medium-pore TS-1 is much less, in contrast to the liquid-phase oxidation reactions, where the efficiency of the former is considerably high for bulky substrates. Thus, the activity trend observed over TS-1 and Ti-β indicates that the carbon–carbon bond formation may probably follow a different reaction pathway from that of conventional oxidation reactions involving H_2O_2.Furthermore, the activity per active site is consistently higher for titanium than the other metals such as Sn or Al, regardless of the pore size. The difference in activity between Na-Y and lanthanum-exchanged Y-zeolites suggests that Lewis acids (since the exchange of rare earths imparts Lewis acidity) play an important role by facilitating the nucleophile formation in the condensation between silyl enol ether and aldehydes. Also, the rare earth-exchanged zeolites exhibit comparatively better TON (Number of moles of product per mole of metal per hour) than that of isomorphously substituted Al- or V-silicates.

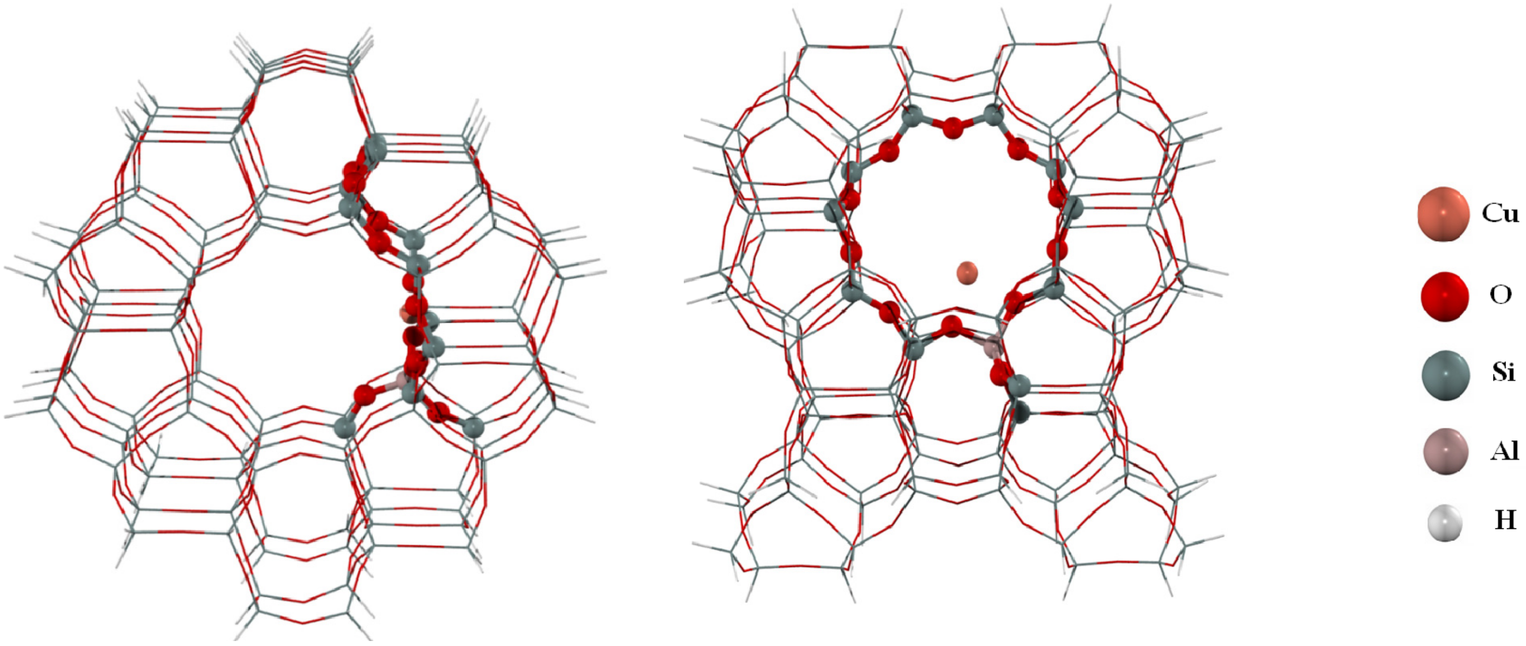
Rowsell *et al.* (2004) stated that metal–organic frameworks (MOFs) are an emerging class of crystalline porous materials. Mostly, these lattices are constructed from clusters of transition-metal ions held in position by ligation to organic molecules. The free space between the metal clusters and ligands shows up as pores in the eventual structure. Gömez-Lor *et al.* (2005) presented that the term MOF covers a wide assembly of hybrid compounds. Because of the exceptionally high pore volume and surface area of MOFs. Many research efforts have been addressed to their application in the sorption of light gases, either as such or after chemical modification. As porous materials, MOFs also find applications in catalysis. The pores of MOFs can theoretically be tailored in a systematic way and hence optimized to a specific catalytic application. Hasegawa *et al.* (2007) investigated the Knoevenage condensation reaction, which is a well-known base-catalyzed model reaction that was selectively promoted in good yield. Casarin *et al.* (2004) investigated a metal organic framework catalyst precursor in the cyclopropanation reaction, showing an interesting selectivity. Choomwattana *et al.* (2008) presented the mechanism of the carbonyl-ene reaction between a metal-organic framework encapsulated formaldehyde and propylene. They also investigated the metal-organic framework structures interacting with formaldehyde and their reaction with propylene, which was studied by two different models: MOF-11 and naked Cu^+. The reaction mechanism is proposed to be intermediate-free concerted, consisting of proton transfer and carbon-carbon bond formation. The activation energy (ΔE_{act}) derived for MOF-11 of 24.1 kcal/mol is similar to that for the faujasite zeolite catalyst of 25.1 kcal/mol, suggesting that MOF-11 is a good candidate for use in catalysis. Horike et al (2008) investigated size-selective Lewis acid catalysis in a microporous metal-organic frameworks for Mukaiyama aldol reaction of an aldehyde with a silyl enolate. It was found to be one of the most fundamental tools for the selective formation of carbon-carbon bonds.

We approach the reaction mechanisms of the Mukaiyama aldol reaction on a molecular level by means of quantum chemical calculations. Because both zeolites and MOFs are micromesoporous materials, the computational methods and schemes used for MOFs can be adopted from the ones used in the study of zeolites. In the same way to zeolites, (J. Sauer *et al.*, 1994, 1989, J. Limtrakul *et al.*, 1995 and 1997) only a small part of the framework affects the electronic properties of the reactive site, thus facilitating the component using quantum chemical methods. To include the contribution of the environmental framework on the adsorption of the reactant, hybrid methods such as embedded cluster or combined quantum mechanics/molecular mechanics (QM/MM) methods (M. Brandle *et al.*, 1998 and R. Z. Khaliullin *et al.*, 2001), as well as the ONIOM schemes, well suit such systems (M. Svensson *et al.*, 1996 and A. H. de Vries *et al.*, 1999). The methodology is frequently exploited to study extended systems and has also been applied to the adsorption of ethylene, benzene, and ethylbenzene over acidic and alkaline faujasite and ZSM-5 zeolites (S. Kasuriya *et al.*, 2003, S. Namuangruk *et al.*, 2004) and the interesting reaction mechanisms over zeolites. (S. Namuangruk *et al.*, 2004) and T. Maihom *et al.*, 2008 investigated and proposed mechanisms of the ethylene oxide hydration reaction within a cluster model of H-ZSM-5 covering the nanocavity, where the straight and zigzag channels intersect of H-ZSM-5 by the ONIOM (B3LYP/6-31G(d,p):UFF).

METHODS OF CALCULATIONS

The MOF-505 and Cu-ZSM-5 zeolite structures were both obtained from crystallographic data. The active part is where molecular adsorption and catalysis most likely take place on. In the ONIOM2 model, the system is separated into two parts. The inner cluster consists of the active region, typically modeled with a small cluster using density function theory, to account for the interactions of adsorbates with the porous structure. The outer layer represents the environmental framework and is described by a molecular mechanics force field to account for the van der Waals interactions due to its confinement. In this present study, we have employed the ONIOM2 (B3LYP/6-31G(d,p):UFF) method to model the copper active site of MOF-505 and Cu-ZSM-5 zeolite. Specifically, we study the reaction mechanism of the Mukaiyama-aldol reaction between encapsulated formaldehyde molecule and silyl enol ether on MOF-505 and Cu-ZSM-5 zeolite. Each system was described by three models for different approaches.

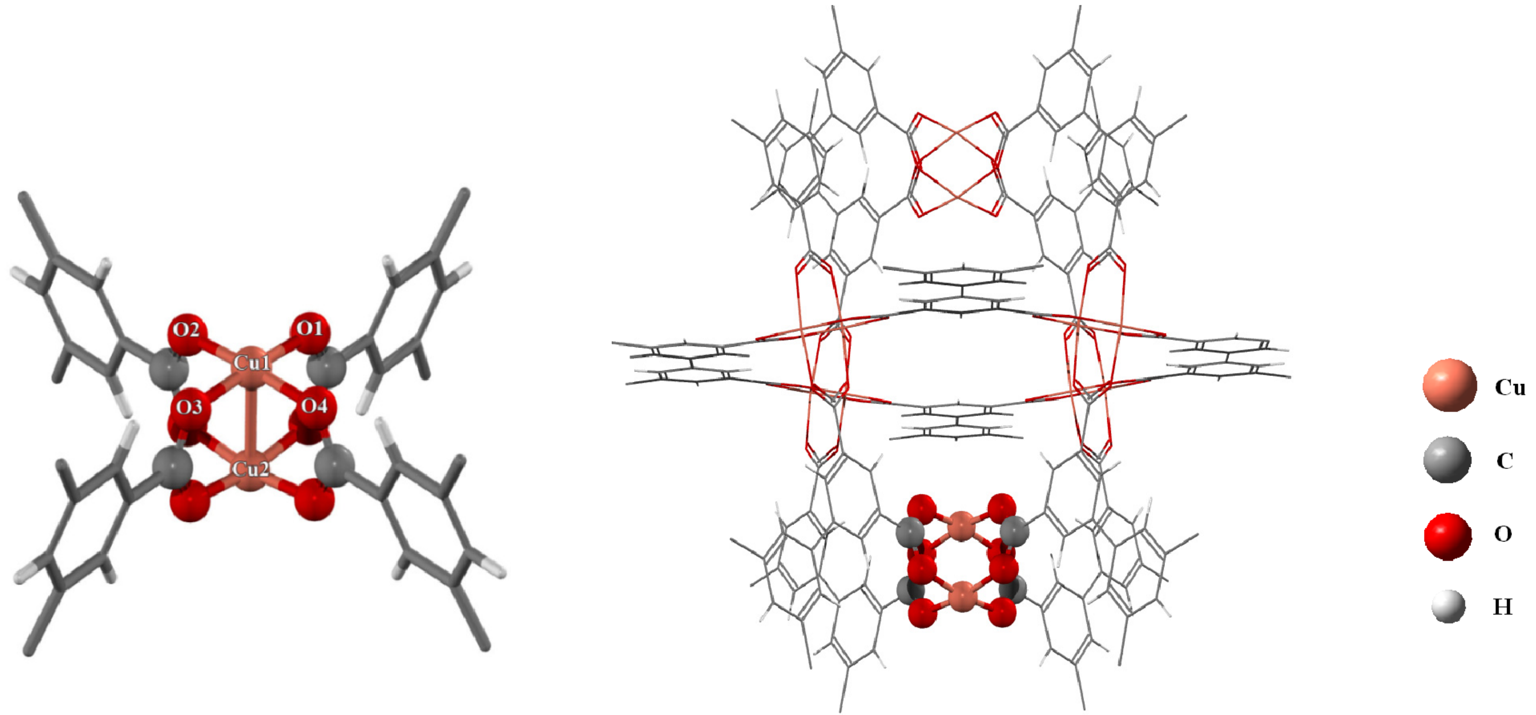
The 128T cluster model of the intersection region of the straight and zigzag channels, as shown in Figure 4, is used for representing the framework structure of Cu-ZSM-5 zeolite. For computational efficiency, the two-layered ONIOM scheme is selected. The B3LYP/6-31G(d,p) level of theory is applied for 12T cluster model, covering the 10-membered ring window of the zigzag channel of the zeolite, which is considered as the active region. The 128T extended framework is treated with the well-calibrated universal force field (UFF) to represent the confinement effect (Derouane *et al.,* 1986, 1988, Zicovich-Wilson *et al.,* 1994) of the zeolite nano-pore structure. This force field has been reported to give a good description of the short-range van der Waals interactions. All calculations were performed using the Gaussian 03 code (Frisch *et al.,* 2003). During optimization, only the 5T cluster of the active region, [$(\equiv SiO)_3Al(OH)Si\equiv$] and the probe molecules were allowed to relax. The frequency calculations were performed at the same level of theory to ensure that the transition state structure has only one imaginary frequency.



(a) (b)

Figure 4 The ONIOM models of the 128T cluster of the H-ZSM-5 zeolite. Atoms belonging to the quantum region were drawn as balls and sticks while the lines represent universal force field (UFF). View from (a) the straight channel and (b) the zigzag channel.

The structure of MOF-505 obtained from XRD data is a 3D channel system with a diameter of 10.10 Å. It consists of square-shaped $Cu_2(CO_2)_4$ paddlewheel building unit connected to 3,3’,5,5’-biphenyl tetracarboxylic acid linkers. The active paddlewheel unit is the effective part where molecular adsorption and catalysis most likely take place on. The B3LYP/6-31G(d,p) level of theory is therefore assigned to the cluster. In order to cover the nanoreactor cavity of MOF-505, the framework environment of 12 linkers and 6 paddlewheel cluster are considered with the universal forcefield for the outer ONIOM layer. In our calculations, the MOF framework was kept at the crystallographic geometry, whereas the upper part of the paddlewheel active site (shown in Figure 5) and the adsorbates ($O{=}CH_2$ and $H_3SiOHC{=}CH_2$) were fully optimized. Normal mode analyses were performed to confirm the transition state to have one imaginary frequency whose mode corresponds to the reaction coordinate.



(a) (b)

Figure 5 Structure of MOF-505. (a) A square-shaped $Cu_2(CO_2)_4$ paddlewheel building unit connected to four units of 3,3’,5,5’-biphenyl group. (b) The ONIOM model for MOF-505 the high layer (DFT region) is represented by ball-bond view and low layer is represented by line view.

Mukaiyama aldol reaction without Lewis acid catalyst calculated using density-functional calculations with the same method and basis set.

The charge distribution in the complexes has been analyzed via the natural population analysis (NPA) (Carpenter and Weinhold, 1988; Foster and Weinhold, 1980; Reed *et al.*, 1988; Reed and Weinhold, 1983; Reed *et al.*, 1985) partitioning scheme using the B3LYP/6-31G(d,p) density.

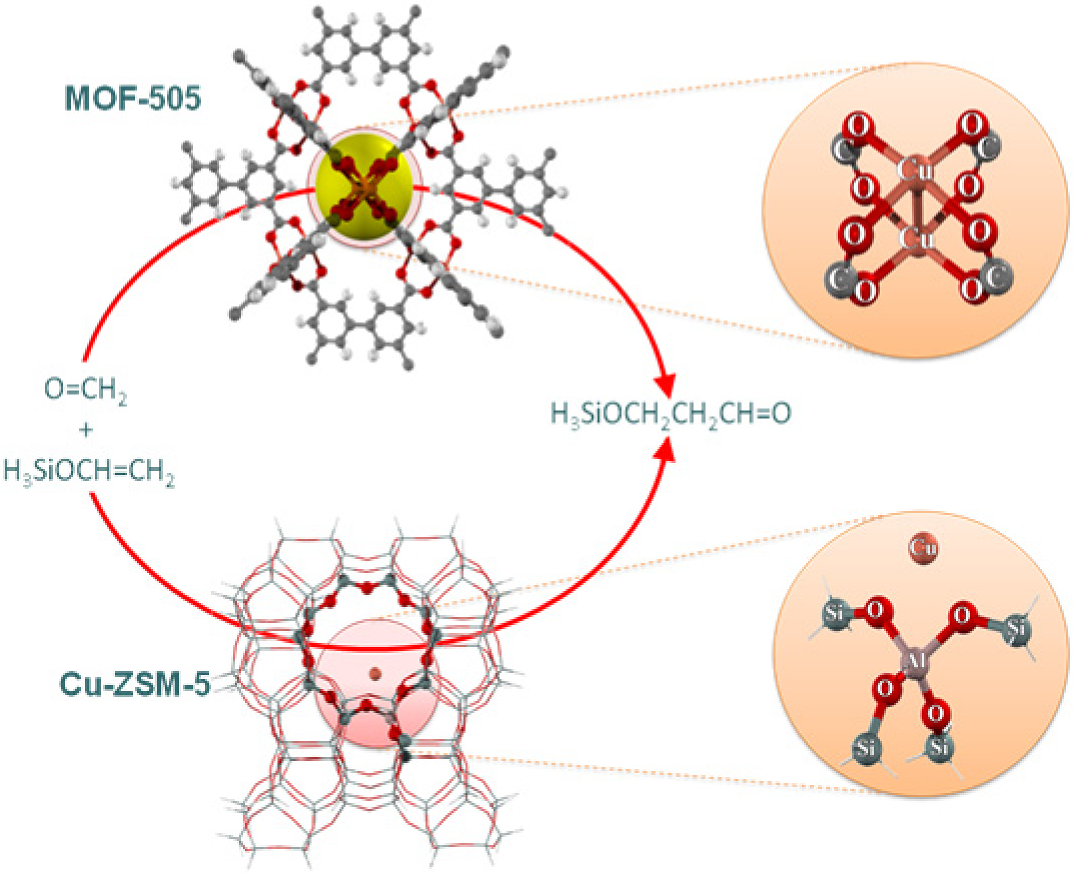


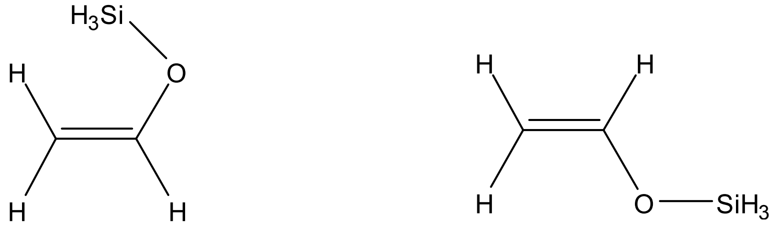
Figure 6 MOF-505 and Cu-ZSM-5 promoted Mukaiyama aldol reaction

RESULTS AND DISCUSSION

This chapter is separated into 3 sections. In the first section, we discuss the reaction without any Lewis acid catalyst. In section 2, the existence and reactivity of encapsulated formaldehyde in MOF-505 ($O=CH_2$@MOF-505) is described. We predict the Mukaiyama-aldol reaction of the MOF-encapsulated formaldehyde with silyl enol ether ($O=CH_2$@MOF-505/$H_3SiOHC=CH_2$). In section 3, we describe the proposed mechanism of the Cu-ZSM-5 catalyzed reaction ($O=CH_2$@Cu-ZSM-5/$H_3SiOHC=CH_2$). Finally, we make the comparison of the two catalyzed cases with the reaction without any Lewis acid catalyst.

1. The Mukaiyama aldol reaction between formaldehyde and silyl enol ether without a Lewis acid catalyst

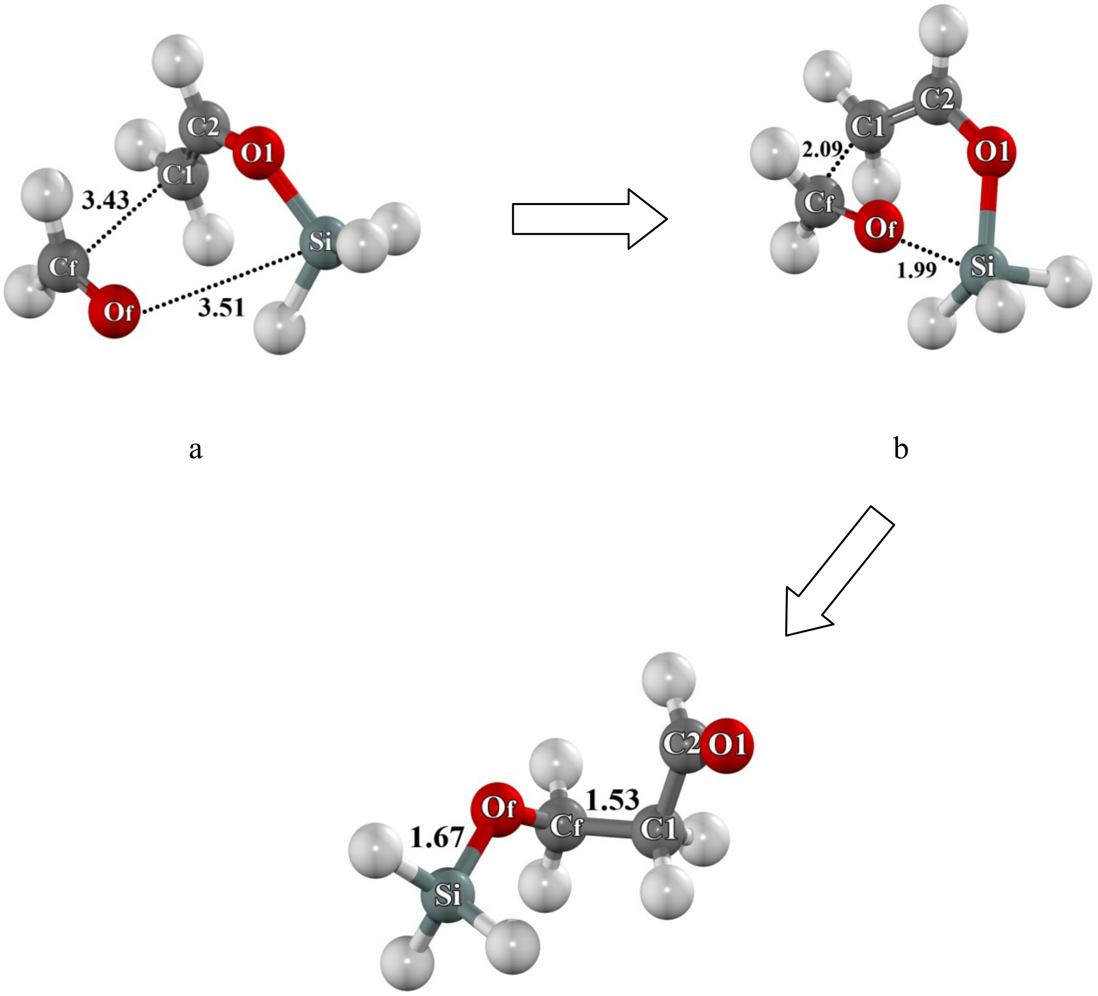
The mechanism of the uncatalyzed Mukaiyama aldol reaction of the parent system, i.e., between silyl enol ether and formaldehyde. The conformational behaviors of the reactant silyl enol ether and the product 3-(silyloxy) propanal have been studied by Gung et al. In this study B3LYP(6-31G(d,p)) calculations confirmed that the s-cis form was slightly more stable, by 2.3 kJ mol^{-1} (shown in figure 7). Hence, the s-cis conformation is chosen to become the preferred starting structure in reaction mechanisms.



(a) *s-cis* (b) *s-trans*

Figure 7 Conformational of the silyl enol ether; (a) s-cis conformation (b) s-trans conformation.

The concerted pathway has been examined previously by Gung *et al.* and Denmark *et al*. The reaction between silyl enol ether and formaldehyde is predicted to be exothermic, by -26.6 kcal/mol. A boat-shaped six-membered-ring transition state is also proposed for the concerted pathway. The transition state involves a simultaneous with C_f-C1 bond formation and silyl group transfer (shown in Figure 8).



a

b

c

Figure 8 Optimized structures of the uncatalyzed Mukaiyama aldol reaction (a) coadsorption complex (b) transition state and (c) product

In the bare system, for the transition state structure as compared to the coadsorption complex, the C_f-C1 bond distance is contracted from 3.43 to 2.09 Å. The distance between silyl enol ether (Si-O_f) is elongated from 1.68 to 1.81 Å whereas the distance between formaldehyde oxygen (O_f) and silyl group becomes 1.99 Å. The lengths of the C1-C2 and C2-O_f bonds in silyl enol ether are change from 1.34 and 1.36 to 1.38 and 1.29 Å, respectively. The reaction coordinate (the normal mode that has an imaginary frequency) indicates again the concerted mechanism of Mukaiyama aldol reaction. The activation energy is 13.7 kcal/mol and the reaction energy is -26.6 kcal/mol (shown in Figure 9).

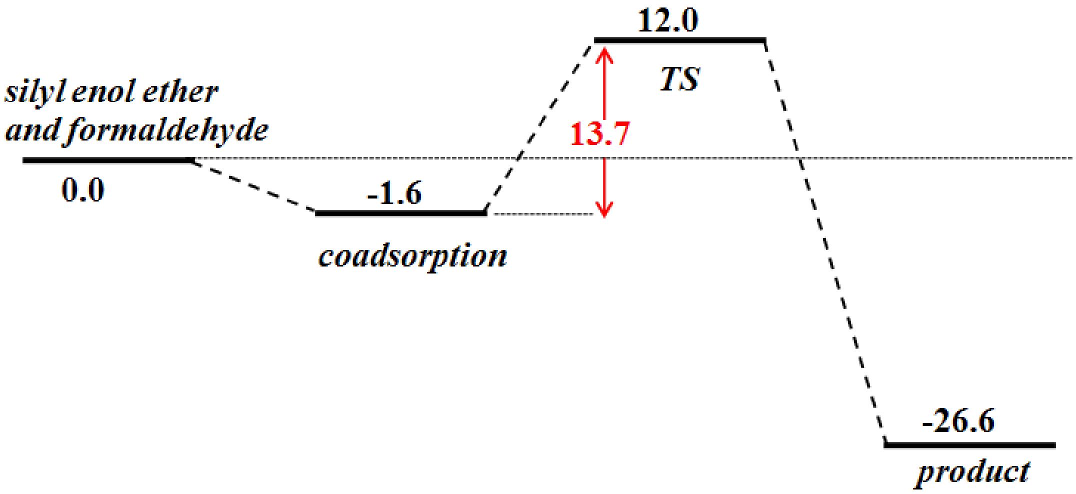


Figure 9 Calculated energy profile (kcal/mol) for the uncatalyzed Mukaiyama aldol reaction between $O=CH_2$and $H_3SiOHC=CH_2$

The optimized geometric parameters and NPA analysis for the uncatalyzed system between silyl enol ether formaldehyde are presented in Table 1 and 2.

Table 1 Optimized geometric parameters of isolated state, coadsorption complex, transition state, and product of the Mukaiyama aldol reaction between formaldehyde and silyl enol ether using B3LYP/6-31G(d,p) method (bond lengths in Å)

Parameter	Isolated molecule	Coadsorption complex	Transition state	Product
C_f-O_f	1.207	1.208	1.278	1.422
C_f-C1	-	3.430	2.092	1.531
C1-C2	1.333	1.336	1.384	1.515
C2-O1	1.365	1.359	1.288	1.209
Si-O1	1.678	1.684	1.813	4.634
Si-O_f	-	3.512	1.992	1.666

Table 2 Atomic charge distribution calculated from the natural population analysis for the Mukaiyama aldol reaction between $O=CH_2$ and $H_3SiOHC=CH_2$.

Atom (q)	Isolated molecule	Coadsorption complex	Transition state	Product
C_f	0.22	0.23	0.33	-0.10
O_f	-0.49	-0.51	-0.72	-0.90
C1	-0.56	-0.57	-0.63	-0.60
C2	0.14	0.14	0.084	0.42
O1	-0.85	-0.84	-0.72	-0.52
Si	1.20	1.20	1.20	1.21

2. MOF-505 encapsulated formaldehyde ($O=CH_2$@MOF-505) and Mukaiyama aldol reaction between the MOF encapsulated formaldehyde and silyl enol ether ($O=CH_2$@MOF-505/$H_3SiOHC=CH_2$)

The optimized geometric parameters are listed in Table 3. Figure 10 (a) illustrates the structure of formaldehyde stabilized in the MOF-505 framework. The Cu unit (Cu1-Cu2) is barely changed upon the adsorption of formaldehyde (0.084 Å and 5^{o} for changes in Cu1-Cu2 bond distance and O-Cu-O bond angles, respectively). The intermolecular distance between formaldehyde and MOF-505 is found to be 2.32 Å. The carbon-oxygen bond of formaldehyde is elongated from 1.207 to 1.215 Å. According the interaction between the hydrogen atoms of formaldehyde and the oxygen atoms of the framework, the corresponding distance between the formaldehyde oxygen and the Cu atom of MOF-505 active site is 2.318 Å. The resulting adsorption energy for the $O=CH_2$@MOF-505 complex is -14.3 kcal/mol. Since the measured C_f-$O_f \cdots$Cu/MOF angle is 119.0^{o}, the active Cu atom moves slightly out of the paddlewheel upper plane toward the adsorbing molecule.

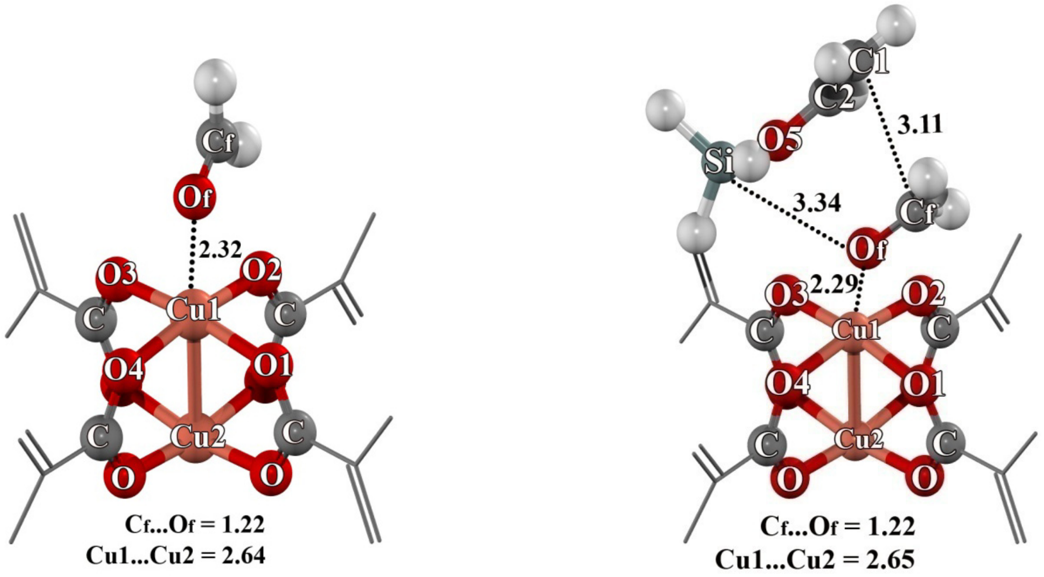
For the Mukaiyama aldol reaction, a concerted mechanism was proposed in which the bond between the carbon atom of formaldehyde (C_f) and the silyl enol ether (C1) is formed and the silyl group is transferred. We suggest the fundamental step of the reaction as follows:

$$O=CH_2 + \text{MOF-505} \longrightarrow O=CH_2\text{@MOF-505} \quad (1)$$

$$SiH_3O\text{-}CH=CH_2 + O=CH_2\text{@MOF-505} \longrightarrow O=CHCH_2CH_2OSiH_3\text{@MOF-505} \quad (2)$$

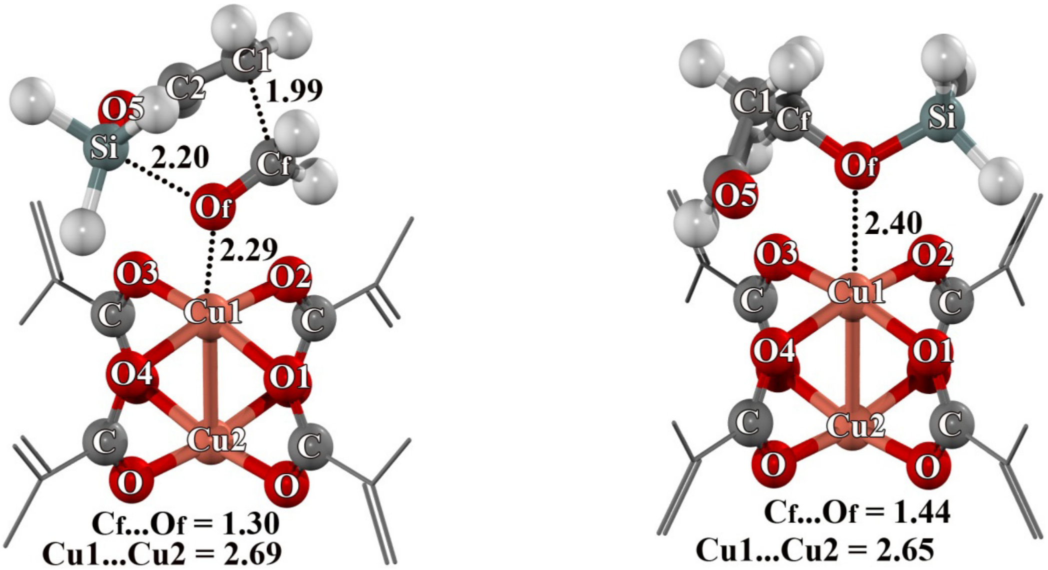
$$O=CHCH_2CH_2OSiH_3\text{@MOF-505} \longrightarrow O=CHCH_2CH_2OSiH_3 + \text{MOF-505} \quad (3)$$

Initially, formaldehyde adsorbs over the paddlewheel active site of MOF-505 via lone pair electron interaction with adsorption energy of -14.3 kcal/mol. Then the encapsulated formaldehyde interacts with silyl enol ether via a π interaction with a coadsorption energy of -23.1 kcal/mol and followed by the chemical reaction in order to produce 3-silyloxy-propanal. The activation energy is 11.0 kcal/mol. The proposed concerted pathway is supported with the calculated transition structure whose imaginary frequency belongs to the mode in which the C_f-C1 bond is formed and silyl group is transferred. The product formation is exothermic by -46.8 kcal/mol. The adsorbed propanal needs 20.2 kcal/mol to desorb from the active site in the final step (3). The optimized geometric parameters of the Mukaiyama aldol reaction between silyl enol ether and MOF-505 encapsulated formaldehyde are presented in Table 3. The energy profile of the reaction is illustrated in Figure 11.



(a) **(b)**

Figure 10 Optimized structures of the $O=CH_2$@MOF-505/$H_3SiOHC=CH_2$ (a) $O=CH_2$@MOF-505 (b) $O=CH_2$@MOF-505/$H_3SiOHC=CH_2$ complex (c) transition state structure and (d) $O=CHCH_2CH_2OSiH_3$@MOF-505 structure (Distance in Å).



(c) **(d)**

Figure 10 (Continued)

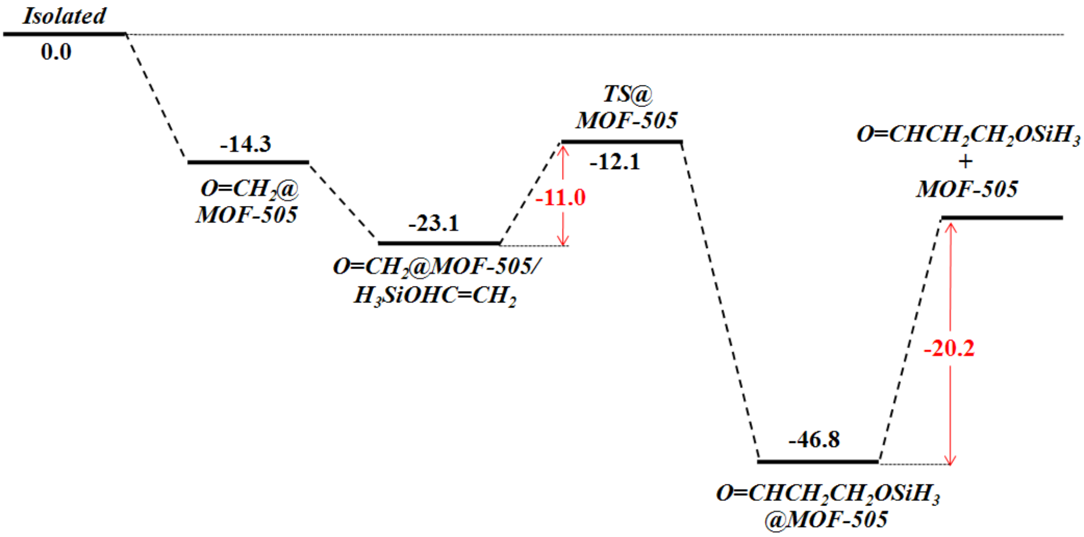


Figure 11 Calculated energy profiles (kcal/mol) for the Mukaiyama aldol reaction between $O{=}CH_2$ and $H_3SiOHC{=}CH_2$ in MOF-505.

As compared to the coadsorption complex, the silyl enol ether Si-O5 bond length in the transition structure is stretched from 1.683 to 1.779 Å whereas the distance between the silicon group (Si) and the formaldehyde oxygen (O_f) is shortened from 3.341 to 2.201 Å. The C_f-O_f double bond of formaldehyde is changed from 1.218 to 1.295 Å as the distance between the silyl enol ether carbon (C1) and formaldehyde carbon (C_f) is contracted from 3.109 to 1.991 Å. We also examined the atomic charges of the molecules involved in the reaction by means of the NPA method, as shown in Table 4. Cu in the upper plane in the MOF structure initially bears a positive charge of 1.27. As formaldehyde adsorbs over the Cu, it becomes slightly more positive due to the electron induction between polar molecules. The adsorption also causes the O_f atom in formaldehyde to become more negative and its C_f atom consequently becomes more positive. In the transition state structure, the negative charge over the silicon accepting O atom of -0.79 is observed. The increased negative charge of O_f facilitates the silyl group transfer. The Cu charge of 1.30 throughout the reaction is stabilized by the extended framework. In order to promote the Mukaiyama aldol reaction, the metal-organic framework not only moderately reduces the reaction barrier but also prevents the polymerization of formaldehyde.

Table 3 Optimized geometric parameters of isolated state, formaldehyde adsorption, coadsorption complex, transition state, and product of the Mukaiyama aldol reaction between formaldehyde and silyl enol ether on MOF-505 using ONIOM (B3LYP/6-31G (d,p):UFF) method.

Parameters	Isolated molecule	Formaldehyde adsorption	Coadsorption complex	Transition state	Product
Distances (Å)					
Cu1-Cu2	2.561	2.645	2.652	2.691	2.648
Cu1-O1	1.939	1.946	1.962	1.959	1.947
Cu1-O2	1.939	1.968	1.958	1.970	1.947
Cu1-O3	1.941	1.957	1.952	1.961	1.957
Cu1-O4	1.942	1.945	1.948	1.948	1.960
Cu1-O_f	-	2.322	2.293	2.287	2.396
C_f-O_f	1.207	1.215	1.218	1.295	1.443
C_f-C1	-	-	3.109	1.991	1.527
C1-C2	1.333	-	1.340	1.391	1.517
C2-O5	1.365	-	1.350	1.286	1.211
Si-O5	1.678	-	1.683	1.779	4.911
O_f-Si	-	-	3.341	2.201	1.690
Angles (degree)					
∠ O1-Cu1-O3	174.6	169.7	169.4	167.2	169.6
∠ O2-Cu2-O4	174.6	169.8	169.3	167.2	169.6

Table 4 Atomic charge distribution calculated from the natural population analysis for the Mukaiyama aldol reaction between $O{=}CH_2$ and $H_3SiOHC{=}CH_2$ in MOF-505.

Atom	Isolated molecule	Formaldehyde adsorption	Coadsorption complex	Transition state	Product
Cu1	1.27	1.31	1.30	1.31	1.30
O_f	-0.49	-0.55	-0.58	-0.79	-0.93
C_f	0.22	0.25	0.26	0.07	-0.11
C1	-0.56	-	-0.59	-0.64	-0.60
C2	0.14	-	0.16	0.37	0.42
O5	-0.85	-	-0.83	-0.72	-0.52
Si	1.20	-	1.20	1.19	1.20

In order to investigate the effect of the framework, we also studied the naked Cu^+ catalyzed system by performing single point calculations on every structures in the reaction coordinate from the MOF-505 system but the framework was removed out. The data for this system are in Table 5 and Figure 12. We found dramatically changes in the energy profile. Formaldehyde adsorbs on Cu^+ with the energy of -39.0 kcal/mol. The coadsorption energy is -47.8 kcal/mol. The bare Cu^+ cation without the shielding effect of surrounding oxygen atom, as found in the paddlewheel active site, thus causing larger electrostatic field than that in the MOF-505 system, which in turn leads to much lower activation energy of 6.9 kcal/mol. The activation energy of Cu^+ system (6.9 kcal/mol) is the lower than that of MOF-505 system (11.0 kcal/mol).

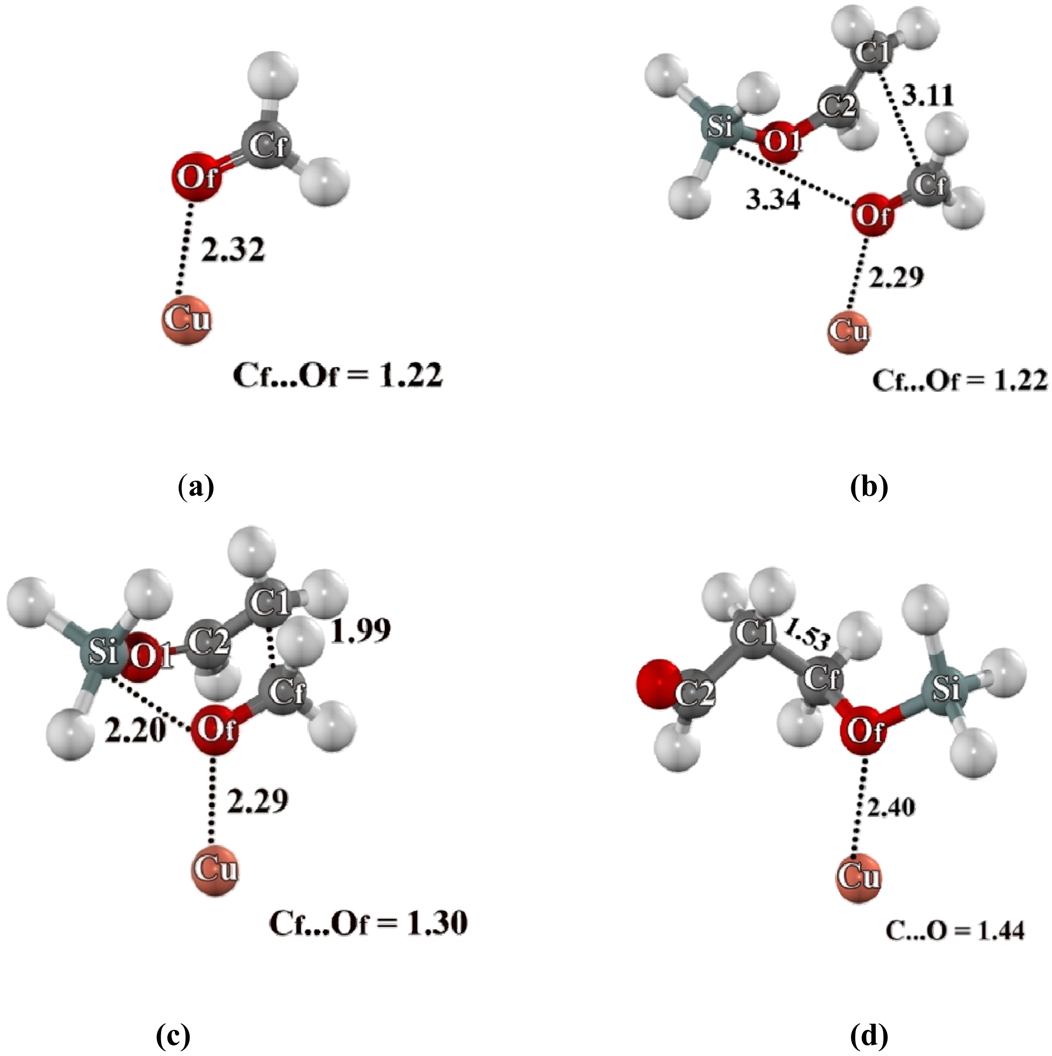


Figure 12 Structures of the $O{=}CH_2@Cu^+/H_3SiOHC{=}CH_2$. (a) $O{=}CH_2@Cu^+$, (b) $O{=}CH_2@Cu^+/H_3SiOHC{=}CH_2$ complex, (c) transition state structure and (d) $O{=}CHCH_2CH_2OSiH_3@Cu^+$.

Table 5 Atomic charge distribution calculated from the natural population analysis for the Mukaiyama aldol reaction between $O=CH_2$ and $H_3SiOHC=CH_2$ in naked Cu^+ system.

Atom (q)	Naked Cu^+ and Isolated molecule	Formaldehyde adsorption	Coadsorption complex	Transition state	Product
Cu	1.00	0.89	0.87	0.82	0.89
O_f	-0.49	-0.60	-0.63	-0.80	-0.96
C_f	0.22	0.31	0.27	0.04	-0.11
C1	-0.56	-	-0.56	-0.61	-0.60
C2	0.14	-	0.15	0.38	0.40
O1	-0.85	-	0.15	-0.71	-0.47
Si	1.20	-	1.19	1.18	1.18

3. Cu-ZSM-5 encapsulated formaldehyde ($O=CH_2$@Cu-ZSM-5) and Mukaiyama aldol reaction between Cu-ZSM-5 encapsulated formaldehyde and silyl enol ether ($O=CH_2$@Cu-ZSM-5/$H_3SiOHC=CH_2$)

The structure of the cation–exchanged site, the location of the Al in the site, and the number of Al atoms associated with the sites was explored. Cu^+ was found to have 2-fold coordination to framework O atoms when present at the intersections of the straight and sinusoidal exchange site**.** ZSM-5 zeolite exchanged with Cu^+ cations [Cu-ZSM-5] is an active catalyst**.** Figure 13 displays the structure of formaldehyde as adsorbed in Cu-ZSM-5 zeolite framework. Selected optimized geometrical parameters are listed in Table 6. Formaldehyde first interacts with the active Lewis acid site by its lone pair electron. The carbon-oxygen bond of formaldehyde is consequently elongated from 1.207 Å to 1.225 Å. The intermolecular distance, measured between the formaldehyde oxygen and the Cu atom of zeolite, is 1.889 Å and the corresponding adsorption energy for the $O=CH_2$@Cu-ZSM-5 complex is -31.8

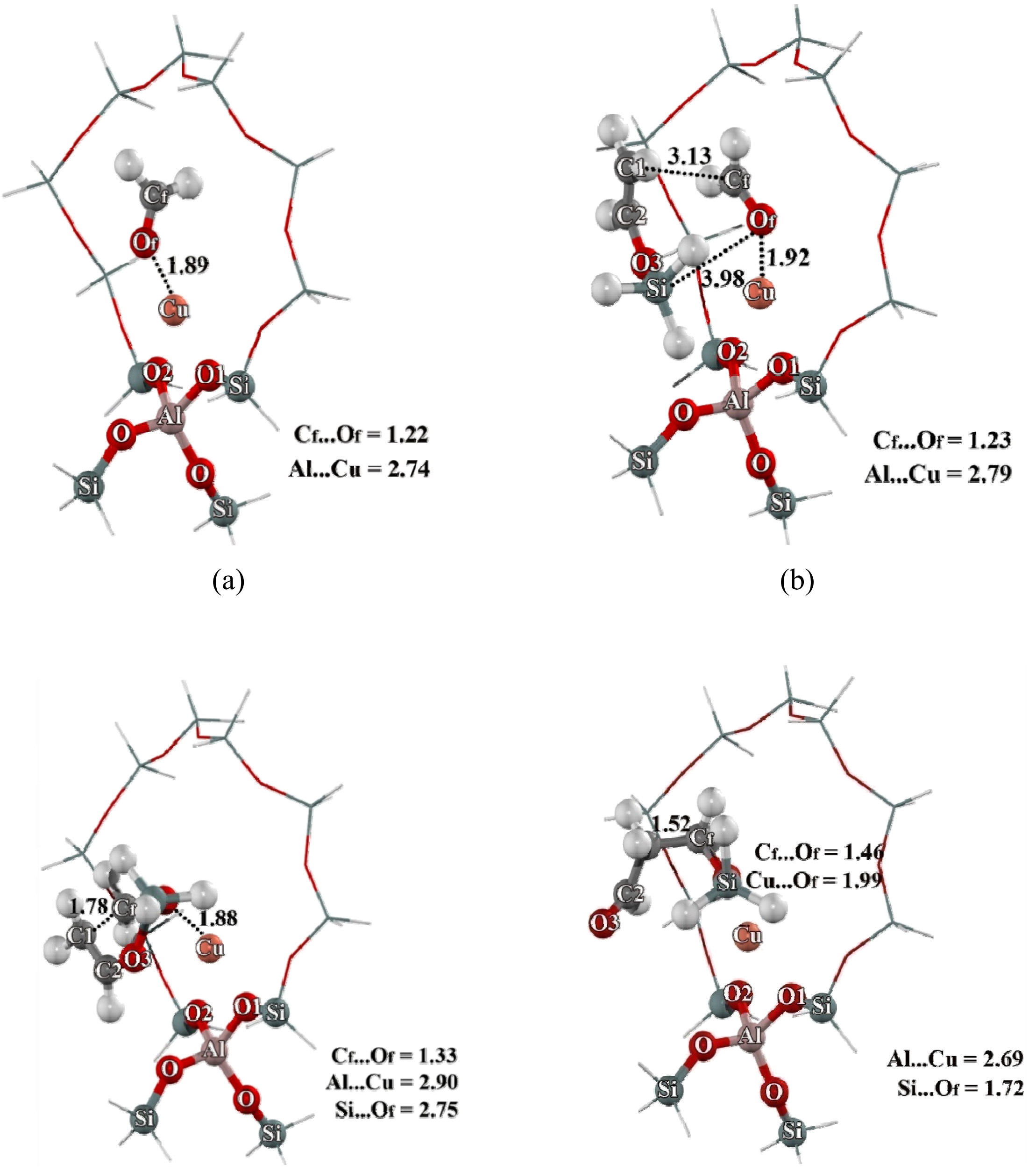
kcal/mol. The C_f-O_f···$Cu_{Cu\text{-}ZSM5}$ angle is 138.0°. Similar to the previous case, the mechanism proposed for the reaction catalyzed with Cu-ZSM-5 is as follows:

$$O{=}CH_2 + \text{Cu-ZSM-5} \longrightarrow O{=}CH_2@\text{Cu-ZSM-5} \quad (4)$$

$$SiH_3O\text{-}CH{=}CH_2 + O{=}CH_2@\text{Cu-ZSM-5} \longrightarrow O{=}CHCH_2CH_2OSiH_3@\text{Cu-ZSM-5} \quad (5)$$

$$O{=}CHCH_2CH_2OSiH_3@\text{Cu-ZSM-5} \longrightarrow O{=}CHCH_2CH_2OSiH_3 + \text{Cu-ZSM-5} \quad (6)$$

The fourth step is the adsorption of formaldehyde onto the Lewis acid site of the zeolite. Then the encapsulated formaldehyde interacts with silyl enol ether via a π interaction with a coadsorption energy, followed by the chemical reaction in order to produce the product. The entire reaction energy profile is presented in Figure 14. The reaction is initiated by coadsorption of silyl enol ether on the encapsulated formaldehyde at the active site of the zeolite. The silyl enol ether molecule diffuses over the adsorbed formaldehyde on the Cu-ZSM-5 with a coadsorption energy of -52.7 kcal/mol. The distance between formaldehyde carbon (C_f) and silyl enol ether (C1) indicates that the carbon of the formaldehyde carbonyl group is more electrophilic when adsorbed on the Cu-ZSM-5 than in the MOF-505 system. The Mukaiyama aldol reaction involves a bond formation between the carbon atom of formaldehyde (C_f) and the silyl enol ether carbon (C1) and the silicon-oxygen bond breaking giving the silicon group to the formaldehyde oxygen (O_f). In the transition state, the complex exhibits one imaginary frequency. The corresponding vibrational motion shows the concerted mechanism of the Mukaiyama aldol reaction: A carbon(C_f) carbon(C1) bond is formed between encapsulated formaldehyde and silyl enol ether and, simultaneously, a silyl enol ether (silyl group) leaves toward the formaldehyde oxygen atom.



(a) (b)

(c) (d)

Figure 13 Optimized structures of the O=CH_2@Cu-ZSM-5/ $H_3SiOHC=CH_2$ (a) O=CH_2@ Cu-ZSM-5 (b) O=CH_2@Cu-ZSM-5/$H_3SiOHC=CH_2$ complex (c) transition state structure and (d) O=$CHCH_2CH_2OSiH_3$@ Cu-ZSM-5 structure (Distance in Å).

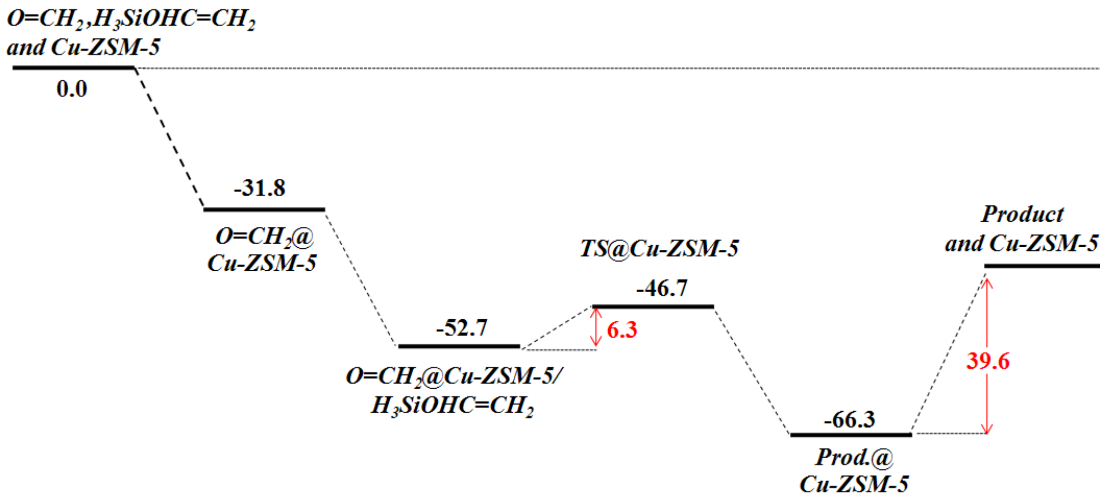


Figure 14 Calculated energy profiles (kcal/mol) for the Mukaiyama aldol reaction between $O=CH_2$ and $H_3SiOHC=CH_2$ in Cu-ZSM-5.

The silyl enol ether Si-O bond length in the transition structure is stretched from 1.692 to 1.754 Å, the distance between the silyl group (SiH_3) and the formaldehyde oxygen (O) is shortened from 3.980 to 2.739 Å. The C_f-O_f double bond of formaldehyde is changed from 1.230 to 1.332 Å as the distance between the silyl enol ether carbon (C1) and formaldehyde carbon (C_f) is constracted from 3.132 to 1.781 Å. We also examined the atomic charges of the molecules involved in the reaction by means of the NPA method, as shown in Table 7. Cu in the ZSM-5 zeolite structure bears a positive charge of 0.83. As formaldehyde adsorbs over the Cu, it becomes slightly more positive. The adsorption also causes the O_f atom in formaldehyde to become more negative and its C_f atom becomes more positive. At the transition state structure, the negative charge over the silicon accepting O_f atom (-0.79). The increased negative charge of O_f facilitates the silicon group transfer. The Cu charge of 0.72 stabilizes the structure. The activation energy is 6.3 kcal/mol. These results demonstrated that the electrostatic contribution from the Cu-ZSM-5 stabilizes the transition state structure.

Table 6 Optimized geometric parameters of isolated state, formaldehyde adsorption, coadsorption complex, transition state, and product of the Mukaiyama aldol reaction between formaldehyde and silyl enol ether on Cu-ZSM-5 using ONIOM (B3LYP/6-31G (d,p):UFF) method (bond lengths is in Å).

Parameters	Isolated molecule	Formaldehyde adsorption	Coadsorption complex	Transition state	Product
Distances (Å)					
Cu-O_f	-	1.889	1.923	1.880	1.991
Cu-Al	2.772	2.742	2.793	2.901	2.687
Cu-O1	1.994	1.990	2.088	1.939	2.118
Cu-O2	2.043	2.148	2.074	2.643	2.094
Al-O1	1.715	1.715	1.701	1.720	1.703
Al-O2	1.717	1.703	1.711	1.675	1.715
Si1-O1	1.612	1.613	1.605	1.614	1.605
Si2-O2	1.593	1.585	1.590	1.570	1.594
C_f-O_f	1.207	1.225	1.230	1.334	1.458
C-C1	-	-	3.132	1.777	1.525
C1-C2	1.333	-	1.341	1.413	1.521
C2-O3	1.365	-	1.354	1.287	1.209
Si-O3	1.678	-	1.692	1.754	4.204
O_f-Si	-	-	3.980	2.748	1.724
Angles (degree)					
∠ Si1-O1-Al	126.6	126.3	126.9	126.6	126.6
∠ Si2-O2-Al	131.6	132.2	131.6	133.5	130.4
∠ O1-Cu-O2	75.1	72.3	72.1	63.4	71.1

The activation energy barrier of Cu-ZSM-5 system is lower than in the MOF-505 system. The product in which the C_f-C1 bond is formed in volves a silyl group transfer from the oxygen atom of silyl enol ether to the formaldehyde oxygen. The adsorbed 3-silyloxy-propanal product is exothermic -66.3 kcal/mol and it requires 26.6 kcal/mol to desorb from the active site in final step. These results indicate that

Cu-ZSM-5 zeolite can be used as a catalyst in Mukaiyama aldol reaction and that they stabilize all species more than in the MOF-505 system.

Table 7 Atomic charge distribution calculated from the natural population analysis for the Mukaiyama aldol reaction between $O{=}CH_2$ and $H_3SiOHC{=}CH_2$ in Cu-ZSM-5.

Atom (q)	Naked Cu^+ and isolated molecules	Formaldehyde absorption	Coadsorption complex	Transition state	Product
Cu	0.83	0.74	0.72	0.58	0.72
O_f	-0.49	-0.58	-0.62	-0.85	-0.96
C_f	0.22	0.27	0.28	0.01	-0.10
C1	-0.56	-	-0.57	-0.63	-0.60
C2	0.14	-	0.14	0.46	0.40
O3	-0.85	-	-0.83	-0.72	-0.49
Si	1.20	-	1.19	1.19	1.19

In order to investigate the effect of the framework like in the case of MOF-505 system, we also studied the naked Cu^+ system where the structures were taken from Cu-ZSM-5 system. The data for this system are in Table 8 and Figure 15. Formaldehyde adsorbs on Cu^+ with the energy of -49.4 kcal/mol. The coadsorption energy is -61.4 kcal/mol. The bare Cu^+ cation without the shielding effect of surrounding oxygen atom, as found in the ZSM-5 framework, causes larger electrostatic field than that in the ZSM-5 system, which in turn leads to much lower activation energy of 0.3 kcal/mol. The activation energy of Cu^+ is the lower than of ZSM-5 system.

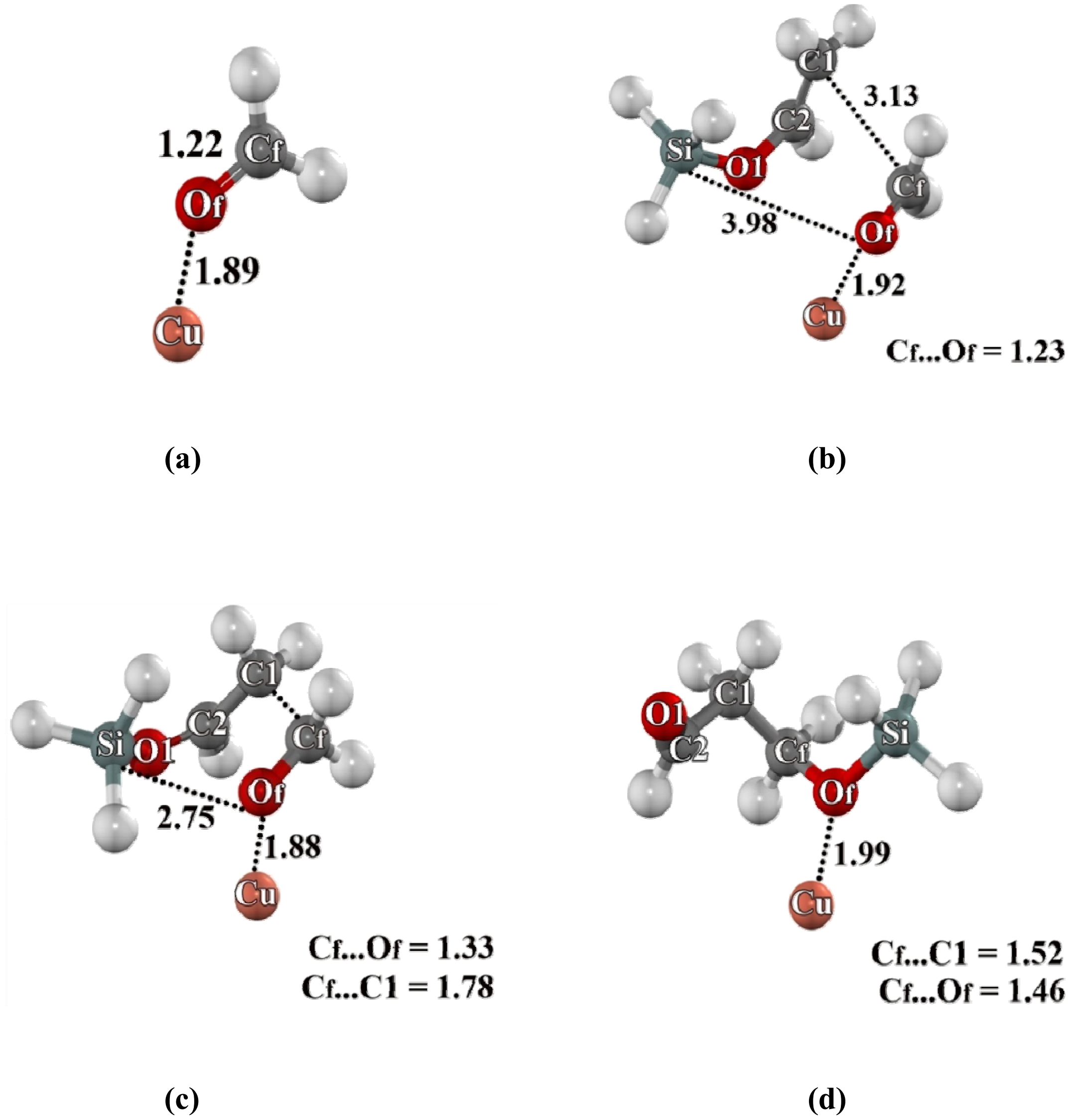


Figure 15 Structures of the $O{=}CH_2@Cu^+$ (Cu-ZSM-5)/$H_3SiOHC{=}CH_2$ (a) $O{=}CH_2@$ Cu^+(Cu-ZSM-5) (b) $O{=}CH_2@Cu^+$(Cu-ZSM-5)/$H_3SiOHC{=}CH_2$ complex (c) transition state structure (d) $O{=}CHCH_2CH_2OSiH_3@$ Cu^+(Cu-ZSM-5).

Table 8 Atomic charge distribution calculated from the natural population analysis for the Mukaiyama aldol reaction between O=CH_2 and $H_3SiOHC{=}CH_2$ in naked Cu^+ system.

Atom (q)	Naked Cu^+ and isolated molecules	Formaldehyde adsorption	Coadsorption complex	Transition state	Product
Cu	1.00	0.90	0.86	0.75	0.87
O_f	-0.49	-0.66	-0.66	-0.82	-0.98
C_f	0.22	0.35	-0.66	-0.01	-0.11
C1	-0.56	-	-0.54	-0.63	-0.61
C2	0.14	-	0.13	0.44	0.39
O1	-0.85	-	-0.85	-0.71	-0.47
Si	1.20	-	1.17	1.16	1.16

4. Comparison of Catalyst of Mukaiyama aldol Reaction

4.1 Energy barrier

The energy diagrams of the three systems are put into one plot in Figure 16. For the bare system, the activation energy of the reaction is 13.7 kcal/mol. The activation barriers of the MOF-505 system (11.0 kcal/mol) and the Cu-ZSM-5 system (6.3 kcal/mol). The results indicate that MOF-505 and Cu-ZSM-5 can be used as a catalyst in the Mukaiyama aldol reaction between carbonyl compound and silyl enol ether. Because both MOF-505 and Cu-ZSM-5 catalysts can lower the activation energy compared to the uncatalyzed reaction and that it stabilizes system. MOF-505 and Cu-ZSM-5 catalysts made carbon atom of formaldehyde is more positive charge which can be attacked by other carbon nucleophile such as carbon in silyl enol ether. Meanwhile, the oxygen atom of formaldehyde is induced to be more negative. It was also found that environmental inclusion of the metal- organic framework and zeolite has an effect on the structure and energetics of the adsorption complexes. The adsorption state in zeolite is more stable than that in MOF-505.

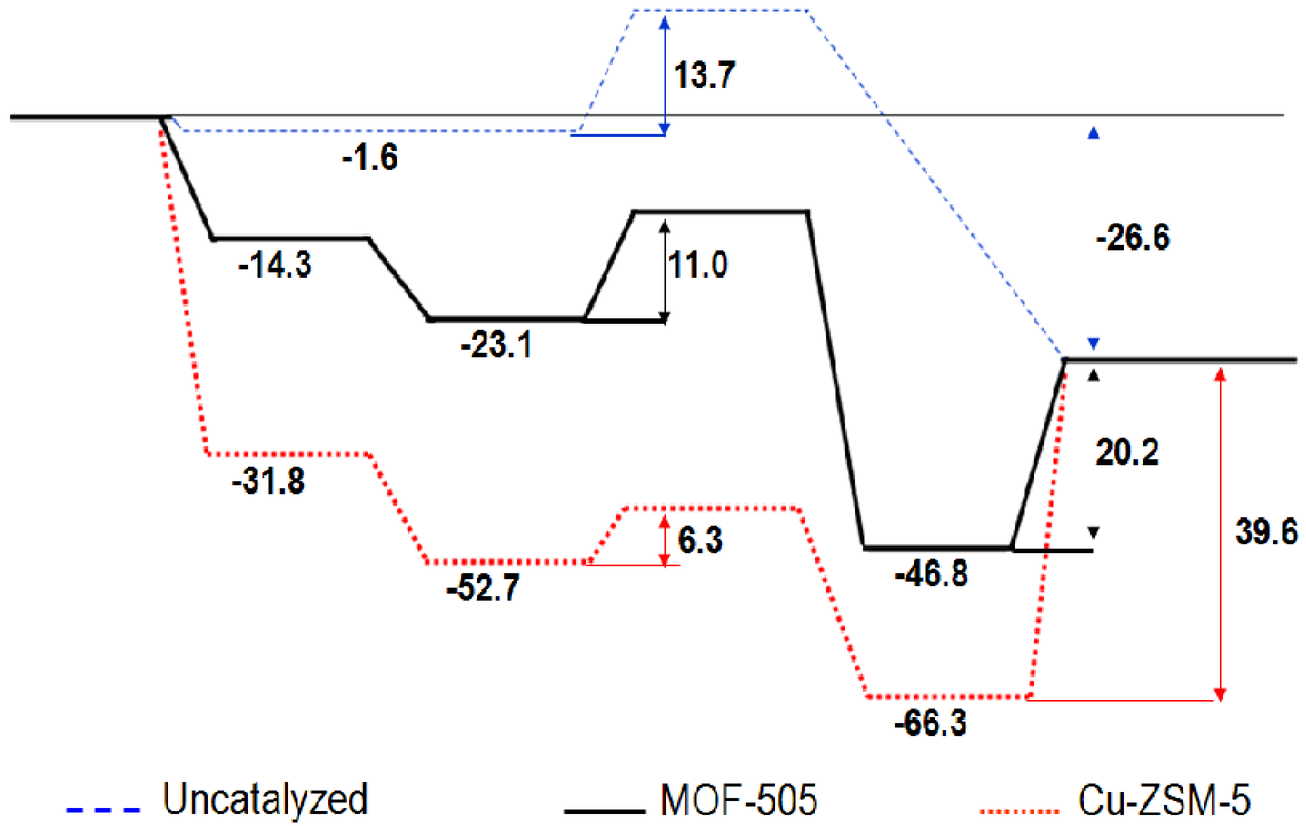


Figure 16 Calculation energy profiles (kcal/mol) for the Mukaiyama aldol reaction between formaldehyde and silyl enol ether in the MOF-505 system (solid line), the Cu-ZSM-5 system (dotted line) and the uncatalyzed system (dashed line).

4.2 Frontier Molecular Orbital (FMO) Energy

Figure 17 illustrates the relative energy of the Frontier Molecular Orbital (FMO) energies (E_{LUMO}) between the formaldehyde without catalyst and formaldehyde activated with catalysts (MOF-505 and Cu-ZSM-5 zeolite) obtained from B3LYP/6-31G(d,p) calculations. As mentioned earlier in the proposed mechanism that electrons are transfer from silyl enol ether to formaldehyde, the energy difference between the LUMO of formaldehyde and the HOMO of the ether is expected reduce upon the formaldehyde adsorption over a catalyst. From the FMO analysis, it is found that the LUMO energy of formaldehyde is reduced from 1.161 eV in the isolated state to -6.264 and -6.669 eV upon the adsorption on the MOF-505 and Cu-ZSM-5, respectively. Compared to the HOMO energy of silyl enol ether (-6.426), the electron transfer from the silyl enol ether is facilitated due to the reduced HOMO-LUMO energy difference. By the MOF-505 catalyst an energy of 0.162 eV is reguired for the electron transfer. Moreover, ZSM-5 is the better catalyst because it makes the E_{LUMO} of encapsulated formaldehyde even lower than E_{LUMO} of ether molecule. Therefore, the FMO analysis results confirm that both catalysts can be applied to facilitate the Mukaiyama aldol reaction between formaldehyde and silyl enol ether and Cu-ZSM-5 is more effective catalyst than MOF-505.

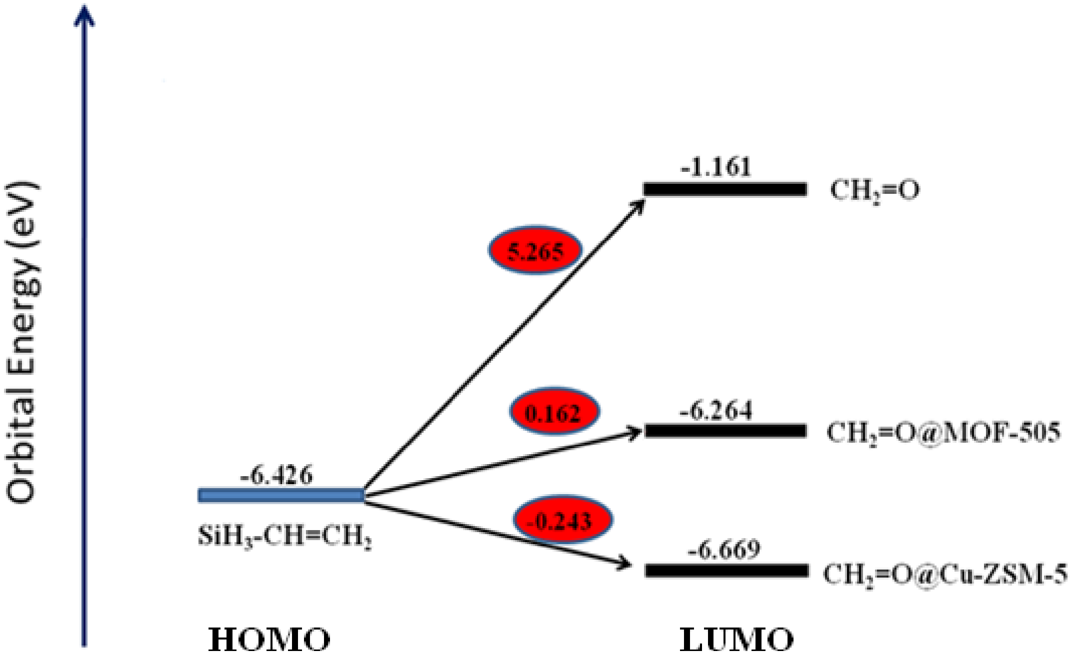


Figure 17 The Frontier Molecular Orbital (FMO) energies obtained from B3LYP/6-31G(d,p) calculations for E_{LUMO} of the formaldehyde without catalyst and formaldehyde activated with catalysts (MOF-505 and Cu-ZSM-5 zeolite) compared to E_{HOMO} of silyl enol ether

4.3 Charge Distribution

The charge distribution and energy evolution of the catalyzed reactions were put into one plot in Figure 18. From the total charge distribution analysis for reactants only where the value of isolated reactants is considered to be 0.0e, the charge of formaldehyde upon the adsorption become positive by 0.032e and 0.046e, for MOF-505 and Cu-ZSM-5 catalysts, respectively. Once the silyl enol ether joins in the coadsorption, the positive charge is even enhanced, revealing the electron transfer from the reactants to the catalyst. Concerning the distribution in the transition structure, the value of reacting species over Cu-ZSM-5 (0.192e) is more positive than that of MOF-505 system (0.035e). It can be discussed that the transition state is in which the electrons were transferred. Cu-ZSM-5 was also found to be more efficient in facilitate the transfer than the MOF-505.

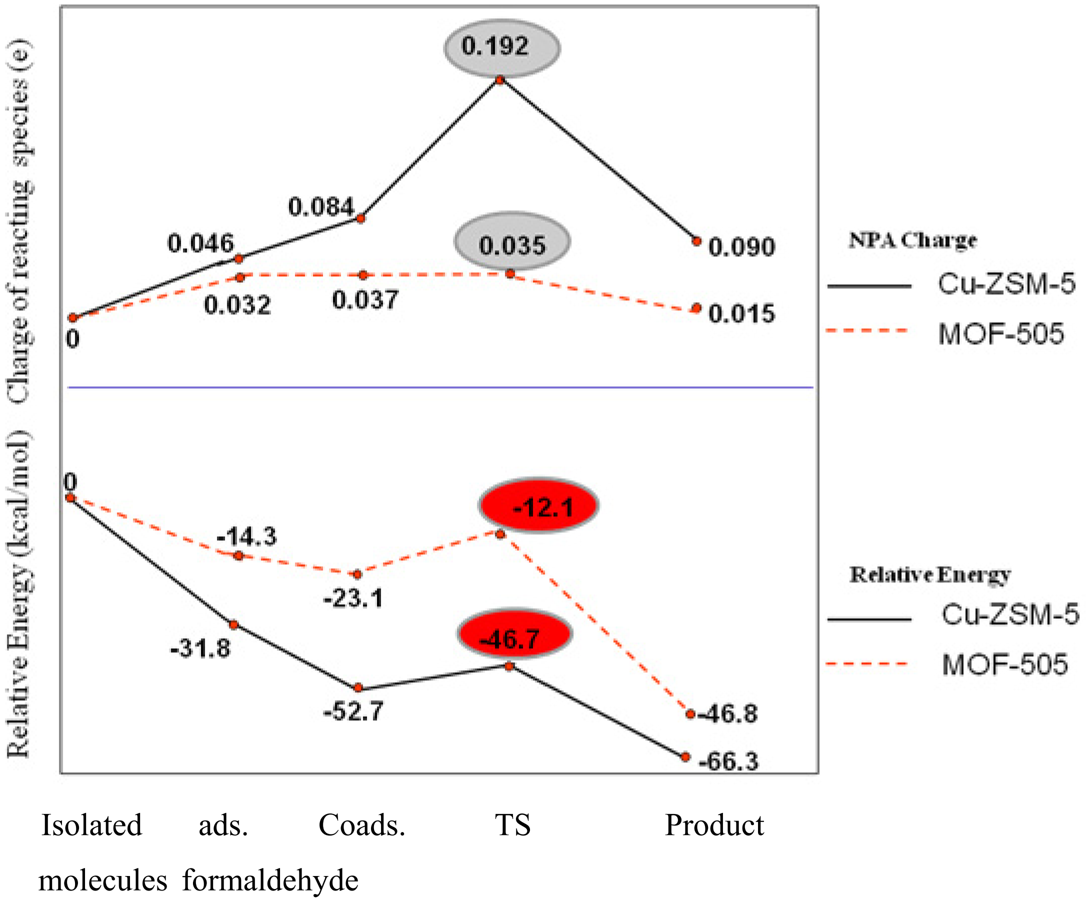


Figure 18 Cu-ZSM-5 and MOF-505 energy evolution (the given charge is the total charge only on the adsorbate)

CONCLUSION

Density-functional theory and the ONIOM approach are used for comparing the catalytic efficiency between metal-organic framework (MOF-505) and zeolite structure (Cu-ZSM-5) on the Mukaiyama aldol reaction of formaldehyde and silyl enol ether. The reaction mechanism is proposed to be intermediate-free concerted, consisting of silyl group transfer and carbon-carbon bond formation. Both MOF-505 and Cu-ZSM-5 contain copper cation which behave as the Lewis acid. Not only the acid in both catalysts is predicted to reduce the energy barrier, it was also found that environmental inclusion of the metal-organic framework and zeolite has an effect on the structure and energetics of the adsorption complexes. As a consequence, it leads to a lower energy barrier (ΔE_{act} = 11.0 and 6.3 kcal/mol) of the reaction as compared to the bare model system (13.7 kcal/mol). MOF-505 and Cu-ZSM-5 catalysts made carbon atom of formaldehyde is more positive charge which can be attacked by other carbon nuclephiles on the carbon atom. The FMO analysis results confirm that Cu-ZSM-5 is more effective catalyst than MOF-505 for the reaction between formaldehyde and silyl enol ether. Morover, it was found that the charge distributions of reacting species in transition state over Cu-ZSM-5 (0.192) system was more positive than that of one 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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APPENDIX

PRESENTATION:

- **Structures and Mechanism of the Mukaiyama Aldol Reactions between Metal Organic Frameworks-505 Encapsulated Formaldehyde and Silyl Enol Ether: An ONIOM study**.

Sudarat Yadnum, Saowapak Choomwatana, Pipat Khongpracha and Jumras Limtrakul. Pure and Applied Chemistry International Conference (PACCON 2009), Naresuan University, Phitsanulok, Thailand, January 14 - 16, 2009. (Poster Presentation)

- **Mechanism of MOF-505 and Cu-ZSM-5 Promoted Mukaiyama Aldol Reaction:An ONIOM study.**

Sudarat Yadnum, Saowapak Choomwattana, Pipat Khongpracha and Jumras Limtrakul. Abstract of paper Congress on The 2009 NSTI Nanotechnology Conference and Trade Show, Houston, United States of America, May 1-8, 2009. (Poster Presentation)

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