THESIS

THEORETICAL STUDY ON REACTION MECHANISMS OF ETHYLENE OXIDE HYDRATION OVER H-ZSM-5: AN ETHYLENE GLYCOL FORMATION

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THESIS

THEORETICAL STUDY ON REACTION MECHANISMS OF ETHYLENE OXIDE HYDRATION OVER H-ZSM-5: AN ETHYLENE GLYCOL FORMATION

THANA MAIHOM

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Stepwise and concerted mechanisms of ethylene oxide hydration reaction within a cluster model covering nanocavity, where the straight and zigzag channels intersect, of H-ZSM-5 have been proposed and investigated by means of the ONIOM(B3LYP/6-31G(d,p):UFF) and embedded-ONIOM(B3LYP/6-31G(d,p): UFF) methods. For the stepwise mechanism, the hydration reaction of ethylene oxide starts from the ring-opening of ethylene oxide by breaking of the C-O bond to form the alkoxide intermediate followed by the hydration of the alkoxide intermediate to produce ethylene glycol as the product of the reaction. The calculated activation energies are computed to be 34.4 and 14.5 kcal/mol for the ring-opening and hydration steps, respectively. For the concerted mechanism, the ring-opening and hydration take place in simultaneously with a small activation barrier of 13.3 kcal/mol. This reaction is suggested as a more economical alternative to the present non-catalytic hydration of ethylene oxide via the concerted mechanism for the production of ethylene glycol, a versatile intermediate in a wide range of applications, and should be of particular interest to industry.

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Student's signature

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Finally, I would like to dedicate this thesis to my lovely parents, my older sister, my older brothers and my grandmother. Their love and support for me is priceless.

Thana Maihom
April 2008

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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
C = Concerted pathway
DFT = Density functional theory
E_a = Activation energy
E_{des} = Desorption energy
FAU = Faujasite zeolite
h = hour
HF = Hartree-Fock
Int = Intermediate structure
ITQ24 = Instituto de Tecnologia Quimica valencia 24
kcal = kilocalories
kJ = kilojoules
LHSV = Liquid Hourly Space Velocity
MM = Molecular Mechanics
mm = millimeter
MO = Molecular Orbital
MOR = Mordenite zeolite
MPa = Mega Pascal
MP2 = The second-order Møller-Plesset perturbation theory
ONIOM = our Own N-layered Integrated molecular Orbital and molecular Mechanics
Prod = Product structure
QM = Quantum Mechanics
QM/MM = Quantum Mechanical/Molecular Mechanical
S = Stepwise pathway
S_N2 = Substitution nucleophilic bimolecular

LIST OF ABBREVIATIONS (Continued)

TS = Transition State structure
UFF = Universal Force Fields
ZSM-5 = Zeolite Socony Mobil 5

THEORETICAL STUDY ON REACTION MECHANISMS OF ETHYLENE OXIDE HYDRATION OVER H-ZSM-5:

AN ETHYLENE GLYCOL FORMATION

INTRODUCTION

Widespread industrial production of ethylene glycol began in 1937 when ethylene oxide, a component in its synthesis, became cheaply available. As an adaptable intermediate, it has now become increasingly important, particularly in the plastics industry, in a wide range of applications, for example, polyester textiles, plasticizers, consumer packaging and lubricants. In addition, ethylene glycol capabilities as an antifreeze coolant make it a prominent constituent of verification.

It can be produced by a well-known process as the hydration of ethylene oxide via the ring-opening reaction. Industrially, the non-catalytic hydration is the main process for the production of ethylene glycol. However, the high conversion and selective production requires a large excess of water which results in costly excessive energy consumption for the product evaporation process. To solve this problem, a number of catalysts have been tested over the years for the effective catalyzation in the hydration of ethylene oxide, for example ion exchange resin (Strickler *et al.,* 1999, Iwakura *et al.,* 1999; Shvets *et al.,* 2000), quaternary phosphonium halides (Kawabe *et al.,* 2000), supported metal oxides (Li *et al.,* 2004, 2005, 2006), polymeric organosilane ammonium salt (Marie *et al.,* 1999), macrocyclic chelating compounds (Kruchten *et al.,* 1999), and zeolite (Li *et al.,* 2004). These catalysts, however, still have some drawbacks for the economic catalyzation in terms of both the conversion and selectivity. In the field of catalysis, zeolite is considered to be one of the best catalysts because it has many advantageous and diverse properties, such as easy product separation, it can be reactivated and it is reusable. In addition, zeolite has increasing benefits from nano-pores size and shape selectivity. Recently, an acidic ZSM-5 zeolite was found to be an active catalyst for the hydration of ethylene oxide (Li *et al.,* 2004). Under the reaction temperature of 150 °C and water to ethylene oxide molar ratio of 22, ethylene oxide conversion and ethylene glycol selectivity can be reached to 98% and 76%, respectively, over H-ZSM-5 catalyst.

Zeolites are microporous aluminosilicates with a large number of atoms in the unit cell. In theoretical studies, small clusters are usually used for representing the models of catalytic zeolite. However, these cluster models do not incorporate the framework effect which has an important role for the reactions inside zeolites (Brändle *et al.,* 1998, Sinclair *et al.,* 1998, Clark *et al.,* 2003). In order to account for the framework effect on the zeolite model various techniques such as the large quantum clusters and periodic *ab initio* calculations are performed. Whilst these techniques are able to produce accurate results, they are not practical for the large unit cell of zeolites since they are computationally too demanding and expensive. In research endeavors to overcome these limitations, researchers discovered various hybrid methods, i.e., the embedded cluster model (Hillier *et al.,* 1999; Ketrat *et al.,* 2003; Treesukol *et al.,* 2005; Sirijaraensre *et al.,* 2005; Jungsuttiwong *et al.,* 2005; Sirijaraensre *et al.,* 2006,), combined quantum mechanics/molecular mechanics (QM/MM) (Greatbanks *et al.,* 1996; Brändle *et al.,* 1998; Limtrakul *et al.,* 2000; Treesukol *et al.,* 2001), as well as the more general ONIOM (our-Own-N-layered Integrated molecular Orbital + molecular Mechanics) (Kasuriya *et al.,* 2003; Panjan *et al.,* 2003; Raksakoon *et al.,* 2003; Boekfa *et al.,* 2004; Namuangruk *et al.,* 2004, 2005, 2006; Pantu *et al.,* 2004, 2007; Pabchanda *et al.,* 2005; Jansang *et al.,* 2006; Lomratsiri *et al.,* 2006). Recently, the ONIOM method has been successfully used to investigate the adsorptions (Kasuriya *et al.,* 2003; Namuangruk *et al.,* 2006; Pantu *et al.,* 2007) and reactions of hydrocarbons over zeolites (Pantu *et al.,* 2004; Namuangruk *et al.,* 2005, 2006; Pabchanda *et al.,* 2005; Jansang *et al.,* 2006).

To the best of our knowledge, the detail of the reaction mechanism of the ethylene oxide hydration over zeolite has not previously been reported in the literature. This is undoubtedly due mainly to its complicated three-dimensional porous structure that limits the ability to observe it experimentally. From an industry point of view, understanding the reaction mechanism in molecular scale could help in optimizing the reaction conditions, which will result in increasing product selectivity.

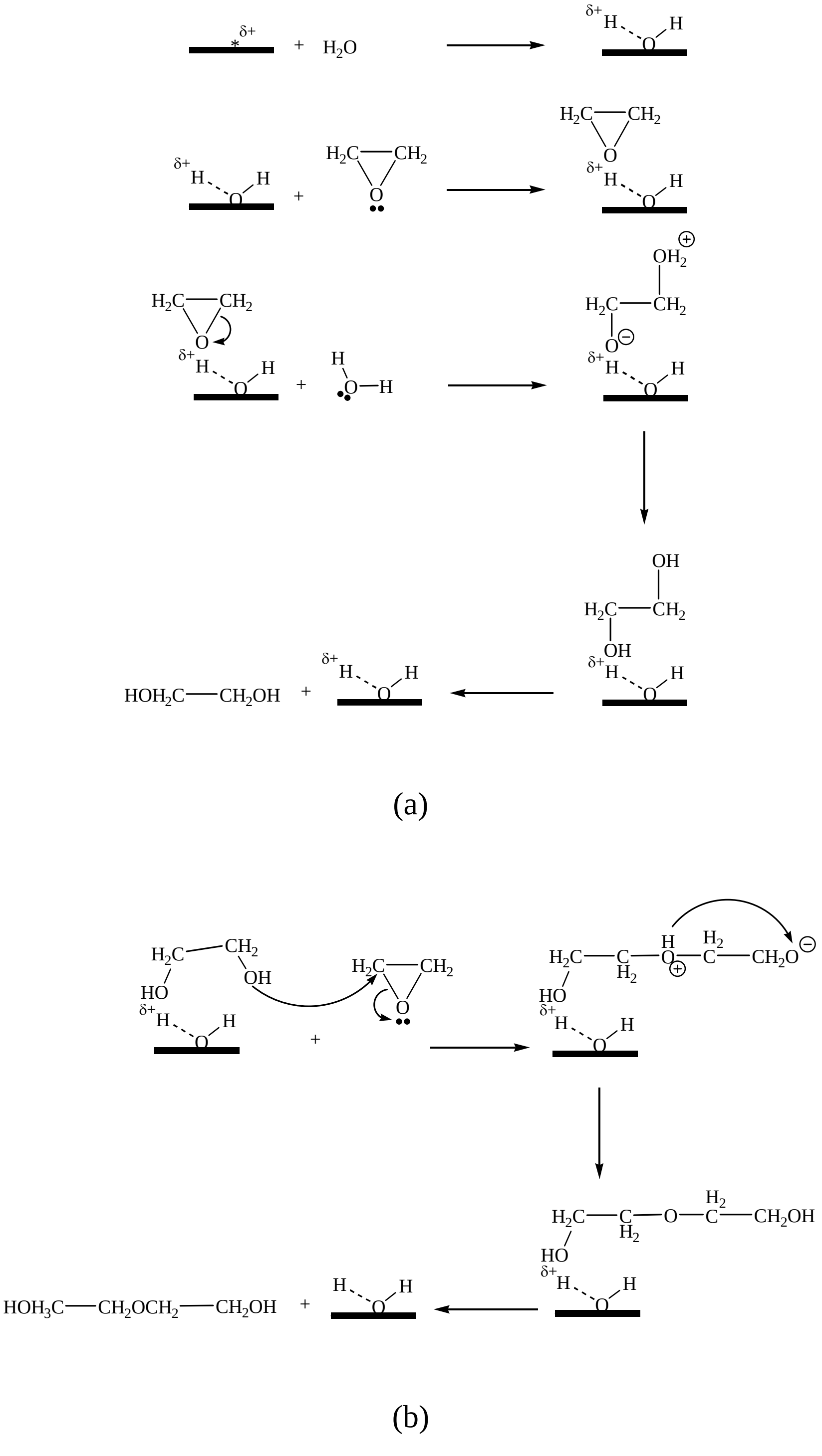
To gain insight into the molecular mechanisms, we present in this study the theoretical investigation on the reaction mechanisms of the ethylene oxide hydration over H-ZSM-5 zeolite by using the ONIOM method. The structures and energetics of the reaction coordinates and reaction mechanisms are discussed.

LITERATURE REVIEW

Numerous catalysts are used for investigating the hydration of ethylene oxide into ethylene glycol. The many patents and literatures evidence these developments. The important point of the hydration of ethylene oxide into ethylene glycol is that the catalysts employed decrease the quantity of water in the reaction processes which results in excessive energy consumption. The catalysts most used in the reaction of ethylene oxide hydration into ethylene glycol are ion exchange resins (Iwakura *et al.,* 1999; Strickler *et al.,* 1999; Shvets *et al.,* 2000). Other catalysts used contain quaternary phosphonium halides (Kawabe *et al.,* 2000), supported metal oxides (Li *et al.,* 2004, 2005, 2006), polymeric organosilane ammonium salt (Marie *et al.,* 1999), macrocyclic chelating compounds (Kruchten *et al.,* 1999), and zeolite (Li *et al.,* 2004).

In 2004, Li and co-worker used a supported metal oxide: the niobium oxide supported on α-Al_2O_3 as the preparation to investigate the hydration of ethylene oxide. In this work, the obtained ethylene glycol selectivity and conversion of ethylene oxide from niobium oxide was compared with the other solid acid catalysts such as acidic ZSM-5 (Si/Al = 61.2), AlPO4–$Cu(NO_3)_2$ and Nafion XR (6%)/SiO_2. The fixed-bed reactor with an inner diameter of 10 mm and a length of 300 mm was used for testing the reaction. The conditions of the reaction were carried out at a temperature of 150 °C and pressure of 1.5 MPa with a water/ethylene oxide mole ratio of 22 and LHSV of 10 h^{-1}. At the optimal conditions, the niobium oxide supported on α-Al_2O_3 showed much better hydration performance in activity and selectivity than other solid acid catalysts. Moreover, Li and others studied the effect of α-Al_2O_3 modification with the $MgAl_2O_4$ for the reaction of ethylene oxide hydration (Li *et al.,* 2005). The α-Al_2O_3 support modified with $MgAl_2O_4$ was able to increase the mechanical strength and basicity. Furthermore, they found that the acidity of the Nb_2O_5, which was supported on α-Al_2O_3 modified with the $MgAl_2O_4$ decreased with increasing of $MgAl_2O_4$ loading and was weaker than the niobic acid. The conversion of ethylene oxide decreased with increasing $MgAl_2O_4$ loading, while the ethylene glycol selectivity showed a maximum at MgAl2O4 loading of 2.23%.

Subsequently, Li and co-worker (2006) studied the effect of tin on Nb_2O_5/α-Al_2O_3 catalyst for ethylene oxide hydration. They added tin 10% by weight of tin to the Nb_2O_5/α-Al_2O_3 catalyst. The tin significantly improved the water adsorption compared with the unpromoted Nb_2O_5/α-Al_2O_3 catalyst and the $MgAl_2O_4$ modified catalyst. The ethylene glycol selectivity was increased in the ethylene oxide hydration. Although the modified niobium oxide gave a high ethylene oxide conversion and ethylene glycol selectivity, the high ratio of water/ethylene oxide (22) was used. Li and a co-worker proposed the mechanisms of ethylene oxide hydration into monoethylene glycol and higher glycols shown in Figures 1a and 1b. These proposed mechanisms were similar to the mechanism in the solid acid catalysts. The reaction started with the adsorption of water onto acidic sites to form positively charged water species. Then, this species that was the actual active site was reacted with ethylene oxide to form the positive charged ethylene oxide species. Subsequently, the positive charged ethylene oxide was attacked by nucleophile water, followed by proton transfer to form positively charged monoethylene glycol. After that, the active site of the positive water species was regenerated by desorption of the monoethylene glycol product (see Figure 1a). As side reactions, the positively charged adsorbed monoethylene glycol may react with another ethylene oxide to form diethylene glycol and other polyglycols (see Figure 1b).



(a)

(b)

Figure 1 Schematic diagram the mechanisms of ethylene oxide hydration over niobium oxide into (a) monoethylene glycol and (b) higher ethylene glycol.

Source: Li *et al.* (2006)

Recently, the heterolytic ring-opening mechanisms for ethylene oxide in acidic, neutral, and alkaline environments using the B3LYP/6-311+G(d,p) theory were studied by Lundin and co-worker (2007). The reactions of the ring-opening for these studies are shown in Figure 2. For this research, they reported their finding in three sections: 1) the hydration of ethylene oxide was shown in two different reaction mechanisms under neutral, acidic and alkaline conditions. Under neutral conditions, the one water molecule was protolyzed in the transition state for the ring-opening reaction. For this reaction, the high activation barrier that was obtained (205 kJ/mol) agrees with the low reaction rate in the experimental observation. Under acidic and alkaline conditions, the S_N2 reaction showed that the water and hydroxide ions acted as nucleophiles while the oxonium ions and water acted as electrophiles. In these reactions, the activation energies of ~80 and ~60 kJ/mol that were obtained were lower than the reaction under neutral conditions, which agrees with experimental results. 2) The mechanism under neutral conditions could be the inspiration for understanding the observed product distribution in experiments for more complex epoxides, i.e., the steric and electronic effects. 3) The ring opening of ethylene oxide, the effect of pH was explored and the role of the nucleophile in both acidic and alkaline was highlighted. While this puts constraints on any successful strategy to produce epoxides in the aqueous system, the stability of the epoxide under neutral conditions was encouraging and could be utilized in the development of an epoxidation catalyst.

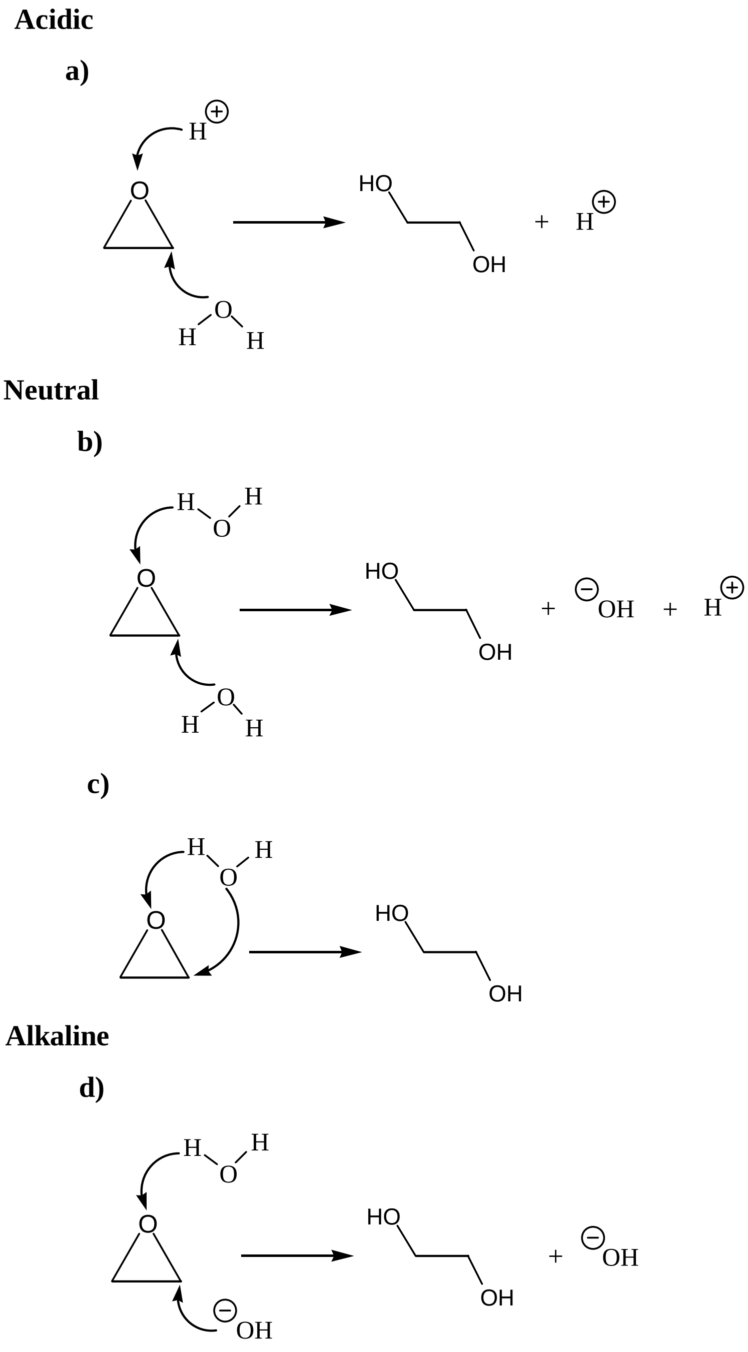


Figure 2 Schematic diagram of (a) the hydrolysis of ethylene oxide under acid, (b and c) neutral and (d) alkaline conditions. Path (c) represents the bare hydrolysis reaction.

Source: Lundin *et al.* (2007)

It is well known that the ring-opening reaction of the epoxides is the common reaction for producing glycol products. Ogawa and co-worker (1992) used the ZSM-5 catalyst, which was treated by octadecyltrichlorosilane to study the ring-opening reaction of epoxides. This catalyst exhibited high activity for the ring-opening reaction of epoxides in a toluene-water solvent. The shape-selectivity of H-ZSM-5-C_{18} in the liquid phase had also been observed by comparing the reaction rates with those over octadecyltrichlorosilane treated SiO_2-Al_2O_3. They concluded that the ZSM-5 catalyst could be used-is this correct in the reaction of epoxides hydration. Moreover, they employed the H-ZSM-5 for catalyzing the ring-opening of 1,2-epoxyalkane with alcohols to give alkoxy alcohols (Ogawa *et al.,* 1996). The reaction proceeded due to the shape-selectivity properties of H-ZSM-5. The ring-opening reaction rate was reserved by using the larger carbon atoms of alcohols. Under basic conditions, through the substitution of nucleophile alcohols at the more hindered position of the epoxide, a higher selectivity could be obtained.

Zeolites are one of the many catalysts that are used for studying the reaction of ethylene oxide hydration to ethylene glycol (Li *et al.,* 2004). To the best of our knowledge, the detailed mechanism of such reaction over zeolite has never been reported in literature. Understanding the reaction mechanisms can help in optimizing the conditions to increase the selectivity of the glycol product. Theoretical study is one of the practical tools that leads to a clear understanding of the reaction mechanisms of ethylene oxide hydration over zeolites that is not possible through experimental investigations due to the complicated three-dimensional porous structure of zeolites.

For the theoretical study of the adsorption and reaction mechanism over zeolites, different models were employed to represent the structures of zeolites that are microporous aluminosilicates with a large number of atoms in the each unit cell. In order to include the zeolite framework effect at an affordable computational cost, hybrid methods were developed, such as the embedded cluster, the combined quantum mechanics/molecular mechanics (QM/MM) methods (Greatbanks *et al.*, 1996; Brandle *et al.*, 1998; Khaliullin *et al.*, 2001; Limtrakul *et al.*, 2001) or our-

Own-N-layered-Integrated molecular Orbital + molecular Mechanics (ONIOM) method (Svensson *et al.*, 1996; de Vries *et al.*, 1999). These methods can be used to accurately describe the confinement effect of the zeolite framework. The ONIOM method has been successfully used to investigate the adsorption of hydrocarbons and interesting reaction mechanisms over zeolites. Kasuriya and co-worker (2003) investigated the adsorption of ethylene, benzene, and ethylbenzene on H-FAU zeolites with three different cluster sizes and methods comprising various two level ONIOM2 schemes. They found that the extended framework significantly enhances their adsorption energy of adsorbates to the zeolites. From the results, they suggested that the ONIOM approach yields a more accurate and practical model in studying the adsorption of unsaturated hydrocarbons on zeolites. More recently, Rungsirisakun and co-worker (2004) used the three-layer ONIOM scheme (B3LYP/6-31G(d,p):HF/3-21G:UFF) to study the interactions of benzene with the important zeolitic catalysts (H-BEA, H-ZSM-5, and H-FAU). The extended zeolitic framework covering the nanocavity had an effect on the adsorption properties and lead to the differentiation of different types of zeolite. The computed adsorption energy for benzene on the H-FAU zeolite can be compared well with the experimental observation. From the results, the researchers suggested that the ONIOM3(MP2/6-31G(d,p):HF/3-21G:UFF) scheme provides a more accurate method for investigating the adsorption of aromatic hydrocarbons on these zeolites.

Moreover, the adsorption of light alkanes and alkenes were studied by using the embedded ONIOM approach (Pantu *et al.,* 2007). The ONIOM2 calculations gave accurate adsorption energies for the adsorption of ethane, propane, and *n*-butane in H-FAU and H-MOR that agrees well with the experimental measurements. They reported that the UFF force field, which is used to model the extended zeolitic framework was found to be essential for describing the confinement effect of the zeolite and led to the differentiation of different types of zeolites.

For the studied of reaction mechanisms, the ONIOM method is used to investigate many reactions in zeolites, for example the alkylation of benzene with ethylene over faujasite zeolite, which was investigated using the ONIOM3 model

(Namuangruk *et al.,* 2004). The ONIOM3 model is shown to be accurate for predicting adsorption energies of the adsorbed reactants and products and compare well with experimental estimates. The results derived from the study suggest that the ONIOM approach yields an accurate and practical model for exploring the structure, adsorption, and reaction mechanisms of zeolites.

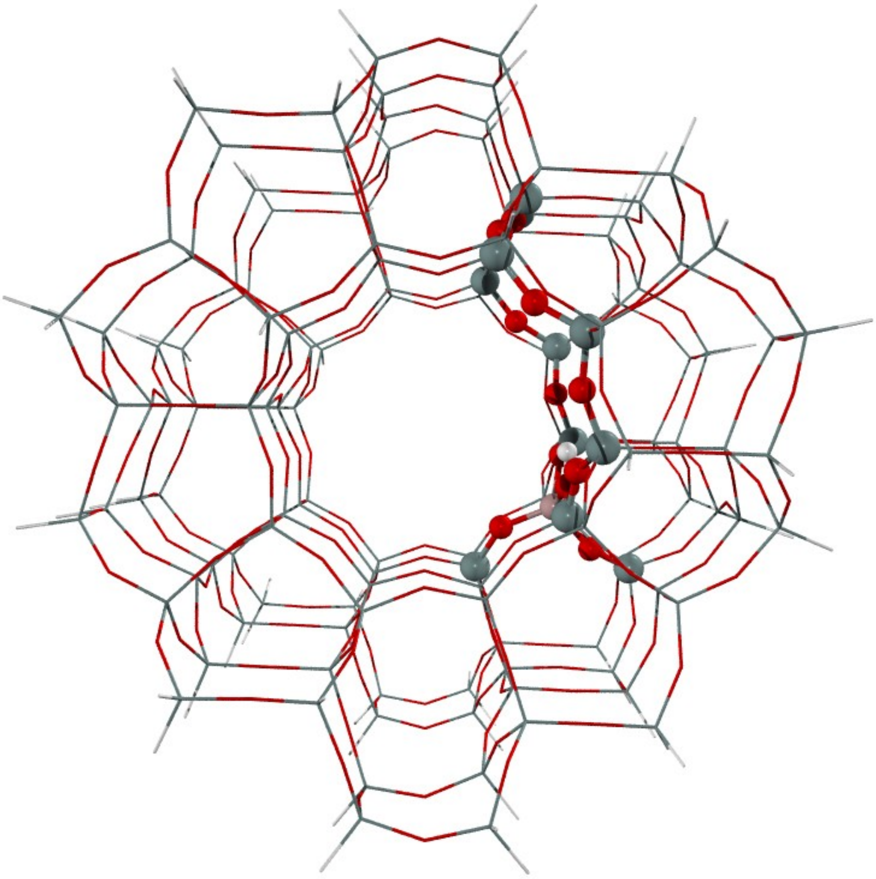
In order to include the long-range effects of the electrostatic Madelung potential from the infinite zeolite lattice, the embedded ONIOM method is employed. This embedded method has been performed in several calculations for both the adsorption and reaction mechanisms. Injan and co-worker (2005) applied the embedded ONIOM method to investigate the adsorption of pyridine on H-Faujasite zeolite. They found that the embedded method accurately gave the adsorption energy of pyridine in Faujasite zeolite, which agrees well with the experimental value. Moreover, the adsorption of pyridine on H-ZSM5 zeolite has been investigated with three different cluster sizes and methods that included the embedded ONIOM (Lomratsiri *et al.,* 2006). Inclusion of the electrostatic contributions of the extended framework via the embedded ONIOM method further significantly enhances the adsorption energy of the pyridine molecule to the zeolite. The predicted adsorption energy of the pyridine/zeolite complex was in good agreement with the experimental data. They suggested that the embedded ONIOM method, together with the quantum chemical methods and the UFF force field, provides an efficient and accurate way for studying the adsorption properties of organic molecules with zeolites. Furthermore, the embedded ONIOM method is found to be a more accurate approach for studying the adsorption of aromatic hydrocarbons on mordenite zeolite (Jansang *et al.,* 2007).

In addition, the embedded ONIOM model is employed to study the reaction mechanisms of cumene formation via benzene alkylation with propylene in a newly synthesized ITQ-24 zeolite (Jansang *et al.,* 2006). The results in this study show that the electrostatic potential from the extended zeolite framework play a major role in stabilizing the transition state and the intermediate in the reaction pathway. Moreover, the activation energy of the ionic system was reduced according to the ionicity of the transition state organic fragment.

MATERIALS AND METHODS

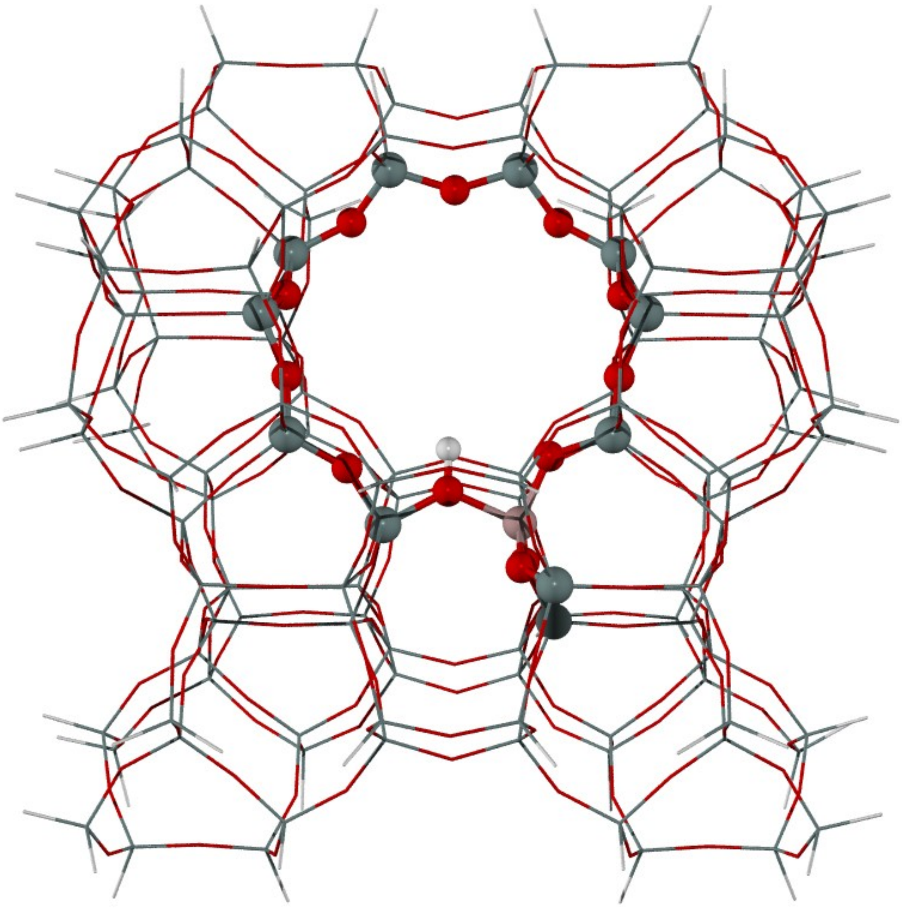
Details of calculations

The structure of the 128T cluster model encompasses the intersection region of the straight and zigzag channels, as shown in Figure 4, is used for representing the lattice structure of an acidic H-ZSM-5 zeolite (Van Koningsveld *et al.,* 1987). For computational efficiency, the two-layered ONIOM scheme is selected. In this ONIOM model, the active region of zeolite and the adsorbate molecules are treated with the high accuracy method, while the rest of the 128T cluster model is treated with the less accurate method to reduce the computational time. 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 are 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)

Figure 3 The ONIOM models of the 128T cluster of the H-ZSM-5 zeolite. Atoms belonging to the quantum region are drawn as balls and sticks while the lines represent universal force field (UFF): viewed from (a) the straight channel (b) the zigzag channel



(b)

Figure 3 (Continued)

According to the ONIOM2 approach, the calculation of energies, the active site is treated with high-level quantum mechanical approach while the extended framework is treated by a less expensive level. The total energy of the whole system can be expressed within the framework of the ONIOM methodology by:

$$E_{ONIOM2} = E_{Low}^{REAL} + \left(E_{High}^{Cluster} - E_{Low}^{Cluster} \right)$$

where the superscript *REAL* means the whole system and the superscript *Cluster* means the active region. Subscripts *High* and *Low* mean high level and low level methodologies. In this work, the quantum cluster is treated by B3LYP method while the extended framework is treated by molecular mechanics force field (UFF).

In order to include the long-range effects of the electrostatic Madelung potential from the infinite zeolite lattice, all optimized ONIOM geometries are embedded in the two sets of point charges and are performed with the single point calculations. The first set is represented by the fixed partial atomic charges (-1.0 e for O and +2.0 e for Si) which are placed in the zeolite lattice positions at 13-17 Å from the 12T quantum cluster, accounting for the medium effect of the electrostatic potential. Another set is placed at the extended lattice framework up to 38 Å from the 12T quantum cluster. These point charges are optimized to reproduce the long-range Madelung potential from the infinite lattice of the zeolite structure. Such method is called “the embedded ONIOM” shown in Figure 5 and has been performed in our previous calculations, such as the pyridine adsorption in zeolites (Lomratsiri *et al.,* 2006, Injan *et al.,* 2005) and the reaction mechanisms of benzene alkylation with propylene in newly synthesized H-ITQ-24 zeolite (Jansang *et al.,* 2006).

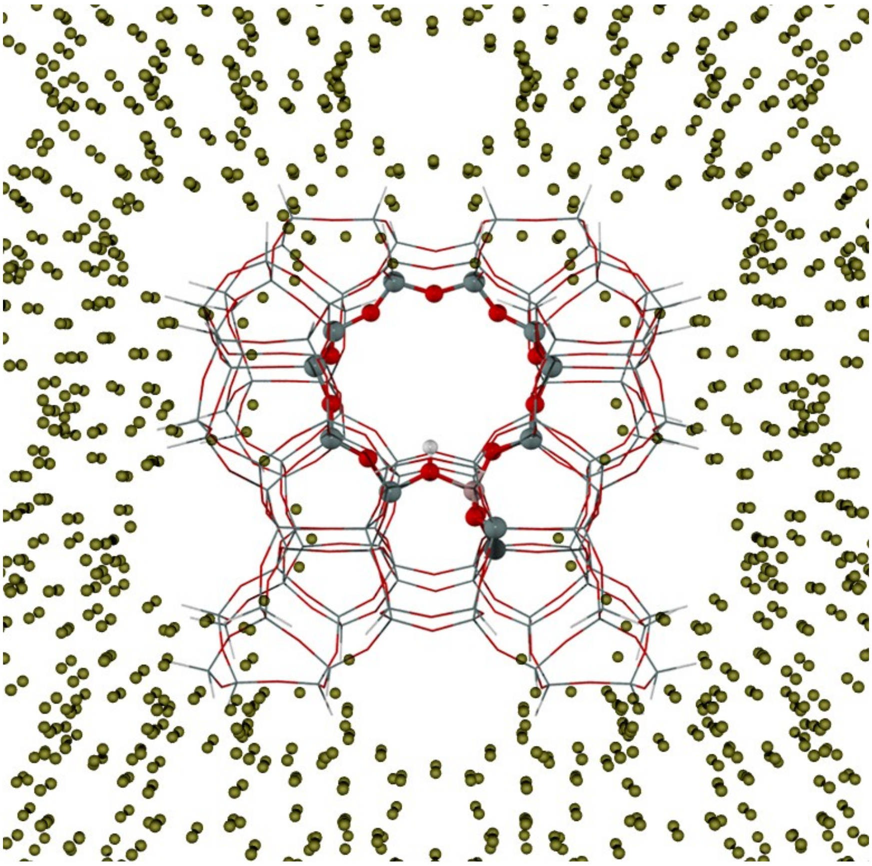
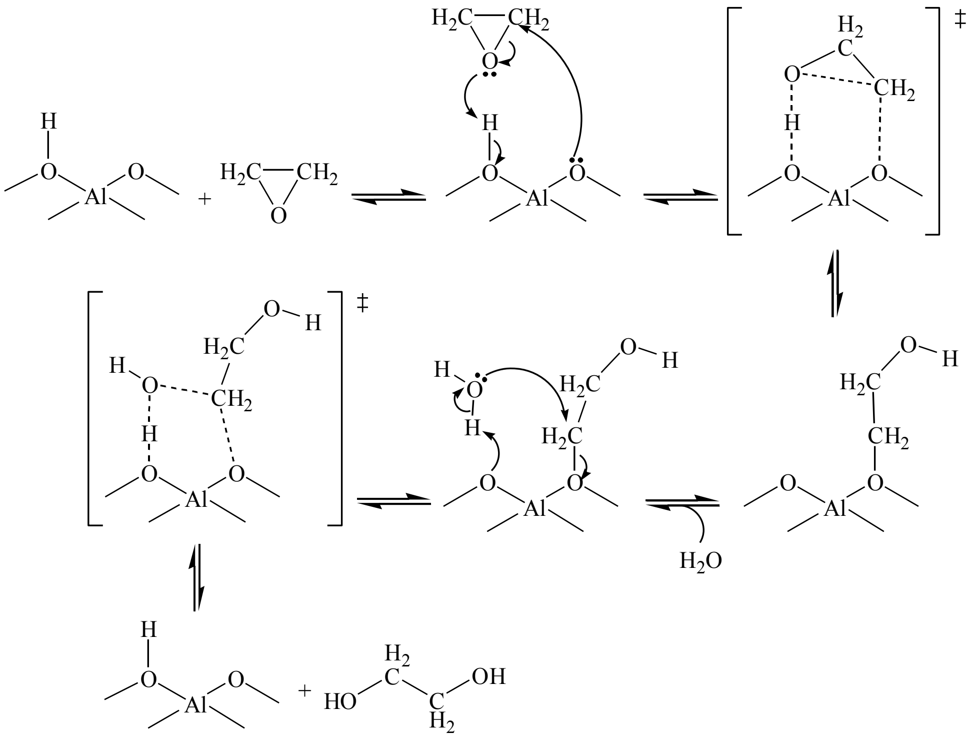


Figure 4 The embedded ONIOM models of the 128T cluster of the H-ZSM-5 zeolite. Atoms belonging to the quantum region are drawn as balls and sticks while the lines represent universal force field (UFF). The dots graphics in embedded ONIOM2 scheme illustrate the Madelung point charges.

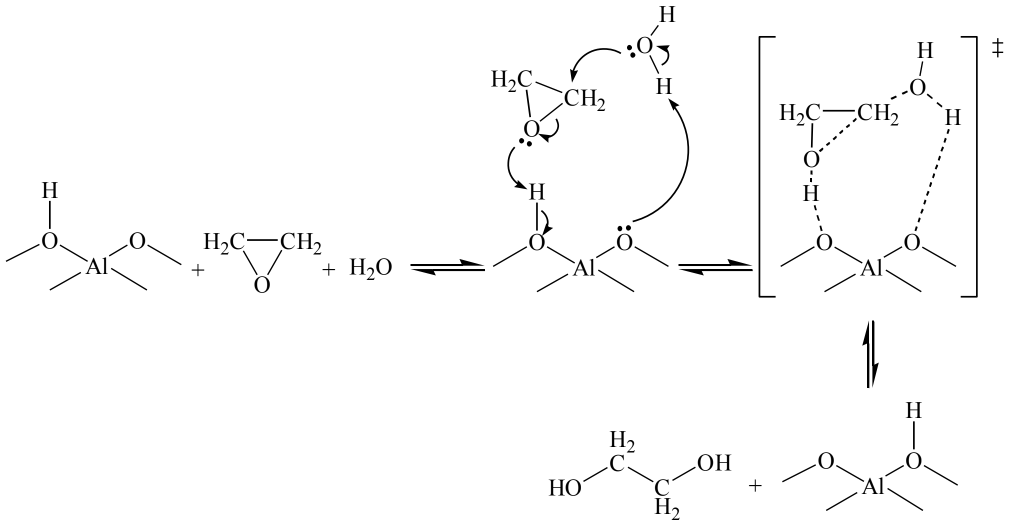
RESULTS AND DISSCUSION

After the ethylene oxide gas molecule diffused into the zeolite pore, it was then adsorbed on the Brønsted acid site, at which stage the ethylene oxide-zeolite adduct is formed via hydrogen bonding. This adduct can be transformed to ethylene glycol by two different types of reaction pathway: the stepwise and the concerted as shown in Figure 5a and 5b, respectively. In this study, the mechanisms for the hydration of ethylene oxide are investigated by using the ONIOM method. In addition, the effects of the infinite lattice structure of zeolite on the reaction pathways are studied by the evaluation of the embedded-ONIOM approach.



(a)

Figure 5 The reaction pathway of (a) stepwise mechanism (b) concerted mechanism for the ethylene oxide hydration into ethylene glycol over zeolite.



(b)

Figure 5 (Continued)

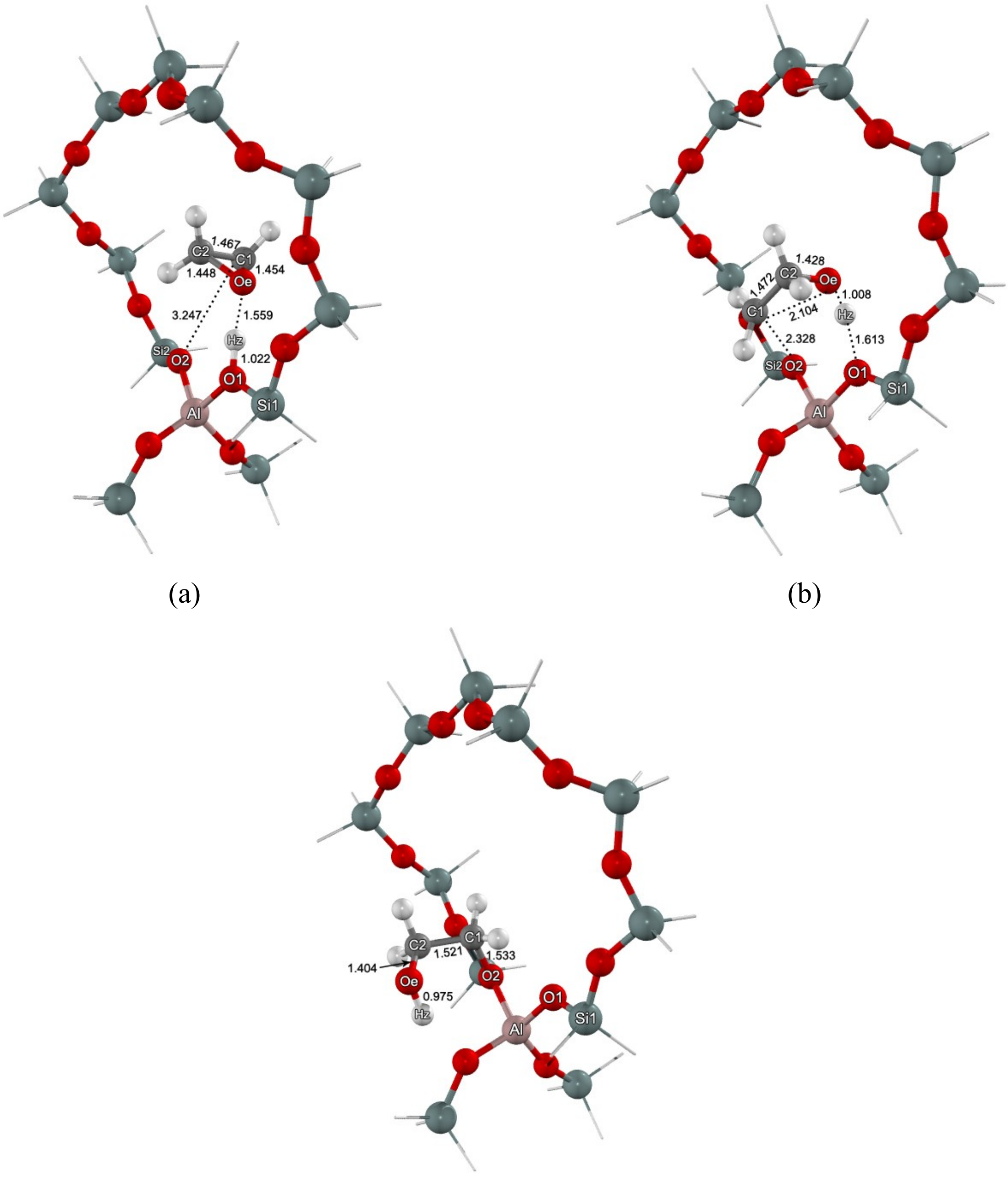
1. Stepwise reaction pathway

The stepwise mechanism commences with ethylene oxide being adsorbed on the Brønsted acid site of H-ZSM-5 zeolite (see Figure 6a) via the hydrogen bonding to form the ethylene oxide-zeolite adsorption complex (Ads1_S). The selected geometric parameters are listed in Table 1. The adsorption energy is calculated to be -23.3 kcal/mol, which is lower than that for propene oxide (-30.8 kcal/mol) due to there being no electron donating group substituted on the epoxide ring (Namuangruk *et al.,* 2006). In this adsorption complex, the hydrogen bonding interaction between the Oe of ethylene oxide and the acidic proton of zeolite (Hz) induces the lengthening of the O1-Hz bond distance from 0.969 to 1.022 Å. In addition, electron transfer from the Oe to the Hz results in the slight elongation of the C1-Oe and C2-Oe bond lengths by about 0.024 Å and 0.018 Å, respectively.

Following this, the C1-Oe bond, which is weaker than C2-Oe bond, ruptures to open the epoxide ring and to then form the surface ethoxide intermediate (Ads2_S) via the primary carbenium-like ion transition state (TS1_S). At the transition structure (cf. Figure 6b), the acidic proton of the zeolite is protonated to the adsorbed ethylene oxide, the C1-Oe bond is broken, and the hybridization of C1 changes from tetrahedral (sp^3) to planar (sp^2). The transition state is confirmed by the frequency calculation with one imaginary frequency at -365.1 cm^{-1}, which is related to the movement of the acidic proton of zeolite (Hz) to the ethylene oxide oxygen (Oe) and the breaking of the C1-Oe bond. This step is called the ring-opening step. The calculated activation energy barrier is 34.4 kcal/mol and the apparent activation energy is 11.1 kcal/mol. The result of this is that, the ethoxide intermediate (Int_S) is formed at the O2 of the zeolite structure and is stabilized by the zeolite framework (Figure 6c). The adsorption energy of this ethoxide species is computed to be -21.5 kcal/mol, which is slightly less stable than that for the ethylene oxide adsorption complex (Ads1_S). The evaluated energy profile of all species involved in this ring-opening step is illustrated in Figure 8.

Table 1 The optimized geometrical parameters and mulliken charge of organic fragments of adsorption complexes for ethylene oxide ring-opening step of stepwise mechanism using the ONIOM2 (distances are in Å, angles are in degrees and charges are in electron).

Parameter	**Isolated cluster**	**Ethylene oxide adsorption (Ads1_S)**	**First transition state (TS1_S)**	**Alkoxide intermediate (Int_S)**
Distances				
O1-Hz	0.969	1.022	1.613	3.418
Oe-Hz	-	1.559	1.008	0.975
C1-Oe	1.430	1.454	2.104	2.461
C1-C2	1.469	1.467	1.472	1.521
C2-Oe	1.430	1.448	1.428	1.404
C1-O2	-	3.247	2.328	1.533
C2-O2	-	3.352	3.267	2.530
Angles				
∠Si1O1Al	128.8	127.0	126.4	127.1
∠Si2O2Al	129.6	131.4	132.5	124.8
∠O1HzOe	-	173.9	162.6	104.2
Charges (q)	-	+0.550	+0.704	+0.440



(a)

(b)

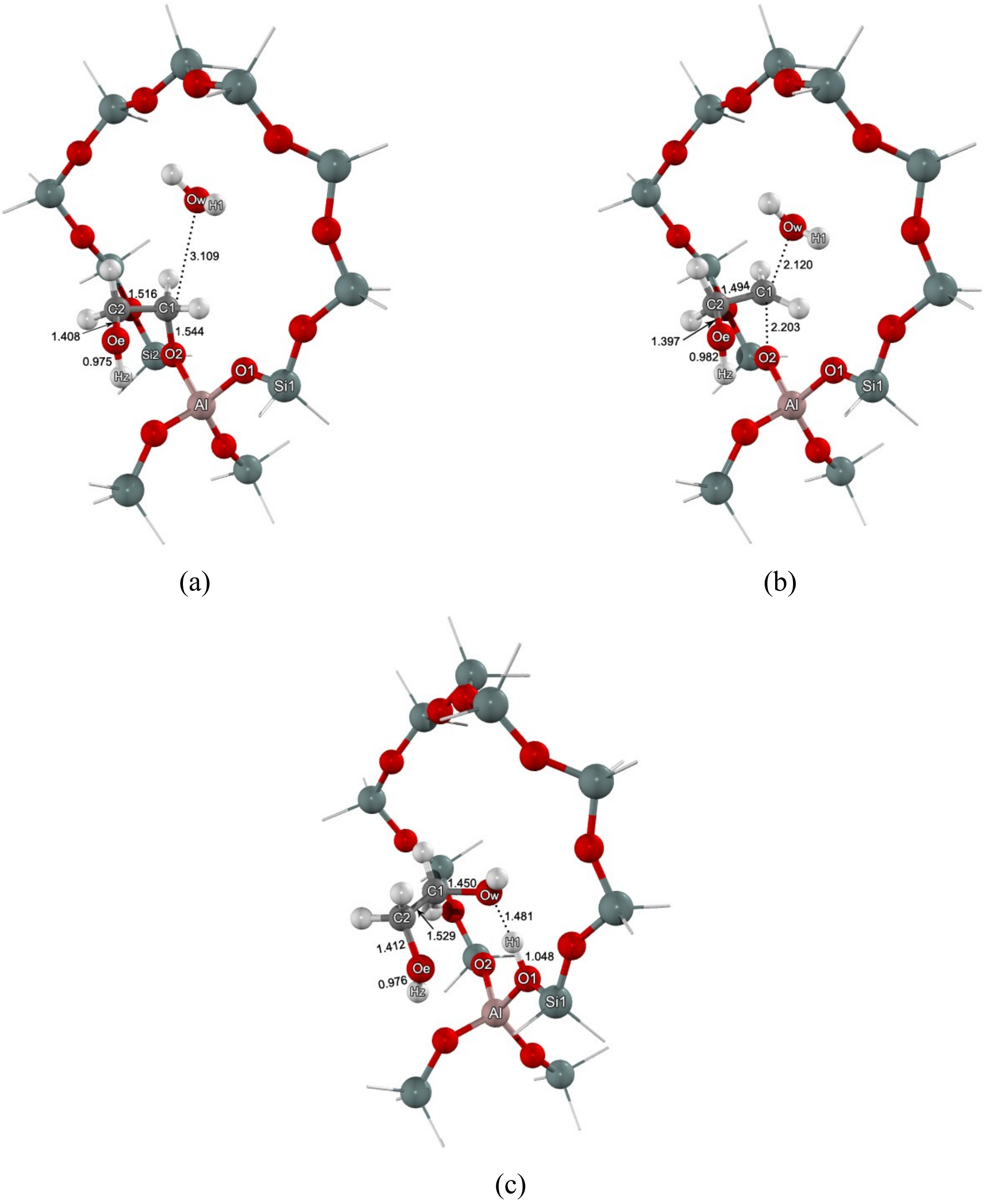
(c)

Figure 6 The optimized structures of (a) the ethylene oxide adsorption complex (Ads1_S), (b) first transition state (TS1_S) and (c) alkoxide intermediate (Int_S) for the ring-opening step of the stepwise mechanism of ethylene oxide hydration calculated at the ONIOM(B3LYP/6-31G(d,p):UFF) level of theory.

The next step is the hydration reaction of the surface ethoxide intermediate and the water molecule to form ethylene glycol. The selected geometric parameters for this are listed in Table 2. After forming the stable ethoxide intermediate, the nucleophilic water molecule adsorbs on the active ethoxide species to form the ethoxide-water coadsorption complex (Ads2_S) which is more stable than the alkoxide intermediate and has an adsorption energy of -33.6 kcal/mol. This coadsorption complex (cf. Figure 7a) is formed as a weak interaction, as can be seen from the lengthening of the C1-O2 covalent bond from 1.533 to 1.544 Å. The transition state (TS2_S) of this step, shown in Figure 7 b, is the S_N2 reaction where the water oxygen atom (Ow) attacks the carbon of the ethoxide intermediate (C1). The activation energy for this step is rather small; it is computed to be 14.5 kcal/mol. Normal mode analysis reveals one imaginary frequency at -619.0 cm^{-1} associated with the transition state, which corresponds to movement along the reaction coordinate in which the O2-C1 bond breaks and the C1-Ow bond forms simultaneously. It is noted that there is no mode of the proton transferring to the zeolite framework. Thus, the protonated ethylene glycol intermediate which might form in the nanocavity of zeolite is optimized to find the local minimum. However, we found from the theoretical calculation that this protonated structure is readily converted to form the ethylene glycol product without requiring a reaction barrier. This may explain why there is no experimental report for the finding of this labile structure. The product of the stepwise reaction (Prod_S) is the *cis*-isomer of ethylene glycol adsorbed on the active site of zeolite due to the transition structure control (Figure 7c). The reaction energy for this reaction pathway is calculated to be -59.2 kcal/mol. Finally, the adsorbed ethylene oxide is desorbed endothermically and requires an energy of -30.5 kcal/mol.

Table 2 The optimized geometrical parameters and mulliken charge of organic fragments of the adsorption complexes for ethylene oxide hydration step of stepwise mechanism using the ONIOM2 (distances are in Å, angles are in degrees and charges are in electron).

Parameter	**Water coadsorption (Ads2_S)**	**Second transition state (TS2_S)**	**Product (Prod_S)**
Distances			
C1-Oe	2.462	2.442	2.467
C1-C2	1.516	1.494	1.529
C2-Oe	1.408	1.397	1.412
C1-O2	1.544	2.203	3.247
C1-O_w	3.109	2.120	1.450
O_w-H1	0.967	0.973	1.481
O1-H1	4.491	3.644	1.048
Angles			
∠Si1O1Al	128.0	128.6	126.2
∠Si2O2Al	124.8	130.5	133.1
∠O2C1O_w	152.1	155.8	72.9
Dihedral			
O_wC1C2O2	-106.0	-84.7	-48.8
Charges (q)	+0.470	+0.728	+0.577



(a)

(b)

(c)

Figure 7 The optimized structures of (a) the water and alkoxide adsorption complex (Ads2_S), (b) second transition state (TS2_S) and (c) the *cis*-ethylene glycol adsorption complex for the hydration step of the stepwise mechanism of ethylene oxide hydration calculated at the ONIOM(B3LYP/6-31G(d,p):UFF) level of theory.

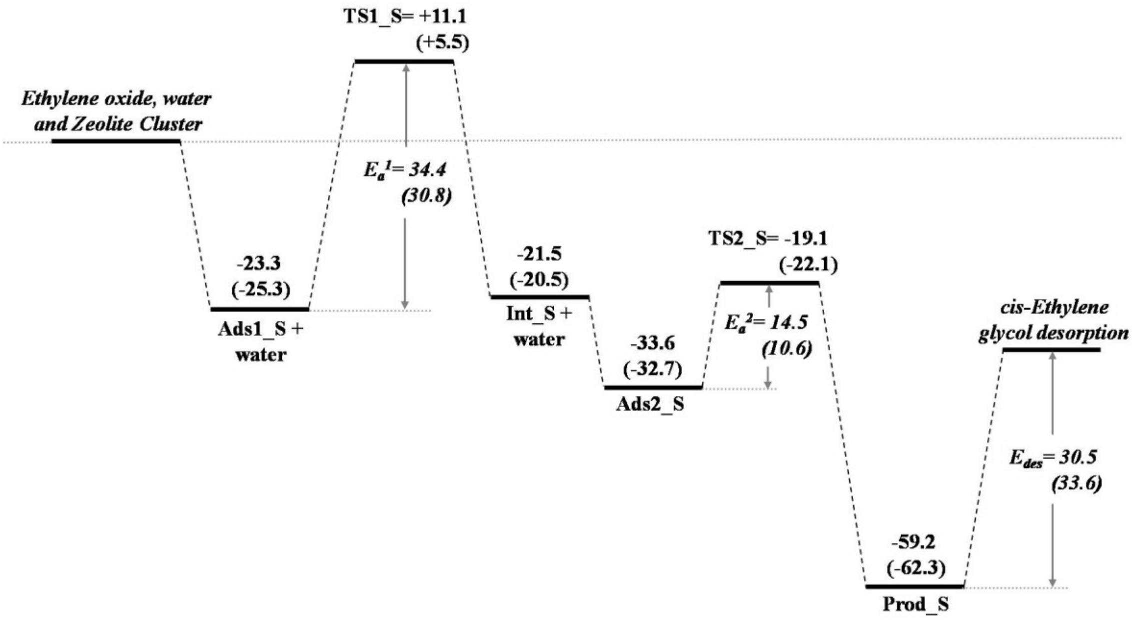


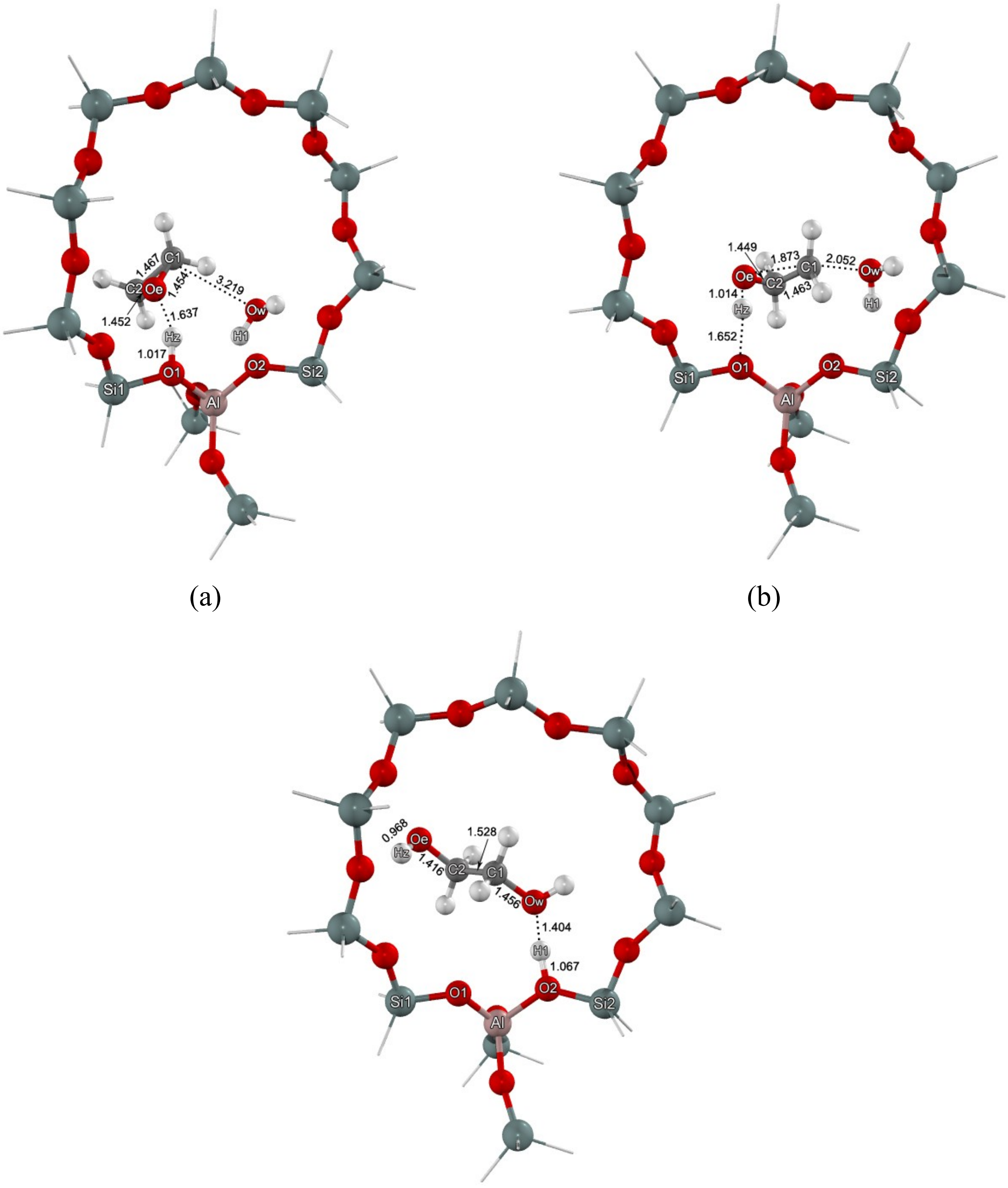
Figure 8 Energetic profile for stepwise mechanism of the ethylene oxide hydration calculated by the ONIOM(B3LYP/6-31G(d,p):UFF) level of theory. The values in parentheses are derived from the embedded ONIOM(B3LYP/6-31G(d,p):UFF) calculations (energies are in kcal/mol).

2. Concerted reaction pathway

In contrast to the stepwise reaction pathway, the ethylene oxide hydration can be considered to proceed in a concerted reaction, the energy profile for which is shown in Figure 10, and selected geometrical parameters are listed in Table 3. The initial step starts with the adsorption of an ethylene oxide on the Brønsted acid site of zeolite with the hydrogen bonding interaction. Then, the water molecule is weakly co-adsorbed next to the adsorbed ethylene oxide to form the coadsorption complex (Ads_C), as shown in Figure 9a. At the Ads_C, the C1-Ow and O2-Ow distances are calculated to be 3.219 and 3.786 Å, respectively. The weak interaction of the water molecule on adsorbed ethylene oxide results in a small binding energy of -8.3 kcal/mol, which is lower than the binding energy of the water molecule adsorbed on the acidic zeolite of –23.9 kcal/mol. Subsequently, the ethylene glycol is formed through the transition state (TS_C), which occurs simultaneously with both the ring-opening and hydration processes (Figure 9b) without forming an alkoxide intermediate. This transition state (TS_C) is considered as the S_N2 attack. The C1-Oe bond is broken by the nucleophilic attack of the water molecule on the C1 of ethylene oxide with OeC1Ow angle of 157.5° and a new C1-Ow bond is formed with the protonation of ethylene oxide at the Oe atom. The C1-Oe bond is lengthened from 1.454 to 1.873 Å, while the C1---Ow distance is decreased from 3.219 to 2.052 Å. At the transition state configuration, the sp^3 hybridization of the ethylene oxide C1 atom is altered to sp^2 hybridization. The transition state is verified by frequency calculation with one imaginary frequency at -309.5 cm^{-1}. The calculated activation energy is evaluated to be 13.3 kcal/mol. After forming the transition state (cf. Figure 9c), the proton (H1) of the water molecule transfers from Ow toward O2 to restore the acid site of zeolite and form the *trans*-ethylene glycol adsorbed on the active site of the zeolite. The product of the reaction, which is *trans*-ethylene glycol adsorbed on zeolite is calculated to be -48.5 kcal/mol and is then desorbed, requiring an energy of 23.06 kcal/mol. The reaction energy for the concerted pathway is exothermic by 25.4 kcal/mol.

Table 3 The optimized geometrical parameters and mulliken charge of organic fragments of the adsorption complexes for concerted ethylene oxide hydration mechanism using the ONIOM2 (distances are in Å, angles are in degrees and charges are in electron).

Parameter	**Ethylene Oxide-Water coadsorption (Ads_C)**	**Transition state (TS_C)**	**Product (Prod_C)**
Distances			
O1-Hz	1.017	1.652	4.154
Oe-Hz	1.637	1.014	0.968
C1-Oe	1.454	1.873	2.421
C1-C2	1.467	1.463	1.528
C2-Oe	1.452	1.449	1.416
O_w-C1	3.219	2.052	1.456
O_w-C2	3.786	2.867	2.435
O_w-H1	0.970	0.970	1.404
H1-O2	2.630	3.212	1.067
Angles			
∠Si1O1Al	127.4	126.5	124.5
∠Si2O2Al	132.3	134.2	131.0
∠OeC1O_w	103.6	157.5	142.5
Charges (q)	+0.534	+0.794	+0.605



(a)

(b)

(c)

Figure 9 The optimized structures of (a) the ethylene oxide and water molecule co-adsorption complex, (b) transition state (TS_C) and (c) *trans*-ethylene glycol adsorption complex for the concerted mechanism of ethylene oxide hydration calculated at the ONIOM(B3LYP/6-31G(d,p):UFF) level of theory.

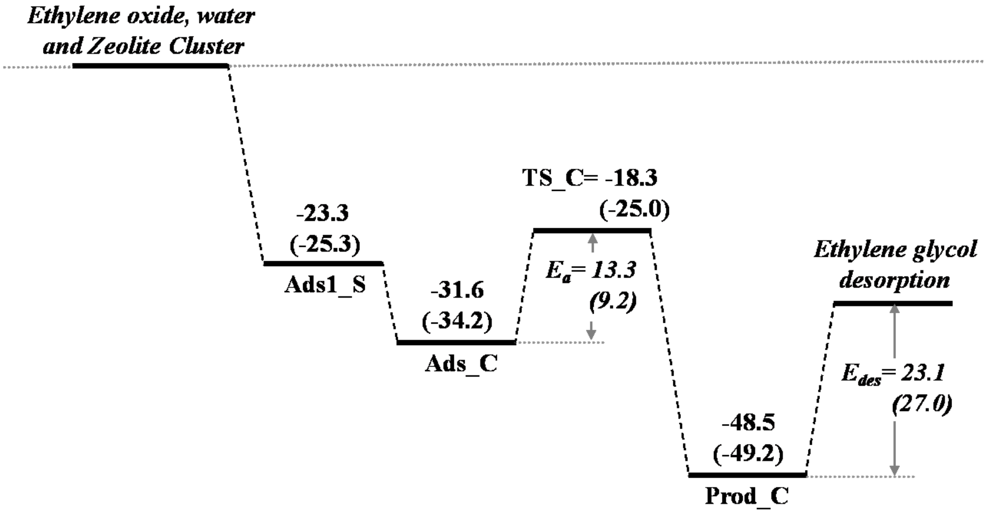


Figure 10 Energetic profile for concerted mechanisms of the ethylene oxide hydration calculated by the ONIOM(B3LYP/6-31G(d,p):UFF) level of theory. The values in parentheses are derived from the embedded ONIOM(B3LYP/6-31G(d,p):UFF) calculations (energies are in kcal/mol).

In order to include the effect of long-range electrostatic interactions of the extended zeolite lattice beyond the ONIOM model, the embedded ONIOM method is employed. For this method, the energy of the system is contributed by the electrostatic interactions, which primarily affect the ionic species especially the transition states. In pervious studies (Jansang *et al.,* 2006), the intermediate and the transition states were stabilized by the electrostatic interactions of the extended zeolite framework. Moreover, the activation energy of the ionic system was reduced due to the ionicity of the transition state organic fragment (cf. Tables 4). In this work, the embedded ONIOM is performed on the ONIOM optimized geometry by single-point energy calculation. With reference to the ONIOM energies, the results show that the adsorption and intermediate complexes are mostly stabilized in the range of 2-4 kcal/mol (see Figures 8 and 10). It is noted that non-ionicity, like Ads2_S in the stepwise mechanism, is not affected by the electrostatic interaction whereas, in the transition states, the activation energies are decreased by 3.6, 3.9 and 4.1 kcal/mol which are in proportion to the ionicity of the organic fragments of the TS1_S, TS2_S and TS_C, respectively. The corrected activation energies accounted from the electrostatic interaction are 30.8 and 10.6 kcal/mol for the ring-opening and hydration of the stepwise mechanism, respectively. The concerted mechanism, in which the transition state is most stabilized from the Madelung potential, is evaluated to be 9.2 kcal/mol.

Table 4 The complexes energy and mulliken charge of organic fragments for ethylene oxide hydration of stepwise and concerted mechanisms (energy are in kcal/mol and charges are in electron).

Complexes	**Energy**		**Charges (q)**
	ONIOM	**Embedded ONIOM**	
Stepwise			
Ethylene oxide adsorption (Ads1_S)	-23.3	-25.3	+0.550
First transition state (TS1_S)	34.4	30.8	+0.704
Alkoxide intermediate (Int_S)	-21.5	20.5	+0.440
Water coadsorption (Ads2_S)	-33.6	-32.7	+0.470
Second transition state (TS2_S)	14.5	10.6	+0.728
Product (Prod_S)	-59.2	-62.3	+0.577
Concerted			
Coadsorption (Ads_C)	-31.6	-34.2	+0.534
Transition state (TS_C)	13.3	9.2	+0.794
Product (Prod_C)	-48.5	-49.2	+0.605

3. Comparison of stepwise and concerted reaction pathways

The complete energetic profiles for the stepwise and concerted reaction pathways are illustrated in Figure 8 and 10, respectively. For the stepwise mechanism, the ring-opening process is found to be the rate-determining step with the activation energy of 34.4 kcal/mol. This is a similar trend to that computed from the embedded ONIOM method of 30.8 kcal/mol. The ethoxide intermediate is destabilized by electrostatic interactions from the zeolite lattice and thus is active for further reaction, which is the ethoxide hydration. This step is more facile than the ring-opening step, and has a small activation barrier of 14.5 kcal/mol for the ONIOM and 10.6 kcal/mol for the embedded ONIOM, respectively. For the concerted mechanism, the activation barrier is calculated to be 13.3 kcal/mol (9.2 kcal/mol for the embedded ONIOM), which is significantly lower than the energy barrier of the rate-determining step in the stepwise mechanism. Moreover, the relative energy of the transition state for the concerted mechanism (TS_C) is lower than that for both transition states for the stepwise mechanism. The long-range electrostatic interaction included by the embedded ONIOM method affects the stability of the adsorbed species inside the zeolite and, most importantly, significantly alters the stability of the ionic species like transition states, which appears to be a key point for this reaction. Therefore, from the energetics of the reactions and relative stability of the transition states, it can be concluded that the formation of ethylene glycol by the hydration of ethylene oxide over H-ZSM-5 zeolite preferably occurs via the concerted mechanism. Moreover, the obtained ethylene glycol products will be *cis*- or *trans*-isomer depending on its reaction mechanism, which is controlled by the transition structure. The *cis*-ethylene glycol is formed by the stepwise mechanism while the *trans*-ethylene glycol is formed by the concerted mechanism. The *trans*-isomer can be desorbed more easily than the *cis*-isomer by 6 kcal/mol. Thus, the adsorbed *trans*-ethylene glycol product produced from the concerted mechanism is more easily separated from the nanocavity of zeolite than the *cis*-ethylene glycol produced from the stepwise mechanism.

CONCLUSION

This study elucidates the reaction mechanism for the hydration of ethylene oxide to ethylene glycol over the nanoporous H-ZSM-5 zeolite with the aim of providing a procedure to reduce the large excess of water which, in the present non-catalytic hydration process, results in costly, excessive energy consumption. The ONIOM and embedded ONIOM methods were used to investigate this reaction mechanism with two different pathways: the stepwise and the concerted mechanisms being considered. For the stepwise mechanism, the hydration reaction proceeds via the ring-opening of ethylene oxide to form the alkoxide intermediate with the energy barrier of 34.4 kcal/mol. Consequently, the alkoxide intermediate is hydrated by a water molecule nearby to form ethylene glycol as the product. The activation energy of this step is calculated to be 14.5 kcal/mol. For the concerted mechanism, the hydration reaction occurs in a single step of simultaneous ring-opening and hydration. The calculated activation energy barrier is only 13.3 kcal/mol.

The results from the embedded ONIOM method indicate that the electrostatics accounted from the infinite lattice of zeolite play an important role in the stabilization of the transition structures and adsorption complexes. These result in lowering the activation barriers for whole reaction pathways, for both the stepwise and concerted mechanisms. For the stepwise mechanism, the calculated activation energies are reduced to 30.8 and 10.6 kcal/mol for the ring-opening and hydration steps, respectively. For the concerted mechanism, the activation barrier is even lower, 9.2 kcal/mol. These results show a similar trend to the computations from the ONIOM method. Therefore, in this study, it can be concluded that the hydration reaction of ethylene oxide to ethylene glycol over H-ZSM-5 zeolite preferably proceeds via the concerted mechanism.

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APPENDIX

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- **Theoretical Study on the Reaction Mechanisms of Ethylene Oxide Hydration over H-ZSM-5: An Ethylene Glycol Formation.**
  Thana Maihom, Tanin Nanok and Jumras Limtrakul. The Proceeding of 33rd Congress on Science and Technology of Thailand, Walailak University, Nakhon Si Thammarat, Thailand, October 18 - 20, 2007. (Oral Presentation)