



## CHAPTER III

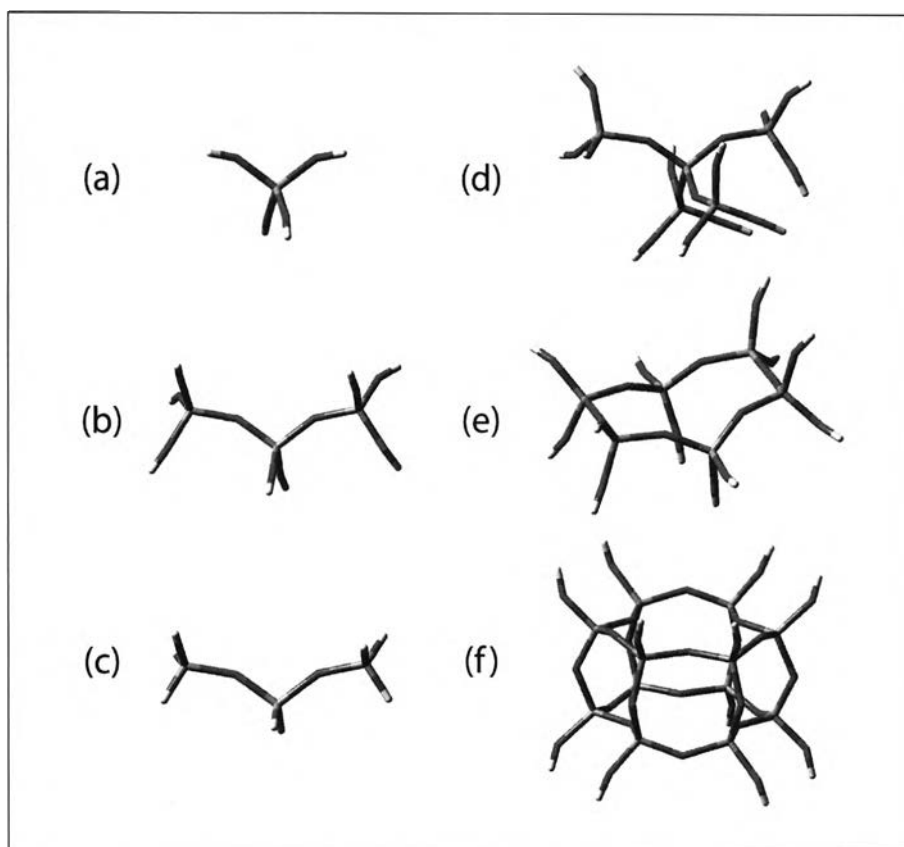
### DETAILS OF THE CALCULATIONS

#### 3.1 Models

The models were used in the theoretical description of zeolites. There are three types of models such as (i) cluster models, (ii) embedded models, and (iii) periodic models. Cluster models have subjected in the zeolite science in the 1980s and 1990s. At present, the application of various embedding schemes [76, 77] and periodic models [78, 79] are successfully used in zeolite science due to the improvement of the computational hardware and the progress in the software.

##### 3.1.1 Cluster Models

Cluster models may consist of several tetrahedral unit(s) ( $\text{SiO}_4$ ,  $\text{AlO}_4$ ) representing a part of the zeolite structure for a description of the zeolite crystal. In addition, charge-compensating cations and adsorbed species can be specified. A simple notation for clusters were obtained from the number of tetrahedral framework (T) and additional structural information could be given in the subscript for the example, d, 1, and r, for tetrahedral, linear, and ring structures, respectively. Other notations could come from the number of shells around central atoms [80] or chemical nomenclature terms [81]. Small cluster models such as 1T, 3T, and 5T (Figure 3.1) that has none of a particular zeolite framework were often used in zeolite modeling. Medium-size cluster models, may consist of 6T to 12T clusters or cluster membered rings. Model of zeolites that is larger than 28T cluster is often referred to as the large cluster model.



**Figure 3.1** Cluster models used in zeolite modeling 1T (a), 3T (b) and (c), 5T (d), 6T (e), and 12T<sub>D6R</sub> (f) cluster models. Note that 3T cluster (c) is H terminated for the rest clusters are O-H terminated. Silicon atoms (Si) and aluminum atoms (Al) are gray color, oxygen atoms (O) are red for hydrogen atoms (H) are white color [57]

Artificial “dangling bonds” are created at the cluster boundaries after the cluster was cut out from the zeolite crystal structure. Usually the dangling bonds were saturated with hydrogen atoms by placing along the direction to the neighboring framework atom. Either silicon or oxygen atoms at the terminal of cluster can be replaced by hydrogen (O-H and H termination). Examples of O-H and H-terminated clusters are depicted in **Figure 3.4** (a) and (b) to (e), respectively. The perturbation on the wavefunction due to the cluster boundary is smaller for the O-H terminated cluster than for the H-terminated cluster of the same size [57]. Moreover, the boundary effect on the wavefunction decreases with the increasing cluster-size.

There are three approaches for obtaining optimized geometries of the cluster models: (1) using experimental geometry (fixed geometry), (2) full geometry optimization (all atoms optimization), and (3) partial geometry optimization (constraining selected atoms). The first two approaches can be used only in some special situations, while their use is very problematic in the majority of applications. Full geometry optimizations can lead to structures that very much differ from realistic zeolites structures. The most common set of constraints is cluster-terminating atoms (either H-terminating atoms or O-H terminal groups) that used in the cluster model optimization. It is apparent that the cluster model approach is not suitable for a large geometry relaxation. When the cluster model is used the long-range interactions were neglected. The importance of the long-range interactions depends on the properties investigated.

### 3.1.2 Embedded Models

The embedding approaches basically include a cluster that is treated quantum mechanically while the influence of the rest of the crystal on the electrons in the cluster is treated by an embedding potential [82]. Alternatively, part of the environment around the cluster can partially be treated at the lower level of theory.

### 3.1.3 Periodic Models

In the periodic approach, the zeolite is represented by a unit cell that periodically repeats in all three crystallographic dimensions. All atoms in the system are treated at equal level, and long-range electrostatic interactions are implicitly included in this model.

The problems from effects of boundary conditions and long-range interactions on the cluster results can be solved in a direct way by periodic models. Periodic quantum chemical calculations can be carried out either with the atomcentered basis set [83, 84] or with the plane-wave basis set [85-87]. The VASP computer code

[12] is based on plane-wave basis set. The number of plane waves satisfying Bloch's theorem increases with the increasing volume of the unit cell for a given energy cutoff. Therefore, calculations using the plane-wave basis set are feasible for zeolites with small- and medium-size unit cells. However there also exists computer code which performed periodic calculations such as Dmol3 program [88] which uses numerical basis functions [89] and CRYSTAL program which employs Gaussian type atomic orbitals [78]. Figure 3.2 shows the advantages and disadvantages of cluster, embedded, and periodic model.


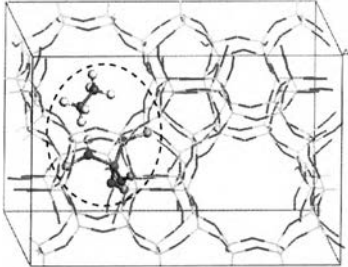

MODELS	ADVANTAGES	DISADVANTAGES
<p><b>Cluster model</b></p> 	<p>Perturbation methods can be used for small cluster models</p>	<p>Problems from effects of boundary conditions - on the wavefunction - on the geometry</p> <p>Does not represent particular zeolite and missing of long-range interactions</p>
<p><b>Embedded model</b></p> 	<p>Full geometry optimization can be performed that included long-range interactions.</p> <p>Possibility to use Perturbation methods.</p>	<p>Problems from effects of cluster boundary - on the wavefunction</p>
<p><b>Periodic structure</b></p> 	<p>The same level of theory can be performed for all atoms.</p> <p>Small effect of boundary conditions - on the wavefunction</p> <p>Full geometry optimization can be performed that included long-range interactions.</p>	<p>Problems from large unit cell (planewave calculations) or large number of centered basis set required computationally very demanding.</p>

Figure 3.2 The example of models of adsorbed ethane on Brønsted acid site in ZSM-5. Advantages and disadvantages individual models are summarized [57]

### 3.2 Preparation of Structures of ZSM-5

The ZSM-5 structure (MFI) was taken from crystallographic data of silicalite-1 [88], and then the Si atom at the intersection between straight and sinusoidal channels, T7, was replaced by the Al atom. This single substitution provides Si/Al ratio of 95. An acidic proton ( $H^+$ ) associated to the substitution was also added to one of O atoms adjacent to the Al to balance the negative charge. This structure was defined as the bare ZSM-5 zeolite structure (Z). This acidic active site or Brønsted acid site was used for the study of proton exchange and degradation reactions. Schematic representations of Al substitution sites of ZSM-5 configurations were shown in Figure 3.3.

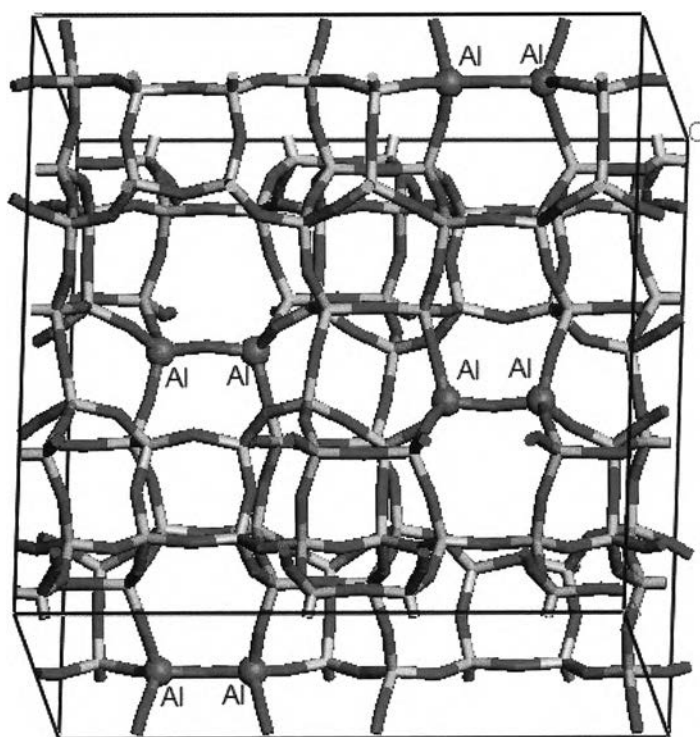
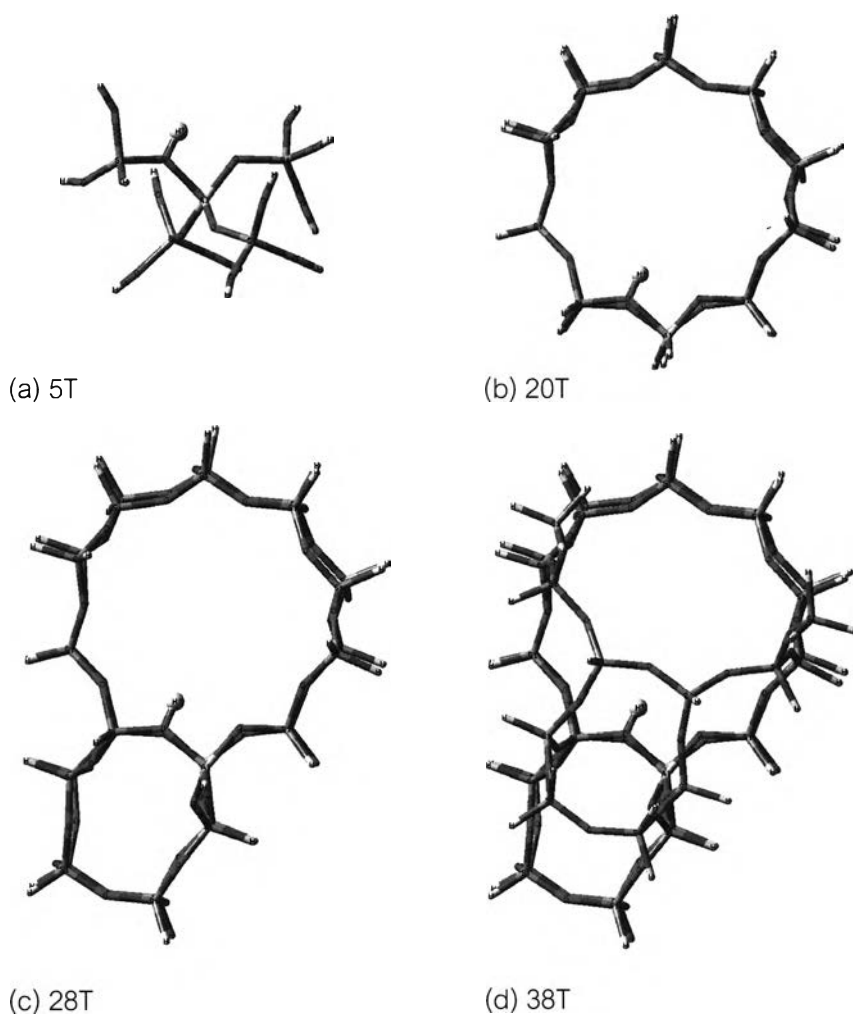
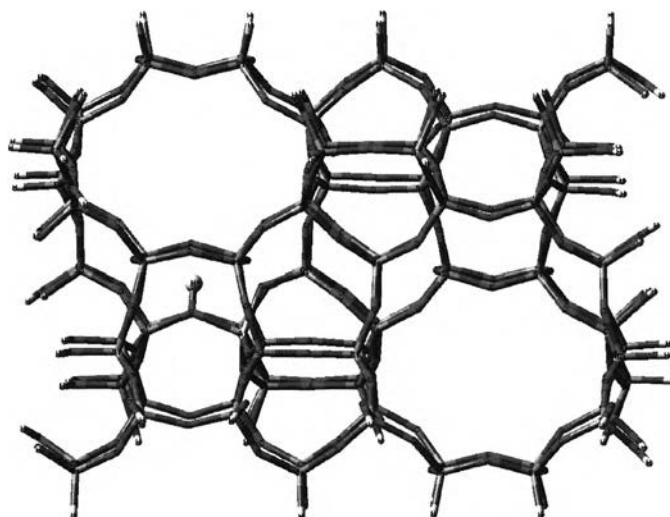


Figure 3.3 Al substitution sites of ZSM-5 configurations

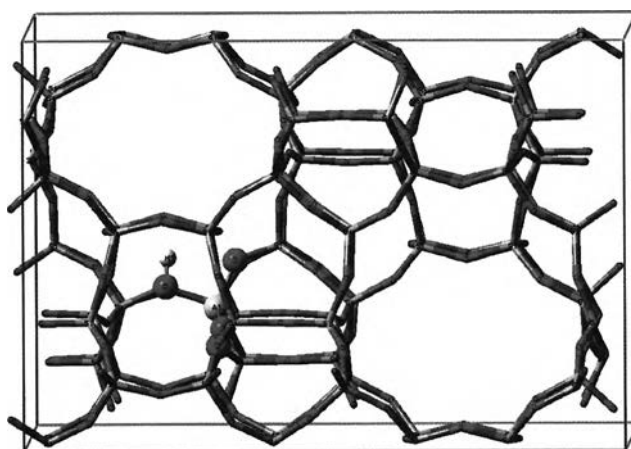
### 3.3 Preparation of Cluster and Periodic Models of ZSM-5

Cluster models were constructed by cut out the bare ZSM-5 zeolite structure. Five cluster models, 5T, 20T, 28T, 38T, and 96T where T represents alumina or silica tetrahedral were employed for the calculations. The 96T model contains the whole unit cell. For 5T model, oxygen atoms at its edge (Si-O bonds) were then saturated with hydrogen atoms represented O-H termination of  $0.96\text{\AA}$  to get rid of the unsaturation. In case of 20T, 28T, 38T, and 96T models, oxygen atoms at their edge were replaced by H atoms and appeared H termination Si-H and Al-H of  $1.50\text{\AA}$ . Directly from the crystal lattice, the silicate components were locally fixed and there is no change even after substituted which other parts. In addition, the periodic model denoted as P was also considered. Illustrations of five cluster models (5T, 20T, 28T, 38T, and 96T) and the periodic model were given in Figure 3.4.





(e) 96T

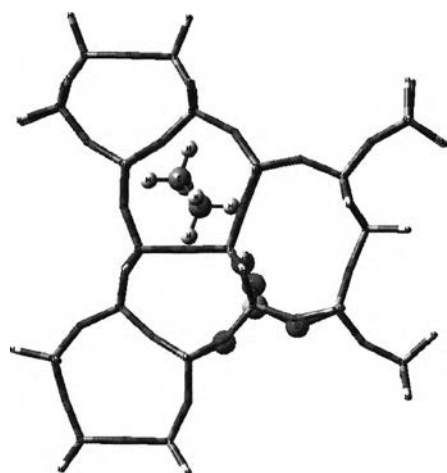


(f) periodic structure

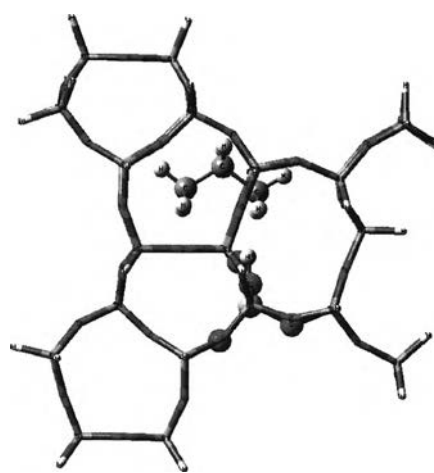
**Figure 3.4** Structures of cluster 5T (a), 20T (b), 28T (c), 38T (d), 96T (e), and periodic structure (f). Acidic proton ( $H^+$ ) is represented in each cluster.

Truitt *et al.* identified an adsorption complex between alkanes and zeolite acidic active sites [90]. The adsorbed alkanes in ZSM-5 represent the important step of the proton exchange, dehydrogenation and cracking reactions and therefore should be investigated. **Figure 3.5** presents the optimized geometries of adsorbed alkanes on ZSM-5 such as the ethane, propane, n-butane, and i-butane, respectively (reactant

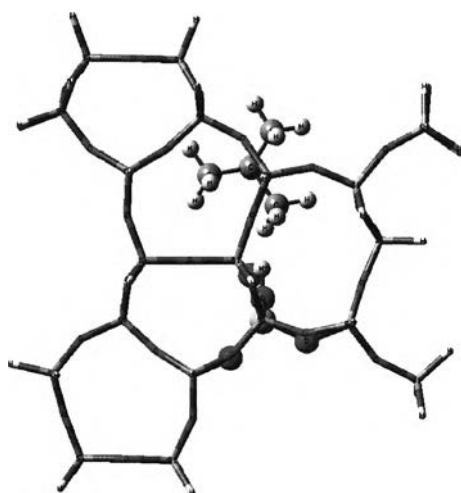
complex). The protonated intermediate (transition state complex) of ZSM-5-catalyzed reactions was converted to transition state structure.



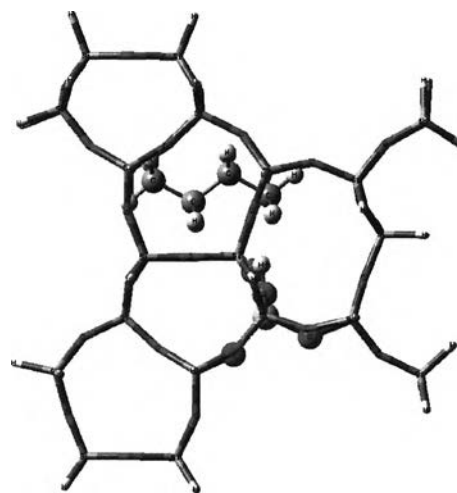
(a) ethane reactant complex



(b) propane reactant complex



(c) i-butane reactant complex



(d) n-butane reactant complex

**Figure 3.5** Adsorbed reactant complexes of ethane (a), propane (b), i-butane (c), and n-butane (d) were in ZSM-5 zeolite 38T cluster model.



## 3.4 Quantum Calculations

### 3.4.1 Geometry Optimizations and Zero-Point Energy Calculations

For 5T, 20T, 28T, and 38T clusters, geometry optimization and Zero-point energy (ZPE) calculations of C2-C4 alkanes (ethane, propane, iso-butane, and normal-butane), bare clusters, reactant complexes (Rcx), and transition-state structures (TS) of proton exchange and degradation reactions were performed using ri-PBE/SVP (the Turburmole [91] program's implementation of the resolution of identity integral approximation (ri) [92] in the density functional theoretical (DFT) calculation with Perdew-Burke-Ernzerhof exchange and correlation functional (PBE) [58, 70] and split valence polarization basis set (SVP) [93-95]). The PBE functional and the double-numeric-polarized basis set (DNP) [89, 96, 97] was also used by Dmol3 program [88]. The DNP is the all-electron basis set which comprises two numerical functions per valence orbital and supplemented with a polarization function. These calculations based on a generalized gradient approximation (GGA) in DFT with the cluster models and periodic models. For the bare cluster, the partial optimization was performed for the acid site on the cluster model and -OH terminals of 5T cluster model while, Si-H or Al-H terminals of the 20T, 28T, and 38T bare clusters were fixed. For both reactant complexes, and transition-state structures, only positions of atoms involved in the reaction were optimized while positions of atoms at the skeleton were fixed. For 96T and P models, optimized structures of Rcx were acquired using PBE/DNP while the optimized structures of TSs were obtained by performing single point calculations on structures which generated by embedding TS structures of 38T to 96T and P models.

### 3.4.2 Adsorption Energy and Reaction Barrier

The measured adsorption energy ( $E_{ads}$ ) and reaction barrier ( $\Delta E^\ddagger$ ) were described in Figure 3.6. The  $E_{ads}$  of C2-C4 alkanes in ZSM-5 were calculated according to



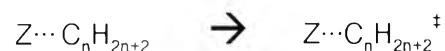
Therefore, 
$$E_{ads} = E(Z) + E(alkane) - E(Rcx) \quad (3.1)$$

where  $E(Rcx)$  is the energy of the reactant complex,

$E(Z)$  is energy of the bare ZSM-5 structure,

and  $E(alkane)$  is the energy of free alkane molecule.

The reaction barrier ( $\Delta E^\ddagger$ ) of the proton exchange reaction was calculated according to



and thus 
$$\Delta E^\ddagger = E(TS) - E(Rcx) \quad (3.2)$$

where  $E(TS)$  is the energy of the transition state

The apparent reaction barrier ( $\Delta E_{app}^\ddagger$ ) is therefore defined as following.

$$\Delta E_{app}^\ddagger = \Delta E^\ddagger - E_{ads} \quad (3.3)$$

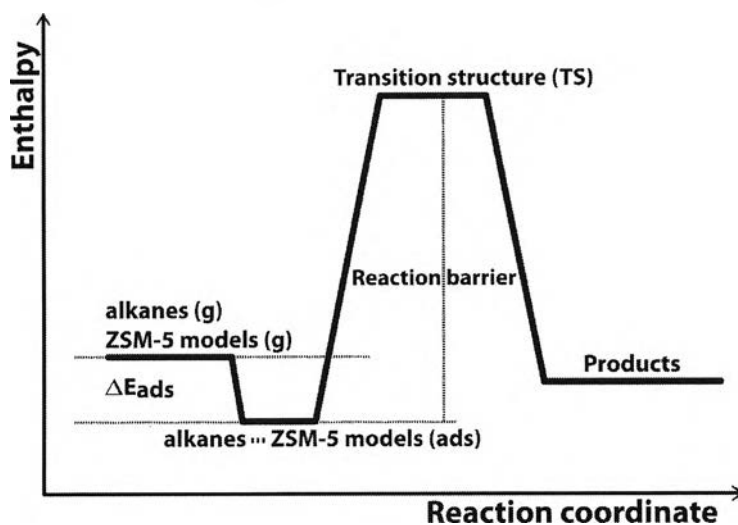


Figure 3.6 Energy diagram for proton exchange and degradation reactions of C2-C4 alkanes.

### 3.4.3 Complete Basis Set (CBS) Extrapolation

Apart from the cluster-size effect, the effect of the quality of basis set was also evaluated. Thus, we extrapolated our result to the complete basis set (CBS) limit according to the scheme suggested by Helgaker *et al.* [98]

$$E_X = E_\infty + AX^{-\alpha} \quad (3.4)$$

where the cardinal number  $X = 2, 3,$  and  $4,$  corresponding to SVP, TZVPPP, and QZVPP basis set, respectively. To obtain  $\alpha$  and  $A,$  quantum calculations for the reactant complexes of various alkanes (ethane, propane, n-butane, and i-butane) on 5T model using SVP, TZVPPP, and QZVPP basis set were carried out.

From the ri-PBE calculations, it was found that various reactant complexes have the very similar value for  $\alpha$  and the value of 6.56 gave the best fit for all 4 systems (*i.e.* ethane, propane, n-butane, and i-butane). As it has been reported, the  $\alpha$  value depends mainly on method and basis set but it does not vary much for the molecular system with the same set of atoms [92]. Thus, this value of  $\alpha$  were used later to determine CBS-limit for ri-PBE calculations of 38T model through Equation (3.5) which proposed by Truhlar *et al.* [92]

$$E_\infty = \left( \frac{3^\alpha}{3^\alpha - 2^\alpha} E_3 - \frac{2^\alpha}{3^\alpha - 2^\alpha} E_2 \right) \quad (3.5)$$

### 3.4.4 Estimation of Dispersion Interaction

To estimate the effect of the level of electron correlation, we performed ri-MP2 calculations with SVP, TZVPPP, and QZVPP basis set using 5T cluster model for the 4 systems. With the same scheme as discussed in the previous section, we obtained ri-MP2/CBS energies for the 4 systems on 5T model. It has been pointed out by Sauer *et al.* [99] that the effect of electron correlation also depends on cluster-size. They

proposed a correction to electron correlation for the periodic model by using DFT-D as suggested by Grimme *et al.* [100].

$$E_{disp} = -S_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{\sqrt{C_6^i C_6^j}}{R_{ij}^6} f_{damp}(R_{ij}) \quad (3.6)$$

However, Sauer *et al.* showed that the DFT-D overestimates the dispersion interaction and suggested to adjust the value with MP2 calculation.

$$[\Delta E_{MP2} - \Delta E_{DFT}]_C \approx E_{disp}(C) + E_{add} = \Delta E_{corr}(C) \quad (3.7)$$

$E_{add}$  is a constant and can be obtained by fitting Equation (3.7) for several cluster-sizes. Here,  $E_{add}$  was acquired from 5T cluster only.

### 3.4.5 Reaction Barriers

The apparent reaction barriers were obtained by combined between the computed reaction barriers using PBE/DNP method with periodic model ( $E_p$ ) and adsorption energy ( $E_{ads}$ ). The calculated values could be improved by taking into accounts other effects such as ZPE, basis set ( $\Delta E_{basis}$ ), and electron correlation ( $\Delta E_{corr}$ ). The extrapolated energy ( $E_{ex}$ ) which includes all above mentioned effects could be evaluated according to Equation (3.8) and it was later used as the representative of “true” interaction energy.

$$E_{ex} = E_p + ZPE + \Delta E_{corr} + \Delta E_{basis} \quad (3.8)$$

where

- $E_{ex}$  = extrapolated reaction barrier
- $E_p$  = energy of periodic model calculated using PBE/DNP
- $ZPE$  = ZPE energy calculated using ri-PBE/SVP on 38T model

$\Delta E_{corr}$  = correction due to level of electron correlation according to Equation (3.6) and (3.7) and corresponding to 96T model  
and  $\Delta E_{basis}$  = correction due to basis-set deficiency which estimated by  $E(38T, riPBE/CBS) - E(38T, PBE/DNP)$ .

The proposed extrapolation scheme as given by Equation (3.8) is in the same light as that has previously been suggested by Sauer *et. al.* [99].