



## CHAPTER IV

### RESULTS AND DISCUSSIONS

#### 4.1 Adsorption of C2-C4 Alkanes in ZSM-5

##### 4.1.1 Adsorbed Structures of C2-C4 Alkanes

Selected geometrical parameters for adsorbed ethane, propane, i-butane, and n-butane obtained using 38T cluster models were provided in Figure 4.1 and Table 4.1.

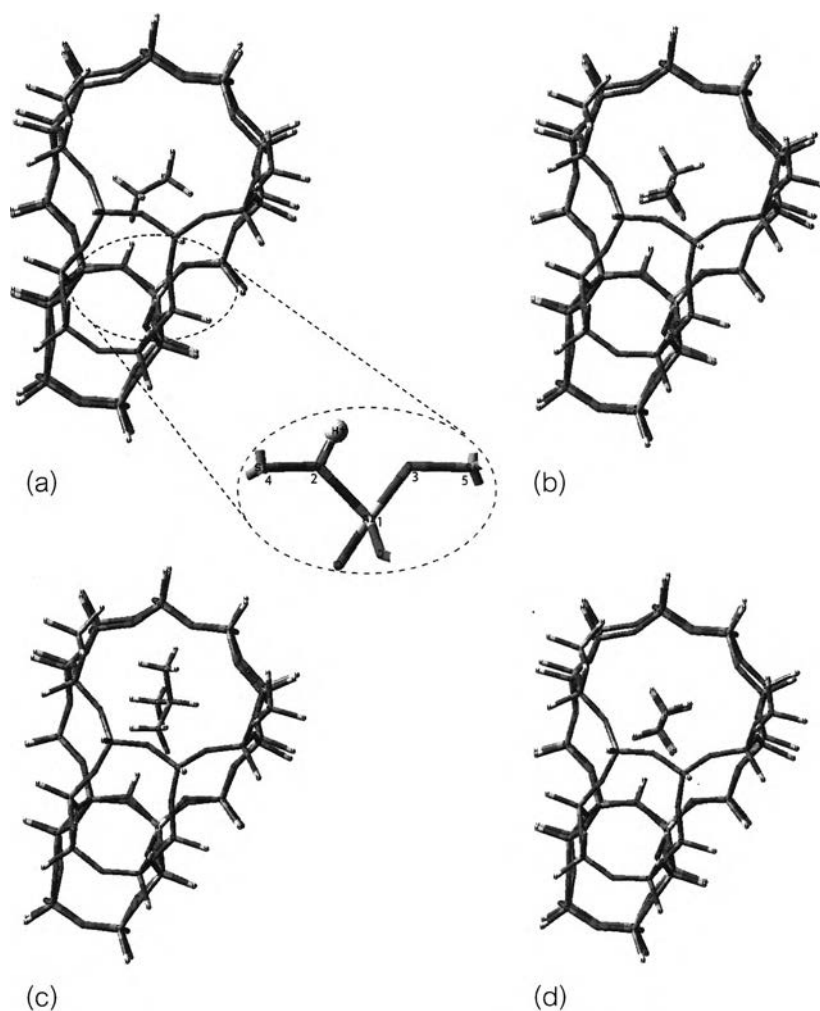


Figure 4.1 The geometries between the adsorbed ethane (a), propane (b), i-butane (c), and n-butane (d) and Brønsted acid site in 38T cluster.

TABLE 4.1 The relevant parameters for the adsorption of the ethane, propane, i-butane, and n-butane in clusters 38T

38T (distances in Å and angles in degrees)										
Alkanes	Al <sub>1</sub> -O <sub>2</sub>	Al <sub>1</sub> -O <sub>3</sub>	Si <sub>4</sub> -O <sub>2</sub> -Al <sub>1</sub>	Si <sub>5</sub> -O <sub>3</sub> -Al <sub>1</sub>	O <sub>2</sub> -Al <sub>1</sub> -O <sub>3</sub>	O <sub>2</sub> -H <sup>+</sup>	C <sub>1</sub> -H <sup>+</sup>	C-H	C-C	Al <sub>1</sub> -C <sub>1</sub>
ethane	1.837	1.697	131.1°	131.5°	87.6°	0.991	2.389	1.107	1.525	4.449
propane	1.830	1.696	131.2°	132.2°	88.3°	0.993	2.296	1.110	1.529	4.341
i-butane	1.828	1.696	131.3°	133.1°	88.6°	0.999	2.171	1.110	1.534	4.149
n-butane	1.831	1.697	131.1°	132.2°	88.3°	0.992	2.305	1.111	1.530	4.354

Noted: O<sub>2</sub>-H<sup>+</sup> is Brønsted acid site, C-H is bond length of alkanes, and C-C is bond length of alkanes

Considering adsorbed structures for the C2-C4 alkanes in Table 4.1, distances between zeolitic oxygen and Brønsted acid ( $O_2-H^+$ ) are in range of 0.991Å-0.999Å. The distance at the primary carbon ( $C_1$ ) with  $H^+$  ( $C_1-H^+$ ) of ethane, propane, i-butane, and n-butane is 2.389Å, 2.296Å, 2.171Å, and 2.305Å, respectively. The order of  $C_1-H^+$  distances corresponds to the order of  $Al_1-C_1$  distances. We found that  $C_1-H^+$  and  $Al_1-C_1$  distance of i-butane is shortest (4.149Å). All alkanes are located in the middle of the ZSM-5 pore (Figure 4.1). Among all alkanes, i-butane has highest steric due to three methyl groups. The C-H bond lengths of all alkanes are in range of 1.107Å-1.111Å. The C-C bond length is 1.525Å for ethane, 1.529Å for propane, 1.534Å for i-butane, and 1.530Å for n-butane, see Table 4.1. Apparently,  $Al_1-O_2$  distances are longer than  $Al_1-O_3$  distances due to binding of  $O_2$  with Brønsted acid forming hydroxyl group.  $Al_1-O_2$  and  $Al_1-O_3$  bond lengths are in range of 1.828Å-1.837Å and 1.696Å-1.697Å, respectively. Bond angles of  $Si_4-O_2-Al_1$  and  $Si_5-O_3-Al_1$  are quiet similar around 131.1°-133.1° and  $O_2-Al_1-O_3$  angles are around 88°.

#### 4.1.2 Estimation of Adsorption Energy

##### 4.1.2.1 Effect of the Cluster Size

For all alkanes, the enhancement of adsorption energies with the increment of cluster-size (from 5T to P model) was observed. This enhancement is as large as 3.4 (i-butane) to 7.1 kcal/mol (n-butane). Evidently, the cluster-size effect is non-negligible and crucial for the determination of the adsorption energy for the C2-C4 alkanes which takes place in ZSM-5. From 38T to 96T model, we saw the enhancement of around 2-5 kcal/mol while extended from 96T to periodic model the increment is approximately 0.8-1.4 kcal/mol. For the periodic model, computed adsorption energies of the C2-C4 alkanes are ranging from 7.1 (ethane) to 11.5 (n-butane) kcal/mol, see Figure 4.2 and Table 4.2. The explanation made for the reaction barriers could be as well used.

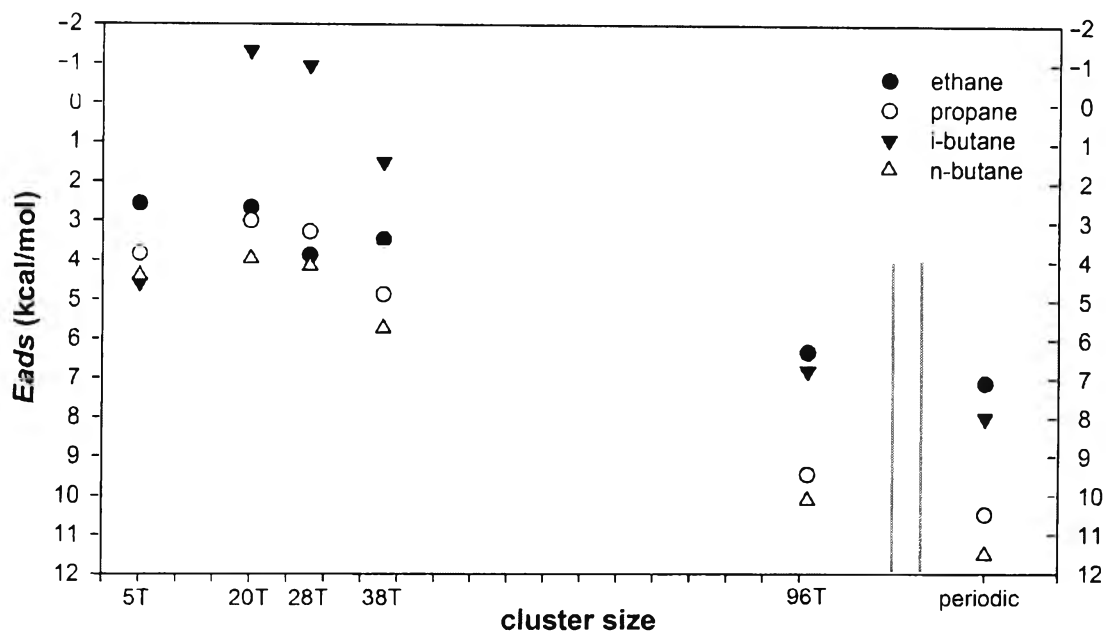


Figure 4.2 Inverse plot of adsorption energy ( $E_{ads}$ ) of C2-C4 alkanes in ZSM-5 calculated using PBE/DNP as function of cluster-size.

In Table 4.2, the comparison between adsorption energies obtained with cluster models 5T, 20T, 28T, and 38T, periodic model and experiments was given. The computed adsorption energies showed good agreement with the experimental values in exception of that of i-butane where the computed values is underestimated by 3 kcal/mol. The adsorption energies proportionally increase with the number of carbon atoms in the hydrocarbon chain, *i.e.* n-butane > propane > ethane.

TABLE 4.2 The adsorption energies ( $E_{ads}$ ) of the ethane, propane, i-butane and n-butane formed complexes with ZSM-5 in cluster 5T, 20T, 28T, and 38T and periodic structure

Alkanes	Adsorption energies ( $E_{ads}$ ) kcal/mol					
	5T	20T	28T	38T	P	experiment
ethane	2.6	2.7	3.9	3.5	7.1	7.3[101], 6.9[102]
propane	3.8	3.0	3.3	4.9	10.5	10.2[2], 9.5[1], 10.9[103]
i-butane	4.6	-1.3	-0.9	1.5	8.0	11.6[104], 12.4[103]
n-butane	4.4	4.0	4.1	5.7	11.5	14.7[2], 11.9[1], 14.3[105]

#### 4.1.2.2 ZPE Correction

According to Table 4.5, the correction by Zero-point energy (ZPE) reduces calculated adsorption energies. For 5T cluster, ZPEs are ranging between -0.4 to -0.7 kcal/mol for all alkanes. The positive contribution was observed.

#### 4.1.2.3 Effect of Basis Set

Table 4.3 listed adsorption energies of C2-C4 alkanes on 5T and 38T cluster models calculated using ri-PBE and various basis sets. It appears that for all alkanes the improvement of basis set decreases computed adsorption energies. Thus, the improvement of the basis set quality has the negative contribution to computed adsorption energies, like cluster-size and ZPE which have the negative contribution. For 5T model, when changing from SVP to TZVPPP adsorption energies were reduced between 3.0 to 5.5 kcal/mol. However, this decrement of adsorption energies is much smaller when changing from TZVPPP to CBS (complete-basis set), *i.e.* between 0.2 to 0.5 kcal/mol. For the larger model (38T), the decrease of adsorption energies are between 5.3 to 9.3 and 0.4 to 0.7 kcal/mol when changing from SVP to TZVPPP and TZVPPP to CBS, respectively. The much smaller decrement of adsorption energies when changing from TZVPPP to CBS implies the quality of the basis set.

TABLE 4.3 Adsorption energies (in kcal/mol) of C2-C4 alkanes on 5T and 38T cluster model computed using ri-PBE and SVP, TZVPP, and CBS basis sets

Alkanes	ri-PBE/SVP		ri-PBE/TZVPPP		ri-PBE/CBS	
	5T	38T	5T	38T	5T	38T
Ethane	-4.1	-6.7	-1.1	-1.4	-0.9	-1.0
Propane	-6.9	-9.2	-2.0	-1.9	-1.7	-1.4
i-butane	-7.0	-6.3	-2.1	2.5	-1.7	3.2
n-butane	-7.5	-11.1	-2.0	-1.8	-1.5	-1.1

#### 4.1.2.4 Effect of Electron Correlation

From Table 4.4 which showed ri-MP2 and ri-PBE energy differences, it is notice that the ri-MP2/ri-PBE difference is not the same for SVP and CBS basis set. The ri-MP2/ri-PBE differences at SVP are between 0.5 to 2.2 kcal/mol whereas they are between 2.0-5.9 kcal/mol for those of at CBS. Thus, the effect of electron correlation on  $E_{ads}$  depends on basis set. However, at both basis set, it was observed that the effect of electron correlation is larger for larger alkanes. The ri-MP2/ri-PBE differences were used as the correction for electron correlation,  $\Delta E_{corr}$ . Their values were listed in Table 4.5 and their contribution is negative.

TABLE 4.4 Differences between ri-MP2 and ri-PBE adsorption energies (in kcal/mol) computed for 5T cluster model with SVP and CBS basis set

Alkanes	E(ri-MP2/SVP)-E(ri-PBE/SVP)	E(ri-MP2/CBS)-E(ri-PBE/CBS)
	5T	5T
Ethane	-0.5	-2.0
Propane	-1.6	-4.6
i-butane	-1.8	-4.9
n-butane	-2.2	-5.9

TABLE 4.5 Adsorption energies (in kcal/mol) of ethane, propane, i-butane, and n-butane in ZSM-5.

Alkanes	$E_p$	ZPE	$\Delta E_{corr}$	$\Delta E_{basis}$	$E_{ex}$	Experiments ( $E_{ads}$ )
ethane	7.1	-0.4	-2.0	2.4	7.9	7.3[101], 6.9[102]
propane	10.5	-0.7	-4.6	3.5	10.1	10.2[2], 9.5[1], 10.9[103]
i-butane	8.0	-0.6	-4.9	4.7	8.4	11.6[104], 12.4[103]
n-butane	11.5	-0.6	-5.9	4.6	10.8	14.7[2], 11.9[1], 14.3[105]

#### 4.1.2.5 Adsorption Energies

Table 4.5 shows computed adsorption energies using PBE/DNP method with periodic model ( $E_p$ ) and corrections due to ZPE, basis-set ( $\Delta E_{basis}$ ), and electron correlation ( $\Delta E_{corr}$ ). The definitions for ZPE and  $\Delta E_{basis}$  is the same as that of equation (3.8) while that for  $\Delta E_{corr}$  was described earlier in 4.1.2.4. Since,  $E_p$  already includes the cluster-size effect, the extrapolated energies ( $E_{ex}$ ) for all alkanes which include effects such as ZPE, basis set, and electron correlation were then calculated by combining  $E_p$  with ZPE,  $\Delta E_{basis}$ , and  $\Delta E_{corr}$  and listed in Table 4.5.

With the extrapolation scheme computed adsorption energies are still in very good agreement with experiments. The  $E_{ex}$  in Table 4.5 are almost the same as  $E_p$ , since ZPE,  $\Delta E_{basis}$  and  $\Delta E_{corr}$  are cancelled each others. Thus, considering only the cluster-size effect is sufficient for determining adsorptions of alkanes in ZSM-5.

## 4.2 Proton Exchange Reactions

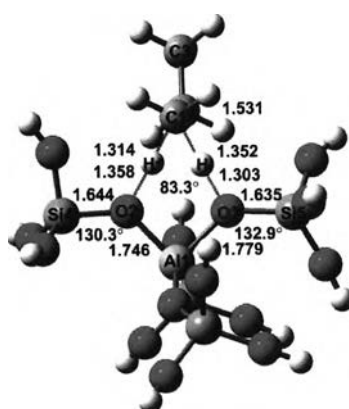
The proton exchange reaction involves the exchange between the Brønsted proton in the zeolitic framework (ZSM-5) and the H atom of alkanes. There are 3 distinct types of hydrogen on alkane carbon atoms, *i.e.* the primary, the secondary, and the tertiary hydrogen, where the exchange with the acidic proton of ZSM-5 could take place. Carbon atoms which connect to these hydrogen atoms are also called primary, secondary, and tertiary carbon, respectively. The proton exchange which occurs at these 3 hydrogen positions was thus referred to the primary, the secondary, and the tertiary proton exchange, respectively. For ethane, there is only one type of proton exchange (primary) since the molecule has only one type of H atom. However, there are 2 types of proton exchange reactions in propane, iso-butane (i-butane), and normal butane (n-butane). The summary of types of proton exchange reactions in the four alkanes was given in Table 4.6.

**TABLE 4.6** Types of proton exchange reactions of C2-C4 alkanes, with notation for further reference in parenthesis.

Alkanes	Types of proton exchange reaction
ethane	primary (ethane)
propane	primary (propane/1); secondary (propane/2)
i-butane	primary (i-butane/1); tertiary (i-butane/3)
n-butane	primary (n-butane/1); secondary (n-butane/2)

#### 4.2.1 Transition State Structures of Proton Exchange Reactions

The example of the TS structure of the proton exchange reaction (5T model) is illustrated in Figure 4.3. It was observed that the proton exchange reaction between the Brønsted acid site of ZSM-5 and alkanes forms the penta-coordinated carbonium ion in the transition state. This mechanism seem to correspond with Olah's monomolecular protolytic mechanism [44, 45] and Haag and Dessau [43]. From the figure, it could be seen that the left zeolitic oxygen has been assigned as the Brønsted acid site, (proton donor) while the right oxygen has been allocated as the Lewis base (proton acceptor).



**Figure 4.3** The penta-coordinated TS structure showing selected geometrical parameters of the proton exchange reaction in propane/1.



Most geometrical parameters of TS structures from the 38T cluster model are very similar to those from the smaller cluster models for all types of alkanes. In exception of the  $Al_1-C_x$ , this bond was found to be shortest in the 5T model because the opened-ring structure of 5T allows alkanes to move close to the active site. In contrast, the  $Al_1-C_x$  bonds are longer in the 20T, 28T, and 38T models due to the closed-ring structures. Selected geometrical parameters for TS structures of ethane, propane/1, propane/2, i-butane/1, i-butane/3, n-butane/1, and n-butane/2 proton exchange reactions, obtained using the 5T, 20T, 28T, and 38T cluster models were provided in Table 4.7, 4.8, 4.9, and 4.10. Figure 4.4 shows TS structures of proton exchange reactions between alkanes and Brønsted acid site in 38T cluster. Structures from (a) to (g) represent only the partial optimized TS structure of 38T model which were cut from the full 38T structure.

TABLE 4.7 The relevant parameters for the transition states of the proton exchange reaction of all alkanes in clusters 5T

5T (distances in Å and angles in degrees)										
Alkanes	Al <sub>1</sub> -O <sub>2</sub>	Al <sub>1</sub> -O <sub>3</sub>	Si <sub>4</sub> -O <sub>2</sub> -Al <sub>1</sub>	Si <sub>5</sub> -O <sub>3</sub> -Al <sub>1</sub>	O <sub>2</sub> -Al <sub>1</sub> -O <sub>3</sub>	O <sub>2</sub> -H <sup>+</sup>	C <sub>1-3</sub> -H <sup>+</sup>	O <sub>3</sub> -H	C <sub>1-3</sub> -H	Al <sub>1</sub> -C <sub>1-3</sub>
ethane	1.746	1.778	130.4°	133.0°	89.4°	1.359	1.314	1.304	1.351	3.581
propane/1	1.746	1.779	130.3°	132.9°	89.3°	1.358	1.314	1.303	1.352	3.581
propane/2	1.741	1.741	131.0°	132.0°	89.4°	1.401	1.294	1.310	1.373	3.615
i-butane/1	1.743	1.782	130.6°	132.3°	89.4°	1.364	1.301	1.302	1.372	3.600
i-butane/3	1.755	1.775	128.0°	131.6°	89.1°	1.406	1.396	1.394	1.334	3.684
n-butane/1	1.746	1.778	130.3°	133.0°	89.4°	1.355	1.316	1.303	1.348	3.580
n-butane/2	1.740	1.785	131.0°	132.0°	89.4°	1.404	1.293	1.311	1.370	3.617

Noted: C<sub>1-3</sub> represents a carbon that can be primary, secondary or tertiary carbon, bond length of C<sub>x</sub>-C<sub>x+1</sub> (x=1-2) is around 1.528Å -1.543Å, O<sub>2</sub> is Brønsted acid site, and O<sub>3</sub> is Lewis acid site.

TABLE 4.8 The relevant parameters for the transition states of the proton exchange reaction of all alkanes in clusters 20T

20T (distances in Å and angles in degrees)										
Alkanes	Al <sub>1</sub> -O <sub>2</sub>	Al <sub>1</sub> -O <sub>3</sub>	Si <sub>4</sub> -O <sub>2</sub> -Al <sub>1</sub>	Si <sub>5</sub> -O <sub>3</sub> -Al <sub>1</sub>	O <sub>2</sub> -Al <sub>1</sub> -O <sub>3</sub>	O <sub>2</sub> -H <sup>+</sup>	C <sub>1-3</sub> -H <sup>+</sup>	O <sub>3</sub> -H	C <sub>1-3</sub> -H	Al <sub>1</sub> -C <sub>1-3</sub>
ethane	1.799	1.792	132.1°	134.5°	85.8°	1.411	1.314	1.406	1.292	3.698
propane/1	1.798	1.790	132.2°	135.1°	86.0°	1.409	1.312	1.402	1.288	3.705
propane/2	1.789	1.803	132.8°	133.0°	85.9°	1.479	1.283	1.403	1.331	3.760
i-butane/1	1.799	1.785	133.2°	135.3°	86.0°	1.396	1.325	1.431	1.271	3.541
i-butane/3	1.809	1.788	129.0°	134.2°	85.3°	1.517	1.396	1.543	1.288	3.898
n-butane/1	1.795	1.791	133.1°	134.6°	86.1°	1.409	1.305	1.416	1.290	3.703
n-butane/2	1.789	1.801	133.0°	133.2°	86.0°	1.484	1.280	1.409	1.326	3.762

Noted: C<sub>1-3</sub> represents a carbon that can be primary, secondary or tertiary carbon, bond length of C<sub>x</sub>-C<sub>x+1</sub> (x=1-2) is around 1.526Å -1.536Å, O<sub>2</sub> is Brønsted acid site, and O<sub>3</sub> is Lewis acid site.

TABLE 4.9 The relevant parameters for the transition states of the proton exchange reaction of all alkanes in clusters 28T

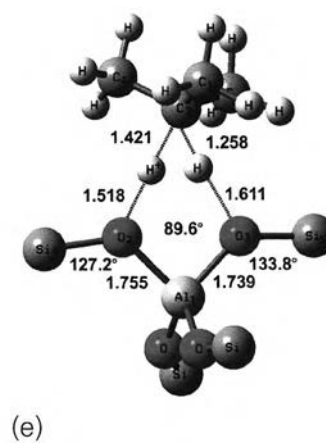
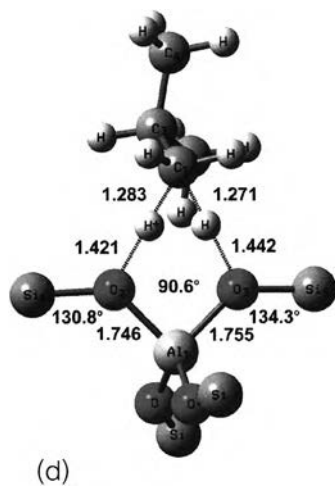
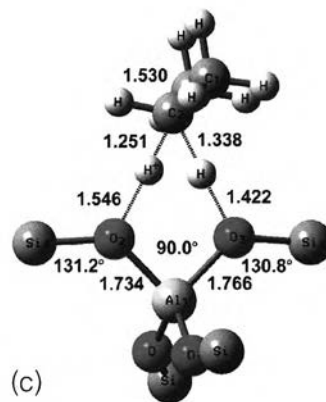
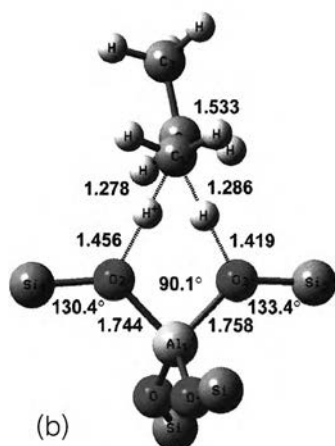
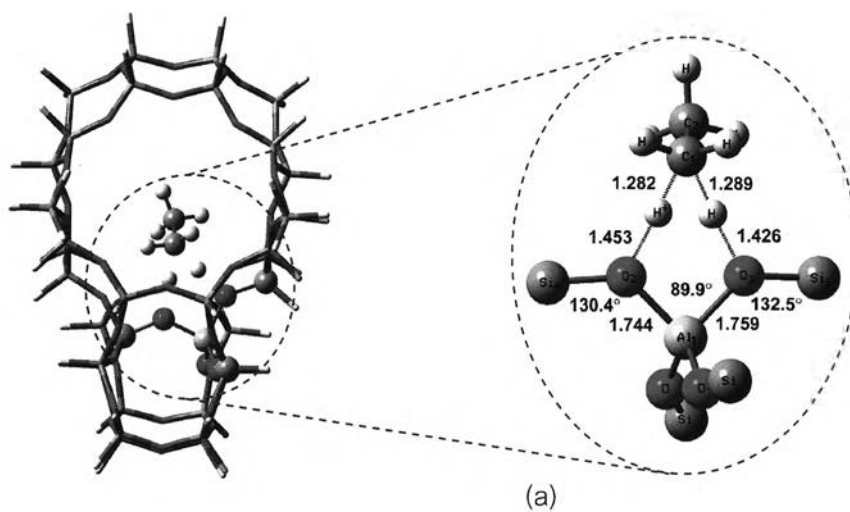
28T (distances in Å and angles in degrees)										
Alkanes	Al <sub>1</sub> -O <sub>2</sub>	Al <sub>1</sub> -O <sub>3</sub>	Si <sub>4</sub> -O <sub>2</sub> -Al <sub>1</sub>	Si <sub>5</sub> -O <sub>3</sub> -Al <sub>1</sub>	O <sub>2</sub> -Al <sub>1</sub> -O <sub>3</sub>	O <sub>2</sub> -H <sup>+</sup>	C <sub>1-3</sub> -H <sup>+</sup>	O <sub>3</sub> -H	C <sub>1-3</sub> -H	Al <sub>1</sub> -C <sub>1-3</sub>
ethane	1.770	1.769	131.1°	131.6°	87.7°	1.420	1.304	1.410	1.289	3.672
propane/1	1.770	1.769	131.1°	132.6°	87.9°	1.420	1.302	1.405	1.286	3.673
propane/2	1.762	1.778	132.0°	130.5°	87.9°	1.486	1.277	1.405	1.324	3.716
i-butane/1	1.773	1.766	132.0°	133.7°	88.1°	1.389	1.306	1.419	1.275	3.605
i-butane/3	1.778	1.763	128.0°	131.8°	87.6°	1.518	1.391	1.556	1.278	3.855
n-butane/1	1.770	1.768	131.5°	132.2°	87.9°	1.416	1.301	1.427	1.285	3.678
n-butane/2	1.761	1.778	132.2°	130.6°	88.0°	1.493	1.272	1.408	1.323	3.724

Noted: C<sub>1-3</sub> represents a carbon that can be primary, secondary or tertiary carbon, bond length of C<sub>x</sub>-C<sub>x+1</sub> (x=1-2) is around 1.528Å -1.532Å, O<sub>2</sub> is Brønsted acid site, and O<sub>3</sub> is Lewis acid site.

TABLE 4.10 The relevant parameters for the transition states of the proton exchange reaction of all alkanes in clusters 38T

38T (distances in Å and angles in degrees)										
Alkanes	Al <sub>1</sub> -O <sub>2</sub>	Al <sub>1</sub> -O <sub>3</sub>	Si <sub>4</sub> -O <sub>2</sub> -Al <sub>1</sub>	Si <sub>5</sub> -O <sub>3</sub> -Al <sub>1</sub>	O <sub>2</sub> -Al <sub>1</sub> -O <sub>3</sub>	O <sub>2</sub> -H <sup>+</sup>	C <sub>1-3</sub> -H <sup>+</sup>	O <sub>3</sub> -H	C <sub>1-3</sub> -H	Al <sub>1</sub> -C <sub>1-3</sub>
ethane	1.744	1.759	130.4°	132.5°	89.9°	1.453	1.282	1.426	1.289	3.663
propane/1	1.744	1.758	130.4°	133.4°	90.1°	1.456	1.278	1.419	1.286	3.651
propane/2	1.734	1.766	131.2°	130.8°	90.0°	1.546	1.251	1.422	1.338	3.723
i-butane/1	1.746	1.755	130.8°	134.3°	90.6°	1.421	1.283	1.442	1.271	3.624
i-butane/3	1.755	1.739	127.2°	133.8°	89.6°	1.518	1.421	1.611	1.258	3.855
n-butane/1	1.746	1.757	130.2°	133.1°	90.1°	1.447	1.285	1.444	1.282	3.644
n-butane/2	1.734	1.765	131.2°	131.3°	90.1°	1.546	1.249	1.421	1.331	3.712

Noted: C<sub>1-3</sub> represents a carbon that can be primary, secondary or tertiary carbon, bond length of C<sub>x</sub>-C<sub>x+1</sub> (x=1-2) is around 1.527Å -1.533Å, O<sub>2</sub> is Brønsted acid site, and O<sub>3</sub> is Lewis acid site.



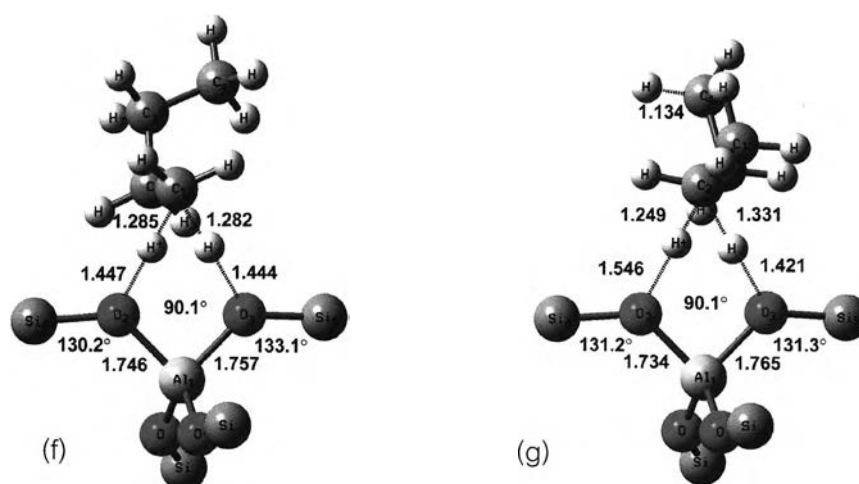


Figure 4.4 The geometries of the transition state structures (TS) of proton exchange reactions between ethane (a), primary propane (b), secondary propane (c), primary i-butane (d), tertiary i-butane (e), primary n-butane (f), and secondary n-butane (g) and Brønsted acid site (distances in Å and angles in degrees) in 38T cluster.

Considering TS structures for the reaction at the primary carbon ( $C_1$ ),  $C_1$ - $H^+$  and  $C_1$ -H distances of ethane are 1.282Å and 1.289Å in the respective order, whereas for those of propane are 1.278Å and 1.286Å, n-butane are 1.285Å and 1.282Å, and those of i-butane are 1.283Å and 1.271Å, see **Table 4.10**. Apparently,  $C_1$ - $H^+$  and  $C_1$ -H distances at the primary carbon are almost the same. For the reaction at the secondary carbon ( $C_2$ ), the information which elucidated from **Table 4.10** revealed that  $C_2$ - $H^+$  distance in the transition state, 1.251Å and 1.249Å for propane and n-butane, is shorter than  $C_2$ -H distance, 1.338Å and 1.331Å for propane and n-butane. In contrast for the reaction at the tertiary position ( $C_3$ ), **Table 4.10** showed that for i-butane  $C_3$ - $H^+$  (1.421Å) is longer than  $C_3$ -H (1.258Å) distance. The difference between  $C_{1-3}$ -H and  $C_{1-3}$ - $H^+$  distances is probably caused by the steric repulsion between the reacting center and neighboring methyl moieties. Also,  $Al_1$ - $O_2$  and  $Al_1$ - $O_3$  bond lengths and  $O_2$ - $Al_1$ - $O_3$  bond angles are dependent to types of reaction centers (primary, secondary, or tertiary). The transition states for the reactions at primary (ethane/1, propane/1, i-butane/1 and n-butane/1) and secondary (propane/2 and n-butane/2) carbons have the shorter  $Al_1$ - $O_2$  bond than  $Al_1$ - $O_3$  bond and  $O_2$ - $Al_1$ - $O_3$  angle around 90°. However, the bond variance for the reaction at the secondary carbon is more evident. For the reaction

with i-butane/3,  $\text{Al}_1\text{-O}_2$  distance is longer than that of  $\text{Al}_1\text{-O}_3$  with  $\text{O}_2\text{-Al}_1\text{-O}_3$  bond angle of  $89.6^\circ$ . In addition, the  $\text{C}_1\text{-C}_2$  bond lengths of ethane are about  $1.526\text{\AA}$ - $1.528\text{\AA}$ , and those of propane/1, propane/2, i-butane/1, i-butane/3, n-butane/1 and n-butane/2 are between  $1.530\text{\AA}$ - $1.543\text{\AA}$ . All of these behaviors could be explained by the steric interaction between the reacting center and the alkane molecule.

## 4.2.2 Estimation of Reaction Barrier

### 4.2.2.1 Effect of the Cluster Size

Values of activation energies (in kcal/mol) for ethane, propane/1, propane/2, n-butane/1, n-butane/2, i-butane/1, and i-butane/3 proton exchange reactions as the function of cluster-size were displayed in Figure 4.5.

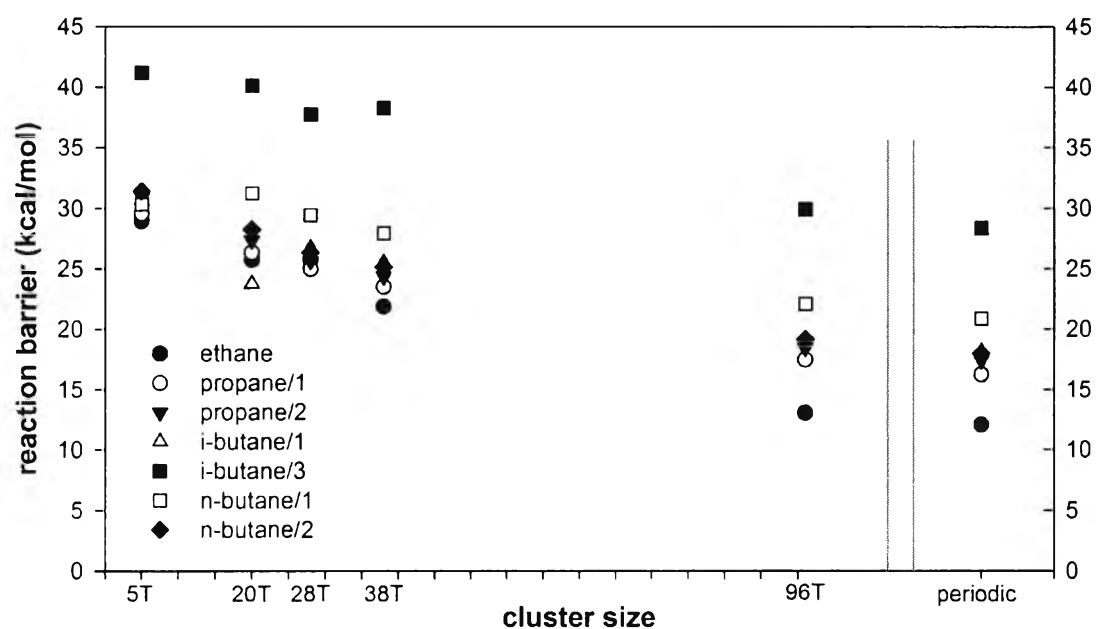


Figure 4.5 Reaction barriers of proton exchange reactions of C2-C4 alkanes in ZSM-5 calculated using PBE/DNP as a function of cluster-size.

For all alkanes, the reduction of the reaction barriers with the increment of cluster-size (from 5T to P model) was observed. The reduction is as large as 10 (butane/1) to 20 kcal/mol (ethane). Evidently, the cluster-size effect is non-



negligible and crucial for the determination of the activation energy for the reaction which takes place in ZSM-5. From 5T to 38T model, we saw the reduction of around 5 kcal/mol while from 38T to 96T model the decrease is approximately 10 kcal/mol and it is only less than 2 kcal/mol when extended from 96T to periodic model. The negative contribution of the cluster-size effect to reaction barriers of the proton exchange reactions of C2-C4 alkanes is probably resulted from electrostatic interactions with the zeolitic frame work as well as bond polarizations. To estimate the cluster-size effect accurately, one must at least consider up to 96T model (unit cell). Hence, there is a large drop in the computed reaction barriers between those using 38T and 96T model. For the periodic model, computed reaction barriers of the proton exchange of C2-C4 alkanes are ranging from 12.1 (ethane) to 28.4 (i-butane/3) kcal/mol, see Figure 4.5 and Table 4.14. Without the deduction of adsorption energies to computed activation energies, the values are already too low when compared to experiments (Table 4.14). Thus, it apparently is not enough when just accounting for the effect of the cluster-size. Moreover, the effect of cluster-size seems to be smaller for the larger alkane. Except for the proton exchange reaction at the tertiary carbon (i-butane/3) which has the reaction barrier of 28.4 kcal/mol, the proton exchange reaction at the primary and the secondary position are around 20 kcal/mol. (All values are from the periodic model.) This different behavior of i-butane/3 is possibly due to its shape. While other alkanes possess the linear or linear-like shape, i-butane/3 has a globular-like structure. This behavior was also observed when compared between TS structures.

#### 4.2.2.2 ZPE Correction

According to Table 4.14, the correction by Zero-point energy (ZPE) reduces the calculated activation energy. ZPE also varies with cluster as shown in Table 4.11. However, the size dependent seems to converge very fast and for the proton exchange reactions of C2-C4 alkanes the ZPE correction already converges at 28T model. For 38T cluster, ZPEs are ranging between -1.6 to -2.5 kcal/mol for all reactions. Again, the negative contribution was observed. If one only adjusts the

reaction barriers computed at the periodic model by ZPE, the computed values will be further underestimated. Thus, other effect should be as well sought.

TABLE 4.11 The Zero-point energies (ZPE) of TS structure of proton exchange reaction of C2-C4 alkanes in kcal/mol

Zero-point energies (ZPE) of proton exchange reaction							
Cluster-size	ethane	propane/1	propane/2	i-butane/1	i-butane/3	n-butane/1	n-butane/2
5T	-2.52	-2.81	-2.64	-2.89	-2.84	-2.87	-2.72
20T	-2.19	-2.16	-2.27	-2.05	-1.61	-1.51	-2.13
28T	-2.24	-2.12	-2.28	-1.53	-1.60	-1.71	-2.13
38T	-2.47	-2.36	-2.32	-1.78	-1.58	-1.78	-2.22

#### 4.1.2.3 Effect of Basis Set

Table 4.12 listed reaction barriers for proton exchange reactions of C2-C4 alkanes on 5T and 38T cluster models calculated using ri-PBE and various basis sets. For 5T model, when changing from SVP to TZVPPP activation energies were raised between 1.9 to 4.6 kcal/mol. In addition, this increment of activation energies is much smaller when changing from TZVPPP to CBS (complete-basis set), *i.e.* between 0.1 to 0.4 kcal/mol. For the larger model (38T), the increase of reaction barriers are between 2.5 to 3.6 and 0.2 to 0.3 kcal/mol when changing from SVP to TZVPPP and TZVPPP to CBS, respectively. The much smaller increment of activation energies when changing from TZVPPP to CBS implies the quality of the basis set. It appears that for all alkanes the improvement of basis set increases computed reaction barriers. Thus, the improvement of the basis set quality has the positive contribution to computed reaction barriers, unlike cluster-size and ZPE which have the negative contribution. The correction using basis-set deficiency ( $\Delta E_{basis}$ ) was estimated from  $E(38T, riPBE/CBS) - E(38T, PBE/DNP)$  which gives positive values because the reaction barriers from CBS were higher than those from DNP, whereas those from SVP show the lowest (Table 4.14).

TABLE 4.12 Reaction barriers (in kcal/mol) of proton exchange reactions of C2-C4 alkanes on 5T and 38T cluster model computed using ri-PBE and SVP, TZVPP, and CBS basis sets

Alkanes	ri-PBE/SVP		ri-PBE/TZVPPP		ri-PBE/CBS	
	5T	38T	5T	38T	5T	38T
ethane	24.4	20.2	28.4	22.8	28.7	23.0
propane/1	26.9	22.1	29.2	24.6	29.4	24.8
propane/2	27.4	22.6	30.5	25.3	30.8	25.5
i-butane/1	26.6	23.0	30.2	26.6	30.4	26.9
i-butane/3	36.1	35.5	40.7	39.1	41.1	39.3
n-butane/1	28.0	26.0	29.9	29.1	30.0	29.3
n-butane/2	28.3	23.5	31.1	26.3	31.3	26.5

#### 4.2.2.4 Effect of Electron Correlation

From **Table 4.13** which listed ri-MP2 and ri-PBE energy differences and dispersion interactions ( $E_{disp}$ ) as a function of cluster-size, we found that estimated dispersion energies for all alkanes are size-dependent and their values converge at 38T model. For 5T cluster, dispersion energies of all alkanes are overestimated by around 2 – 3 kcal/mol when compared to the difference of activation energies computed by ri-MP2/CBS and ri-PBE/CBS. However, the ri-MP2/ri-PBE difference is not the same for SVP and CBS basis set. For a particular system, the overestimation of the dispersion interaction obtained using Equation (3.6) does not depend on types of alkanes. Using **Table 4.13**, we determined the overestimation of the dispersion interaction by Equation (3.6) or  $E_{add}$  and then used it to adjust  $E_{disp}$  for  $\Delta E_{corr}$  as shown in Equation (3.7). The value of  $\Delta E_{corr}$  listed in **Table 4.14** can, however, be positive or negative according to types of alkanes. It is positive for ethane and propane while it is negative for n- and i-butane. In the case of the proton exchange reaction of C2-C4 alkanes, the magnitude of  $\Delta E_{corr}$  for 96T model is between 0.1 to 3.5 kcal/mol. It is 2.8 kcal/mol for ethane and -3.5 kcal/mol for i-butane/1. Values of  $\Delta E_{corr}$  for 96T model for all alkanes were given in **Table 4.14**.

TABLE 4.13 Differences between ri-MP2 and ri-PBE activation energies (in kcal/mol) computed for 5T cluster model with SVP and CBS basis set and dispersion interactions estimated using Equation (3.6) for 5T, 20T, 28T, 38T, and 96T models.

Alkanes	E(ri-MP2/SVP)-E(ri-PBE/SVP)	E(ri-MP2/CBS)-E(ri-PBE/CBS)	$E_{disp}$				
	5T	5T	5T	20T	28T	38T	96T
ethane	3.3	-1	-4.2	0	-0.7	-0.4	-0.4
propane/1	0.3	1.1	-1.7	-2.1	-1.9	-2.4	-2.1
propane/2	-1.1	-0.9	-3.1	-1	-0.3	-2.2	-2.1
i-butane/1	-0.6	-0.2	-3.2	2.9	-1.5	-4.7	-4.1
i-butane/3	-2	-3.7	-5.9	-2.8	-2.7	-6	-5.7
n-butane/1	-0.7	1.6	-1.6	-7.1	-6.8	-5	-4.6
n-butane/2	-2.3	-0.5	-3	-3.9	-3.6	-2.8	-2.6

TABLE 4.14 Reaction barriers (in kcal/mol) of proton exchange reactions of alkanes in ZSM-5.

Alkanes	$E_p$	ZPE	$\Delta E_{corr}$	$\Delta E_{basis}$	$E_{ex}$	$E_{ads}$	$E_{ex}-E_{ads}$	$-T\Delta S$	$E_{ex}-E_{ads}-T\Delta S$	Other theoretical works ( $\Delta E_{app}^\ddagger$ )	Experiments ( $\Delta E_{app}^\ddagger$ )
ethane	12.1	-2.5	2.8	1.1	13.5	7.1	6.4	3.1	9.5	28.2[6], 31.4[7], 31.0[106]	
propane/1	16.3	-2.4	0.6	1.2	15.7	10.5	5.2	19.1	24.3	30.6[7], 30.4[106]	25.7±1.6[4], 25.5±2.4[107]
propane/2	17.4	-2.3	0.1	1.1	16.3	10.5	5.8	19.4	25.2	30.6[7], 29.8[106]	27.8±1.6[4], 29.7±1.4[107]
i-butane/1	18.1	-1.8	-1.2	1.4	16.5	8.0	8.5	19.4	27.9	32.3[7], 29.4[108]	25.9[109]
i-butane/3	28.4	-1.6	-3.5	1.0	24.3	8.0	16.3	21.4	37.7	36.2[7], 29.9[108]	
n-butane/1	20.9	-1.8	-1.5	1.4	19.0	11.5	7.5	18.9	26.4	29.9[106]	19.0[2, 110], 20.2[105], 25.7±2.4[111]
n-butane/2	18.0	-2.2	-0.1	1.4	17.1	11.5	5.6	19.8	25.4	28.3[106]	25.7±2.4[111]

Noted:  $\Delta E_{app}^\ddagger = E_{ex} - E_{ads}$

#### 4.2.2.5 Reaction Barriers

Table 4.14 shows computed reaction barriers using PBE/DNP method with periodic model ( $E_p$ ). When combining with adsorption energy ( $E_{ads}$ ), the computed apparent reaction barriers are only 10 kcal/mol or less (in exception of i-butane/3 which has the apparent reaction barrier of 20 kcal/mol). The obtained reaction barriers are way lower than corresponding experimental results (also shown on Table 4.14). Since,  $E_p$  only considers for the cluster-size effect, the calculated values could be improved by taking into accounts other effects such as ZPE, basis set, and electron correlation. The corrections to the activation energies owing to ZPE, basis set ( $\Delta E_{basis}$ ), and electron correlation ( $\Delta E_{corr}$ ) were listed in Table 4.14. Also in this table, extrapolated energies ( $E_{ex}$ ) which include corrections due to the above mentioned effects according to Equation (3.8) were given.

However, even with the extrapolation scheme computed reaction barriers are heavily underestimated by up to 25 kcal/mol. When compared to other theoretical studies [6, 7, 106, 108], our predicted apparent reaction barriers are too small. Moreover, most theoretical works often overestimated their computed barriers. It seems that at a glance those previous calculations had better agreement with experiments. However, small cluster-size models (3T) with limited level of accuracy and basis set have been employed in those works. We have shown that the cluster-size has a drastic effect on the reaction barrier while other effects (ZPE, basis set, correlation) are smaller (but still significant) and cancelled out. The agreement between previous theoretical works and experiments suggests that there should be another effect which has not yet been considered and this effect will cancelled out with the effect from the cluster-size. We, thus, considered the entropic term. The entropic contributions ( $T\Delta S$ ) were included in Table 4.14. Their values are non-negligible and around 20 kcal/mol, the same size as the cluster-size effect, except in the case of ethane. When including  $T\Delta S$ , the predicted apparent reaction barriers are now in good agreement with corresponding experimental values. The entropic term is indeed very important and has an opposite sign to the cluster-size effect.



From Table 4.14, the proton exchange reactions at primary and secondary positions have very similar barriers, 24 – 27 kcal/mol while the reaction at the tertiary position has a strikingly higher barrier (37.7 kcal/mol). This trend is similar to that discussed on geometries of TS where structures of TS complexes at primary and secondary positions are very alike but they are distinct to those at the tertiary position. Thus, reaction barrier of the proton exchange reaction of C2-C4 alkanes in ZSM-5 could be described by steric interaction. However, the reaction barrier for ethane is only 9.5 kcal/mol, the value that differs from other alkanes. This is probably because ethane has only one C-C bond which is already fixed to the zeolitic framework. Thus, the degree of freedom and hence the entropy are much reduced. It is also worth to note that the estimated barrier of the proton exchange reaction of ethane is much lower than other predictions [6, 7, 108]. For ethane, the entropic effect though has opposite sign to the cluster-size effect but its value is very small and thus the two effects are not cancelled. Very small reaction barrier is then observed.

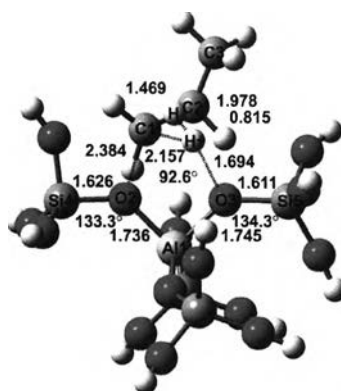
### 4.3 Dehydrogenation Reactions

The dehydrogenation reaction is referred to the reaction where C-H bond of alkane is cleaved by the zeolitic Brønsted acid proton and formed hydrogen molecule. Similar to the proton exchange reactions there are three positions where alkanes' C-H bonds can be broken with the Brønsted proton of ZSM-5, *i.e.* at the primary, the secondary, and the tertiary carbon atom of the alkanes. The assignment of types of dehydrogenation reactions is similar to that of the proton exchange in Table 4.6.

#### 4.3.1 Transition State Structures of Dehydrogenation Reactions

An optimized TS structure of the dehydrogenation reaction obtained using 5T model is shown in Figure 4.6. From Figure 4.6, it appears that the bond between carbon and hydrogen atom of alkane is lengthened while the hydrogen atom moves closer to the protonic hydrogen of ZSM-5 forming hydrogen-hydrogen bond.

Interestingly, a penta-coordinated carbonium ion is formed in the transition state. TS form agrees with the mechanism of Olah [44, 45], Haag, and Dessau [43].



**Figure 4.6** The transition-state structure with selected geometrical parameters of the dehydrogenation reaction in propane/1.

Selected geometrical parameters for TS structures of ethane, propane/1, propane/2, i-butane/1, i-butane/3, n-butane/1, and n-butane/2, obtained using 5T, 20T, 28T, and 38T cluster models were provided in Table 4.15, 4.16, 4.17, and 4.18. From TS structures of dehydrogenation reactions, the bond length of  $Al_1-C_x$  in 5T is about 3.383Å-4.382Å shorter than other  $Al_1-C_x$  distances in 20T, 28T, and 38T which are in a range of 3.608Å-4.511Å. Consequently,  $C_x-C_{x+1}$  bond length at primary carbon is 1.465Å -1.481Å longer than that at secondary and tertiary carbon which is 1.432Å-1.460Å. However, in the larger clusters, the results are opposite. In the 38T model, for example,  $C_x-C_{x+1}$  bond length at primary carbon is shorter than that at secondary and tertiary carbon. The cluster-size has an effect not only on the true reaction barriers, but also the calculated TS structures.

Geometries of TS structures for above reactions obtained using 38T cluster model were shown in Figure 4.7.

TABLE 4.15 The relevant parameters for the transition states of the dehydrogenation reaction of all alkanes in clusters 5T

5T (distances in Å and angles in degrees)										
Alkanes	Al <sub>1</sub> -O <sub>2</sub>	Al <sub>1</sub> -O <sub>3</sub>	Si <sub>4</sub> -O <sub>2</sub> -Al <sub>1</sub>	Si <sub>5</sub> -O <sub>3</sub> -Al <sub>1</sub>	O <sub>2</sub> -Al <sub>1</sub> -O <sub>3</sub>	O <sub>2</sub> -C <sub>1,3</sub>	O <sub>3</sub> -H <sup>+</sup>	C <sub>1,3</sub> -H	C <sub>1,3</sub> -H <sup>+</sup>	H-H <sup>+</sup>
ethane	1.732	1.748	134.2°	133.6°	92.8°	2.454	1.745	1.989	2.122	0.812
propane/1	1.736	1.745	133.3°	134.3°	92.6°	2.384	1.694	1.978	2.157	0.815
propane/2	1.705	1.789	131.4°	134.9°	92.3°	2.969	1.741	1.780	2.138	0.819
i-butane/1	1.741	1.741	132.9°	134.4°	92.6°	2.351	1.703	1.993	2.173	0.813
i-butane/3	1.745	1.754	132.2°	132.6°	91.7°	3.405	1.609	1.796	2.277	0.836
n-butane/1	1.737	1.744	133.3°	134.3°	92.7°	2.377	1.684	1.975	2.166	0.817
n-butane/2	1.709	1.760	134.0°	134.7°	94.1°	3.014	1.733	2.152	2.303	0.807

Noted: C<sub>1,3</sub> represents a carbon that can be primary, secondary or tertiary carbon, bond length of C<sub>x</sub>-C<sub>x+1</sub> (x=1, 2) is around 1.432Å-1.481Å, and O<sub>2</sub> is Brønsted acid site.

TABLE 4.16 The relevant parameters for the transition states of the dehydrogenation reaction of all alkanes in clusters 20T

20T (distances in Å and angles in degrees)										
Alkanes	Al <sub>1</sub> -O <sub>2</sub>	Al <sub>1</sub> -O <sub>3</sub>	Si <sub>4</sub> -O <sub>2</sub> -Al <sub>1</sub>	Si <sub>5</sub> -O <sub>3</sub> -Al <sub>1</sub>	O <sub>2</sub> -Al <sub>1</sub> -O <sub>3</sub>	O <sub>2</sub> -C <sub>1-3</sub>	O <sub>3</sub> -H <sup>+</sup>	C <sub>1-3</sub> -H	C <sub>1-3</sub> -H <sup>+</sup>	H-H <sup>+</sup>
ethane	1.735	1.756	138.2°	136.9°	91.4°	2.977	2.340	2.594	2.413	0.776
propane/1	1.744	1.762	137.4°	137.2°	90.8°	2.867	2.380	2.556	2.364	0.774
propane/2	1.745	1.804	132.5°	137.9°	91.9°	3.307	1.827	1.864	2.223	0.806
i-butane/1	1.753	1.777	136.4°	137.5°	90.6°	2.894	2.208	1.970	1.987	0.797
i-butane/3	1.766	1.774	134.7°	136.9°	89.9°	3.758	1.870	2.043	2.376	0.795
n-butane/1	1.758	1.755	136.9°	136.5°	90.7°	2.961	3.198	2.150	1.898	0.784
n-butane/2	1.766	1.781	136.3°	134.8°	90.2°	3.451	2.525	1.896	2.231	0.806

Noted: C<sub>1-3</sub> represents a carbon that can be primary, secondary or tertiary carbon, bond length of C<sub>x</sub>-C<sub>x+1</sub> (x=1, 2) is around 1.433Å-1.453Å, and O<sub>2</sub> is Brønsted acid site.

TABLE 4.17 The relevant parameters for the transition states of the dehydrogenation reaction of all alkanes in clusters 28T

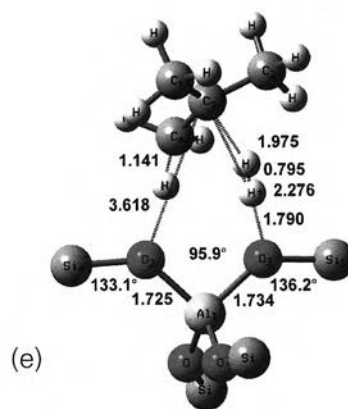
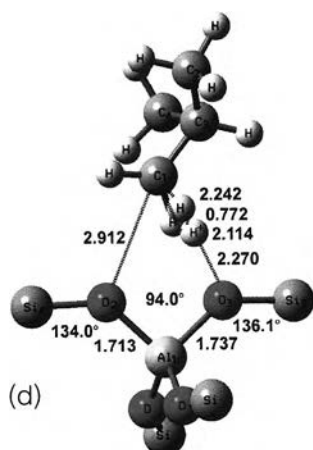
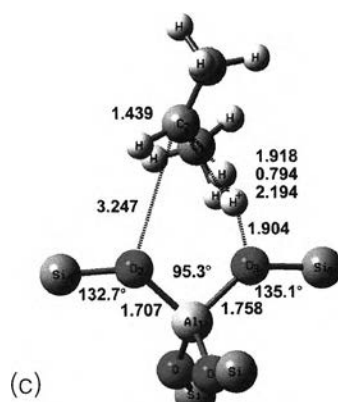
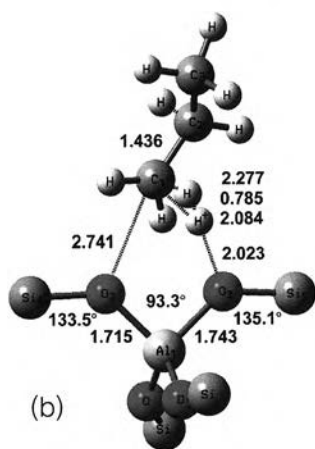
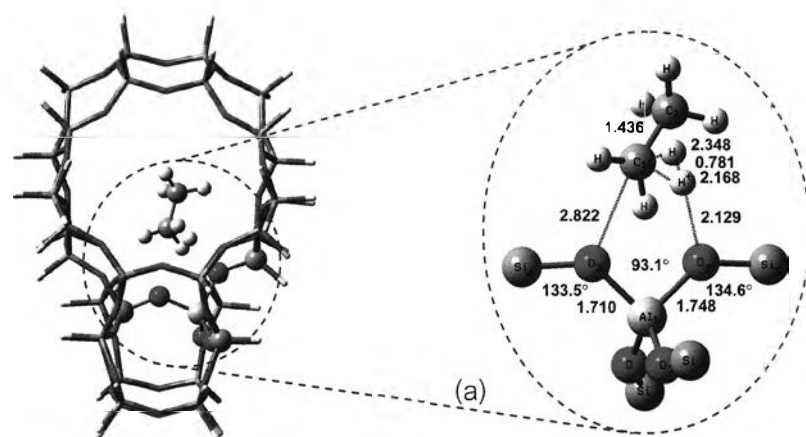
28T (distances in Å and angles in degrees)										
Alkanes	Al <sub>1</sub> -O <sub>2</sub>	Al <sub>1</sub> -O <sub>3</sub>	Si <sub>4</sub> -O <sub>2</sub> -Al <sub>1</sub>	Si <sub>5</sub> -O <sub>3</sub> -Al <sub>1</sub>	O <sub>2</sub> -Al <sub>1</sub> -O <sub>3</sub>	O <sub>2</sub> -C <sub>1-3</sub>	O <sub>3</sub> -H <sup>+</sup>	C <sub>1-3</sub> -H	C <sub>1-3</sub> -H <sup>+</sup>	H-H <sup>+</sup>
ethane	1.735	1.747	137.7°	135.4°	96.6°	2.811	2.402	2.406	2.275	0.777
propane/1	1.736	1.760	132.1°	135.9°	96.8°	2.896	2.452	2.149	2.088	0.782
propane/2	1.725	1.781	130.8°	135.6°	96.1°	3.296	1.816	1.876	2.227	0.805
i-butane/1	1.735	1.756	132.4°	137.5°	97.3°	2.851	1.973	2.070	2.059	0.790
i-butane/3	1.749	1.752	131.1°	135.8°	96.7°	3.676	1.758	1.955	2.321	0.806
n-butane/1	1.750	1.753	136.9°	136.5°	90.7°	2.961	2.105	2.341	2.254	0.784
n-butane/2	1.745	1.761	131.6°	134.5°	95.1°	3.466	2.626	1.923	2.240	0.805

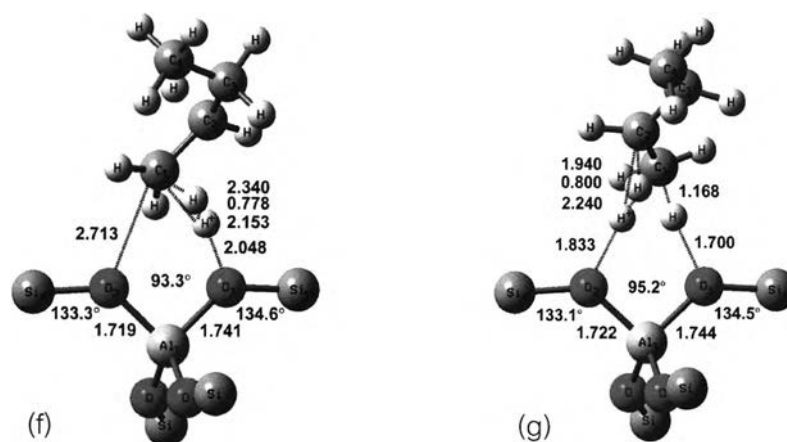
Noted: C<sub>1-3</sub> represents a carbon that can be primary, secondary or tertiary carbon, bond length of C<sub>x</sub>-C<sub>x+1</sub> (x=1, 2) is around 1.412Å-1.465Å, and O<sub>2</sub> is Brønsted acid site.

TABLE 4.18 The relevant parameters for the transition states of the dehydrogenation reaction of all alkanes in clusters 38T

38T (distances in Å and angles in degrees)										
Alkanes	Al <sub>1</sub> -O <sub>2</sub>	Al <sub>1</sub> -O <sub>3</sub>	Si <sub>4</sub> -O <sub>2</sub> -Al <sub>1</sub>	Si <sub>5</sub> -O <sub>3</sub> -Al <sub>1</sub>	O <sub>2</sub> -Al <sub>1</sub> -O <sub>3</sub>	O <sub>2</sub> -C <sub>1-3</sub>	O <sub>3</sub> -H <sup>+</sup>	C <sub>1-3</sub> -H	C <sub>1-3</sub> -H <sup>+</sup>	H-H <sup>+</sup>
ethane	1.710	1.748	133.5°	134.6°	93.1°	2.822	2.129	2.348	2.168	0.781
propane/1	1.715	1.743	133.5°	135.1°	93.3°	2.741	2.023	2.277	2.084	0.785
propane/2	1.707	1.758	132.7°	135.1°	95.3°	3.247	1.904	1.918	2.194	0.794
i-butane/1	1.713	1.737	134.0°	136.1°	94.0°	2.912	2.270	2.242	2.114	0.772
i-butane/3	1.725	1.734	133.1°	136.2°	95.9°	3.618	1.790	1.975	2.276	0.795
n-butane/1	1.719	1.741	133.3°	134.6°	93.3°	2.713	2.048	2.340	2.153	0.778
n-butane/2	1.722	1.744	133.1°	134.5°	95.2°	3.511	2.687	1.940	2.240	0.800

Noted: C<sub>1-3</sub> represents a carbon that can be primary, secondary or tertiary carbon, bond length of C<sub>x</sub>-C<sub>x+1</sub> is around 1.425Å-1.454Å, and O<sub>2</sub> is Brønsted acid site.





**Figure 4.7** Geometries of transition state structures (TS) between ethane (a), propane/1 (b), propane/2 (c), n-butane/1 (d), n-butane/2 (e), i-butane/1 (f), and i-butane/3 (g) of dehydrogenation reaction (distances in Å and angles in degree) obtained using 38T cluster.

Considering the TS structures for the dehydrogenation reaction at the primary carbon ( $C_1$ ),  $C_1$ -H and  $C_1$ -H<sup>+</sup> distances of ethane are 2.348Å and 2.168Å in the respective order, those of propane/1 are 2.277Å and 2.084Å, those of i-butane/1 are 2.242Å and 2.114Å, and those of n-butane/1 are 2.340Å and 2.153Å. Evidently,  $C_1$ -H bond is longer than  $C_1$ -H<sup>+</sup> bond and their values are almost equal at the primary position for all alkanes. For the dehydrogenation reaction which occurred at the secondary carbon ( $C_2$ ),  $C_2$ -H distance in the transition state is shorter than and  $C_2$ -H<sup>+</sup> distance, i.e 1.918Å and 2.194Å for propane/2 and 1.940Å and 2.240Å for n-butane/2. For the reaction at the tertiary position ( $C_3$ ), it was observed that  $C_3$ -H<sup>+</sup> is longer than  $C_3$ -H distance like in the case of the primary carbon, 2.276Å and 1.975Å for i-butane/3. Moreover,  $O_2$ -C distances of the secondary and the tertiary carbon is longer than that of the primary carbon. For example,  $O_2$ - $C_3$  distance of i-butane/3 is the longest (3.618Å) because of the highest steric effect. The  $O_2$ - $C_2$  distance of propane/2 is 3.247Å and that of n-butane/2 is 3.511Å. In case of  $O_2$ - $C_1$  distance of ethane is 2.822Å, that of propane/1 is 2.741Å, that of i-butane/1 is 2.912Å, and that of n-butane/1 is 2.713Å. The difference between  $C_{1-3}$ -H,  $C_{1-3}$ -H<sup>+</sup>, and  $O_2$ - $C_{1-3}$  distances could probably be as well explained by the steric between the reacting center and neighboring methyl moieties. Similar to the



proton exchange reaction,  $O_2-Al_1-O_3$  bond angles were found to be depended on types of reaction centers (primary, secondary, or tertiary). The transition states for the reactions at primary (ethane, propane/1, i-butane/1 and n-butane/1) and secondary/tertiary (propane/2, n-butane/2, and i-butane/3) carbons have  $O_2-Al_1-O_3$  angles around  $93^\circ-94^\circ$  and  $95-96^\circ$ , respectively. We found that the  $O_2-Al_1-O_3$  angles of dehydrogenation reaction are higher than the  $O_2-Al_1-O_3$  angles of proton exchange reaction in range of  $3^\circ-6^\circ$ . At all types of reaction center, the  $Al_1-O_3$  bond lengths are longer than  $Al_1-O_2$  bond lengths because H of alkanes or acidic proton ( $H^+$ ) can bond with  $O_3$  of zeolite. The protonating proton withdraws electron from the  $Al_1-O_3$  bond; as a result, the  $Al_1-O_3$  bond is weakened and lengthened. When the hydrogen atom moves closer to the protonic hydrogen of ZSM-5 forming  $H_2$ , we found that  $C_x-C_{x+1}$  bond length of all alkanes are shorten due to their hybridization orbital are changed. The  $C_x-C_{x+1}$  bond length of ethane, propane/1, propane/2, i-butane/1, i-butane/2, n-butane/1, and n-butane/2 is 1.436Å, 1.436Å, 1.439Å, 1.425Å, 1.454Å, 1.434Å, and 1.436Å, respectively. Additionally, the  $H-H^+$  distances for  $H_2$  molecule are in ranges of 0.772Å-0.800Å. We found that the  $H-H^+$  distances of the secondary or tertiary carbon are slightly longer than those of the primary carbon. The steric effect between the reacting center and the alkane molecule plays an important role for all of these behaviors.

## 4.3.2 Estimation of Reaction Barrier

### 4.3.2.1 Effect of the Cluster Size

Values of activation energies (in kcal/mol) for ethane, propane/1, propane/2, n-butane/1, n-butane/2, i-butane/1, and i-butane/3 dehydrogenation reaction as the function of cluster-size are displayed in **Figure 4.8**.

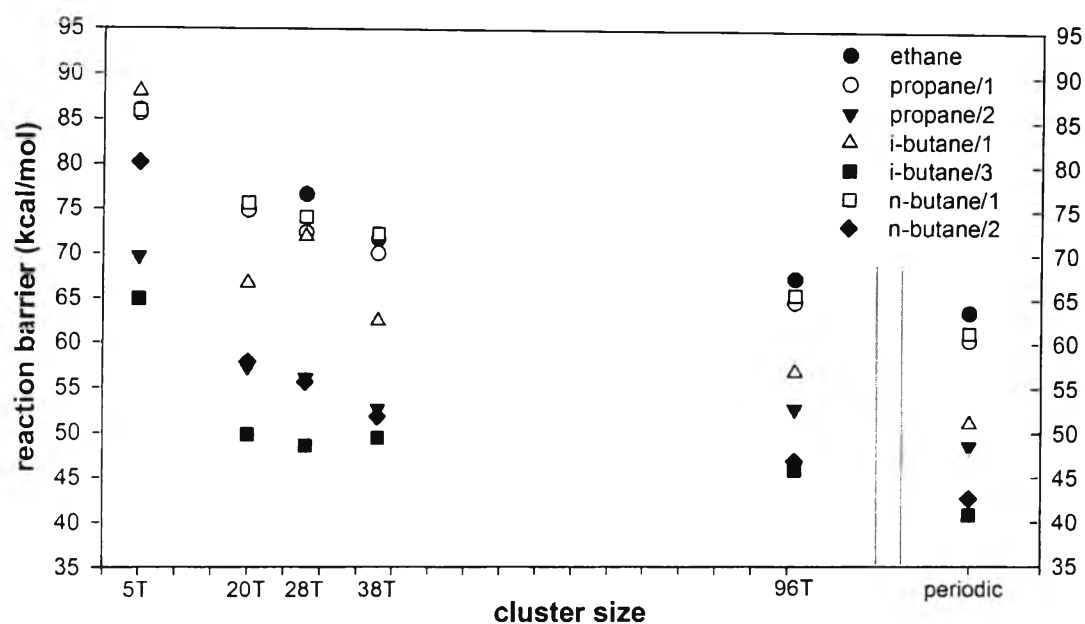


Figure 4.8 Reaction barriers of dehydrogenation reactions of C2-C4 alkanes in ZSM-5 calculated using PBE/DNP as a function of cluster-size.

For all alkanes, the reaction barriers decrease as the size of cluster increases (from 5T to P). The reduction is as large as 21.2 kcal/mol for propane/2 (the smallest) to 37.5 kcal/mol for n-butane/2 (the largest). Evidently, the cluster-size effect is non-negligible and crucial for the determination of the activation energy for the reaction which takes place in ZSM-5. From 5T to 38T models, the reduction of reaction barriers was around 13-28 kcal/mol while from 38T to 96T the decrease is approximately 3-7 kcal/mol in 38T to 96T model, and the reaction barriers decrease less than 5 kcal/mol when structure was extended to the periodic model. The negative contribution of the cluster-size effect to the reaction barrier of the dehydrogenation reaction of C2-C4 alkanes is probably resulted from electrostatic interactions and bond polarizations between the TS structure and the zeolitic framework. Because of the carbonium ion has positive charge, the negative charge of the framework stabilizes the TS. The large cluster shows more negatively-charge framework than the smaller one. Thus, the reaction barrier is lower in the big cluster. To estimate the cluster-size effect accurately, one must at least consider up to 96T model (unit cell). Hence, there is a large drop in the computed reaction barriers between those using 5T and 38T models. For periodic

model, computed reaction barriers of the dehydrogenation reactions of C2-C4 alkanes are ranging from 40.8 (i-butane/3) to 63.5 (ethane) kcal/mol, see Figure 4.8 and Table 4.22. With further deduction by adsorption energies, computed reaction barriers are still too high as compared to experiments (Table 4.22). Thus, it apparently is not enough when just accounting for the effect of the cluster-size. Moreover, the effect of cluster-size seems to be smaller for the larger alkane. The activation energies of dehydrogenation reactions at the primary and the secondary/tertiary carbon of alkanes are around 63.5-51.1 kcal/mol and 48.5-40.8 kcal/mol, respectively. (All values are from the periodic model.)

#### 4.3.2.2 ZPE Correction

According to Table 4.22, the Zero-point energy (ZPE) correction reduces the calculated activation energy and also varies with the cluster-size. However, the size dependence seems to converge very fast, and for the dehydrogenation reactions of C2-C4 alkanes the ZPE correction already converges at 28T model in Table 4.19. For 38T cluster, ZPEs are ranging between -4.3 to -5.8 kcal/mol. Adjusting the reaction barriers computed at the periodic model by ZPE, the computed values are still overestimated. Thus, other effect should be as well sought.

TABLE 4.19 The Zero-point energies (ZPE) of TS structure of dehydrogenation reaction of C2-C4 alkanes in kcal/mol

Zero-point energies (ZPE) of dehydrogenation reaction							
Cluster-size	ethane	propane/1	propane/2	i-butane/1	i-butane/3	n-butane/1	n-butane/2
5T	-4.61	-4.89	-5.37	-4.39	-5.72	-4.77	-6.03
20T	-4.37	-6.95	-5.22	-5.03	-5.50	-4.36	-5.37
28T	-4.30	-6.63	-5.15	-4.21	-4.76	-6.27	-5.41
38T	-4.75	-5.82	-5.42	-4.92	-4.35	-5.46	-5.56

### 4.3.2.3 Effect of Basis Set

Table 4.20 listed the reaction barriers for dehydrogenation reactions of C2-C4 alkanes on 5T and 38T cluster models calculated using ri-PBE and various basis sets. For 5T model, when changing from SVP to TZVPPP activation energies were reduced between 0.8 to 4.7 kcal/mol. Moreover, this decrement of activation energies is smaller when changing from TZVPPP to CBS, *i.e.* between 0.1 to 0.4 kcal/mol. For the larger model (38T), the decrease of reaction barriers are between 0.5 to 3.3 and 0.1 to 0.3 kcal/mol when changing from SVP to TZVPPP and TZVPPP to CBS, respectively. The much smaller decrement of activation energies when changing from TZVPPP to CBS again implies the quality of the basis set. It appears that for all alkanes the improvement of basis set decreases computed reaction barriers. However, the improvement of the basis set quality adds the positive contribution to computed reaction barriers, unlike cluster-size and ZPE which have the negative contribution. The correction using basis-set deficiency ( $\Delta E_{basis}$ ) was estimated from  $E(38T, riPBE/CBS) - E(38T, PBE/DNP)$  which gives positive values because the reaction barriers from CBS were higher than those from DNP, whereas those from SVP show highest (Table 4.22).

TABLE 4.20 Reaction barriers (in kcal/mol) of dehydrogenation reactions of C2-C4 alkanes on 5T and 38T cluster model computed using ri-PBE and SVP, TZVPP, and CBS basis sets.

Alkanes	ri-PBE/SVP		ri-PBE/TZVPPP		ri-PBE/CBS	
	5T	38T	5T	38T	5T	38T
ethane	87.7	77.3	86.5	74.0	86.4	73.7
propane/1	88.5	75.8	86.0	72.5	85.8	72.3
propane/2	72.3	56.2	70.1	55.2	70.0	55.1
i-butane/1	90.3	67.9	88.2	63.8	88.0	63.5
i-butane/3	65.6	52.2	64.8	51.6	64.7	51.6
n-butane/1	89.1	77.8	86.3	74.7	86.1	74.4
n-butane/2	84.7	55.2	80.0	54.0	79.7	53.9

#### 4.3.2.4 Effect of Electron Correlation

From **Table 4.21** which showed ri-MP2 and ri-PBE energy differences and dispersion interactions ( $E_{disp}$ ) as a function of cluster-size, we found that estimated dispersion energies for all alkanes are size-dependent and their values converge at 38T model. For 5T cluster, dispersion energies of all alkanes are overestimated by around 11-14 kcal/mol when compared to the difference of activation energies computed by ri-MP2/CBS and ri-PBE/CBS. However, the ri-MP2/ri-PBE difference is not the same for SVP and CBS basis set. For a particular system, the overestimation of the dispersion interaction obtained using equation (3.6) does not depend on types of alkanes. Using **Table 4.21**, we determined the overestimation of the dispersion interaction by equation (3.6) or  $E_{add}$  and then used it to adjust  $E_{disp}$  for  $\Delta E_{corr}$  as shown in equation (3.7). The values of  $\Delta E_{corr}$  listed in **Table 4.22** are positive for all alkanes in the case of the dehydrogenation reaction. The magnitude of  $\Delta E_{corr}$  for 96T model is between 9.1 to 11.1 kcal/mol. It is 11.1 kcal/mol for ethane and n-butane/1 and 9.1 kcal/mol for -butane/2. Values of  $\Delta E_{corr}$  for 96T model for all alkanes were given in **Table 4.22**.

TABLE 4.21 Differences between ri-MP2 and ri-PBE activation energies (in kcal/mol) computed for 5T cluster model with SVP and CBS basis set and dispersion interactions estimated using Equation (3.6) for 5T, 20T, 28T, 38T, and 96T models.

Alkanes	E(ri-MP2/SVP)-E(ri-PBE/SVP)	E(ri-MP2/CBS)-E(ri-PBE/CBS)	$E_{disp}$				
	5T	5T	5T	20T	28T	38T	96T
ethane	15.5	6.8	-5.9	-1.5	-2.6	-1.5	-1.6
propane/1	16.5	8.3	-4.6	-4.2	-3.0	-2.6	-2.3
propane/2	15.9	7.5	-3.8	-0.9	-0.4	-2.3	-2.1
i-butane/1	15.9	7.2	-5.5	2.5	-2.7	-2.1	-1.6
i-butane/3	18.8	10.7	-4.0	4.2	2.1	-5.6	-5.4
n-butane/1	16.6	8.7	-4.5	-6.2	0.2	-3.8	-3.7
n-butane/2	15.1	7.5	-4.3	-2.7	-1.1	-1.3	-1.2

TABLE 4.22 Reaction barriers (in kcal/mol) of dehydrogenation reactions of alkanes in ZSM-5

Alkanes	$E_p$	ZPE	$\Delta E_{corr}$	$\Delta E_{basis}$	$E_{ex}$	$E_{ads}$	$E_{ex}-E_{ads}$	$-T\Delta S$	$E_{ex}-E_{ads}-T\Delta S$	Other theoretical works ( $\Delta E_{app}^\ddagger$ )	Experiments ( $\Delta E_{app}^\ddagger$ )
ethane	63.5	-4.8	11.1	2.1	72.0	7.1	64.9	1.9	66.7	75.95[10], 70.9[6]	
propane/1	60.4	-5.8	10.6	2.2	67.3	10.5	56.9	18.1	75.0	76.7[112], 73.0[11]	22.7[2, 113]
propane/2	48.5	-5.4	9.1	2.5	54.8	10.5	44.3	19.7	64.0		
i-butane/1	61.2	-4.9	9.5	1.1	58.3	8.0	50.3	19.3	69.7	59.4[108], 66.9[114], 74.7[114], 53.5[11]	29.4±0.3[104], 23.9[2, 113], 32.5±1.4[115]
i-butane/3	42.7	-4.3	10.7	2.2	47.9	8.0	39.9	19.9	59.9		
n-butane/1	51.1	-5.5	11.1	2.2	67.5	11.5	56.0	19.3	75.3		27.5[2, 113], 25.0[105], 35.6[116]
n-butane/2	40.8	-5.6	9.3	2.1	49.8	11.5	38.3	20.7	59.0		

Noted:  $\Delta E_{app}^\ddagger = E_{ex} - E_{ads}$



#### 4.3.2.5 Reaction Barriers

Table 4.22 shows computed reaction barriers using PBE/DNP method with periodic model ( $E_p$ ). When combining with adsorption energy ( $E_{ads}$ ), the computed apparent reaction barriers are range of 38 to 65 kcal/mol. The obtained reaction barriers are way higher than corresponding experimental results (also shown on Table 4.22). The corrections to the activation energies owing to ZPE, basis set ( $\Delta E_{basis}$ ), and electron correlation ( $\Delta E_{corr}$ ) were listed in Table 4.22. Also in this table, extrapolated energies ( $E_{ex}$ ) which include corrections due to the above mentioned effects according to Equation (3.8) were given.

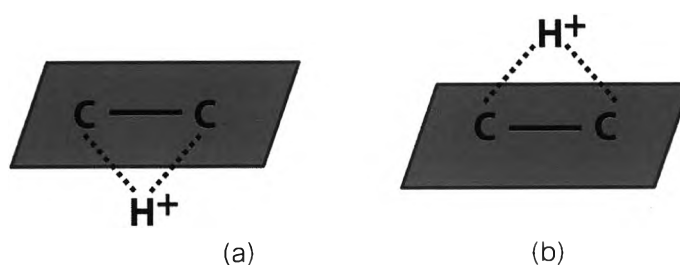
However, even with the extrapolation scheme computed reaction barriers are heavily overestimated by up to 72 kcal/mol. When compared to other theoretical studies [10, 11, 36, 108, 112, 114, 117], our predicted apparent reaction barriers are still lower. Thus, most theoretical works are as well heavily overestimated their computed barriers. Our TS geometries and those given by other works are in good agreement and perhaps this explains the similar behavior. We have shown that the cluster-size has a drastic effect on the reaction barrier while other effects (ZPE, basis set, correlation) are smaller but still significant. In the same light as in the proton exchange reaction, the entropic contribution ( $T\Delta S$ ) was also considered and its values were included in Table 4.22. They are non-negligible and around 20 kcal/mol, the same size as the cluster-size effect, except in the case of ethane (1.9 kcal/mol). This is probably because ethane has only one C-C bond which is already fixed to the zeolitic framework. Although, including  $T\Delta S$ , the predicted apparent reaction barriers are still overestimated. Probably, there is another TS structure which has lower energy but this structure has not yet found.

From Table 4.22, the reaction barriers at primary position of dehydrogenation reactions has a higher barrier (70-75 kcal/mol) while the reaction at secondary and tertiary positions have very similar barriers, 60-65 kcal/mol. This trend is similar to that discussed on geometries of TS where structures of TS complexes at

secondary and tertiary positions are very alike but they are distinct to those at the primary position. Thus, reaction barrier of the dehydrogenation reactions of C2-C4 alkanes in ZSM-5 could be described by steric interaction.

#### 4.4 Cracking Reactions

The acid catalyzed cracking reaction involves the protonation of acidic proton of ZSM-5 to alkanes's C-C bond. There are two possible pathways for the cracking reaction as shown in **Figure 4.9**. In the pathway 1 (P1), the protonation takes place under the plane of C-C bond, and for the pathway 2 (P2) the protonation takes place above the plane of C-C bond (another side of the plane).



**Figure 4.9** The model showing cracking reactions pathway 1 (P1) (a) and cracking reactions pathway 2 (P2) (b).

For ethane, propane, and i-butane, there is only one possible position (terminal C-C bond) for cracking reactions since the molecule has only one type of C-C bond. The cracking reactions in n-butane, however, have two possible positions, terminal and internal C-C bond. The summary of possible positions for cracking reactions in all alkanes is given in **Table 4.23**.

TABLE 4.23 Possible positions for cracking reactions of C2-C4 alkanes, with notation for further reference in parenthesis.

Alkanes	Types of cracking reaction
ethane/terminal	pathway 1 (ethane/P1t); pathway (ethane/P2t)
propane/terminal	pathway 1 (propane/P1t); pathway 2 (propane/P2t)
i-butane/terminal	pathway 1 (i-butane/P1t); pathway 2 (i-butane/P2t)
n-butane/terminal	pathway 1 (n-butane/P1t); pathway 2 (n-butane/P2t)
n-butane/internal	pathway 1 (n-butane/P1i); pathway 2(n-butane/P2i)

#### 4.4.1 Transition State Structures of Cracking Reactions

In the TS, the zeolitic proton was located almost in the middle between the C-C bond. From normal mode analysis, the TS of cracking reaction involves the breaking of C-C bond into two smaller alkyl groups where the acidic proton leaves with one of the alkyl groups forming alkane while the other alkyl group forming the carbenium ion. The carbenium ion cloud later transform into alkane or its isomer inside ZSM-5. This mechanism is agreement with Collins and O'Malley [3]. The geometry of TS for cracking reaction of propane/P2t obtained using 5T model is shown in Figure 4.10.

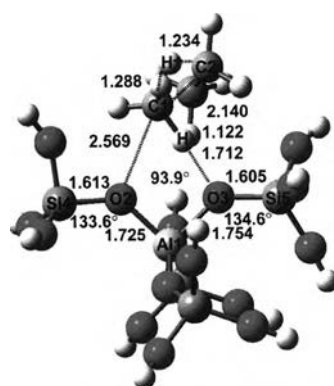


Figure 4.10 The transition state structure with selected geometrical parameters for the cracking reaction in propane/P2t.

Selected geometrical parameters for TS structures of the cracking reactions with ethane/P1t, ethane/P2t, propane/P1t, propane/P2t, i-butane/P1t, i-butane/P2t, n-butane/P1t, n-butane/P2t, n-butane/P1i, and n-butane/P2i, for the 5T and 38T cluster model are provided in **Table 4.24** and **Table 4.25**. Geometries of TS structures for the 38T cluster model are very similar to ones obtained from the smaller cluster models for all types of alkanes **Figure 4.11**.

TABLE 4.24 The relevant parameters for the transition states of the cracking reaction of all alkanes in clusters 5T

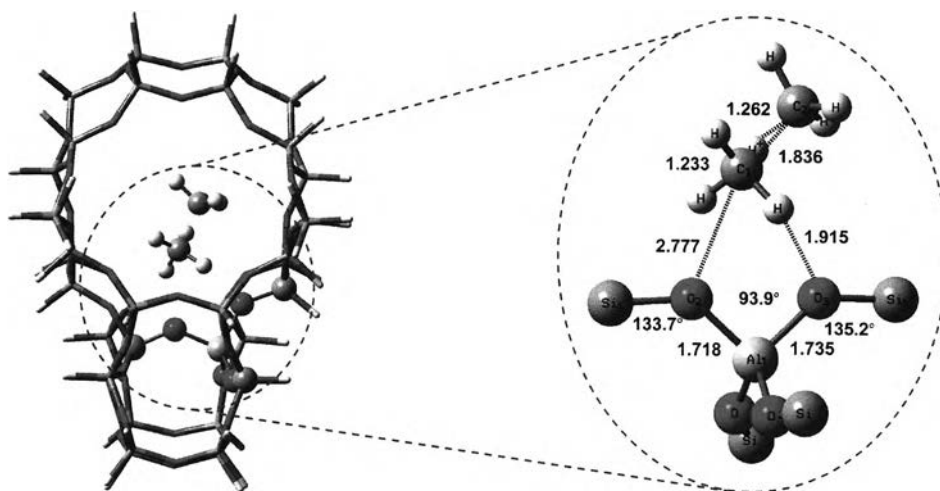
5T (distances in Å and angles in degrees)										
Alkanes	Al <sub>1</sub> -O <sub>2</sub>	Al <sub>1</sub> -O <sub>3</sub>	Si <sub>4</sub> -O <sub>2</sub> -Al <sub>1</sub>	Si <sub>5</sub> -O <sub>3</sub> -Al <sub>1</sub>	O <sub>2</sub> -Al <sub>1</sub> -O <sub>3</sub>	O <sub>2</sub> -C <sub>x</sub>	O <sub>3</sub> -H	C <sub>x</sub> -H <sup>+</sup>	C <sub>x+1</sub> H <sup>+</sup>	C <sub>x</sub> -C <sub>x+1</sub>
ethane/P1t	1.742	1.740	134.6°	133.9°	93.2°	2.463	2.475	1.326	1.205	2.235
ethane/P2t	1.728	1.750	135.0°	133.3°	94.0°	2.551	2.410	1.270	1.230	1.857
propane/P1t	1.742	1.734	134.6°	134.4°	93.4°	2.495	2.480	1.292	1.230	2.337
propane/P2t	1.725	1.754	133.6°	134.6°	93.9°	2.569	1.713	1.288	1.234	2.140
i-butane/P1t	1.736	1.737	135.0°	134.0°	93.8°	2.544	2.629	1.257	1.268	2.417
i-butane/P2t	1.728	1.747	133.7°	134.6°	94.0°	2.603	1.784	1.275	1.265	2.429
n-butane/P1t	1.745	1.731	134.1°	133.6°	92.6°	2.496	2.383	1.279	1.231	2.377
n-butane/P2t	1.732	1.746	133.1°	135.1°	93.8°	2.560	1.743	1.301	1.230	2.189
n-butane/P1i	1.741	1.733	134.6°	134.6°	93.5°	2.657	2.502	1.356	1.209	2.486
n-butane/P2i	1.720	1.754	133.7°	135.0°	93.9°	2.748	1.800	1.314	1.221	2.311

Noted: C<sub>x</sub> and C<sub>x+1</sub> represent carbon at the breaking C-C bond

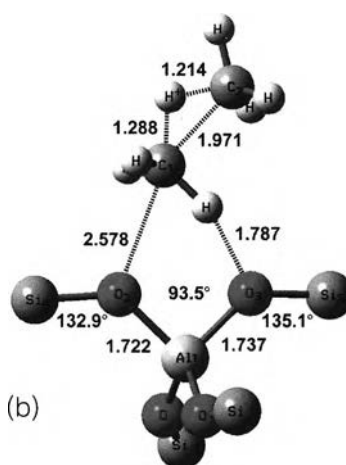
TABLE 4.25 The relevant parameters for the transition states of the cracking reaction of all alkanes in clusters 38T

38T (distances in Å and angles in degrees)										
Alkanes	Al <sub>1</sub> -O <sub>2</sub>	Al <sub>1</sub> -O <sub>3</sub>	Si <sub>4</sub> -O <sub>2</sub> -Al <sub>1</sub>	Si <sub>5</sub> -O <sub>3</sub> -Al <sub>1</sub>	O <sub>2</sub> -Al <sub>1</sub> -O <sub>3</sub>	O <sub>2</sub> -C <sub>x</sub>	O <sub>3</sub> -H	C <sub>x</sub> -H <sup>†</sup>	C <sub>x+1</sub> H <sup>†</sup>	C <sub>x</sub> -C <sub>x+1</sub>
ethane/P1t	1.718	1.735	133.7°	135.2°	93.9°	2.777	1.915	1.233	1.262	1.835
ethane/P2t	1.722	1.737	132.9°	135.1°	93.5°	2.578	1.787	1.288	1.214	1.971
propane/P1t	1.732	1.730	131.5°	137.4°	93.8°	2.452	1.734	1.295	1.229	2.264
propane/P2t	1.731	1.729	131.9°	136.4°	94.0°	2.489	1.855	1.298	1.231	2.245
i-butane/P1t	1.739	1.724	132.3°	138.2°	93.9°	2.231	1.745	1.281	1.215	2.342
i-butane/P2t	1.740	1.720	131.8°	137.4°	93.9°	2.236	1.768	1.331	1.220	2.461
n-butane/P1t	1.719	1.729	134.3°	135.5°	94.1°	2.791	2.226	1.222	1.280	2.040
n-butane/P2t	1.736	1.725	131.5°	137.2°	93.9°	2.399	1.833	1.325	1.222	2.427
n-butane/P1i	1.720	1.738	133.1°	135.7°	93.7°	2.600	1.737	1.240	1.262	2.081
n-butane/P2i	1.716	1.735	134.1°	138.1°	94.3°	2.677	1.942	1.284	1.210	2.089

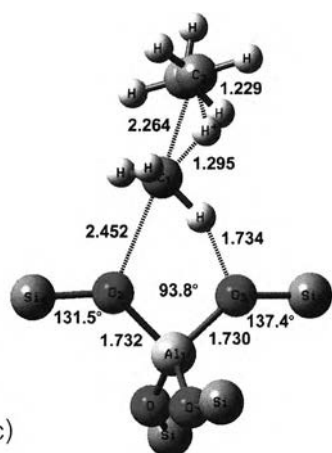
Noted: C<sub>x</sub> and C<sub>x+1</sub> represent carbon at the breaking C-C bond



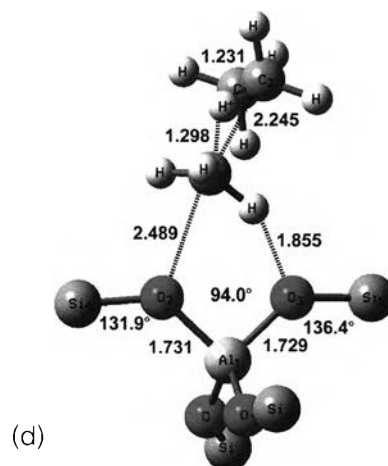
(a)



(b)



(c)



(d)

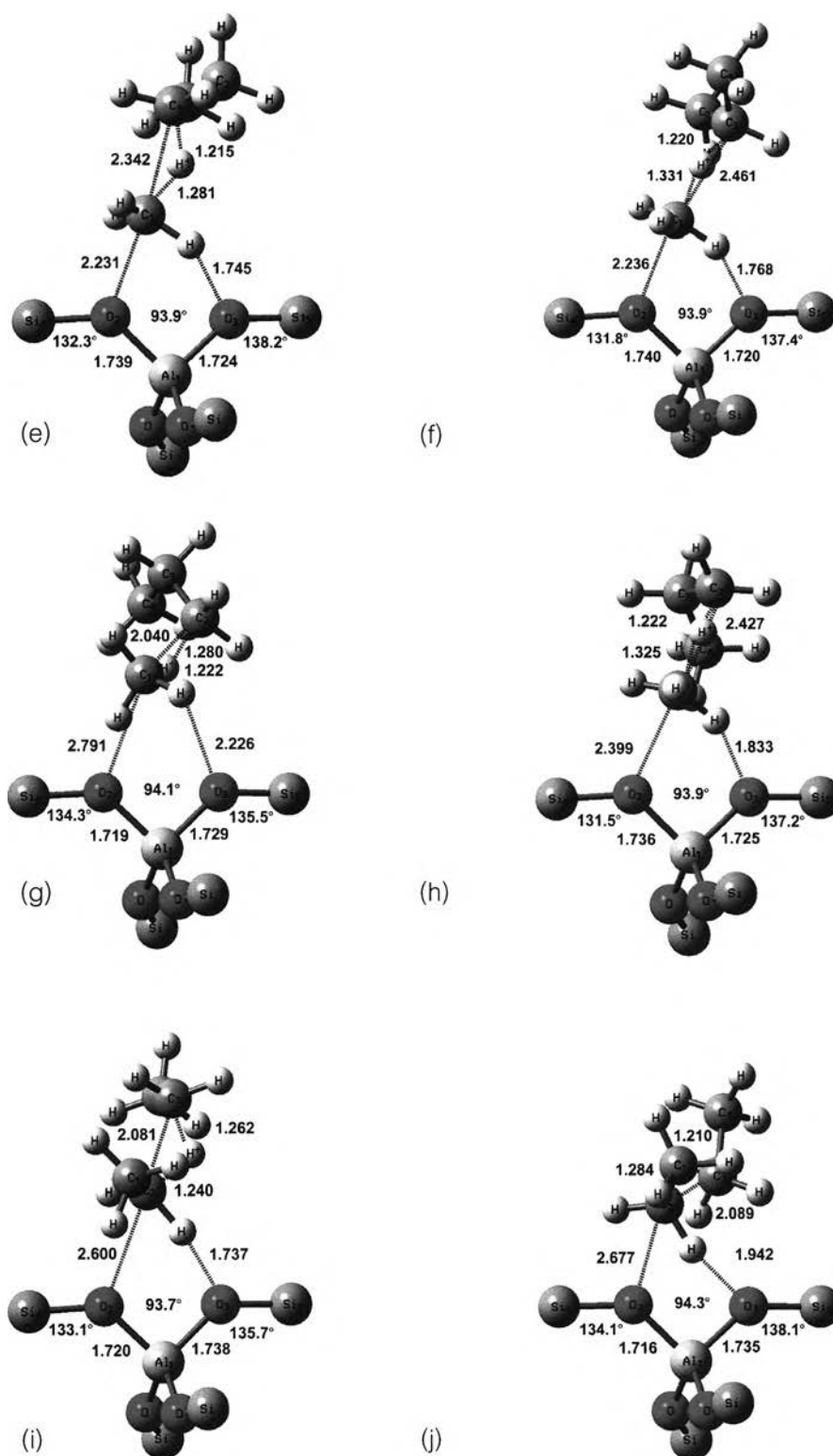


Figure 4.11 Geometries of transition state structures (TS) of cracking reaction in 38T cluster; ethane/P1t (a), ethane/P2t (b), propane/P1t (c), propane/P2t (d),



i-butane/P1t (e), i-butane/P2t (f), n-butane/P1t (g), n-butane/P2t (h), n-butane/P1i (i), and n-butane/P2i (j) (distances in Å and angles in degree).

Considering TS structures of pathway 1 and pathway 2,  $C_x-H^+$  distances are longer than  $C_{x+1}-H^+$  distances for all alkanes and reaction sites. The difference is approximately 0.06Å -0.1Å for most alkanes, in exception of ethane/P1t and n-butane/P1t, where a smaller variation, 0.03Å and 0.06Å respectively, is observed. In contrary, for the cracking reaction in pathway 2 of n-butane at the internal C-C bond (n-butane/P2i),  $C_x-H^+$  (1.284Å) is longer than  $C_{x+1}-H^+$  (1.210Å) distance. The larger variation is probably due to the position of proton over the C-C bond. This position of proton generates more steric repulsion with neighboring methyl moieties. For the TS structure of which  $C_x-H^+$  is longer than  $C_{x+1}-H^+$ , it was observed that the further C atom ( $C_{x+1}$ ) forms an alkane while the nearer C atom ( $C_x$ ) form a carbenium ion which attaches to zeolitic oxygen. For the TS structure of which  $C_x-H^+$  is shorter than  $C_{x+1}-H^+$ , the nearer C atom forms alkane while the further C atom form carbenium ion which does not attach to zeolitic oxygen (Figure 4.11). It was found that the reaction barrier for TS of which carbenium ion is attached to zeolitic oxygen is lower than that which is unattached by around 2-3 kcal/mol (Table 4.29). Thus, zeolitic oxygen ( $O_2$ ) acts as lewis acid and stabilizes the TS. Examples are ethane/P2t, propane/P1t, propane/P2t, i-butane/P1t, i-butane/P2t, and n-butane/P2t. It is worth noting that the carbenium ion could proceed to form bond an alkoxide ion with the zeolitic framework. In addition  $O_2-C_x$  distance in pathway 1 and 2 are quite similar, except for that of ethane/t and n-butane/t in which the distance in pathway 1 is longer than pathway 2 (2.777Å and 2.578Å for ethane/t and 2.791Å and 2.399Å for n-butane/t). The  $C_x-C_{x+1}$  bonds are in range of 1.835Å -2.461Å, indicating that the C-C bond cleavage already occurs. The transition states for pathway 1 and pathway 2 reactions have almost equal  $Al_1-O_3$  and  $Al_1-O_2$  bond lengths and  $O_2-Al_1-O_3$  angle around 94°.

## 4.4.2 Estimation of Reaction Barrier

### 4.4.2.1 Effect of the Cluster Size

Values of activation energies (in kcal/mol) ethane/P1t, ethane/P2t, propane/P1t, propane/P2t, i-butane/P1t, i-butane/P2t, n-butane/P1t, n-butane/P2t, n-butane/P1i and n-butane/P2i cracking reactions as the function of cluster-size were displayed in Figure 4.12.

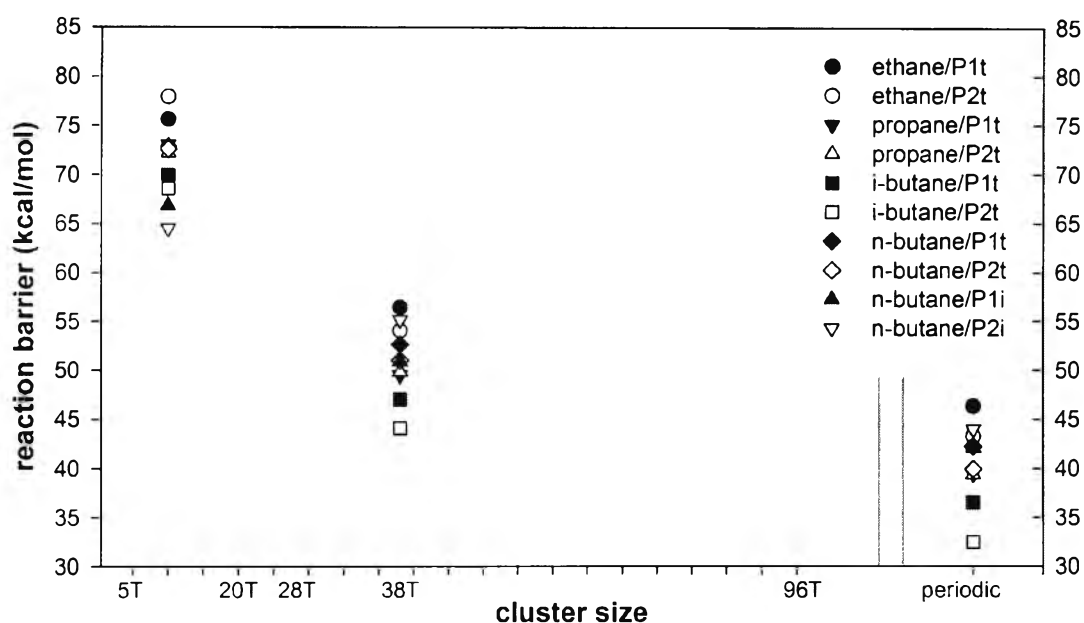


Figure 4.12 Reaction barriers of cracking reactions of C2-C4 alkanes in ZSM-5 calculated using PBE/DNP as a function of cluster-size.

For all alkanes and cracking reactions, the reduction of the reaction barrier as the size of cluster increases (from 5T to P) was observed. The reduction is as large as 20.5 kcal/mol for n-butane/P2i (the smallest) to 36.1 kcal/mol for i-butane/P2t (the largest). Evidently, the cluster-size effect is non-negligible and crucial for the determination of the activation energy for the reaction which takes place in ZSM-5. From 5T to 38T models, we saw the reduction of around 9-24 kcal/mol while from 38T to P the decrease is approximately 8-11 kcal/mol. The negative contribution of the cluster-size effect to reaction barriers of the cracking reactions of C2-C4 alkanes is probably resulted from electrostatic interactions with the zeolitic framework as well as

bond polarizations. To estimate the cluster-size effect accurately, one considers up to periodic model model. For periodic model, computed reaction barriers of the cracking reactions of C2-C4 alkanes are ranging from 32.5 (i-butane/P2t) to 46.3 (ethane/P1t) kcal/mol, see Figure 4.12 and Table 4.29. The activation energies of cracking reactions of alkanes at the terminal and the internal C-C bond are around 36.6-46.3 kcal/mol and 32.5-44.0 kcal/mol in pathway 1 and pathway 2, respectively. (All values are from the periodic model.) This behavior was also observed when compared TS structures.

#### 4.4.2.2 ZPE Correction

According to Table 4.29, the Zero-point energy (ZPE) correction reduces the calculated activation energy. It also varies with cluster-size. However, the size dependent seems to converge. For 38T cluster, ZPEs are ranging between -0.6 to -2.1 kcal/mol in Table 4.26.

TABLE 4.26 The Zero-point energies (ZPE) of TS structure of cracking reaction of C2-C4 alkanes in kcal/mol

Zero-point energies (ZPE) of cracking reaction					
Pathway 1					
Cluster-size	ethane/t	propane/t	i-butane/t	n-butane/t	n-butane/i
5T	-2.63	-2.90	-3.01	-3.31	-2.79
38T	-1.60	-1.76	-0.57	-1.51	-0.78
Pathway 2					
5T	-1.92	-2.06	-2.95	-3.39	-2.51
38T	-1.54	-1.69	-1.39	-2.11	-0.28

#### 4.4.2.3 Effect of Basis Set

Table 4.27 listed reaction barriers for cracking reactions of C2-C4 alkanes on 5T and 38T cluster models calculated using ri-PBE and various basis sets. For 5T model, when changing from SVP to TZVPPP activation energies were reduced between 4.7 to 6.4 kcal/mol. However, this decrement of activation energies is smaller when changing from TZVPPP to CBS (complete-basis set), *i.e.* between 0.4 to 0.5 kcal/mol. For the larger model (38T), the decrease of reaction barriers are between 1.6 to 3.3 and 0.1 to 0.2 kcal/mol when changing from SVP to TZVPPP and TZVPPP to CBS, respectively. The much smaller decrement of activation energies when changing from TZVPPP to CBS implies the quality of the basis set.

TABLE 4.27 Reaction barriers (in kcal/mol) of cracking reactions of C2-C4 alkanes on 5T and 38T cluster model computed using ri-PBE and SVP, TZVPP, and CBS basis sets.

Alkanes	ri-PBE/SVP		ri-PBE/TZVPPP		ri-PBE/CBS	
	5T	38T	5T	38T	5T	38T
ethane/P1t	80.2	60.8	75.5	58.3	75.1	58.1
ethane/P2t	82.1	58.8	76.9	56.4	76.6	56.2
propane/P1t	79.5	54.0	73.1	51.9	72.6	51.7
propane/P2t	76.9	54.6	71.7	52.2	71.3	52.0
i-butane/P1t	75.3	51.2	69.9	49.3	69.5	49.1
i-butane/P2t	73.5	48.9	68.6	46.6	68.3	46.4
n-butane/P1t	78.8	58.0	73.2	54.7	72.7	54.5
n-butane/P2t	77.0	55.3	72.1	53.6	71.7	53.5
n-butane/P1i	72.0	55.0	66.9	53.2	66.5	53.0
n-butane/P2i	69.8	60.4	64.6	57.2	64.2	57.0

It appears that for all alkanes the improvement of basis set decreases computed reaction barriers. However, the improvement of the basis set quality has the positive contribution to computed reaction barriers, unlike cluster-size and ZPE which have the negative contribution. The correction using basis-set deficiency

( $\Delta E_{basis}$ ) was estimated from  $E(38T, riPBE/CBS) - E(38T, PBE/DNP)$  which gives positive values because the reaction barriers from CBS were higher than those from DNP, whereas those from SVP show highest (Table 4.29).

#### 4.4.2.4 Effect of Electron Correlation

From Table 4.28 which showed ri-MP2 and ri-PBE energy differences and dispersion interactions ( $E_{disp}$ ) as a function of cluster-size, we found that estimated dispersion energies for all alkanes are size-dependent and their values converge at 38T model. For 5T cluster, dispersion energies of all alkanes are overestimated by around 2.5-11.7 kcal/mol when compared to the difference of activation energies computed by ri-MP2/CBS and ri-PBE/CBS. However, the ri-MP2/ri-PBE difference is not the same for SVP and CBS basis set. For a particular system, the overestimation of the dispersion interaction obtained using Equation (3.6) does not depend on types of alkanes. Using Table 4.28, we determined the overestimation of the dispersion interaction by Equation (3.6) or  $E_{add}$  and then used it to adjust  $E_{disp}$  for  $\Delta E_{corr}$  as shown in Equation (3.7). Value of  $\Delta E_{corr}$  listed in Table 4.29 can, are positive for all alkanes. In the case of the cracking reactions of C2-C4 alkanes, the magnitude of  $\Delta E_{corr}$  for 96T model is between 0.7 to 9.4 kcal/mol. It is 9.4 kcal/mol for n-butane/P1t and 0.7 kcal/mol for ethane/P2t.

TABLE 4.28 Differences between ri-MP2 and ri-PBE activation energies computed for 5T cluster model with SVP and CBS basis set and dispersion interactions estimated using Equation (3.6) for 5T, 20T, 28T, 38T, and 96T models.

Alkanes	E(ri-MP2/SVP)-E(ri-PBE/SVP)	E(ri-MP2/CBS)-E(ri-PBE/CBS)	$E_{\text{disp}}$		
	5T	5T	5T	38T	96T
ethane/P1t	10.0	2.8	-5.0	-1.6	-1.6
ethane/P2t	7.3	-2.0	-4.5	-1.8	-1.8
propane/P1t	13.1	7.6	-1.9	-2.1	-1.9
propane/P2t	9.2	2.6	-2.6	-2.1	-1.9
i-butane/P1t	14.6	8.7	-1.8	-2.2	-1.5
i-butane/P2t	13.3	7.4	-1.9	-1.5	-0.8
n-butane/P1t	14.5	10.2	-1.5	-2.4	-2.2
n-butane/P2t	9.4	3.1	-3.2	-3.6	-3.2
n-butane/P1i	14.9	9.4	-2.3	-5.1	-5.0
n-butane/P2i	10.4	4.7	-2.7	-5.1	-4.6

TABLE 4.29 Reaction barriers (in kcal/mol) of cracking reactions of alkanes in ZSM-5.

Alkanes	$E_p$	ZPE	$\Delta E_{corr}$	$\Delta E_{basis}$	$E_{ex}$	$E_{ads}$	$E_{ex}-E_{ads}$	$-T\Delta S$	$E_{ex}-E_{ads}-T\Delta S$	Other theoretical works ( $\Delta E_{app}^\ddagger$ )	Experiments ( $\Delta E_{app}^\ddagger$ )
ethane/P1t	46.3	-1.6	6.2	1.7	52.6	7.1	45.5	6.8	52.3	71.39[10], 69.78[6], 78.00[8], 73.70/54.10[9]	
ethane/P2t	43.3	-1.5	0.7	2.2	44.7	7.1	37.5	8.3	45.8		
propane/P1t	39.4	-1.8	7.6	2.2	47.5	10.5	37.0	22.3	59.3	62.1/62.6[112], 68.0[8]	37.02[113]
propane/P2t	39.4	-1.7	3.2	2.2	43.1	10.5	32.6	24.7	57.2		
i-butane/P1t	36.6	-0.6	9.0	2.1	47.2	8.0	39.2	23.0	62.1	53.45/44.86[118]	29.86[113], 9.0±0.4[104], 57.0[119], 24.8±1.2[115]
i-butane/P2t	32.5	-1.4	8.5	2.3	41.9	8.0	33.9	23.6	57.5		
n-butane/P1t	42.3	-1.5	9.4	1.9	52.1	11.5	40.5	20.9	61.4		32.25[113], 33.4[105], 33.9[116], 31.7[116]
n-butane/P2t	39.9	-2.1	3.1	2.5	43.4	11.5	31.9	25.2	57.1		
n-butane/P1i	42.1	-0.8	6.8	2.2	50.2	11.5	38.7	23.3	62.0		32.0[116]
n-butane/P2i	44.0	-0.3	2.8	1.9	48.4	11.5	36.9	23.7	60.6		

Noted:  $\Delta E_{app}^\ddagger = E_{ex}-E_{ads}$ , Ref. [117], the  $\Delta E_{app}^\ddagger$  of n-butane depend on type of product that is methane (33.9), propane (31.7), and ethane (32.0)



#### 4.4.2.5 Reaction Barriers

Table 4.29 shows computed reaction barriers using PBE/DNP method with periodic model ( $E_p$ ). The obtained reaction barriers are in good agreement with experimental results (also shown on Table 4.29). The corrections to the activation energies owing to ZPE, basis set ( $\Delta E_{basis}$ ), and electron correlation ( $\Delta E_{corr}$ ) were listed in Table 4.29. Also in this table, extrapolated energies ( $E_{ex}$ ) which include corrections due to the above mentioned effects according to Equation (3.8) were given.

When combining with adsorption energy ( $E_{ads}$ ), the computed extrapolated apparent reaction barriers are range of 31.9 to 45.5 kcal/mol. The extrapolated apparent reaction barriers of cracking reactions of C2-C4 alkanes in ZSM-5 are 45.5, 37.5, 37.0, 32.6, 39.2, 33.9, 40.5, 31.9, 38.7, and 36.9 kcal/mol for ethane/P1t, ethane/P2t, propane/P1t, propane/P2t, i-butane/P1t, i-butane/P2t, n-butane/P1t, n-butane/P1i, n-butane/P2t, and n-butane/P2i, respectively. Therefore, pathway 2 is the predominant reaction for the cracking due to the low reaction barriers, compared with pathway 1. These values are in good agreement with experiments. The cracking reaction occurs easier for n-butane/P2t, propane/P2t, i-butane/P2t, n-butane/P2i, ethane/P2t, respectively.

When compared to other theoretical studies [6, 8-10, 112, 119], our predicted apparent reaction barriers are lower. Moreover, most theoretical works often overestimated their computed barriers due to small cluster-size models (3T) with limited level of accuracy and basis set. We have shown that the cluster-size has a drastic effect on the reaction barrier while other effects (ZPE, basis set, correlation) are smaller (but still significant). The entropic contributions ( $T\Delta S$ ) that has an opposite sign to the cluster-size effect were included in Table 4.29. Their values are non-negligible and around 20 to 25 kcal/mol, the same size as the cluster-size effect, except in the case of ethane. When including  $T\Delta S$ , the reaction barriers in pathway 1 of cracking reactions has barrier between 52.3-62.1 kcal/mol while the reaction in pathway 2 have barriers, 45.8-60.6 kcal/mol in Table 4.29. Moreover, the reaction barriers of all alkanes

in pathway 1 have higher barriers than those in pathway 2. The differences between reaction barriers in pathway 1 and 2 are 6.5, 2.0, 4.6, 4.3, and 1.4 kcal/mol, for ethane/t, propane/t, i-butane/t, n-butane/t, and n-butane/l, respectively. However, when including  $T\Delta S$ , the predicted apparent reaction barriers are heavily overestimated. Thus, inclusion of entropic contribution does not improved computed reaction barriers.