สำนักงานวิทยทรัพยากร จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER V

CONCLUSIONS

5.1 Adsorption Energies

The adsorption energies are obtained on periodic model of ZSM-5. The results show good agreement with the experimental values except of i-butane where the computed values is around 3 kcal/mol underestimated. The computed adsorption energies are 7.1, 10.5, 8.0, and 11.5 kcal/mol for ethane, propane, i-butane, and n-butane, respectively. The adsorption energies as a function of the cluster-size proportionally increase with the number of carbon atoms in the hydrocarbon chain, *i.e.* n-butane > propane > ethane. The cluster-size (from 5T to P) has a effect on the reaction barrier in range of 3.4 to 7 kcal/mol while ZPE, basis set, electron correlation effects are smaller and in the range of -0.4 to -0.7, 2.4 to 4.7, and -2.0 to -5.9 kcal/mol, respectively. Although effects of ZPE, basis-set, and electron correlation are not as large as the cluster-size effect and their values deem to cancel each other. The extrapolated energies (E_{ex}) of C2-C4 alkanes in ZSM-5 which combined corrections due to cluster-size, ZPE, basis set, and electron correlation are still in very good agreement with experiments.

5.2 Proton Exchange Reactions

The penta-coordinated carbonium ion was observed for the transition state structure of the proton exchange reaction for the C2-C4 alkanes. The transition state geometries of the proton exchange reactions of these alkanes seem to depend on types of carbon atom in alkanes. At the transition state, $C_{1\text{-}3}$-H, $C_{1\text{-}3}$-H^+, Al_1-O_2, and Al_1-O_3 distances as well as O_2-Al_1-O_3 bond angles for all reactions have similar values for the same types of reaction center (carbon atom). For instance, while reactions at primary or secondary carbon atom have $C_{1\text{-}2}$-H^+ shorter than $C_{1\text{-}2}$-H distance, the reaction at tertiary carbon atom has C_3-H^+ longer than C_3-H distance. This behavior of the TS of the proton exchange reaction could probably be explained by the steric interaction between the reacting centers (primary, secondary, or tertiary) and neighboring methyl moieties. The cluster-size (from 5T to P) has a drastic effect on the reaction barrier in range of -10 to -20 kcal/mol while ZPE, basis set, electron correlation effects are smaller and in the range of -1.6 to -2.5, 1.0 to 1.4, and -3.5 to 2.8 kcal/mol, respectively. Although effects of ZPE, basis-set, and electron correlation are not as large as the cluster-size effect and their values deem to cancel each other, their effects are still significant. To report on reaction barriers of the proton exchange reaction of C2-C4 alkanes in ZSM-5, the extrapolated energies (E_{ex}) which combined corrections due to cluster-size, ZPE, basis set, and electron correlation was proposed.

With inclusion of adsorption energy (E_{ads}) to E_{ex}, apparent reaction barriers of proton exchange reactions of C2-C4 alkanes in ZSM-5 was obtained and compared to available experimental values. The values of 6.2, 5.4, 5.8, 8.5, 16.3, 7.5, and 5.6 kcal/mol were reported for ethane, propane/1, propane/2, i-butane/1, i-butane/3, n-butane/1, and n-butane/2, respectively. The activation energies show the same trend with geometries of TS. Thus, we can group the proton exchange reactions according to types of reaction center. While the reactions at primary and secondary carbon have similar barrier heights (5-8 kcal/mol), the reaction at tertiary carbon has a much larger barrier height. Although the trend of barrier heights for different alkanes is the same as observed in experiments, computed values are very much underestimated. Experimentally, reaction barriers for the proton exchange reaction of C2-C4 alkanes in ZSM-5 were reported to be between 28-36 kcal/mol. The great difference between our computed values and experiments needs to be explained. Entropies of these reactions were computed. If entropic contributions ($T\Delta S$) have been included to reaction barriers, apparent reaction barriers will be between 9.5 to 37.7 kcal/mol which in good agreement with corresponding experimental values.

5.3 Dehydrogenation Reactions

Similar to the proton exchange reaction, a penta-coordinated carbonium ion is observed for TS structures of the dehydrogenation reactions of the C2-C4 alkanes in ZSM-5 framework. For the primary-carbon reacting center, the distance of C_1-H was found to be longer than C_1-H^+ at for all types of reactions. For the secondary and the tertiary carbon, however C_{2-3}-H is shorter than C_{2-3}-H^+. The distances of O_2-C_{1-3} at secondary and tertiary carbon are longer than that at the primary carbon. The H-H^+ distances for H_2 molecule are in ranges of 0.772Å-0.800Å. At the secondary or tertiary carbon, the distances of H-H^+ are slightly longer than those of the primary carbon. Geometries of TS for the dehydrogenation reaction could be well explained by the steric interactions between the reacting center and environments. Interestingly, obtained TS structures for the dehydrogenation and those of the proton exchange reaction are very comparable. Thus, it could be that the proton exchange reaction is a precursor or a competitor to the dehydrogentation reaction.

For reaction barriers of the dyhydrogenation of C2-C4 alkanes in ZSM-5, the cluster-size again shows a drastic effect on the reaction barrier and it reduces reaction barriers (computed using 5T model) in the range of -21.2 to -37.5 kcal/mol. Still computed reaction barriers after inclusion of adsorption energies are overestimated by up to 28 kcal/mol. Corrections due to ZPE, basis-set, electron correlation are smaller than those of cluster-size and, respectively, in the range of -4.3 to -5.8, 1.1 to 2.5, and 9.1 to 11.1 kcal/mol. Corrections due to basis-set and electron correlation are positive and, thus, it makes the situation even worse. The extrapolated apparent reaction barriers of dehydrogenation reactions of C2-C4 alkanes in ZSM-5 are 64.9, 56.9, 46.3, 50.3, 39.9, 56.0, and 38.3 kcal/mol for ethane, propane/1, propane/2, i-butane/1, i-butane/3, n-butane/1, and n-butane/3, respectively. While experimental values were between 22.7-35.6 kcal/mol. The predicted values are very much deviated from experiments but they are in-line with other theoretical predictions. When entropic contributions ($T\Delta S$) were included, values between 59.0 to 75.3 kcal/mol were yielded. The values of entropic terms are around 20 kcal/mol and non-negligible and that causes the overestimation of apparent reaction barriers even more serious. The apparent reaction barriers of dehydrogenation reactions at the primary carbon (70-75 kcal/mol) are higher than at the secondary and tertiary carbons (60-65 kcal/mol).

5.4 Cracking Reactions

There are 2 pathways for the cracking reaction of alkanes in ZSM-5 in which the C-C bond breaking leads to alkane and alkyl group. Again the formation of carbenium ion was observed for TS structures of cracking reactions of the C2-C4 alkanes. The steric effect between the reacting center and neighboring methyl moieties probably causes the difference between C_x-H^+ and C_{x+1}-H^+ distances for all alkanes and reaction pathways. For ethane/P1t, n-butane/P1t, and n-butane/P1i, TS structures have C_x-H^+ is shorter than C_{x+1}-H^+. For this case, it was found that alkane formed from the reaction is located closer to the zeolitic framework. For the case where C_x-H^+ is longer than C_{x+1}-H^+ such as propane/P1t, propane/P2t, i-butane/P1t, and i-butane/P2t, the alkane part is located far from the zeolitic framework.

As for the other 2 reactions, the cluster-size has a drastic effect on the reaction barrier and it decreases reaction barriers computed using 5T model in the range of -20.5 to -36.1 kcal/mol. However, the effect of cluster-size seems to be smaller for the larger alkane. Effects of ZPE, basis set, and electron correlation again have a smaller impact on the barriers. Decrements as a result of such effects are in range of -0.6 to -2.1, 1.7 to 2.5, and 0.7 to 9.4 kcal/mol, respectively for ZPE, basis-set, and electron correlation, respectively. 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. However, when entropic contributions ($T\Delta S$) were included, computed reaction barriers become too high.

It is interesting that the C-C bond lengths of TS in proton exchange, dehydrogenation, and cracking reaction are significantly different. In case of proton exchange, the C-C bond length in TS is not much changed from that of alkane reactant. On the other hand, the changes of C-C bond lengths in dehydrogenation and cracking reaction are large. The C-C bond in dehydrogenation is shortened to 1.412Å-1.481Å, and it can form double bond (C=C) of alkene if the bond length is reduced to 1.33Å. In contrast, the C-C distance in cracking reaction increases to about 1.835Å-2.486Å, indicating the bond cleavage already occurs.

TS structures of proton exchange, dehydrogenation, and cracking reactions of ethane, propane, i-butane and n-butane in ZSM-5 have very similar nature. The proton exchange seems to be the precursor for the dehydrogenation reaction. Using extrapolation scheme proposed, computed reaction barriers for proton exchange reactions are underestimated while they were overestimated for dehydrogenation reactions and shows good agreement with experiments for the cracking reaction. The overestimation for dehydrogenation reaction suggests that there might exist another TS structures with lower energy. Inclusion of corrections such as ZPE, basis-set, electron correlation, and especially cluster-size deem to be very important and necessary.