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Regioselectivity of carbonium ion transition states in zeolites

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ABSTRACT

Alkane proton exchange reaction and pentacoordinated carbonium ion transition state formation confined inside nanopores of H-ZSM-5 zeolites have been investigated by DFT theoretical calculations. By including both steric and long-range electrostatic effects associated with the zeolite framework structure, the transition state structures and activation barriers associated with the hydrogen exchange reaction may be predicted accurately. Unlike the reaction mechanisms found in typical homogeneous catalytic systems such as liquid superacids, it is found that the synergetic effect from electrostatic interactions and steric constraints dictates the regioselectivity of propane and isobutene carbonium ion transition state formation in the heterogeneous systems, such as microporous zeolites.

1. Introduction

Pentacoordinated carbonium ions have been proposed as the key intermediates during alkane C–H bond activation reactions in liquid superacids. For the formations of carbonium ion transition states in liquid superacids, Olah et al. concluded that the reactivities follow the trend: *tert*-C–H > *sec*-C–H > *prim*-C–H > CH_4, which is in accordance with the charge distribution capacities of the corresponding carbonium ions [1–3]. Zeolites, which possess unique framework structures with periodic arrangements of cages and channels in nanometer-scale, are eco-friendly solid acid catalysts and have been widely used for alkanes C–H bonds activation, especially for proton exchange reactions [4–12]. However, it is intriguing that notable differences in reactivities were observed for alkane C–H activations when catalyzed by heterogeneous zeolite catalysts. While experimental evidences revealing the significance of regioselectivity of the *prim*-C–H ($-CH_3$) groups during propane and isobutane proton exchange reactions over 10-membered rings (10-MR) ZSM-5 zeolites had been made available recently [10–12], detailed transition state structures and basis for the observed product regioselectivity remain to be addressed.

Accurate quantum chemical calculations should be useful in providing theoretical supports to the aforementioned issues [13–21]. The structural parameters of the transition states, activation barrier heights, as well as reaction energies can be deduced from the theoretical predictions. On the basis of the calculated activation barriers, the reaction mechanism and reaction selectivities can be determinated. In our previous works, comprehensive studies have been made on product selectivity and detailed reaction pathway invoked during propene hydrogenation reaction over H-ZSM-5 zeolite by DFT calculations [18–21].

Due to limitations in computational resources, previous theoretical studies on H/D exchange reaction mostly employed small clusters, such as 3T (tetrahedral atoms) or 5T models to represent the zeolite structure [22,23], thus incapable of taking into account the electrostatic effects and steric repulsions associated with the zeolite framework. Consequently, such theoretical calculations failed to provide accurate predictions for molecular conformations and hence detailed reaction mechanism occurring in the intracrystalline cavities of zeolites. For example, the experimental activation energies observed for methyl and methylene group carbons were 25.0 and 29.0 kcal/mol [10], respectively, however, the corresponding activation barriers predicted based on a 5T cluster model [23] were overestimated by about 10–15 kcal/mol. More importantly, the aforementioned theoretical predictions also led to an *opposite* trend (40.5 and 39.2 kcal/mol for $-CH_3$ and $-CH_2-$, respectively) for selective activation. Since it is anticipated that the zeolite framework should have considerable effect on reaction mechanism, thus, it is inevitable to adopt a larger cluster model to represent the zeolite structure during theoretical calculations. It is only with such extended representation of zeolite structure that more precise descriptions for electrostatic and adsorbate–adsorbent interactions, and hence more accurate reaction mechanism (*viz.* transition

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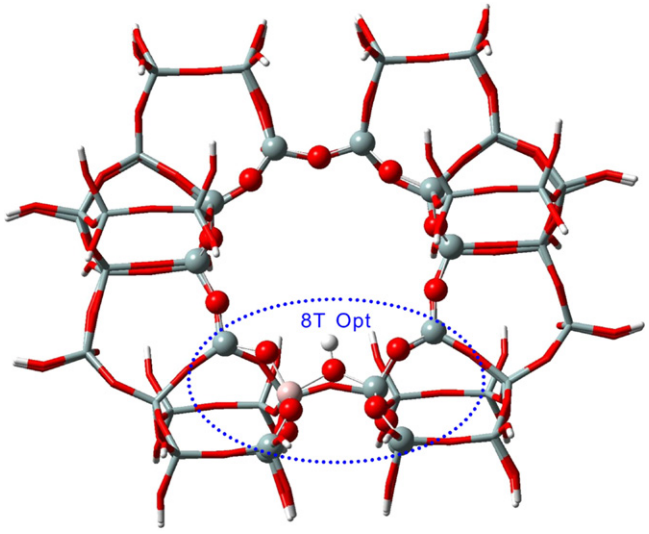

Fig. 1. Representation of zeolite H-ZSM-5 framework structure by the 64T cluster model (viewing along the [1 0 0] direction). The 14T cluster represented as ball and stick view was treated as the high-layer atoms during the ONIOM calculations.

state structures and activation barriers), could be predicted [18–21].

To unravel the origins of regioselectivity associated with alkane hydrogen exchange in zeolites, theoretical quantum chemical calculations were carried out by adopting an extended 64T cluster model to represent the zeolite framework structure to elucidate H/D exchange reaction mechanisms for methane, ethane, propane, and isobutane. For comparison, calculations based on a simplified 8T cluster model were also performed for the above systems.

2. Computational method

In view of the fact that the long-range forces and steric constraints prevailing in the framework structures of zeolites should have considerable effect on the reaction pathways of heterogeneous catalysis systems, H-ZSM-5 zeolite modeled by a 64T cluster model ($AlSi_{63}O_{156}H_{57}$) consisting of a 10-MR channel and one Brønsted acid site with a total of 277 atoms (see Fig. 1) was adopted during calculations. The structure parameters adopted during the calculations were extracted from the crystallographic structural data of ZSM-5 [24]. The terminal O–H was fixed at a bond length of 0.96 Å, oriented along the direction of the corresponding O–Si bond. The combined theoretical ONIOM (Our-own-N-layered Integrated molecular Orbital & molecular Mechanics) method was applied to predict the geometries of various adsorption structures and transition states (TS) [25–29], whereas semiempirical AM1 and the hybrid density functional B3LYP method with 6-31+G(d,p) basis set were employed for the low- and high-level treatments, respectively. It is well known that the ONIOM method, which adopts an electronic embedded cluster approach by incorporating partial charges of the low-layer region into the high-layer quantum mechanical Hamiltonian, provides a much better description of the long-range electrostatic effects arising from the Medelung potential of the zeolite framework as well as the local environments surrounding the targeted atoms. Such combined method can thus provide much more accurate predictions for the locations of acidic proton in zeolites [18], the structures of adsorbed base molecules [19], as well as the reaction mechanisms [20,21]. To preserve the integrity of ZSM-5 zeolite structure during the ONIOM calculations, only partial optimization of the cluster was performed [18–21]. This was carried out by relaxing the atoms of the $(SiO)_3$–Si–OH–Al–$(SiO)_3$ (total 28 atoms) in the high-level layer while keeping the rest of atoms fixed at their crystallographic locations [27–29]. Moreover, the substituted Al atom was placed at the T12 site of the crystallographic position during structural optimization, whereas the acidic proton was located at the O24 site [19]. None of the atoms in the alkane molecules were constrained throughout all configuration optimizations of the adsorption complexes and the transition state structures. It is noteworthy that since frequency calculations of the 64T cluster model (which contains a total of 291 atoms in the case of isobutene) are impractical in terms of computation time, thus, the transition state (TS) of hydrogen exchange with the Brønsted acid sites was not confirmed by frequency calculations after the QST3 search. In order to investigate the effect of the zeolite framework on the activation barriers, the calculated results were also compared with those predicted from system with a smaller (8T) cluster model at the same theoretical level. However, while the latter model can be used to represent the activated center of zeolite, it fails to take into account the constraint effect provoked by the zeolite framework. Furthermore, we define herein the activation barrier (ΔE) as the single-point energy difference between the absorption complex and transition state of the guest–host (alkane–zeolite) systems, i.e., $\Delta E = E_{(TS)} - E_{(ads)}$. All calculations were performed using the GAUSSIAN03 program [30].

3. Results and discussion

3.1. Hydrogen exchange of methane and ethane

Fig. 2 illustrates the transition state structures for alkane proton exchange reaction over H-ZSM-5; the corresponding structural parameters are depicted in Table 1. It is noted that previous study on TS of methane based on a simplified 3T cluster model showed that the hydrogen atoms under exchange were half-way between the carbon atom on the CH_4 and an acidic oxygen atom on the catalyst, as such, all of the r values, *viz.* r_1 (O_1–H_1), r_2 (O_2–H_2), r_3 (C–H_1), and r_4 (C–H_2), were found to be identical (1.322 Å) [22]. Consequently, the theoretical results predicted by the 3T cluster model

Table 1
Selected transition state bond lengths (Å) and activation energies (kcal/mol) for alkane hydrogen exchange reaction over H-ZSM-5 zeolite predicted by the 8T cluster model.[a]

Parameter	Methane	Ethane	Propane		Isobutane	
			CH_3	CH_2	CH_3	CH
r_1	1.392	1.438	1.428	1.498	1.430	1.563
r_2	1.377	1.421	1.417	1.433	1.435	1.562
r_3	1.288	1.275	1.278	1.260	1.279	1.285
r_4	1.294	1.283	1.283	1.297	1.283	1.282
δ_q	−0.68	−0.33	−0.37	−0.24	−0.37	−0.11
ΔE_{cal}	33.7	33.0	33.3	33.6	33.6	37.8
ΔE_{exp}	29.2–35.9 [7]	–	25.0 [10]	29.0 [10]	12–13.7 [11,12]	–

[a] r_1, r_2, r_3, and r_4 denote the bond distances of O_1–H_1, O_2–H_2, C–H_1, and C–H_2, respectively, whereas H_1 and H_2 represent the Brønsted proton and hydrogen of the alkanes, respectively, as indicated in Figs. 4 and 5. ΔE_{cal} and ΔE_{exp} represent theoretical and experimental activation energies, respectively. δ_q represents Mulliken Charges (|e|) on the attacked carbon of the transition states.

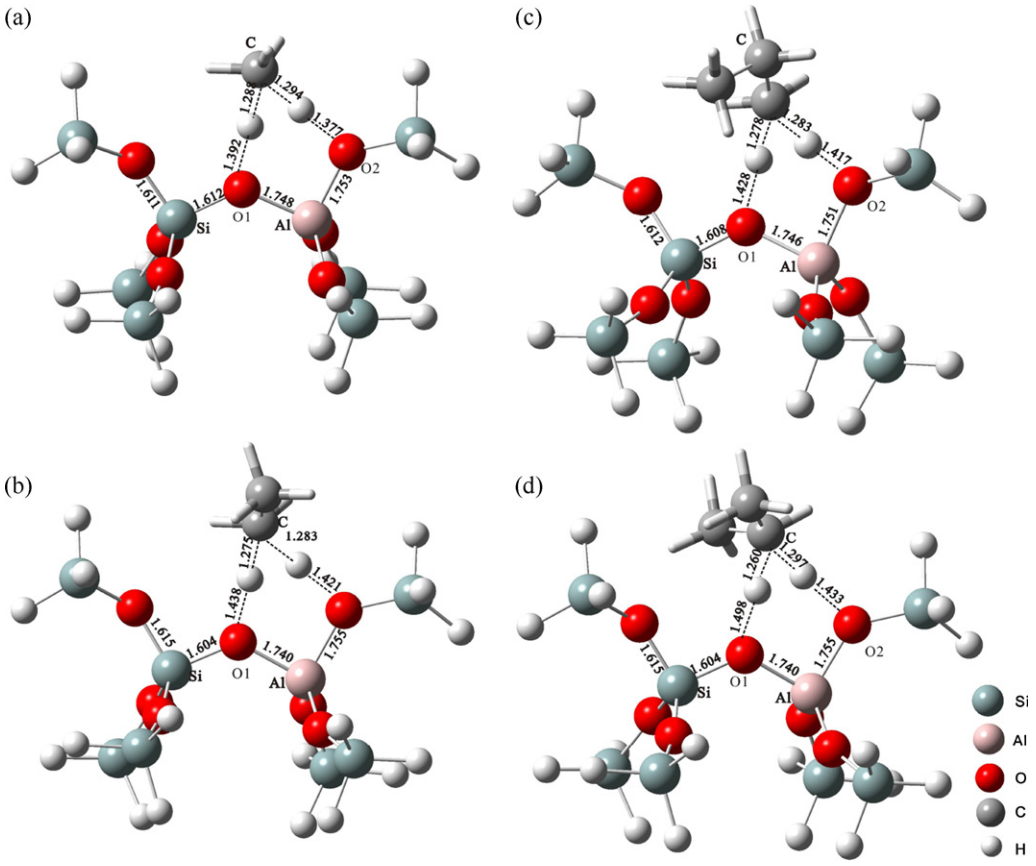

Fig. 2. Local transition state structures predicted for alkane hydrogen exchange with the Brønsted acid sites in zeolite based on the 8T cluster model for (a) methane, (b) ethane, (c) methyl and (d) methylene groups in propane. Selected interatomic distances (Å) are indicated.

failed to support the existence of the carbonium ion TS being identified experimentally by infrared spectroscopy [31]. On the other hand, based on a 5T cluster model, Ryder et al. [23] reported a same value for r_3 and r_4 (1.282 Å) and for r_1 and r_2 (1.399 Å) for methane proton exchange reaction. For comparison, the TS structures and bond lengths predicted for methane, ethane, propane and isobutane proton exchange based on the 8T cluster model are shown in Figs. 2 and 3 and the results are also depicted in Table 1.

For methane proton exchange reaction, the predicted TS structure based on the 8T cluster model was found to show no significant differences compared to that obtained by the 5T cluster model [23]. Moreover, by comparing with the experimental activation energy (33.4 kcal/mol) [7], it is indicative that a considerable improvement in value predicted by the 8T cluster model (33.7 kcal/mol) vs. those by the 3T (37.7 kcal/mol) and 5T (40.7 kcal/mol) models. On the other hand, by adopting an extended 64T cluster model, a much smaller r_3 value was obtained compared to those predicted by the

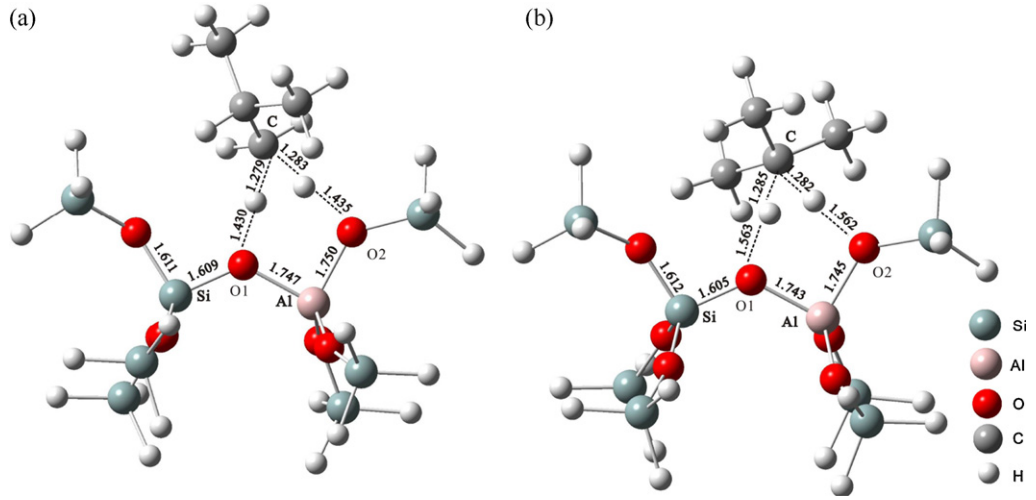

Fig. 3. Local transition state structures predicted for alkane hydrogen exchange with the Brønsted acid sites in zeolite based on the 8T cluster model for (a) methyl and (b) methine groups in isobutane. Selected interatomic distances (Å) are indicated.

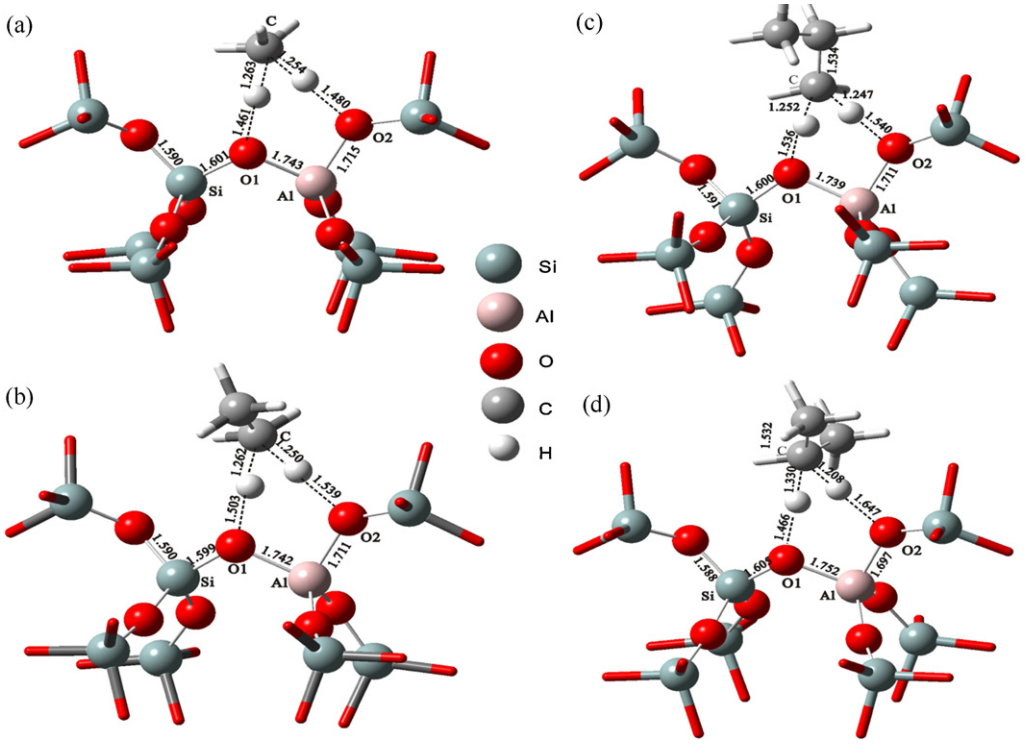

Fig. 4. Local transition state structures predicted for alkane hydrogen exchange with the Brønsted acid sites in zeolite based on the 64T cluster model for (a) methane, (b) ethane, (c) methyl and (d) methylene group in propane. Selected interatomic distances (Å) are indicated.

3T, 5T, and 8T cluster models. For methane proton exchange reaction, a r_3 and r_4 bond length of 1.263 and 1.254 Å was respectively obtained, which are much shorter than r_1 (1.461 Å) and r_2 (1.480 Å) (see Fig. 4 and Table 2). These results indicate an enhance property of the carbonium ion TS, which is in good agreement with the experimental observation [31]. Moreover, by taking the long-range electrostatic interactions between zeolite adsorbent and adsorbate species in the extended (64T) model, more accurate activation energies were obtained, as compared to the existing experimental data. Again, taking the case of methane proton exchange as an example, a predicted activation energy of 29.8 kcal/mol (Table 2) was obtained. Clearly, this value is much closer to the experimental values (29.2–35.9 kcal/mol) [7] and is more reliable compared to the values 37.7 [22], 40.7 [23] and 33.7 kcal/mol predicted by the simplified 3T, 5T, and 8T models (Table 3), respectively. Similar observations may also be referred for the ethane proton exchange

Table 2
Selected transition state bond lengths (Å) and activation energies (kcal/mol) for alkane hydrogen exchange reaction over H-ZSM-5 zeolite predicted by the 64T cluster models.[a]

Parameter	Methane	Ethane	Propane		Isobutane	
			CH_3	CH_2	CH_3	CH
r_1	1.461	1.503	1.536	1.466	1.587	1.592
r_2	1.480	1.539	1.540	1.647	1.557	1.778
r_3	1.263	1.262	1.252	1.330	1.244	1.339
r_4	1.254	1.250	1.247	1.209	1.247	1.226
δ_q	−0.33	−0.37	−0.37	−0.23	−0.37	−0.18
ΔE_{cal}	29.8	26.9	28.7	30.0	17.8	21.7
ΔE_{exp}	29.2–35.9 [7]	–	25.0 [10]	29.0 [10]	13.7 [11,12]	–

[a] r_1, r_2, r_3, and r_4 denote the bond distances of O_1–H_1, O_2–H_2, C–H_1, and C–H_2, respectively, whereas H_1 and H_2 represent the Brønsted proton and hydrogen of the alkanes, respectively, as indicated in Figs. 4 and 5. ΔE_{cal} and ΔE_{exp} represent theoretical and experimental activation energies, respectively. δ_q represents Mulliken Charges (|e|) on the attacked carbon of the transition states.

Table 3
The activation energies (kcal/mol) for alkane hydrogen exchange reaction over H-ZSM-5 zeolite predicted by different cluster models.

Model	Methane	Ethane	Propane		Isobutane	
			CH_3	CH_2	CH_3	CH
3T	37.7[a], 31.1[b]	31.4[b]	30.6[b]	30.6	29.8[b]	31.5[b]
5T	40.7[a]	40.0[a]	40.5[a]	39.2[a]	–	–
8T	33.7	33.0	33.3	33.6	33.6	37.8
64T	29.8	26.9	28.7	30.0	17.8	21.7
ΔE_{exp}	29.2–35.9 [7]	–	25.0 [10]	29.0 [10]	13.7 [11,12]	–

[a] Obtained at the level DFT-BH&HLYP/6-31G(**++) [23].
[b] Obtained at the level MP2/6-31G**//HF/6-31G** [22].

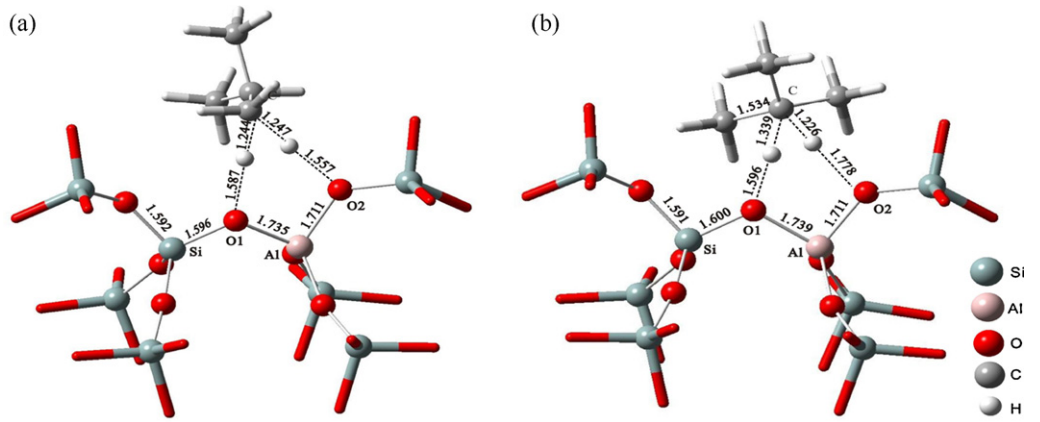

Fig. 5. Local transition state structures predicted for alkane proton exchange with the Brønsted acid proton in zeolite based on the 64T cluster model for (a) methyl and (b) methine groups in isobutane. Selected interatomic distances (Å) are indicated.

reaction. In this case, by extending the cluster size from 8T to 64T, a notable decrease in activation energy from 33.0 to 26.9 kcal/mol (see Tables 1–3) was observed. Such a dramatic decrease (ca. 6 kcal/mol) in activation barrier indicates that the carbonium ions are effectively stabilized by the electrostatic effects provoked by the zeolite framework and that more reliable reaction mechanisms for alkane transformation reaction over zeolite may also be predicted.

3.2. Hydrogen exchange of propane and isobutane

Aside from the methyl ($-CH_3$) group, the methylene ($-CH_2-$) group in propane molecule should also play an important role during proton exchange reaction. In terms of the capability of spreading the positive charges, methylene group should surpass the methyl group and hence should have a lower reaction barrier (i.e., more stable TS) in most cases. As such, the methylene group should be more preferable than the methyl group during activation reaction in liquid superacids [1–3]. However, this is not the case for propane confined in the zeolites due to a relatively larger steric effect for the methylene than the methyl group. The activation barriers predicted for similar systems based on a 5T cluster model [23] were typically overestimated by *ca.* 10–15 kcal/mol. For examples, the predicted activation energies were 40.5 and 39.2 kcal/mol for methyl ($-CH_3$) and methylene ($-CH_2-$), respectively, suggesting that the latter is more easily activated than the former, thus leading to a faulty *opposite* trend for selective activation as compared with the experiment results [10]. Clearly, this arises from the inadequacy in representing the zeolite framework by simplified (smaller) clusters, by which the interactions between the zeolite frameworks and adsorbed alkanes were been ignored. The adoption of a larger cluster model to represent the sophisticated zeolite framework structure, i.e., to include the electrostatic effect and steric constraint during theoretical calculations, is thus inevitable for precise prediction of reaction mechanism. The structure and energy parameters of TS state so obtained for propane based on the 64T cluster model are depicted in Fig. 4 and Table 2. Indeed, our calculations based on the extended (64T) cluster model revealed a slightly higher activation barrier for the methylene group (30.0 kcal/mol) than the methyl group (28.7 kcal/mol) in propane. Moreover, these predicted activation energy values are in good agreement with the experimental results [10]. The Mulliken charges of the propane TS were found to be −0.37 and −0.23|e| for the carbon atom in methyl and methylene groups (Table 2), respectively, indicating that the TS of methylene group is more stable than methyl group for the propane carbonium. Nevertheless, in terms of reaction activity, it was observed that the methyl group tends to be more preferentially exchange with the Brønsted acid sites in zeolites obtained from NMR experiments [10] as well as theoretical calculations reported herein, revealing an *opposite* trend with capability of spreading in liquid superacids [1–3]. Thus, it is indicative that the alkane hydrogen exchange reactions within the microporous zeolites are not determined by the stabilities of the corresponding carbonium ions. Rather, their TS selectivities are dictated by the steric constraints between the alkane group and zeolite framework.

Fig. 5 illustrates the TS structure for isobutane proton exchange reaction over H-ZSM-5; their corresponding structural parameters are depicted in Table 2. Based on the 64T cluster model, the activation energies predicted for the methyl ($-CH_3$) and methine ($-CH$) groups in isobutane were 17.8 and 21.7 kcal/mol, respectively. As shown in Table 3, the activation barriers predicted based on the extended cluster model for the methyl group in isobutane (17.8 kcal/mol) are much closer to the value of 12–13.7 kcal/mol recently reported in an experimental NMR study [11,12]. Compared with the two methyl groups in propane, it is clear that the three methyl groups in isobutane have a relatively stronger steric constraint. As such, the difference in activation energies for the methyl and methine groups in isobutane during hydrogen exchange reaction, $\Delta\Delta E_{(isobutane)} = \Delta E_{(CH_3)} - \Delta E_{(CH)} = -3.9$ kcal/mol, is notably larger than the barrier difference for the $-CH_3$ and $-CH_2-$ group in propane, $\Delta\Delta E_{(propane)} = \Delta E_{(CH_3)} - \Delta E_{(CH_2)} = -1.30$ kcal/mol. The greater difference in reaction barrier observed for isobutane indicates that the primary C–H activation reaction is more dynamically favored over the tertiary C–H bond activation for isobutane trapped inside the pore channels of zeolite ZSM-5. The above results are consistent with those obtained from experimental study, which revealed that only the methyl group in isobutane was involved during CH bond activation in zeolite H-ZSM-5 due to fact that considerably more steric constraints are provoked by the methine group [11,12].

3.3. Relative reaction rates

To afford a direct comparison with the experimental results obtained from hydrogen exchange reaction over microporous zeolites, we also estimated the relative reaction rates of methyl and methylene groups based on the transition state theory (TST). The reaction rate (k_{TST}) can be derived by using the Eyring equation [33–35]:

$$k_{TST}(T) = \frac{k_B T}{h} \exp\left(-\frac{\Delta E}{RT}\right) \quad (1)$$

where h is Planck's constant, k_B is the Boltzmann constant, and R is the ideal gas constant. Accordingly, the relative reaction rate

constants (K_{TST}) may be determinated by:

$$K_{TST}(T) = \frac{k_1}{k_2} = \exp\left(-\frac{\Delta\Delta E}{RT}\right)) = \exp\left(-\frac{\Delta E_1 - \Delta E_2}{RT}\right) \quad (2)$$

As such, the calculated activation energies may readily be used to deduce the relative reaction rate of competitive proton exchange reaction of the alkanes with Brønsted acid sites in zeolites. For the 8T cluster model case (see Table 3), the activation energy predicted for the methyl and methylene groups during propane proton exchange reaction was 33.3 and 33.6 kcal/mol, respectively, which leads to nearly identical reaction rates ($K_{TST} = k_{CH_3}/k_{CH_2} = 1.4$) based on Eq. (2). Such a result clearly does not agree with the experimental observations [10]. On the other hand, the difference in activation energies of methyl (28.7 kcal/mol) and methylene (30.0 kcal/mol) groups is much larger when predicted based on the 64T cluster model, rendering further derivation of proton exchange reaction rates (k_{TST}) by Eq. (2). Accordingly, the reaction rate derived for the methyl group (k_{CH_3}) in propane is found to be faster than that of methylene (k_{CH_2}) by about four folds at $T = 473$ K, in good agreement with the experimental results, which observed a relative reaction rate of $K_{TST} = k_{CH_3}/k_{CH_2} = 3$ [10]. Since an activation energy difference, $\Delta\Delta E = \Delta E_{(CH_3)} - \Delta E_{(CH)}$, of −3.9 kcal/mol was observed for isobutane, leading to a relative reaction rate constant $K_{(isobutane)} = k_{(CH_3)}/k_{(CH)}$ of ca. 10^3, which justify that only the methyl group carbonium ions TS, i.e., $(CH_3)_2$–CH–CH_4^+, can be formed for isobutane adsorbed on the Brønsted acid sites of zeolites at room temperature (298 K); in perfect agreement with the experimental findings [11,12]. Furthermore, that the relative reaction rate constant K_{TST} deviates from unity may be accounted for the observed regioselectivity of propane (or isobutane) proton exchange reaction occurring within the microporous channels of zeolite H-ZSM-5. In addition, one may also conclude from the transition-state theory that the selectivity for the C–H activation of the methyl group tends to deteriorate with increasing reaction temperature.

4. Conclusions

The transition state structures and activation energies for a series of alkane proton exchange reactions confined inside nanosize channels of zeolite H-ZSM-5 have been predicted by DFT calculations based on an extended 64T cluster model, in which both the long-range forces and steric constraints associated with the zeolite frameworks were included. Such a treatment is found to be crucial not only for accurate predictions of transition state structures and activation barriers during alkane C–H bond activations over zeolites, but also make possible for quantitative determination of the relative reaction rates. For isobutane proton exchange reaction and pentacoordinated carbonium ion transition state formation confined in the pore channels of zeolite H-ZSM-5, the lower reaction energy observed for the methyl group compared to the methylene (or methine) group is attributed to the regioselectivity during alkane transformation reaction. As compared to the results obtained from homogeneous liquid superacid systems, our results clearly indicate that synergetic effects from electrostatic interactions and steric constraints dictate the regioselectivity of the carbonium ion transition state formation in heterogeneous solid acid systems, such as microporous zeolites.

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