

Theoretical study of conversion reactions of ketone to hydroxyalkylene in cluster models of zeolite H-ZSM-5

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Abstract

Conversions of acetaldehyde to hydroxyethylene, acetone to 2-hydroxypropylene, butanone to 2-hydroxybutene and 2-pentanone to 2-hydroxypentene catalyzed by H-ZSM-5 have been theoretically studied using quantum chemical methods. Geometry optimizations of the local structures of species reacting with H-ZSM-5 zeolite using 3T-DFT and 5T-DFT cluster models computed at B3LYP/6-31G(d) level and 50/3T-ONIOM2 cluster model computed at ONIOM(B3LYP/6-31G(d):AM1) level have been carried out. Three steps of the reaction mechanism were found and thermodynamic properties of each reaction steps and equilibrium constants of overall reaction have been obtained. The overall reaction of the conversion for all systems is endothermic reaction. The activation energies of all conversion reactions derived at three different methods are reported.

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1. Introduction

The few last decade up to present, zeolites have played very important role in the petroleum and petrochemical industries. They have been known as the one of the most important heterogeneous catalysts [1–4]. Therefore, zeolites were widely studied for their acidic properties of Brønsted acid sites [5,6] using several techniques [7–21]. The hydrogen-bonded complexes due to the interaction between waters and Brønsted acids of zeolites were studied [20–22]. ZSM-5 (Zeolite SOCONY Mobile-5) is one of the most useful catalysts that have been widely used in the petroleum and petrochemical industries. H-ZSM-5 was widely used in the conversion of light alkanes to aromatics with low selectivity because of cracking side reactions [23–29]. The catalysts of exchanged cations on H-ZSM-5 were used in many reactions. The Zn/H-ZSM-5 was used to increase propane conversion turnover rates, hydrogen formation rates, and

selectivity to aromatics [30]. The methane reactions in Mo/H-ZSM5 were investigated [31] and the Co/H-ZSM-5 was used for propane conversion to propene and to C6–C8 aromatics for dehydrogenation and dehydrocyclization of alkanes [32]. The siting and coordination of Cu⁺ ions in zeolite ZSM-5 have been studied by a combined quantum mechanics and interatomic potential function technique [33]. The reaction pathways and the energetics for the direct methane-methanol and benzene-phenol conversions that occur on the surface of Fe-ZSM-5 zeolite were analyzed using density functional theory (DFT) computations [34]. The coordination of divalent metal cations to ZSM-5 has been investigated using gradient-corrected DFT method. Coordination at both isolated charge-exchange sites and pairs of charge-exchange sites was considered for many divalent transition metal cations [35].

Protolytic cracking of ethane in ZSM-5 zeolites has been investigated using quantum-chemical techniques and a cluster model of the zeolite acid site. An aluminosilicate cluster model containing five tetrahedral atoms was used to locate all of the stationary points along a reaction

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path for ethane cracking at the HF/6-31G(d), B3LYP/6-31G(d), and MP2(FC)/6-31G(d) levels of theory [36]. A theoretical study of the cracking reaction of thiophene by small zeolitic cluster catalysts has been reported and it has been shown that the cracking of thiophene was catalyzed by Lewis basic oxygen atoms [37]. The isomerization and transalkylation reactions of aromatic species catalyzed by acidic zeolite were theoretically studied using the cluster DFT calculations. All different reported mechanisms of isomerization and transalkylation have been investigated and analyzed [38]. The structures and electronic properties of the Brønsted acid site in B, Al or Ga isomorphously substituted ZSM-5 zeolites were studied by ab initio Hartree-Fock (HF) and DFT methods [39]. The interactions of methane with Brønsted acid sites in H-ZSM-5 were investigated both experimentally and theoretically [40]. The dehydrogenation and cracking reactions of isobutane over zeolite H-ZSM-5 represented by double-ring 20T cluster were studied at the DFT/B3LYP level of theory [41]. The propene, 1-hexene, and 3-hexene protonation over representative H-ZSM-5 clusters to give covalent alkoxide intermediates were theoretically studied using DFT method [42]. The vibrational frequencies, structural, energetic, and spectroscopic properties of the acid sites of zeolite ZSM-5 were studied [43,44] using three-layered ONIOM(B3LYP/6-311+G(d, p):HF/3-21G(d):MNDO) method. To rationalize and get more understanding on the experiments of conversion reaction of aldehyde to unsaturated alcohols, the aim of this work is therefore to theoretically study the reaction mechanisms of the conversion reactions of acetaldehyde to hydroxyethylene, acetone to 2-hydroxypropylene, butanone to 2-hydroxybutene and 2-pentanone to 2-hydroxypentene catalyzed by H-ZSM-5 using various cluster models. These conversion reactions have been theoretically investigated employing the calculations at B3LYP/6-31G(d) level of theory for 3T, 5T cluster models and ONIOM(B3LYP/6-31G(d):AM1) level of theory for 50T cluster model. The energetics and thermodynamic quantities of these catalytic reactions of all models have been determined and compared with non-catalytic and water-catalyzed models.

2. Computational details

2.1. Zeolite cluster models

Three sizes of the H-ZSM-5 clusters 3T, 5T and 50T are modeled as the molecular catalyst interacting with the adsorbent. These H-ZSM-5 cluster models were employed in the computation of the interaction between the modeled structure and interacting species. The 3T and 5T, respectively defined as the structures $\text{H}_3\text{Si}(\text{OH})\text{Al}(\text{OH})_2(\text{O})\text{SiH}_3$ and $\text{H}_3\text{Si}(\text{OH})\text{Al}(\text{O SiH}_3)_2(\text{O})\text{SiH}_3$ are shown in Fig. S1 (Supplementary data). The 50T cluster consisting of forty-nine silicon and one aluminum tetrahedral (Si/Al = 49) shown in Fig. S2 (Supplementary data) is modeled with the integrated

molecular orbital + molecular orbital (IMOMO) method [45] which is implemented as the two-layered ONIOM(MO:MO) methodology [46]. The geometries of these clusters were prepared from the ZSM-5 crystal lattice structure reported in the literature [47]. The 50T cluster employed with the two-layered ONIOM calculation is finally called as the 50/3T-ONIOM2 model.

2.2. Methods of calculation

Full geometry optimizations of the configuration of species interacting with the 3T and 5T clusters were carried out for all stationary points using DFT method. The DFT calculations have been performed with the Becke's three parameters hybrid density functional using the Lee, Yang and Parr correlation functional (B3LYP) [48–50]. Geometry optimizations of the 50T cluster model have been carried out using the hybrid ONIOM methodology [51,52], known as the 50/3T-ONIOM2 calculation model. The ONIOM2(MO:MO) approach employed for the 50T cluster subdivides the real system in two different layers, each one being described at a high and low levels of theory. The active site of H-ZSM-5 zeolite and reacting compounds called as the model system is described at the highest level of theory whereas the rest of the zeolite is computed at a lower level. The real and model systems of H-ZSM-5 zeolite and reacting compounds used for the two-layered ONIOM(MO:MO) calculations are shown in Fig. S2 (Supplementary data). The energies computed at the B3LYP/6-31G(d) for 3T (3T-DFT) and 5T (5T-DFT) cluster models and the ONIOM2(B3LYP/6-31G(d):AM1) [53,54] for 50/3T model have been carried out with the zero-point vibration energy corrections.

The transition-state structures of 3T-DFT and 5T-DFT cluster models optimized at B3LYP/6-31G(d) level of theory have been located using the reaction coordinate method referred to the synchronous transit-guided quasi-newton (STQN) calculation [55]. The transition states were confirmed by one imaginary frequency. The intrinsic reaction coordinate (IRC) method [56] was used to track minimum energy paths from transition structures to the corresponding minimum. For 50/3T-ONIOM2 calculation model, the transition structures of all related species have been located using the B3LYP/6-31G(d)-optimized transition structure of the 3T cluster model as an initial geometry of the computation. The reaction energy ΔE^{298} , standard enthalpy ΔH^{298} and Gibbs free energy changes ΔG^{298} of all reactions have been derived from the frequency calculations at B3LYP/6-31G(d) level of theory. The reaction entropies ΔS^{298} of all reactions were derived from individual value of entropy of related species obtained at the same level of theory. All computations were performed using the GAUSSIAN 03 program package [57]. The MOLDEN 3.7 program [58] was utilized to observe molecular energies and geometries convergence via the Gaussian output files. The molecular graphics of all species were generated with the MOLEKEL program [59].

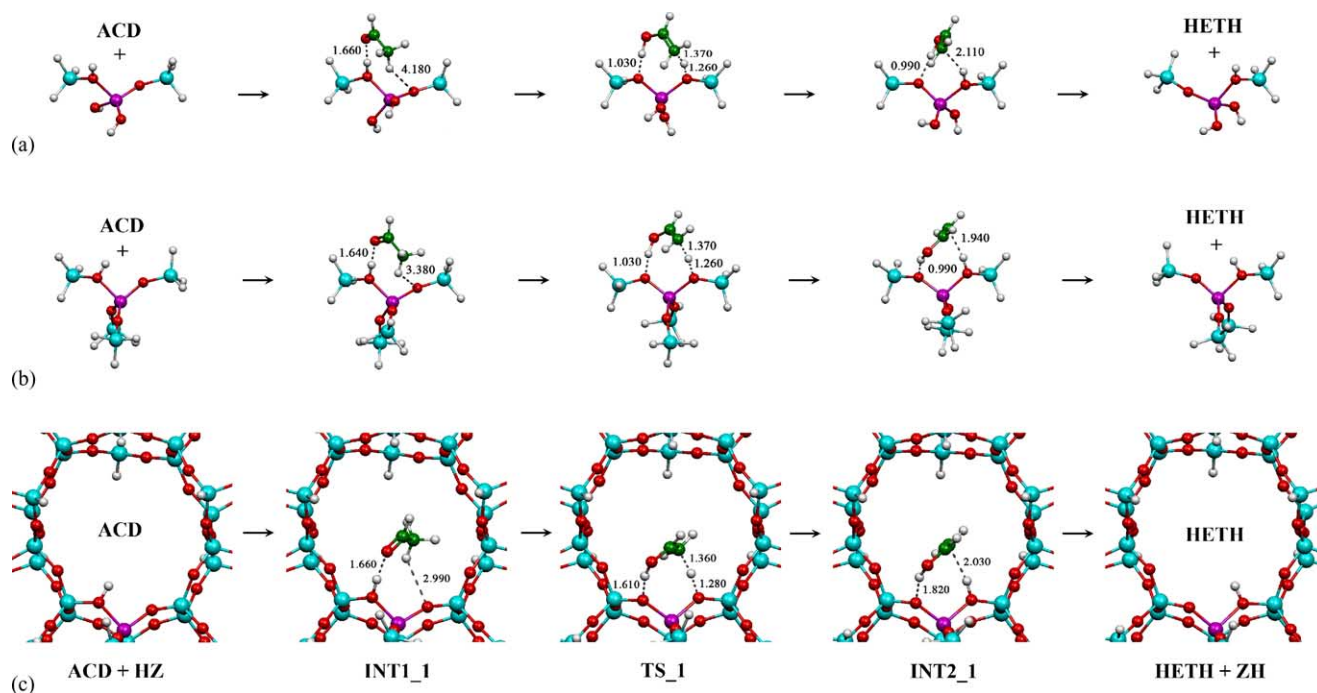


Fig. 1. Reaction steps for acetaldehyde conversion on (a) 3T-DFT, (b) 5T-DFT and (c) 50/3T ONIOM2 cluster models.

3. Results and discussion

Conversion reactions of acetaldehyde (ACD) to hydroxyethylene (HETH), acetone (ACT) to 2-hydroxypropylene (HPRO), butanone (BTN) to 2-hydroxybutene (HBUT) and 2-pentanone (PTN) to 2-hydroxypentene (HPEN) were investigated on the 3T, 5T and 50T clusters of H-ZSM-5 catalyst compared to non-catalytic and water-catalyzed models. The systems of conversion reactions according to the reactants acetaldehyde, acetone, butanone and 2-pentanone are also designated as ACD, ACT, BTN and PTN systems, respectively. Relative energies and thermodynamic properties of all systems and models were computed from the frequency calculations at the B3LYP/6-31G(d) level of theory.

3.1. Geometrical structures, energetics and thermodynamic quantities

The geometrical structures of reactants acetaldehyde, acetone, butanone and 2-pentanone were optimized at B3LYP/6-31G(d) level of theory. Geometrical data for these reactants, their corresponding transition-state structures and products of non-catalytic (gas phase) and water-catalyzed models are listed in Table S1 and S2 (Supplementary data), respectively; their atomic numbering are shown in Fig. S1. The geometrical structures of the involved species of the systems acetaldehyde (ACD), acetone (ACT), butanone (BTN) and 2-pentanone (PTN) employing the 3T-DFT and 5T-DFT calculation models are shown in Figs. 1a–b, 2a–b, 3a–b and 4a–b, respectively.

The computed stretching vibrational frequencies of hydroxyl groups at the reaction-involved oxygen atoms (O_2 and O_3) and the selected geometry parameters (bond distance and bond angle) on the 3T and 5T clusters of H-ZSM-5 zeolite are tabulated in Table S3. Table S3 shows that the computed OH stretching vibrational frequencies of H-ZSM-5 at atoms O_2 (3734.9 cm^{-1}) and O_3 (3735.7 cm^{-1}) are almost the same positions. The computed stretching vibrational frequencies of hydroxyl groups at atoms O_2 for reactant-side intermediate and O_3 for product-side intermediate for all systems are hardly ever different but smaller than their corresponding isolated-H-ZSM-5 OH vibrational frequencies by approximate 700 cm^{-1} . Relative energies and thermodynamic quantities of related species of systems acetaldehyde, acetone, butanone and 2-pentanone for 3T and 5T cluster model are listed in Table 1. The order of the reaction energies for all models is in decreasing order: systems $PTN > ACT > BTN > ACD$. The conversion constants of the reaction systems ACD, ACT, BTN and PTN of the 5T and 3T (in parentheses) cluster models are $\log K = -13.35$ (-14.72), -14.46 (-16.33), -14.65 (-17.35) and -14.70 (-16.42), respectively.

The computed stretching vibrational frequencies of hydroxyl groups at the reaction-involved oxygen atoms (O_2 and O_3) and selected geometry parameters (bond distances and bond angles) on 50T cluster of H-ZSM-5 are tabulated in Table S4. It shows that the computed OH stretching vibrational frequencies of H-ZSM-5 at atoms O_2 (3752.4 cm^{-1}) and O_3 (3750.5 cm^{-1}) are almost the same positions. The computed stretching vibrational frequencies of hydroxyl groups at atoms O_2 for reactant-side interme-

Table 1
Relative energies and thermodynamic quantities of related species of various systems on 3T and 5T cluster models

System/energy ^a	$\Delta E^{\ddagger b}$	ΔE^{298c}	ΔH^{298c}	ΔG^{298c}	ΔS^{298d}	log <i>K</i>
ACD system						
ACD + HZ	–	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	
INT1_1	–	–14.52(–14.76)	–14.92(–15.02)	–1.87(–3.75)	–43.79(–37.81)	
TS_1	18.33(20.39)	3.81(5.63)	2.70(4.82)	19.16(18.92)	–55.20(–47.29)	
INT2_1	–	1.92(2.90)	1.37(2.09)	16.35(16.34)	–50.23(–47.79)	
HETH + ZH	–	17.75(17.21)	17.76(17.15)	18.63(17.20)	–2.95(–0.18)	–13.35 (–14.72)
ACT system						
ACT + HZ	–	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	
INT1_2	–	–17.90(–17.94)	–16.90(–16.74)	–6.26(–9.02)	–35.68(–25.91)	
TS_2	18.56(20.79)	0.66(2.85)	0.72(3.17)	14.40(15.01)	–45.91(–39.72)	
INT2_2	–	0.37(1.91)	0.79(2.61)	13.48(13.27)	–42.56(–35.74)	
HPRO + ZH	–	20.08(19.53)	20.52(19.91)	20.48(19.05)	0.13(2.90)	–14.46 (–16.33)
BTN system						
BTN + HZ	–	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	
INT1_3	–	–16.43(–16.35)	–16.22(–16.05)	–4.35(–6.34)	–39.83(–32.56)	
TS_3	17.89(20.04)	1.46(3.69)	0.63(3.13)	16.82(17.25)	–54.32(–47.37)	
INT2_3	–	1.43(2.99)	1.01(2.21)	15.63(17.34)	–49.05(–50.72)	
HBUT + ZH	–	18.75(18.20)	18.66(18.05)	20.05(18.62)	–4.67(–1.90)	–14.65 (–17.35)
PTN system						
PTN + HZ	–	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	
INT1_4	–	–14.92(–14.89)	–15.80(–14.65)	–0.56(–3.47)	–51.14(–37.50)	
TS_4	17.92(20.15)	3.00(5.26)	2.14(4.65)	18.62(19.20)	–55.26(–48.80)	
INT2_4	–	3.10(4.45)	2.14(3.68)	18.72(18.94)	–55.62(–51.18)	
HPEN + ZH	–	20.37(19.83)	20.19(19.58)	22.08(20.65)	–6.34(–3.58)	–14.70 (–16.42)

^a For 5T and 3T (in parenthesis) cluster models of H-ZSM-5, computed at B3LYP/6-31G(d) level of theory.

^b Activation energy, in kcal mol^{–1}.

^c In kcal mol^{–1}.

^d In cal mol^{–1} K^{–1}.

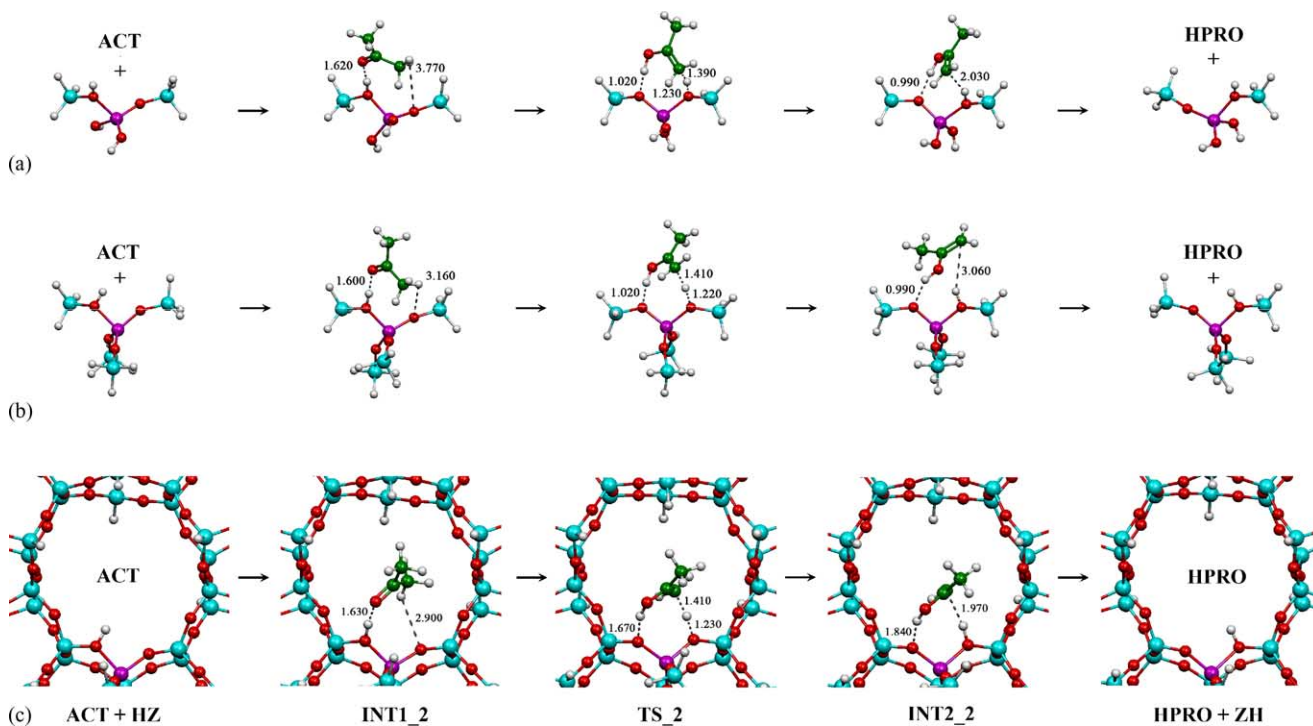


Fig. 2. Reaction steps for acetone conversion on (a) 3T-DFT, (b) 5T-DFT and (c) 50/3T ONIOM2 cluster models.

Table 2

Relative energies and thermodynamic quantities of related species of various systems on 50T cluster model

System/energy ^a	$\Delta E^{\ddagger b}$	ΔE^{298c}	ΔH^{298c}	ΔG^{298c}	ΔS^{298d}	log <i>K</i>
ACD system						
ACD + HZ	–	0.00	0.00	0.00	0.00	
INT1.1	–	–11.23	–11.11	–0.66	–35.07	
TS_1	19.39	8.16	7.33	20.76	–45.06	
INT2.1	–	3.60	3.32	15.69	–41.51	
HETH + ZH	–	17.89	17.90	17.85	0.17	–11.98
ACT system						
ACT +	–	0.00	0.00	0.00	0.00	
INT1.2	–	–14.06	–12.94	–3.59	–31.36	
TS_2	19.34	5.28	5.49	17.63	–40.74	
INT2.2	–	3.39	4.02	15.24	–37.64	
HPRO + ZH	–	20.22	20.66	19.69	3.25	–13.80
BTN system						
BTN + HZ	–	0.00	0.00	0.00	0.00	
INT1.3	–	–13.86	–13.56	–2.42	–37.35	
TS_3	20.01	6.15	5.44	20.37	–50.10	
INT2.3	–	4.30	4.07	17.73	–45.80	
HBUT + ZH	–	18.89	18.81	19.27	–1.55	–14.77
PTN system						
PTN + HZ	–	0.00	0.00	0.00	00.00	
INT1.4	–	–12.13	–11.90	0.48	–41.52	
TS_4	19.98	7.85	7.16	22.08	–50.05	
INT2.4	–	5.84	5.65	19.14	–45.26	
HPEN + ZH	–	20.51	20.33	21.29	–3.22	–13.68

^a For 50/3T cluster model of H-ZSM-5, computed at ONIOM2(B3LYP/6-31G(d):AM1) level of theory.^b Activation energy, in kcal mol^{–1}.^c In kcal mol^{–1}.^d In cal mol^{–1} K^{–1}.

diate and O₃ for product-side intermediate for all systems are hardly ever different but smaller than their corresponding isolated-H-ZSM-5 OH vibrational frequencies by approximate 700 cm^{–1}. Relative energies and thermodynamic quantities of related species of systems acetaldehyde, acetone, butanone and 2-pentanone are listed in Table 2. The conversion constants of the reaction systems ACD, ACT, BTN and PTN of the 50T cluster model are log *K* = –11.98, –13.80, –14.77 and –13.68, respectively. Relative energies and thermodynamic quantities of related species of various systems on the 50T cluster model are listed in Table 2. The geometrical structures of the involved species of the systems ACD, ACT, BTN and PTN of the 50/3T-ONIOM2 model are shown in Figs. 1c, 2c, 3c and 4c, respectively. The order of magnitudes of the conversion constants is in decreasing order: ACD > ACT > BTN > PTN for 3T-DFT and 5T-DFT calculation models and ACD > PTN > ACT > BTN for 50/3T-ONIOM2 calculation model.

3.2. Molecular arrangement on different cluster models

Due to the molecular configurations of acetaldehyde interacting with H-ZSM-5 zeolite as three different clusters 3T, 5T and 50T, shown in Fig. 1, the molecular arrangement of acetaldehyde on these clusters are quite similar. All cluster models employed for this system (ACD) should give the correct computational results, because the small molecule

of acetaldehyde is hardly ever affected by double 10T-membered ring of 50T cluster. For the ACT system, the molecules of acetone and acetaldehyde are hardly different but the molecular arrangement of acetone on the 50/3T cluster model are quite different from the 5T and 3T models (see Fig. 2). However, the molecular arrangements of the species interacting with 5T and 3T cluster models for ACT system are still different. As the molecules of butanone (BTN) and 2-pentanone (PTN) are bigger than the acetaldehyde and acetone, the molecular arrangements of butanone and 2-pentanone on the 50/3T cluster model are obviously different from the 5T and 3T models, see Figs. 3 and 4. The 50/3T-ONIOM2 calculation model is an appropriate tool for the electronic calculation in the H-ZSM-5 catalyst system.

3.3. Reaction coordinate

The potential energy surfaces for keto-enol isomerization of acetaldehyde, acetone, butanone and 2-pentanone of non-catalytic shown in Fig. S3 (Supplementary data), water-catalyzed in Fig. S4 (Supplementary data) and 3T-DFT, 5T-DFT and 50/3T-ONIOM2 in Fig. 5 are presented. The activation of non-catalytic reactions of systems ACD, ACT, BTN and PTN, shown in Fig. S3 (Supplementary data) are 69.38, 65.92, 66.22 and 67.87 kcal/mol, respectively. Activation energies due to the activation steps of the water-catalyzed model of the systems ACD, ACT, BTN and PTN, shown in

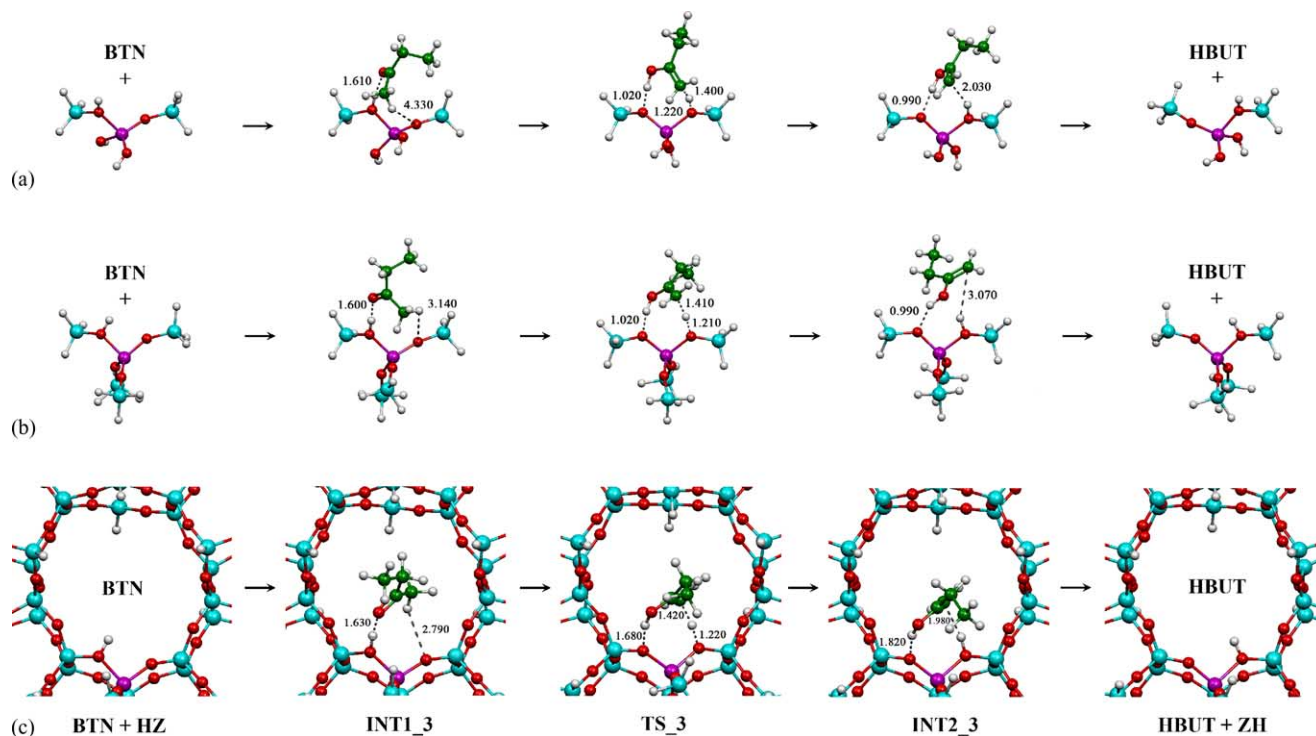


Fig. 3. Reaction steps for butanone conversion on (a) 3T-DFT, (b) 5T-DFT and (c) 50/3T ONIOM2 cluster models.

Fig. S4 (Supplementary data) are 38.07, 38.29, 39.30 and 41.59 kcal/mol, respectively. Activation energies due to the activation steps of the 5T and 3T (in parentheses) cluster models of the systems ACD, ACT, BTN and PTN shown in Fig. 5 are 18.33 (20.39), 18.56 (20.79), 17.89 (20.04) and

17.92 (20.15) kcal/mol, respectively. Activation energies due to the activation steps of the 50T cluster model of the systems ACD, ACT, BTN and PTN shown in Fig. 5 are 19.39, 19.34, 20.01 and 19.98 kcal/mol, respectively. In this work, the relative energies computed by the 3T-DFT and 5T-DFT

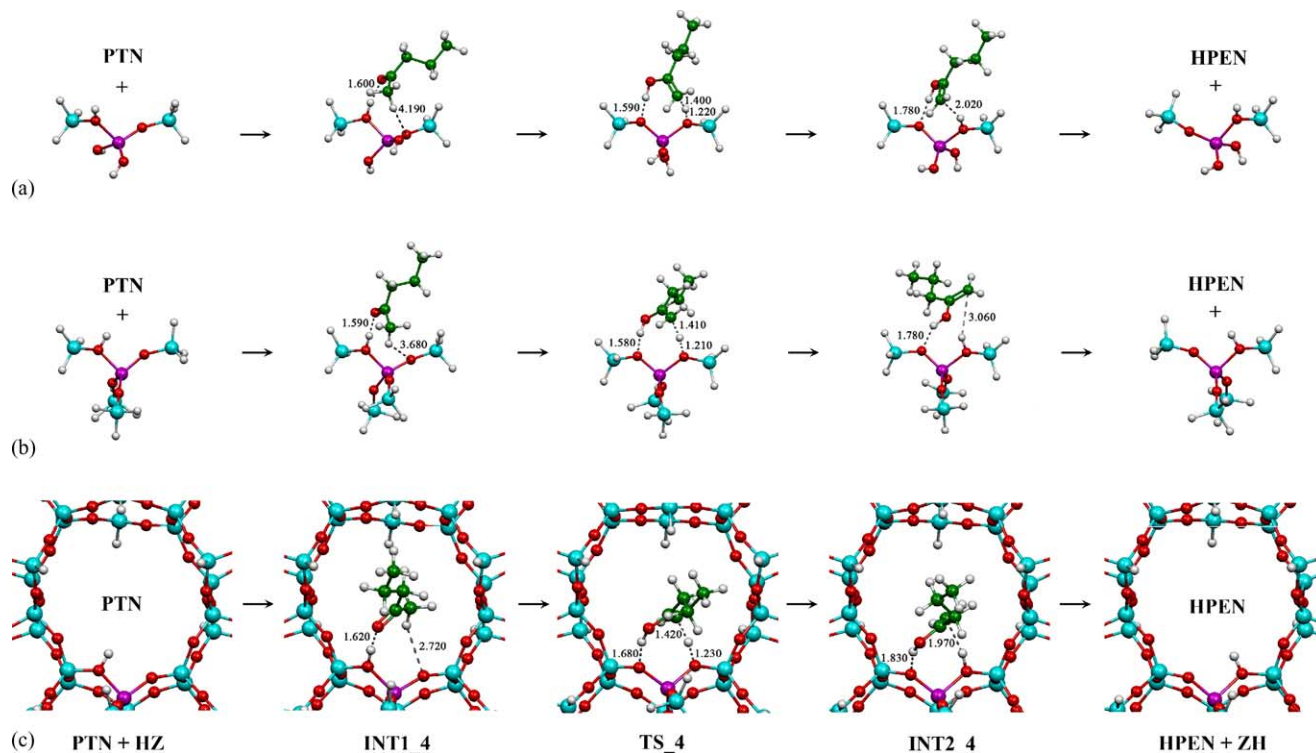


Fig. 4. Reaction steps for 2-pentanone conversion on (a) 3T-DFT, (b) 5T-DFT and (c) 50/3T ONIOM2 cluster models.

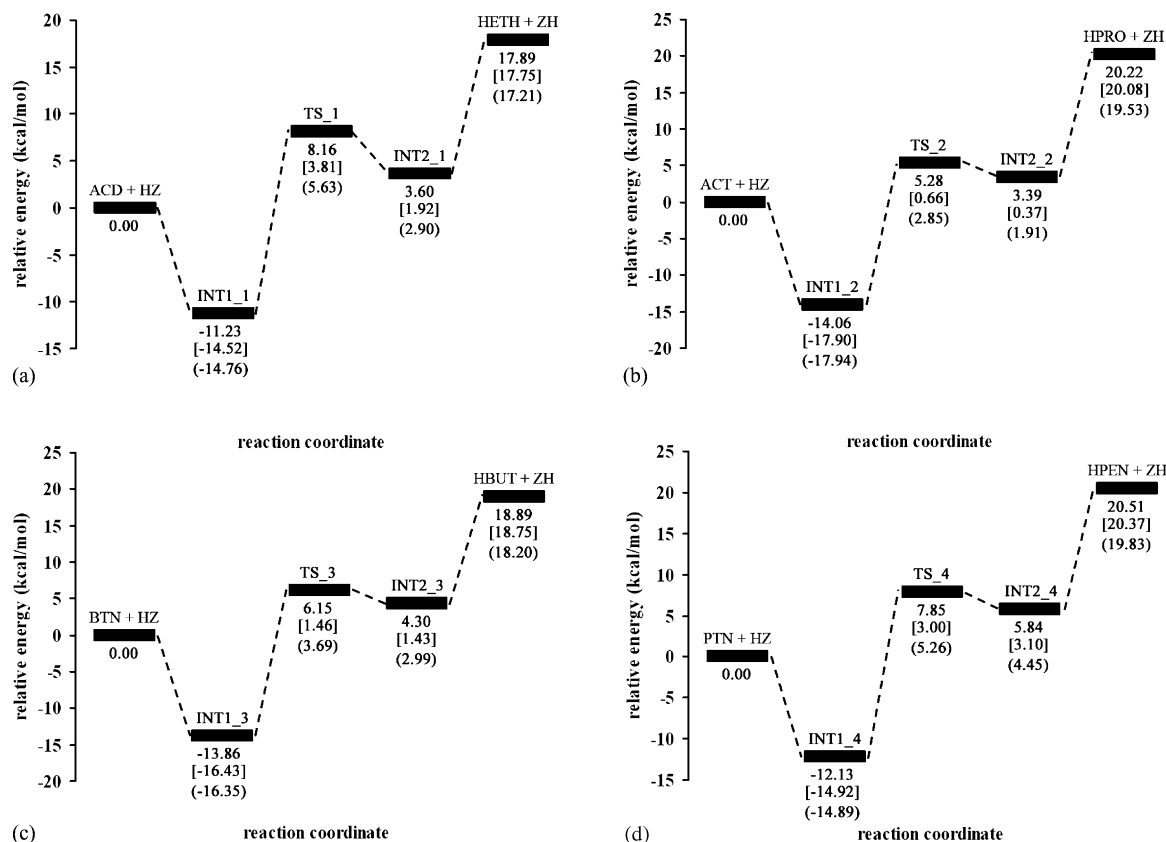


Fig. 5. Potential energy surface for keto-enol isomerization of (a) acetaldehyde, (b) acetone, (c) butanone and (d) 2-pentanone on three cluster models of H-ZSM-5. Relative energies are derived from the 50/3T-ONIOM2, 5T-DFT [in bracket] and 3T-DFT (in parenthesis).

models show the underestimated values as compared to the 50/3T-ONIOM2 model.

4. Conclusion

Conversions of acetaldehyde to hydroxyethylene, acetone to 2-hydroxypropylene, butanone to 2-hydroxybutene and 2-pentanone to 2-hydroxypentene catalyzed by H-ZSM-5 have been theoretically studied using 3T-DFT and 5T-DFT cluster models computed at the B3LYP/6-31G(d) level and 50/3T-ONIOM cluster model computed at the ONIOM(B3LYP/6-31G(d):AM1) level have been carried out. The activation energies of all systems ACD, ACT, BTN and PTN catalyzed by H-ZSM-5 zeolite are obviously lower than non catalytic and water-catalyzed models. As catalytic ability of H-ZSM-5 zeolite depending on the activation of these conversion reactions, the H-ZSM-5 can be applied in the production of some unsaturated alcohols. The 50/3T-ONIOM2 calculation model is an appropriate tool for the electronic calculation in the H-ZSM-5 catalyst system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2005.06.012.

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