Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Isobutane aromatization over complete Lewis-acid Zn/HZSM-5 zeolite catalyst: performance and mechanism

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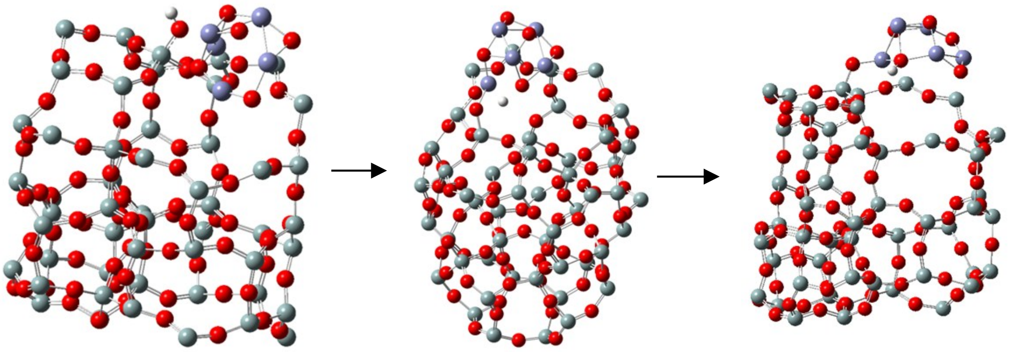
Content

Table S1 DFT calculation of ZnO structure inside of zeolite channel

n	1	3	5	6	7
ΔG (kcal/mol)	2.99	2.85	31.52	-303.28	-305.08

The thermodynamic stability of ZnO cluster inside of channel (873K)

$$\text{Zeolite@(ZnO)}_n \longrightarrow \text{Zeolite} + \text{(ZnO)}_n$$



Zeolite_5ZnO
0.00 kcal/mol

Transition state
6.84kcal/mol

Zeolite_5ZnO_2
-28.10 kcal/mol

Based on the calculation, it was found that if n is not bigger than 5, the Gibbs free energies were positive, while n is bigger than 5, the Gibbs free energies were negative. It dictates that in the intersection of ZSM5, $(ZnO)_5$ cluster is the biggest and stable cluster.

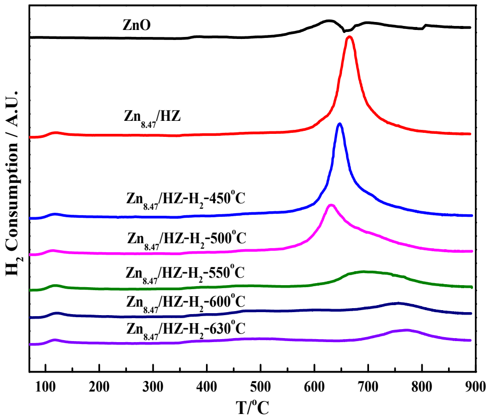


Figure S1 H_2-TPR profiles of ZnO reference and $Zn_{8.47}$/HZSM-5 catalyst pretreated by H_2 flow at the speed of 3ml/min for 6 hours at different temperatures.

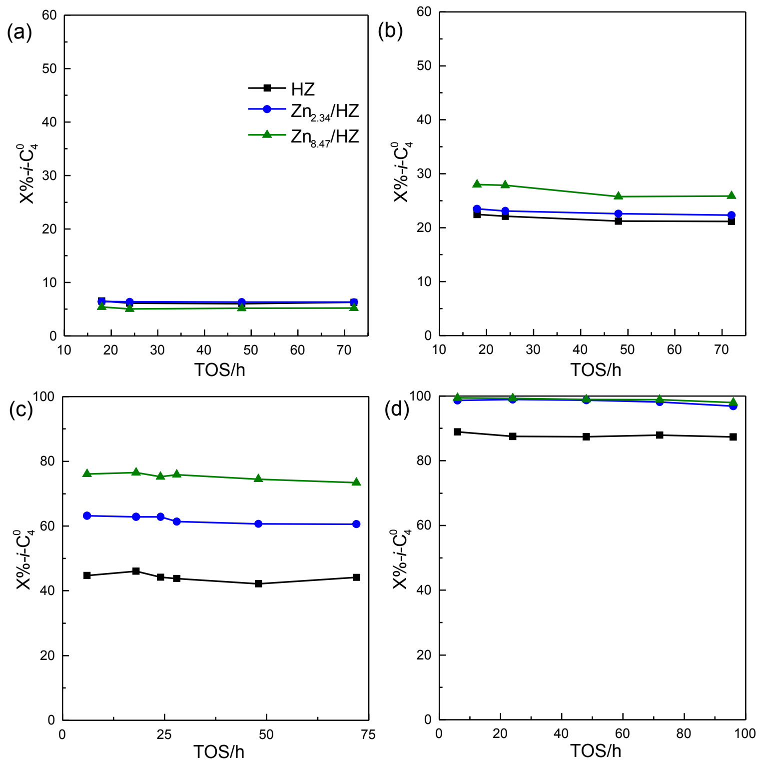


Figure S2 Reaction stability of isobutane conversion over HZSM-5 and Zn/HZSM-5 catalysts. (a) 400℃, (b) 450℃, (c) 500℃, (d) 560℃. Reaction conditions: P=0.1 MPa, WHSV=0.75 h^{-1}.

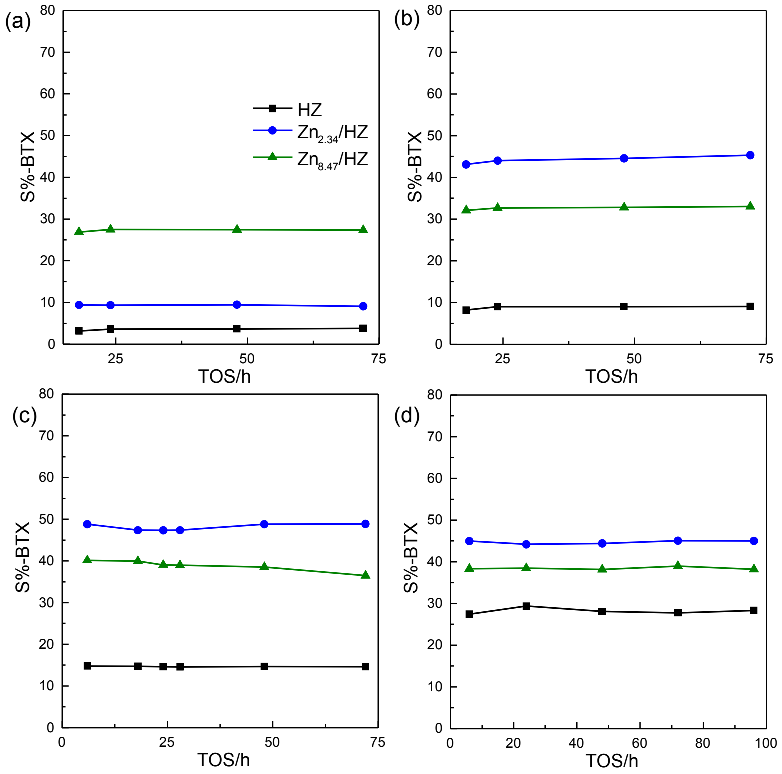


Figure S3 Reaction stability of BTX selectivity over HZSM-5 and Zn/HZSM-5 catalysts. (a) 400℃ (b) 450℃ (c) 500℃ (d) 560℃. Reaction conditions: P=0.1 MPa, WHSV=0.75 h^{-1}.

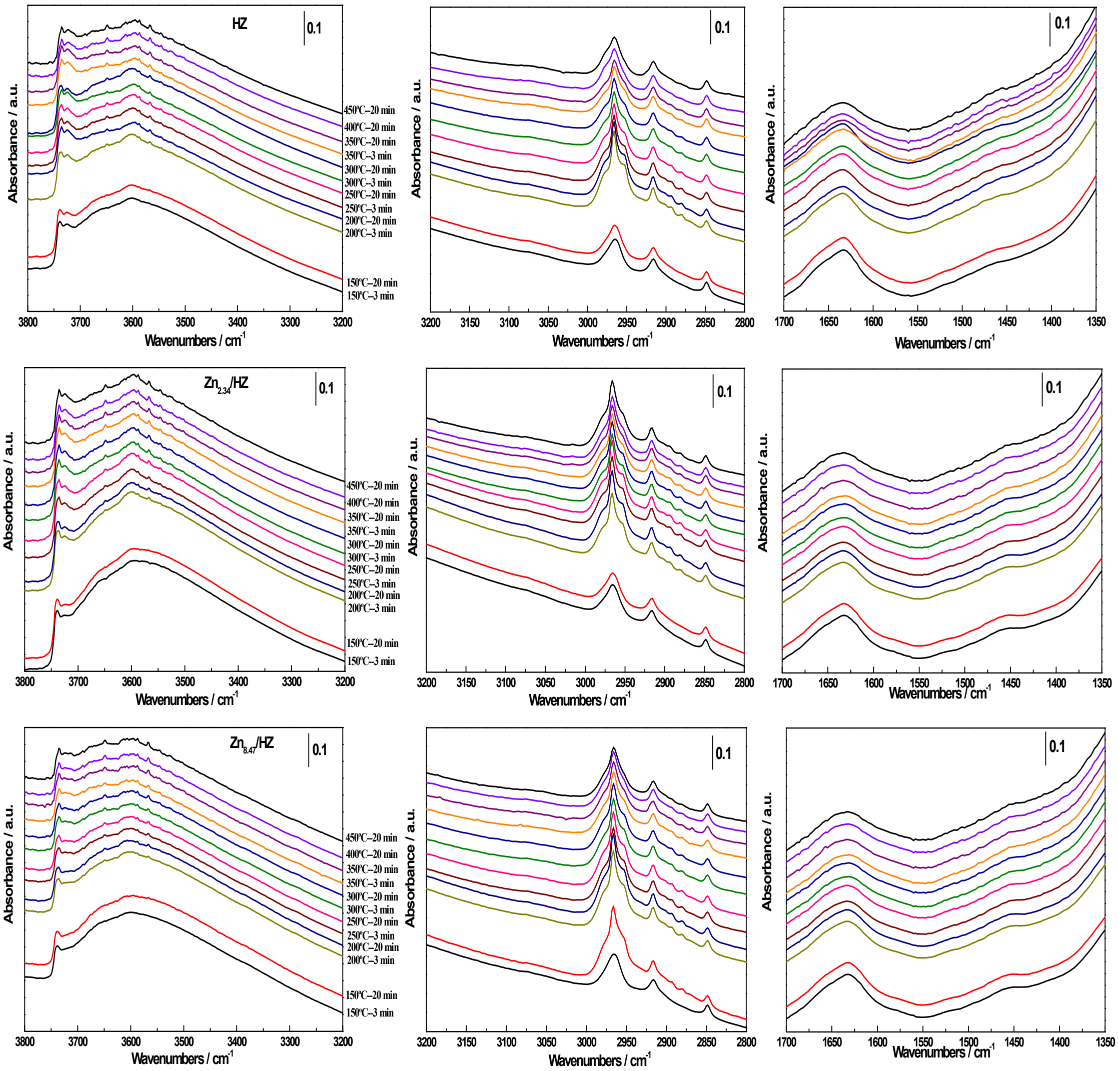


Figure S4 DB-FTIR profiles of isobutane aromatization on nano-sized HZSM-5, $Zn_{2.34}$/HZSM-5 and $Zn_{8.47}$/HZSM-5 catalysts at different temperatures 150-450°C and 101.33 kPa obtained using a DB-FTIR spectrometer in a flowing mixture of isobutane and nitrogen gas (2 % isobutane - 98 % nitrogen), GHSV=1080 h^{-1}.

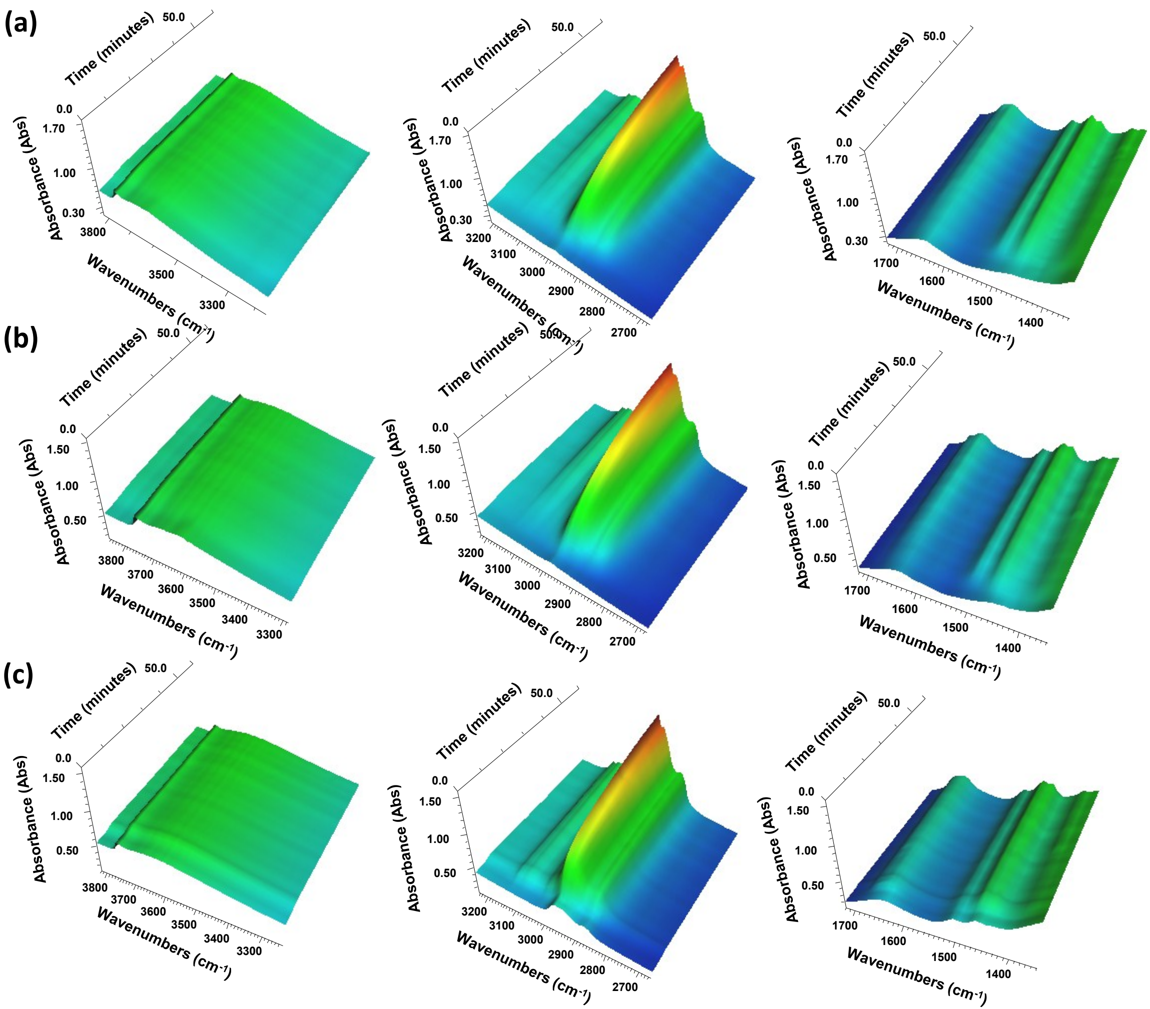
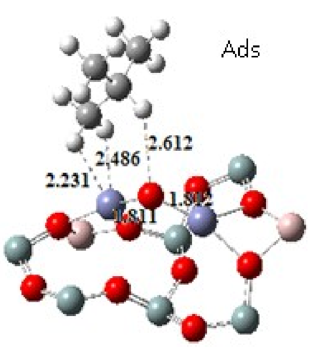
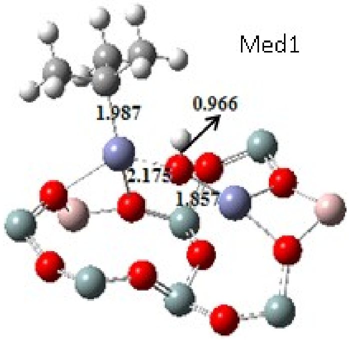


Figure S5 Three-dimensional DB-FTIR profiles of propene aromatization on (a) nano-sized HZSM-5, (b) $Zn_{2.34}$/HZSM-5 and (c) $Zn_{8.47}$/HZSM-5 catalysts at 250°C and 101.33 kPa obtained using a DB-FTIR spectrometer in a flowing mixture of propene and nitrogen gas (6 % propene - 94 % nitrogen), GHSV=1080 h^{-1}.


Ads
2.612
2.486
2.231
1.812
1.811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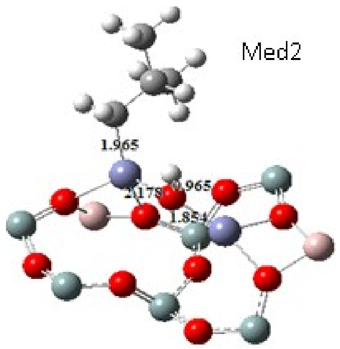
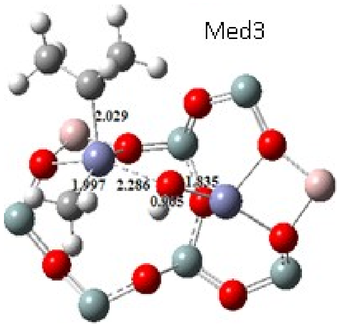
0.966
1.987
2.175
1.857


Med2
1.965
0.965
2.178
1.854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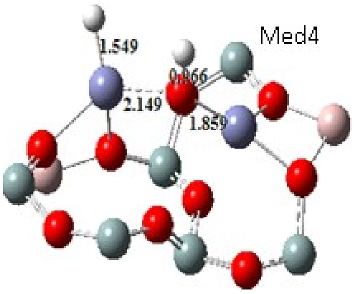
2.029
1.997
2.286
1.835
0.965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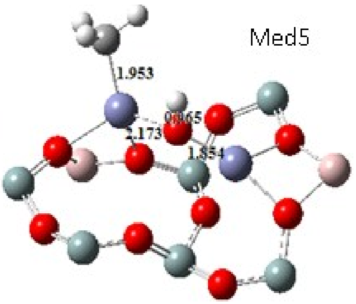
1.549
0.966
2.149
1.859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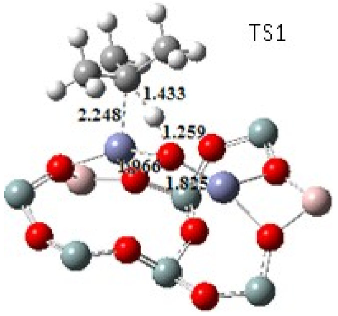
1.953
0.865
2.173
1.854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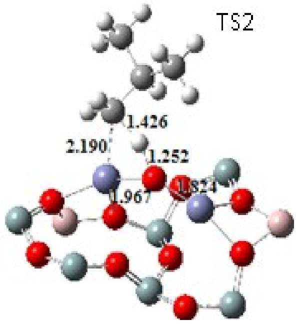
1.433
2.248
1.259
1.966
1.825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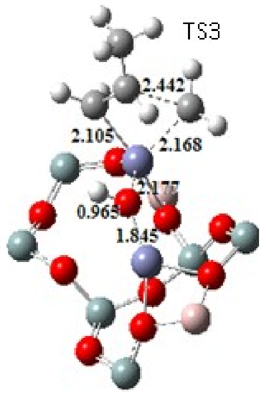
2.190
1.252
1.967
1.824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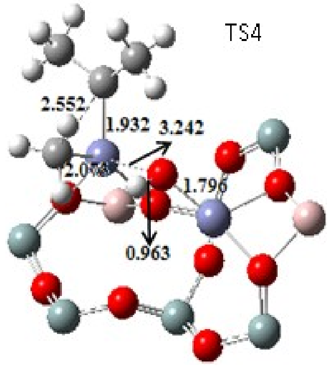
2.105
2.168
2.177
0.965
1.845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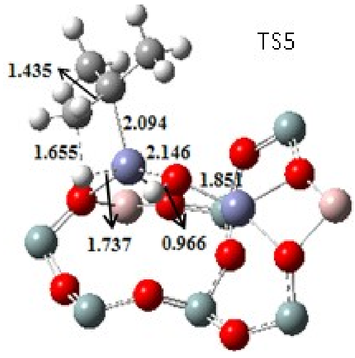
2.552
1.932
3.242
2.078
1.796
0.963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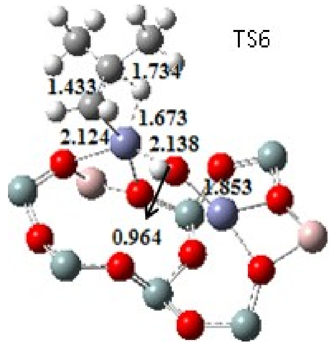
1.435
2.094
1.655
2.146
1.851
1.737
0.966


TS6
1.734
1.433
1.673
2.124
2.138
1.853
0.964

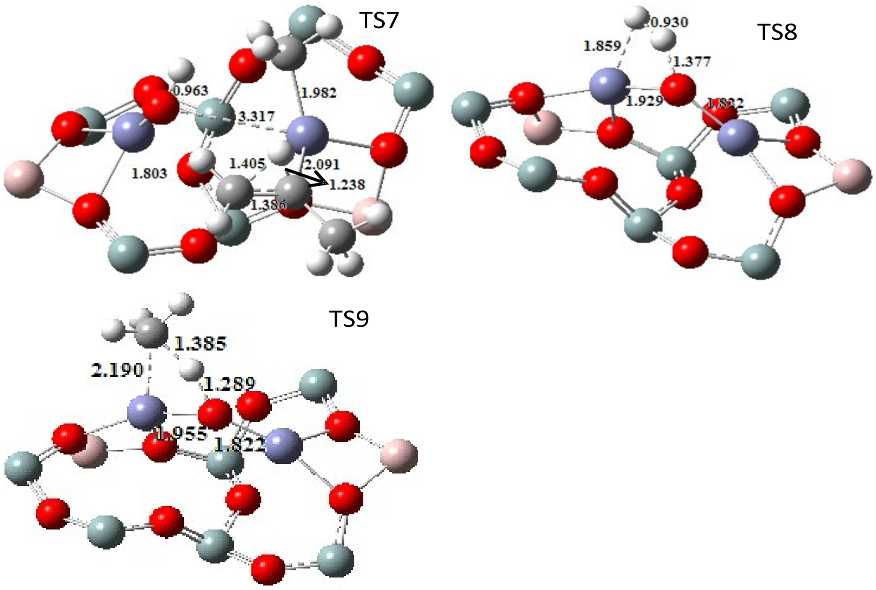
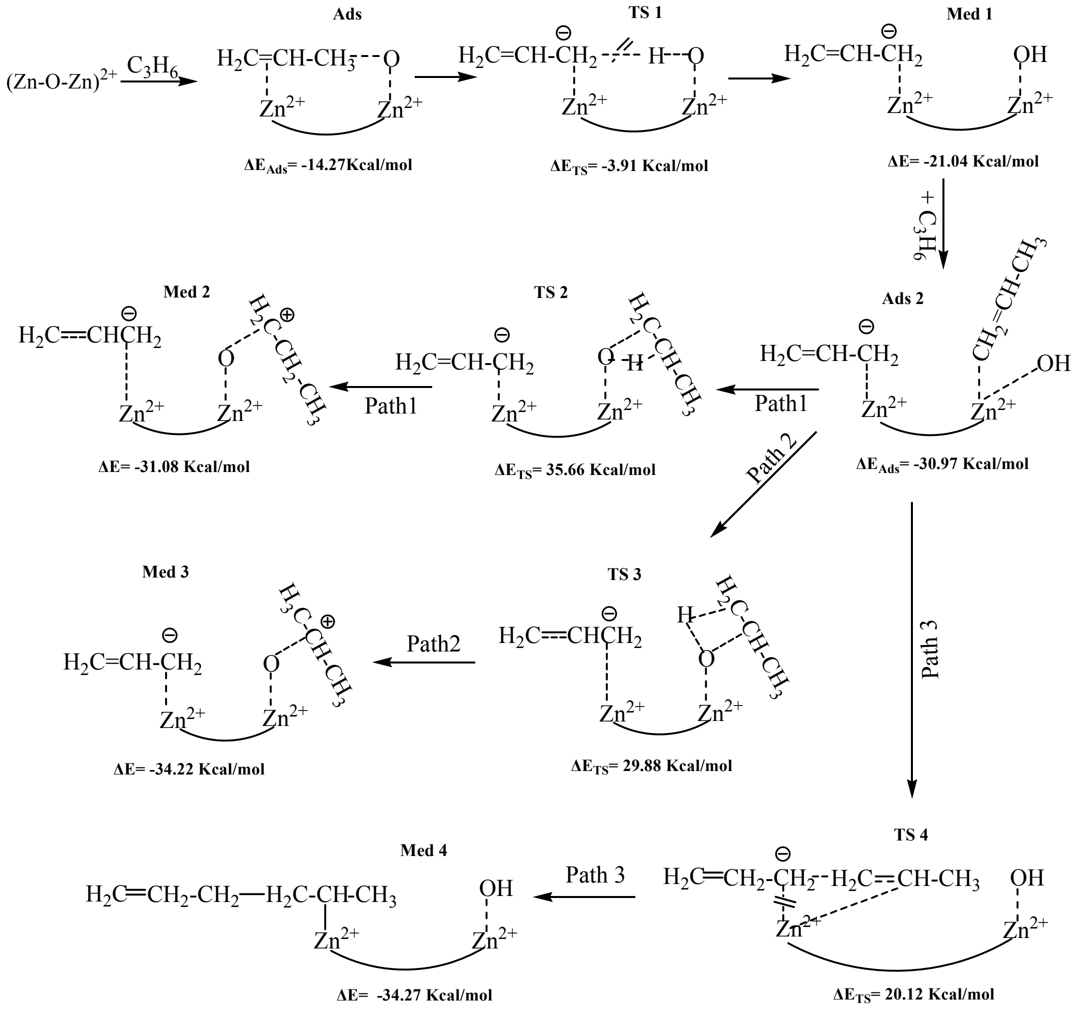
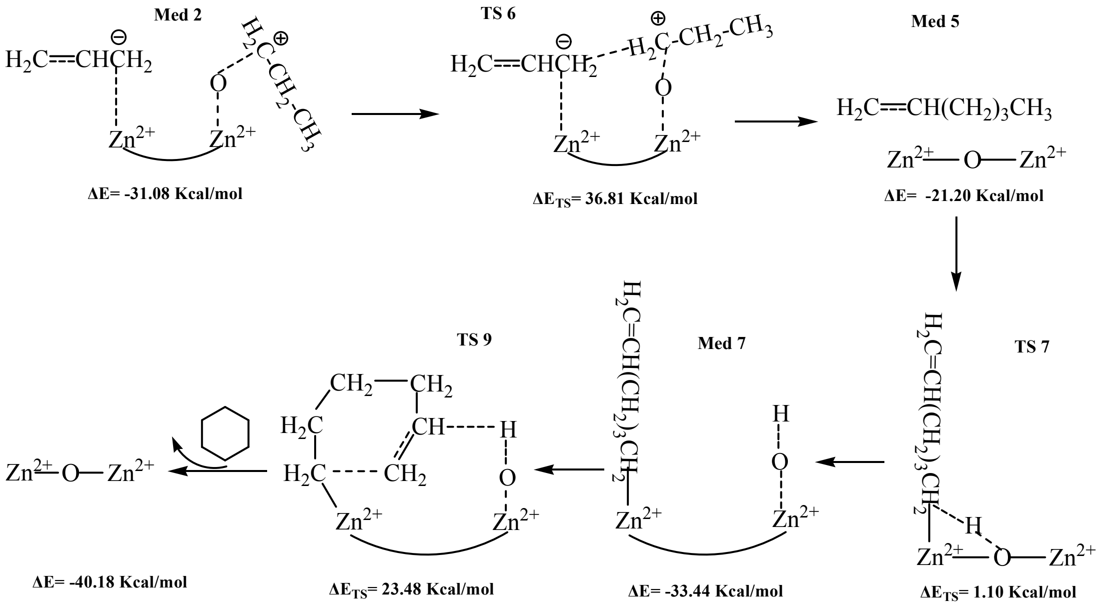


Figure S6 Geometric structures of reaction intermediates and transition states in primary activation of isobutane (the unit for bond length is Å)

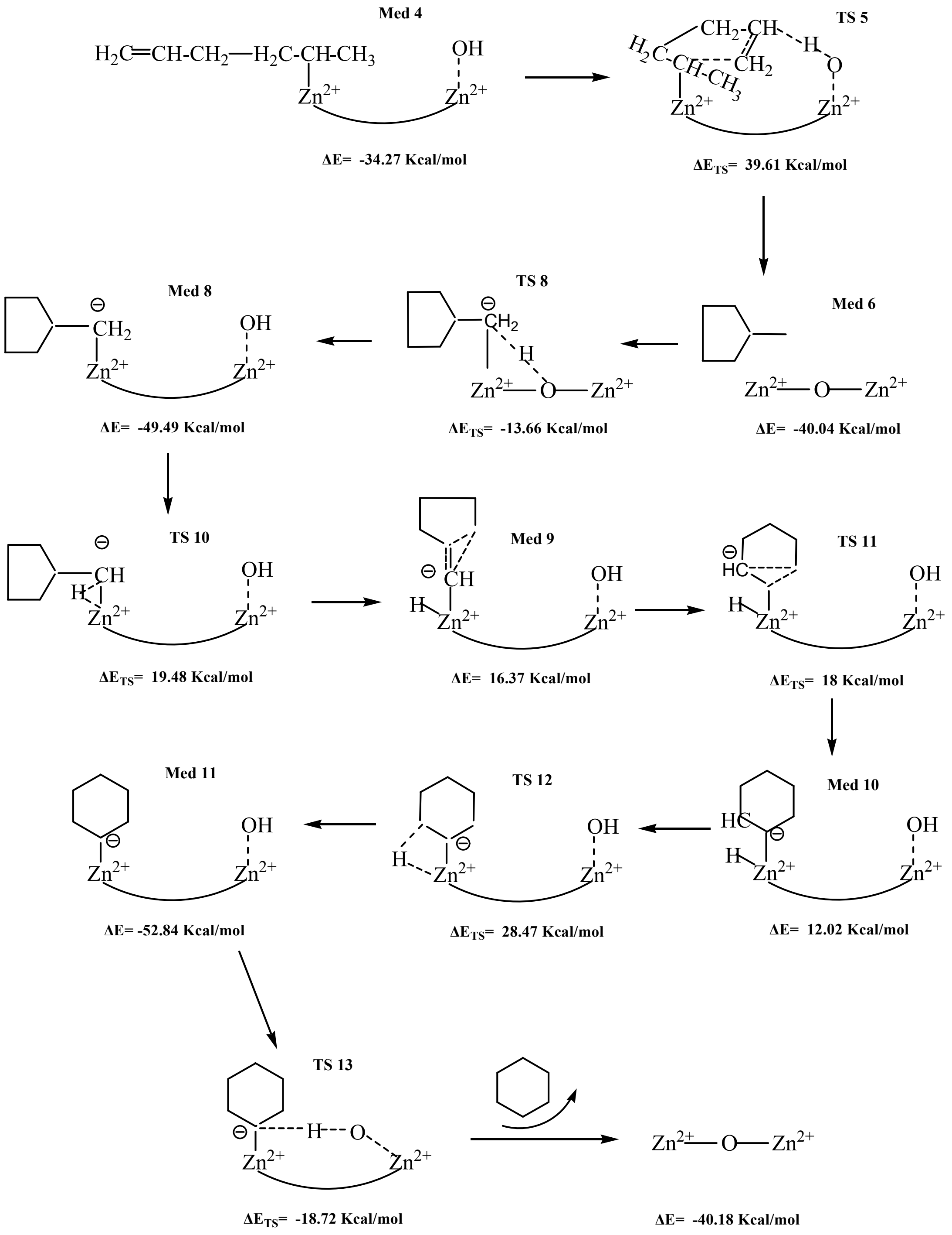


Scheme S1 Propylene oligomerization over $(Zn\text{-}O\text{-}Zn)^{2+}$ active center

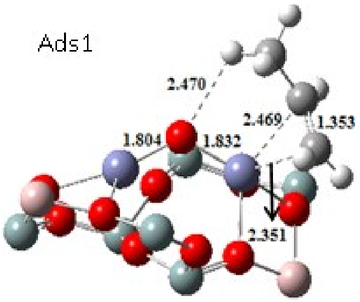
Path 1 and 2: propylene oligomerization over $[ZnOH]^{+}$ according to carbocation mechanism; Path 3: propylene oligomerization over $[Zn\text{-}(C_3H_5)^{-}]^{+}$ according to carbanion mechanism



Scheme S2 The cyclization of propylene dimmer (formed by Path1) over (Zn-O-Zn)$^{2+}$ active center with the participation of adjacent [ZnOH]$^{+}$



Scheme S3 The cyclization of propylene dimer (formed by Path 3) over $(Zn\text{-}O\text{-}Zn)^{2+}$ active center with the participation of adjacent $[ZnOH]^+$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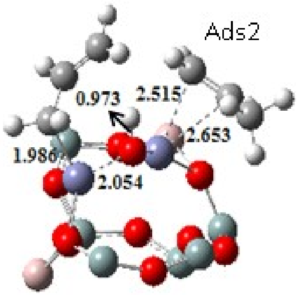
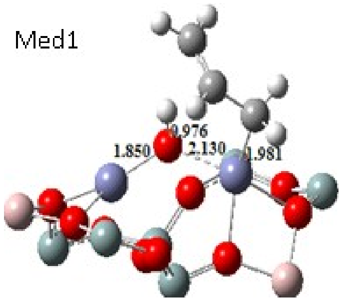

Ads2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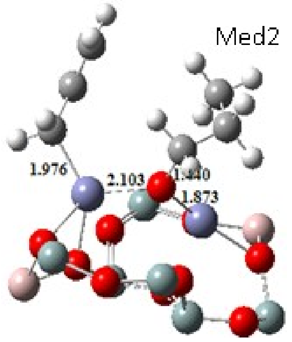
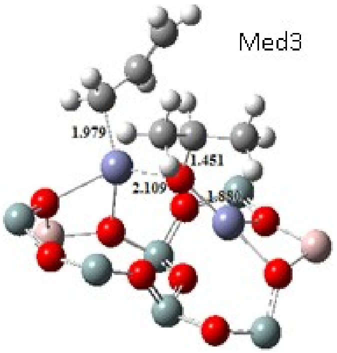

Med2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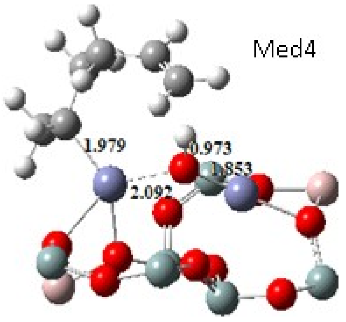
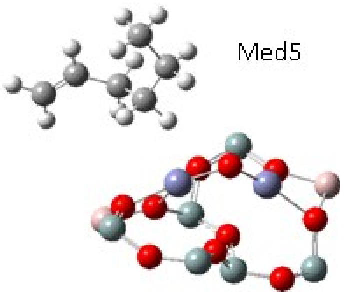

Med4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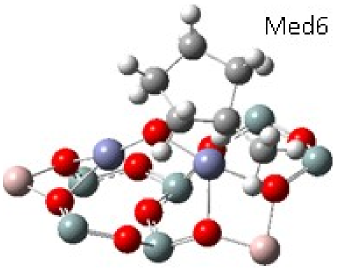
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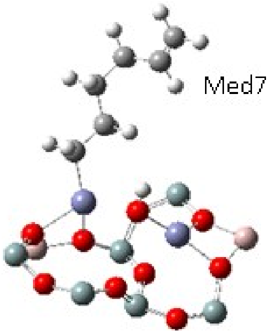
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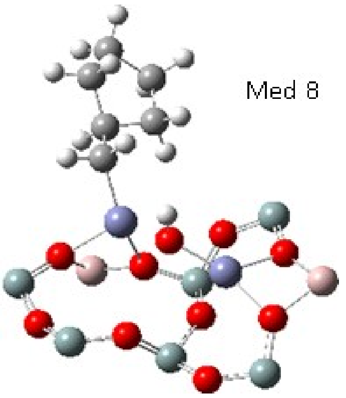
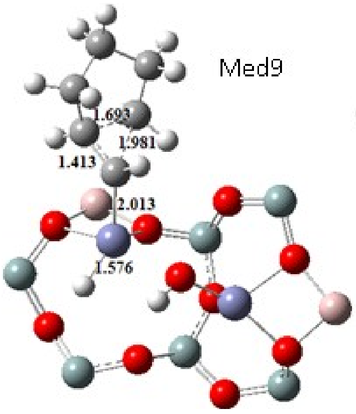

Med 8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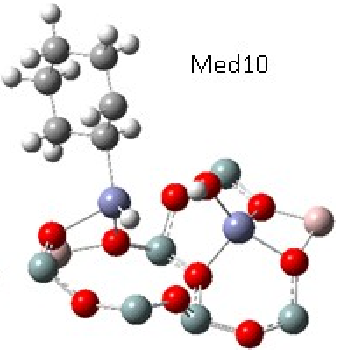
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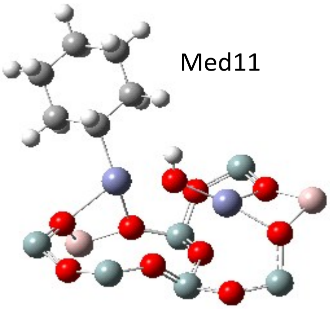
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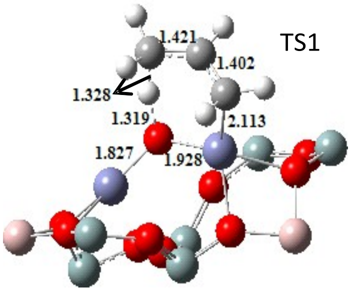
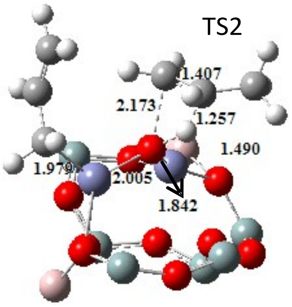

TS1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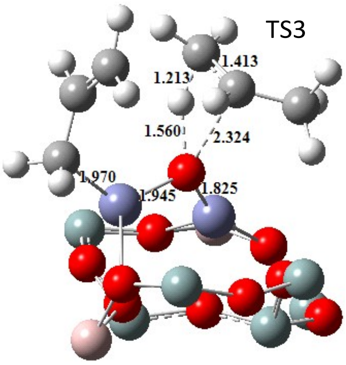
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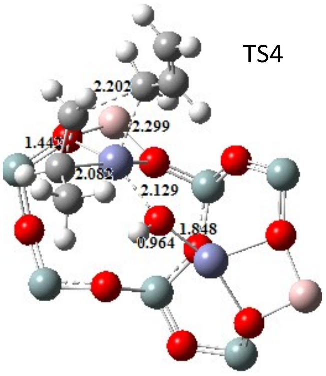
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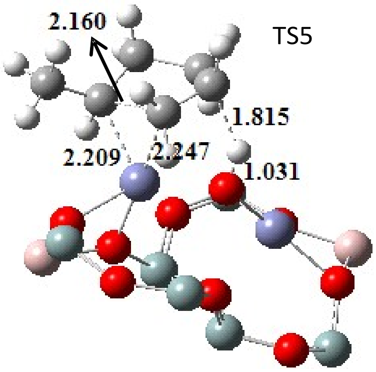
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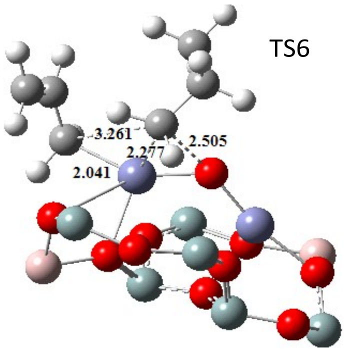
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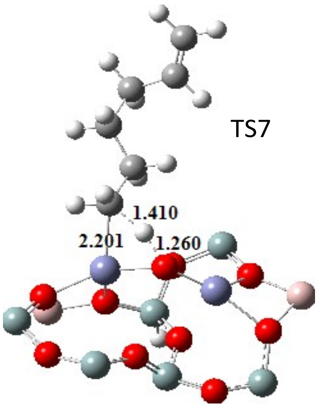
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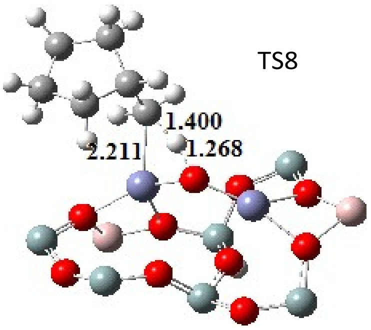
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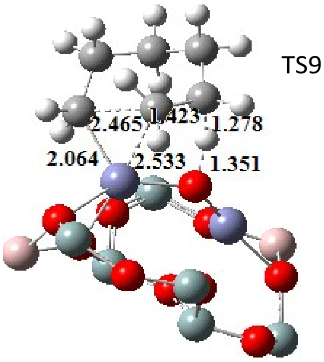
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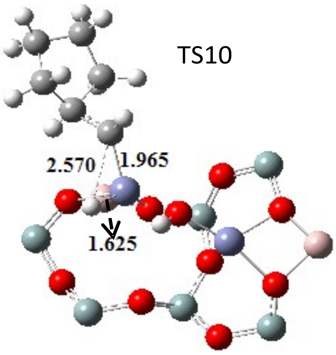
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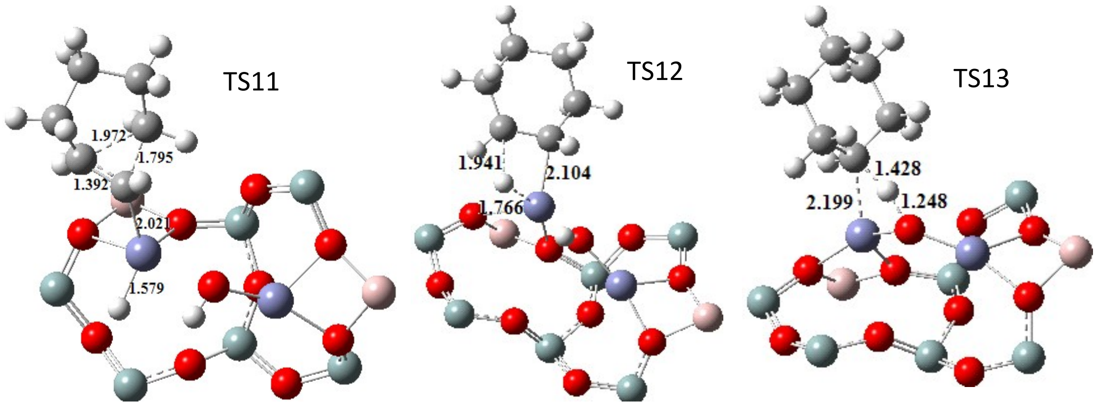

Figure S7 Geometric structures of reaction intermediates and transition states of propylene oligomerization and cyclization (the unit for bond length is Å)