Supplementary Information

# The catalytic activity and adsorption in faujasite and ZSM-5 zeolites: the role of differential stabilization and charge delocalization

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Definition of harmonic vibrational terms.

$$E_{\mathrm{ZPE}} = \sum_{a=1}^{K} R\frac{\tilde{\nu}_a}{2} \tag{1}$$

$$H^T = \sum_{a=1}^{K} R\frac{\tilde{\nu}_a}{\exp(\tilde{\nu}_a/T)-1} \tag{2}$$

$$S = \sum_{a=1}^{K} R\left[\frac{\tilde{\nu}_a/T}{\exp(\tilde{\nu}_a/T)-1} - \ln\left(1-\exp\left(-\tilde{\nu}_a/T\right)\right)\right] \tag{3}$$

$$G = E_{\mathrm{ZPE}} + H^T - TS = H - TS \tag{4}$$

where $a$ numbers vibrational modes with frequencies $\nu_a$, $\tilde{\nu}_a = h\nu_a/k$, $h$ is the Plank's constant, $k$ is the Boltzmann's constant, $R$ is the gas constant and $T$ is the temperature. $K$ is the number of normal modes.

The absolute values of thermodynamic quantities are subtracted to compute binding contributions such as $\Delta G$ (subtracting the values for the complex and isolated systems).

Table S1. Adsorption energy (kcal/mol) for the most stable and second isomer ZSM-5 at the full DFTB/PBC level.

| Adsorbed molecule | Most stable isomer | Second isomer |
|---|---|---|
| Water | -10.1 | -10.8 |
| Methanol | -17.9 | -16.0 |
| Ethanol | -25.9 | -22.2 |
| Propanol | -32.1 | -26.4 |

Table S2. The energies of transition states (TS) and intermediates (I) plotted in Fig. 7.

| Stationary point | $\Delta E$ | $\Delta H_{ZPE}$ | $\Delta H$ | $\Delta G$ |
|---|---|---|---|---|
| Reactants | 0.0 | 0.0 | 0.0 | 0.0 |
| I1 | -35.3 | -35.2 | -30.1 | -41.6 |
| TS1 | -13.9 | -14.1 | -10.1 | -17.3 |
| I2 | -47.4 | -42.5 | -41.1 | -40.9 |
| TS2 | -42.1 | -44.6 | -42.0 | -44.9 |
| I3 | -55.1 | -50.9 | -49.4 | -49.5 |
| TS3 | -38.2 | -37.8 | -34.7 | -39.8 |
| I4 | -50.0 | -48.4 | -45.1 | -50.6 |
| TS4 | -40.2 | -40.6 | -37.0 | -42.6 |
| I5 | -66.9 | -62.8 | -60.2 | -63.0 |
| TS5 | -59.1 | -58.9 | -55.5 | -60.5 |
| I6 | -80.5 | -78.7 | -74.7 | -82.3 |
| TS6 | -77.0 | -77.7 | -73.7 | -80.7 |
| I7 | -89.8 | -84.8 | -82.2 | -86.1 |
| TS7 | -87.6 | -88.3 | -84.2 | -92.4 |
| I8 | -105.7 | -102.2 | -97.8 | -106.3 |
| Products | -68.5 | -69.1 | -68.4 | -74.7 |

If the reaction is analyzed based on $\Delta H_{ZPE}$, $\Delta H$, or $\Delta G$, the barriers for TS2 and TS7 disappear.

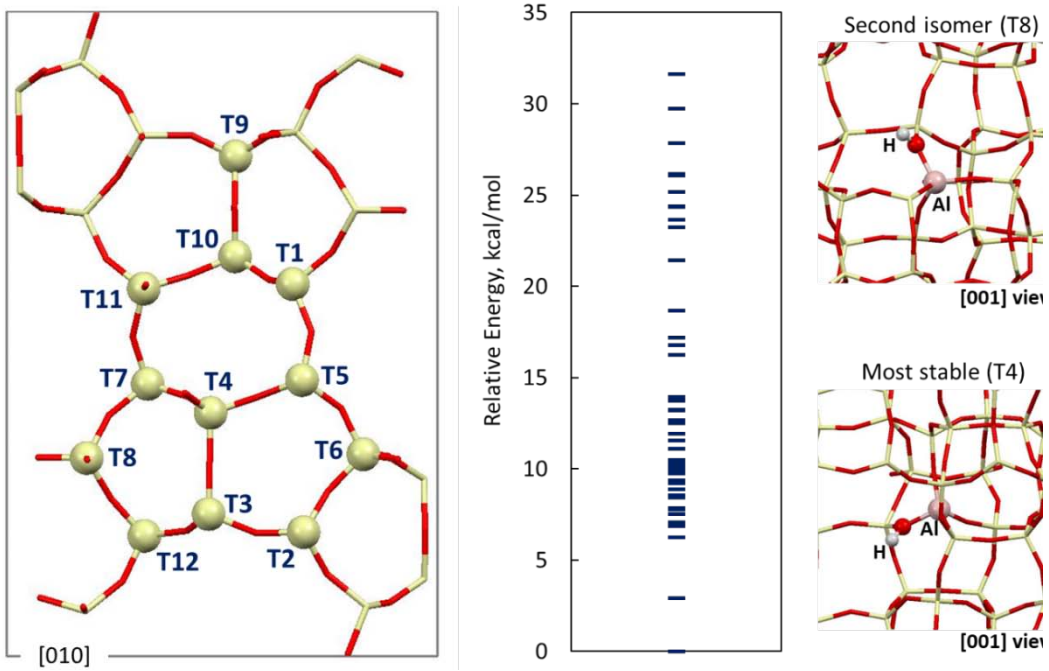


Figure S1. Position of all 12 distinct T sites (T1-T12) in ZSM-5 structure and relative stability of 48 isomers of H-ZSM-5 (every T site has 4 adjacent oxygens that can be protonated).

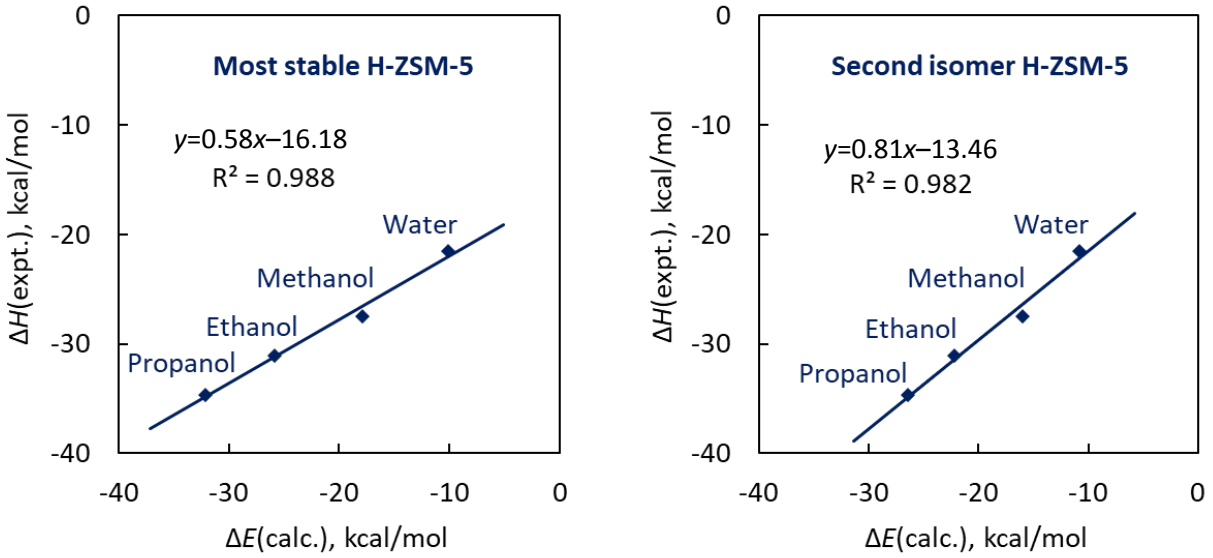


Figure S2. Correlation between the experimental[1] and calculated adsorption energy at the full DFTB/PBC level for the most stable and second isomers of H-ZSM-5 (isomers refer to Al sites).

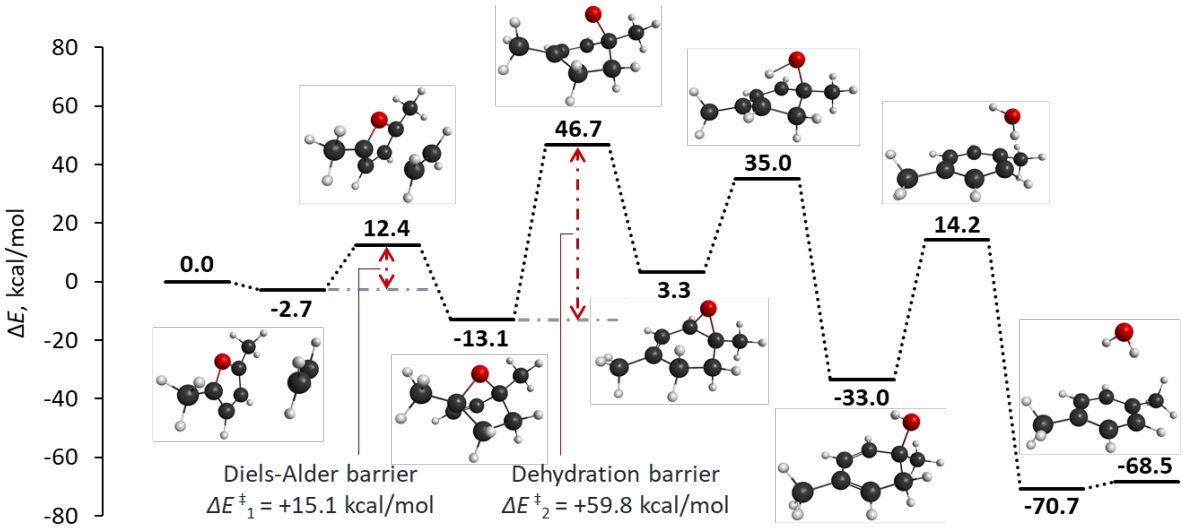


Figure S3. Reaction profile of the non-catalytic *p*-xylene production from 2,5-dimethylfuran (DMF) and ethylene at the DFTB level. Note that no zeolite is used in these reactions.

References

[1] C.-C. Lee, R. J. Gorte and W. E. Farneth, *J. Phys. Chem. B* 1997, **101**, 3811–3817.