Theoretical Determination of Size Effects in Zeolite-catalyzed Alcohol Dehydration

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Supporting Information

Diffusion measurement The Hill-Sauer force field [1,2] was used for the zeolite and the TraPPE force field [3] was used for the alcohol molecules. The super cell of H-ZSM-5 contains 576 zeolite atoms (1 x 1 x 2 unit cell) and the ratio of Si atoms to Al atoms is 31. The loadings of the alcohol molecules were 12, 12, and 6 for ethanol, iso-propyl alcohol, and tert-amyl alcohol, respectively. Each system was conditioned with initial energy minimization and subsequent 500,000 steps of equilibration. Production runs of 40 ns with a time step of 0.1 fs were performed for all systems in the NVT ensemble using a Nosé-Hoover thermostat. The cutoff radius for Lennard-Jones potentials was 10 Å and Ewald summation was used for electrostatics. Three independent MD simulations were conducted for each system. The mean square displacement (MSD) of alcohol molecules was measured every 1000 steps. The Einstein relation shown in Equation 1 was used to calculate the self-diffusion coefficient.

$$D_S = \frac{1}{6}\lim_{t\to\infty}\frac{d}{dt}\langle|r(t) - r(0)|^2\rangle \qquad \text{Eq. 1}$$

where r(t) and r(0) denote the positions of the alcohol molecule at time t and 0.

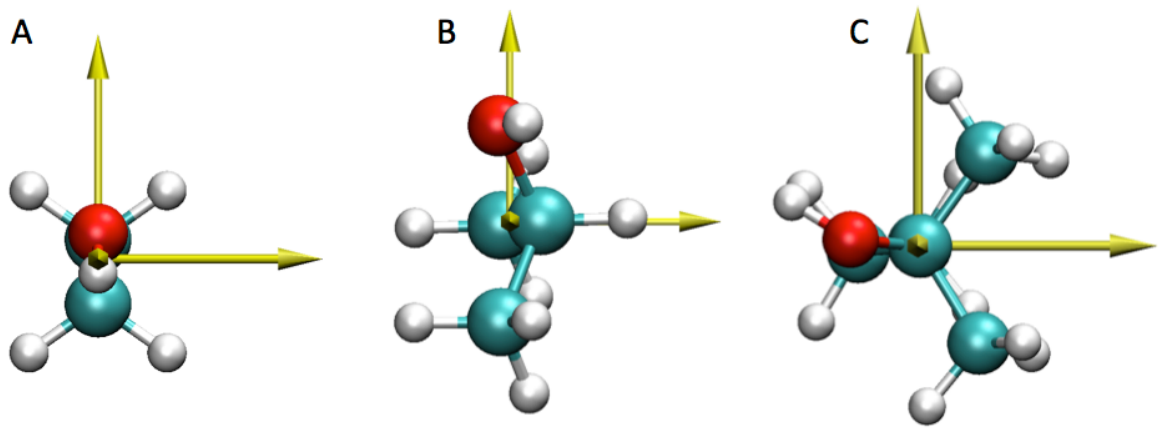

Figure S1. The measured size of ethanol (A), IPA (B), and TAA (C) is defined as the dimension of the three principal axes of each molecule at its most stable geometry, which is calculated using Gaussian 09 programs with M06-2X functional and 6-311++g(d,p) basis set. The optimized molecule is oriented with the three principal axes aligned in the *x*-, *y*-, and *z*-directions using the VMD program. The minimum distances along these three directions are measured and a correction of the vdW radius of H-atom was added to these distances to take into account the molecular surface.

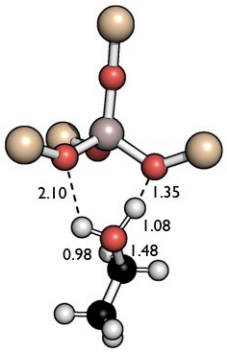

Figure S2. Optimized geometries (distances in Å) of adsorbed ethanol in H-BEA using ONIOM (M06-2X/6-311G(d,p):HF/3-21G) in Gaussian 09 (G09).

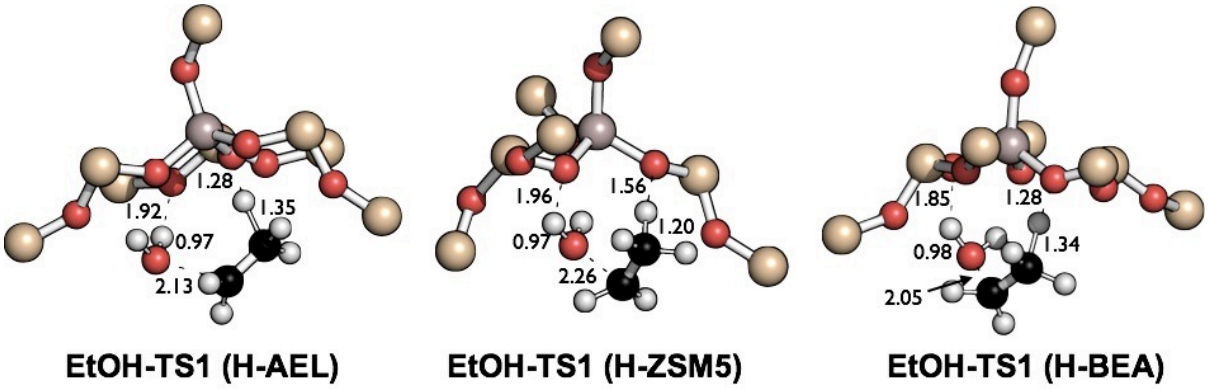

Figure S3. Optimized geometries of transition states of ethanol in H-AEL, H-ZSM-5 and H-BEA. Distances are given in Angstroms.

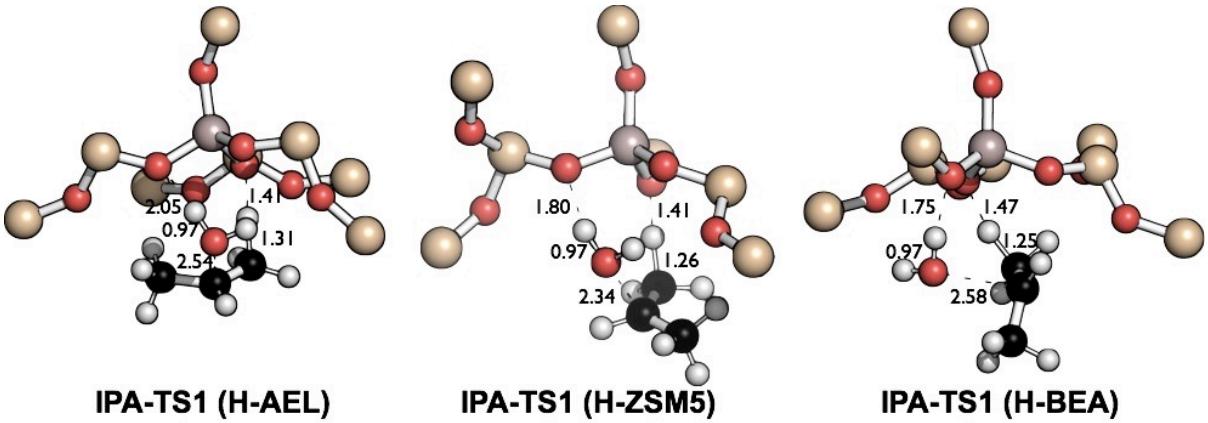

Figure S4. Optimized geometries of transition states of IPA in H-AEL, H-ZSM-5 and H-BEA. Distances are given in Angstroms.

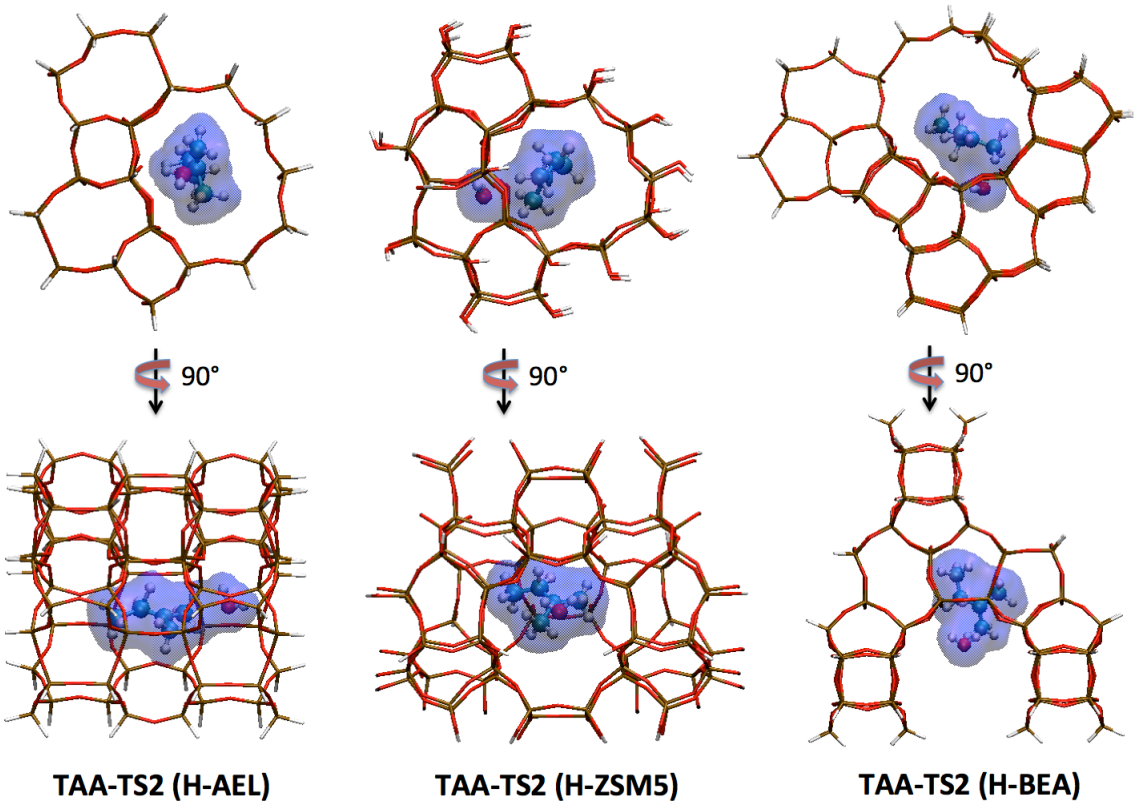

Figure S5. Transition states of TAA in H-AEL, H-ZSM-5 and H-BEA.

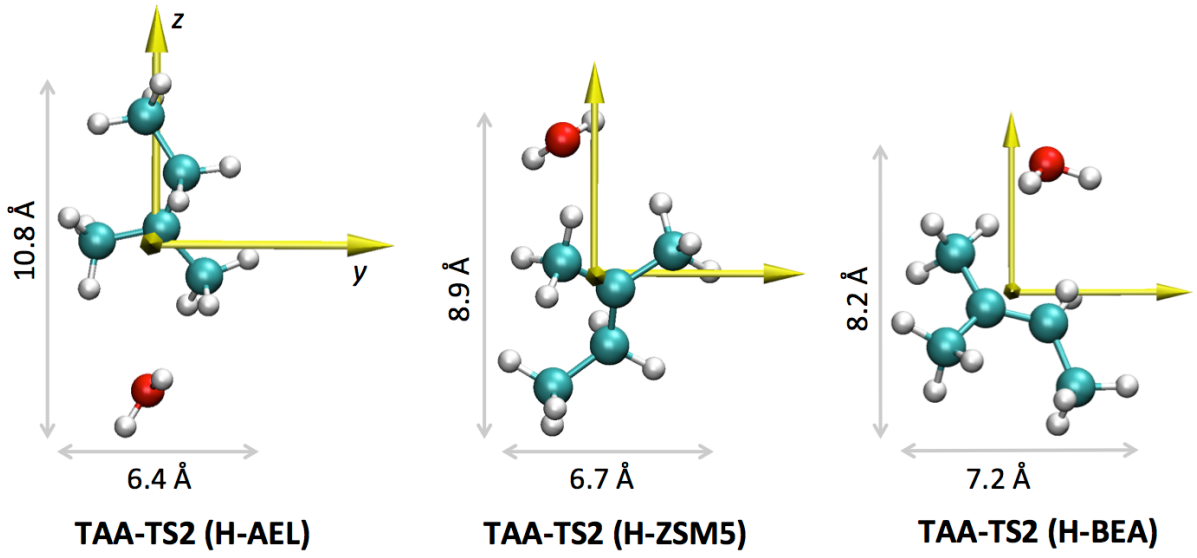

Figure S6. The measured size of transition states of TAA in H-AEL, H-ZSM-5 and H-BEA.

References

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3. Chen, B.; Potoff, J.J.; Siepmann, J.I. Monte Carlo calculations for alcohols and their mixtures with alkanes. Transferable potentials for phase equilibria. 5. United-atom description of primary, secondary, and tertiary alcohols. *J. Phys. Chem. B* **2001**, *105*, 3093-3104.