

Predicting diffusion barriers and diffusivities of C₆-C₁₂ methylbenzenes in MFI zeolites

Supplemental Information

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S1. Details of framework structures

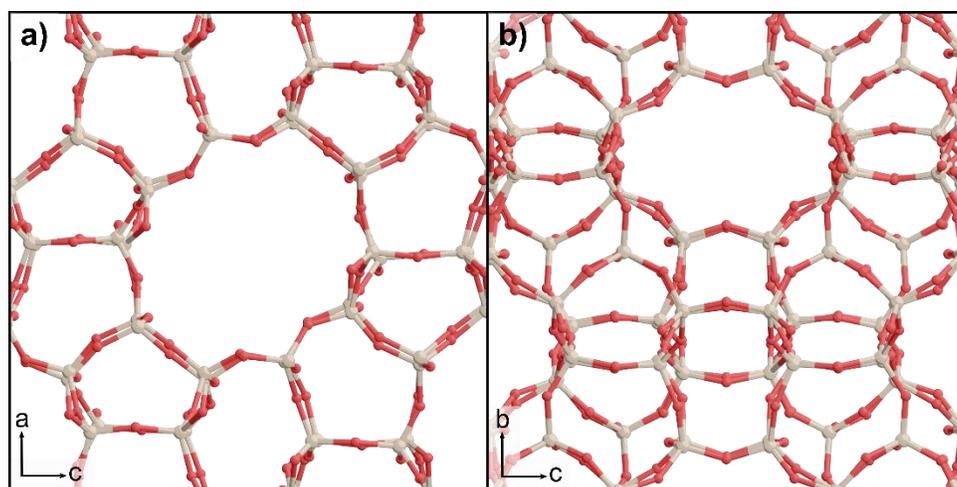


Figure S1. View down the straight (a) and sinusoidal (b) channels of silicalite-1 (MFI framework).

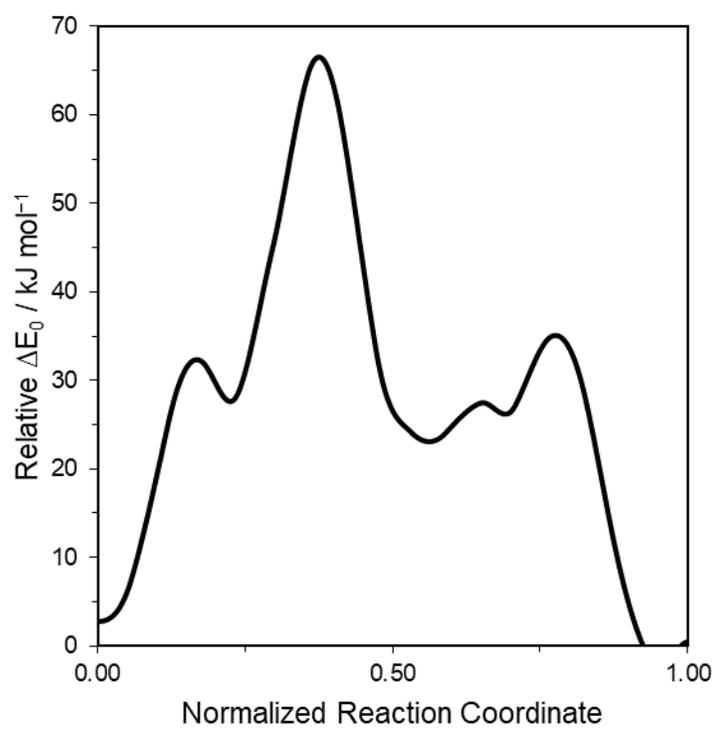


Figure S2. Potential energy surface of benzene diffusion in a 1x2x1 supercell.

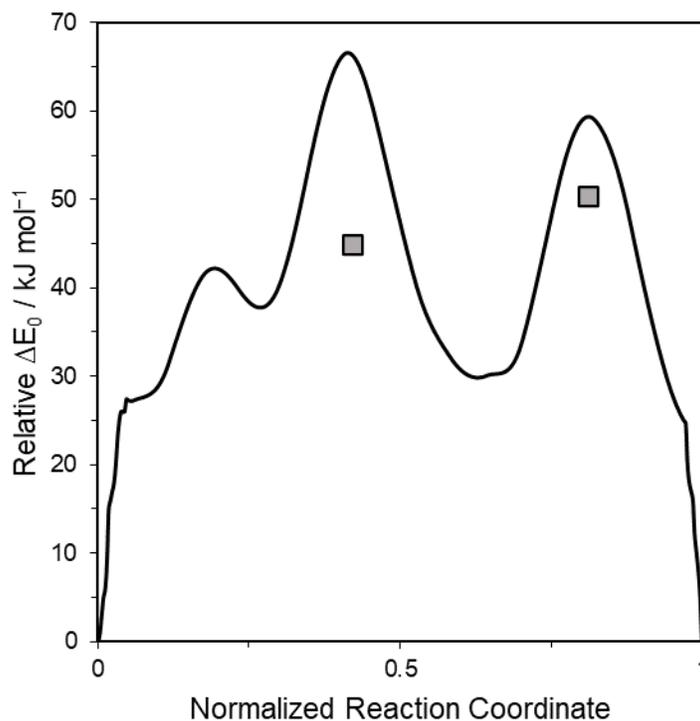


Figure S3. Potential energy surface of benzene diffusion through the sinusoidal channel in the framework obtained from Olson et. al. Gray squares represent converged transition states.

S2. Details of frequency calculations and entropy corrections

Frequency calculations were performed on the lowest energy adsorbed aromatic in the channel intersection (reactant state) and highest energy transition state associated with the potential energy surface (Dimer calculation). Frequency calculations are normal mode analyses and are used to determine zero-point vibrational energy (ZPVE), vibrational enthalpy (H_{vib}), and vibrational free energy (G_{vib}) for adsorbed species to calculate enthalpy (H):

$$H = E_0 + \text{ZPVE} + H_{\text{vib}} \quad (\text{S1})$$

and free energies (G):

$$G = E_0 + \text{ZPVE} + G_{\text{vib}} \quad (\text{S2})$$

enthalpy and free energy are used to calculate entropies.

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (\text{S3})$$

Translational and rotational enthalpies and free energies are also calculated for gas phase species to determine gas phase enthalpy:

$$H = E_0 + \text{ZPVE} + H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} \quad (\text{S4})$$

and free energy:

$$G = E_0 + \text{ZPVE} + G_{\text{trans}} + G_{\text{rot}} + G_{\text{vib}} \quad (\text{S5})$$

Low modes of frequency calculations, corresponding to frustrated rotations and translations within the confinement of the zeolite, contribute to entropy and enthalpy calculations. As such, frequencies below 60 cm^{-1} , typically corresponding to frustrated motions, are replaced with 60 cm^{-1} as discussed in the manuscript. Yet, even with these corrections we find that the adsorption energy of aromatics is significantly underestimated, because the harmonic oscillator approximation underestimate vibrational frequencies within zeolites. We correct for this underestimation when calculating diffusivities using a correlation developed for adsorption of linear $\text{C}_3\text{--}\text{C}_9$ hydrocarbons:

$$\Delta S = (S_{2\text{D,trans,gas}} + F_{\text{rot}} S_{1\text{D,rot,gas}} + S_{\text{vib,gas}}) - S_{\text{gas}} \quad (\text{S6})$$

where the adsorption entropy is approximated assuming gas phase species will lose 1 degree of translational freedom and a fraction of their rotational freedom, depending on the cavity diameter of the framework. Within MFI, F_{rot} is approximated as 1.28 by prior work.

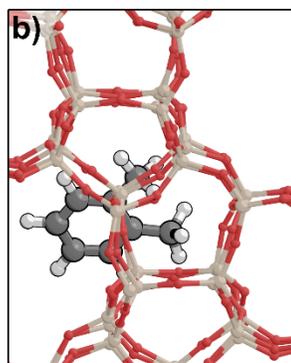
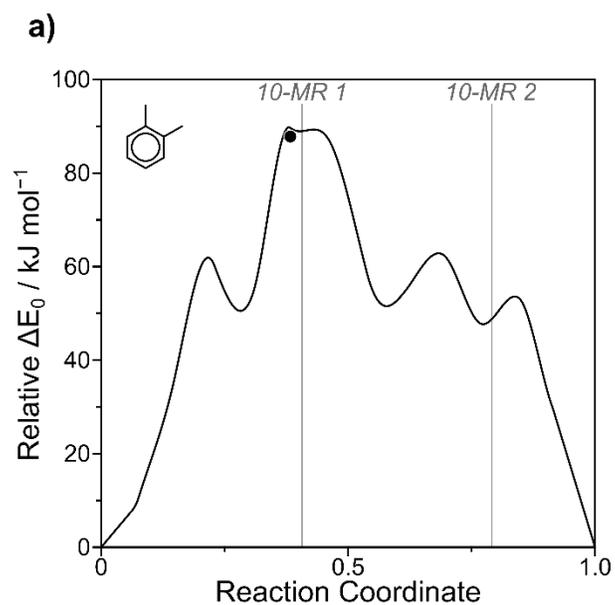
S3. Summary of straight and sinusoidal channel diffusion transition states

Table 1. Straight and sinusoidal barriers, framework distortion, and arene distortion for C₆–C₁₂ species.

Species	Straight Channel Diffusion				Sinusoidal Channel Diffusion		
	C _d Å	ΔE ₀ kJ mol ⁻¹	Framework Dist. Å	Arene Dist. Å	ΔE ₀ kJ mol ⁻¹	Framework Dist. Å	Arene Dist. Å
Benzene	6.6	15	0.38	0.05	52	1.41	0.06
Toluene	6.6	15	0.93	0.05	56	1.43	0.06
<i>Ortho</i> -xylene	7.3	37	2.42	0.09	88	5.52	0.09
<i>Meta</i> -xylene	7.3	40	1.90	0.09	71	6.59	0.08
<i>Para</i> -xylene	6.6	13	0.97	0.04	50	1.57	0.10
1,2,3-trimethylbenzene	7.6	106	3.23	0.10	131	7.20	0.23
1,2,4-trimethylbenzene	7.3	51	2.16	0.22	74	6.62	0.20
1,3,5-trimethylbenzene	8.2	189	3.84	0.31	231	8.98	0.20
1,2,3,4-tetramethylbenzene	7.6	112	3.38	0.17	121	7.16	0.25
1,2,3,5-tetramethylbenzene	8.2	190	4.29	0.27	–	–	–
1,2,4,5-tetramethylbenzene	7.3	23	2.15	0.18	70	6.15	0.45
Pentamethylbenzene	8.2	199	3.64	0.40	282	10.77	0.58
hexamethylbenzene	9.1	244	4.97	0.63	–	–	–

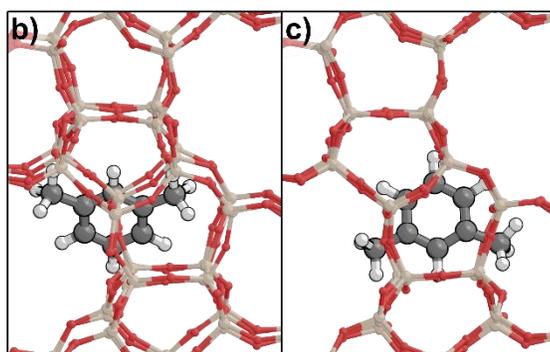
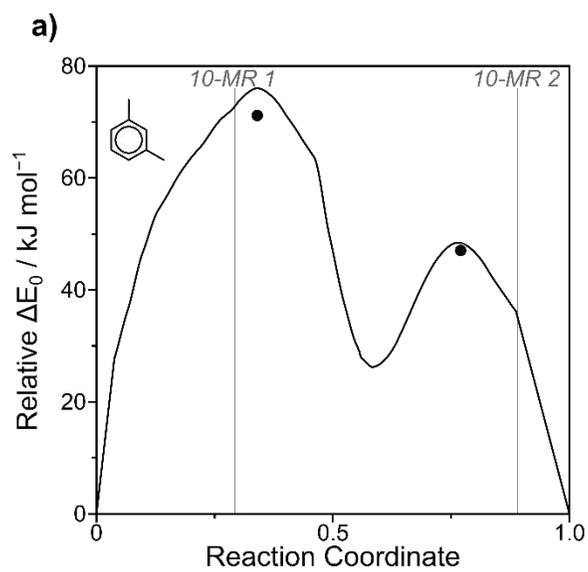
S4. Sinusoidal channel diffusion potential energy surfaces

The potential energy surfaces and transition states of benzene, toluene, *para*-xylene, 1,2,3-trimethylbenzene, 1,2,4,5-tetramethylbenzene, and pentamethylbenzene sinusoidal channel diffusion are shown in the main text (Section 3.1.2).



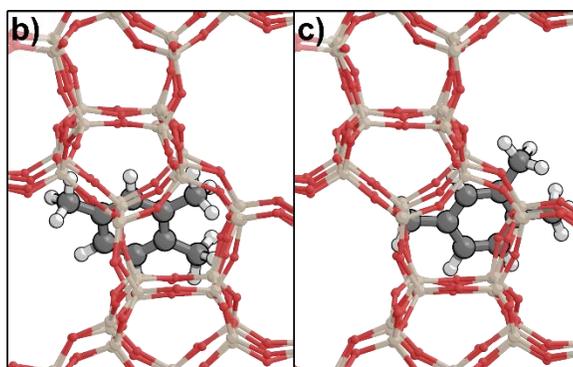
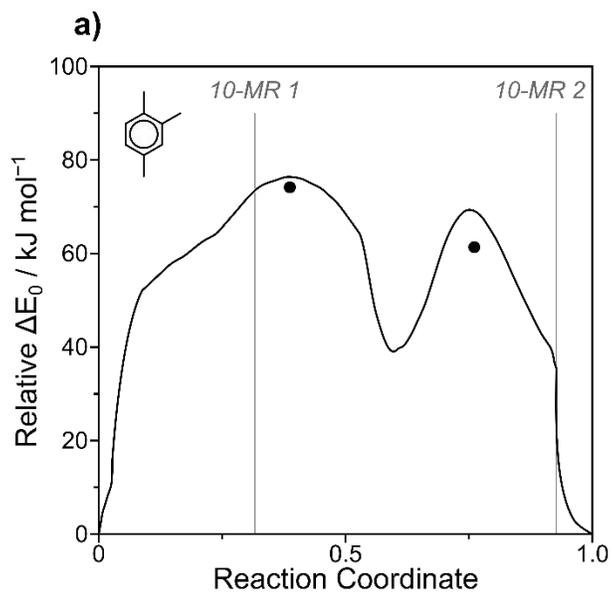
Dist. -0.06
 ΔE_0 88

Figure S4. a) Potential energy surface and b) transition state of ortho-xylene sinusoidal channel diffusion. The distance of the transition state relative to the two 10 MRs (gray lines) and potential energy of the transition states (kJ mol^{-1}) are also reported.



Dist.	0.03	0.75
ΔE_0	71	47

Figure S5. a) Potential energy surface and b, c) transition states of *meta*-xylene sinusoidal channel diffusion. The distance of the transition state relative to the two 10 MRs (gray lines) and potential energy of the transition states (kJ mol^{-1}) are also reported.



Dist.	0.12	0.73
ΔE_0	74	61

Figure S6. a) Potential energy surface and b, c) transition states of 1,2,4-trimethylbenzene sinusoidal channel diffusion. The distance of the transition state relative to the two 10 MRs (gray lines) and potential energy of the transition states (kJ mol^{-1}) are also reported.

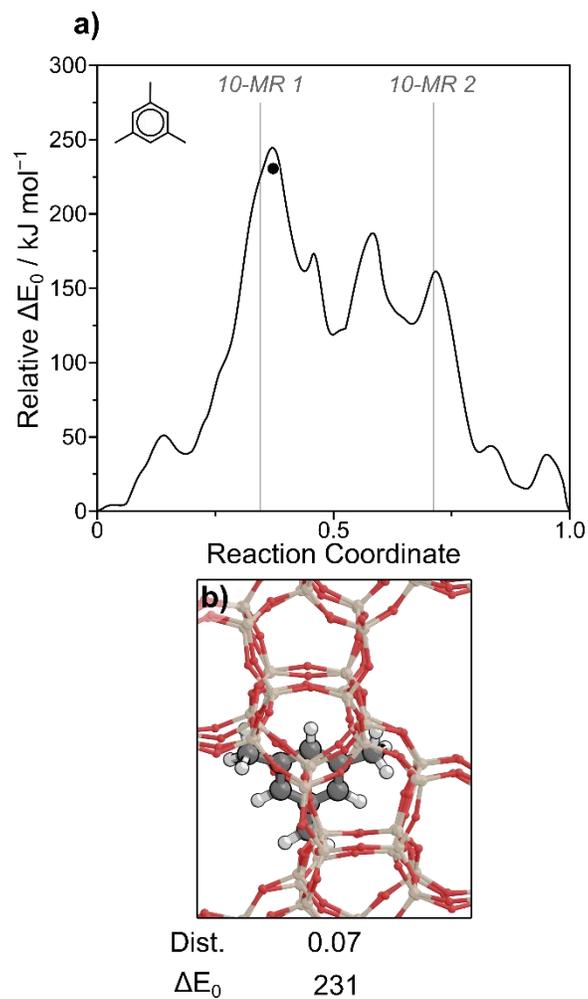


Figure S7. a) Potential energy surface and b) transition states of 1,3,5-trimethylbenzene sinusoidal channel diffusion. The distance of the transition state relative to the two 10 MRs (gray lines) and potential energy of the transition states (kJ mol^{-1}) are also reported.

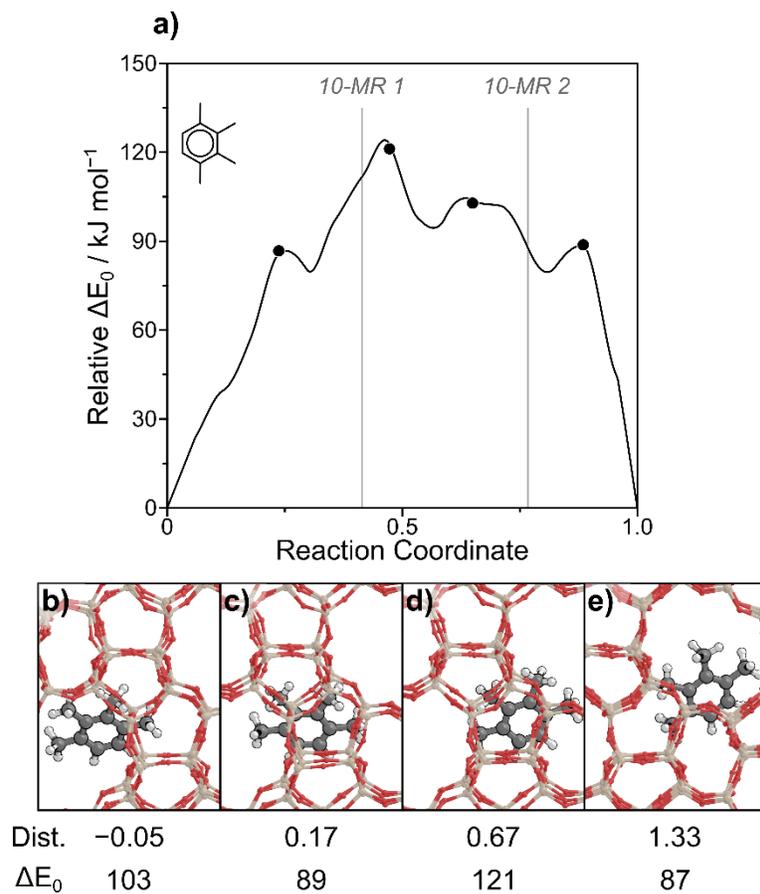


Figure S8. a) Potential energy surface and b–e) transition states of 1,2,3,4-tetramethylbenzene sinusoidal channel diffusion. The distance of the transition state relative to the two 10 MRs (gray lines) and potential energy of the transition states (kJ mol^{-1}) are also reported.

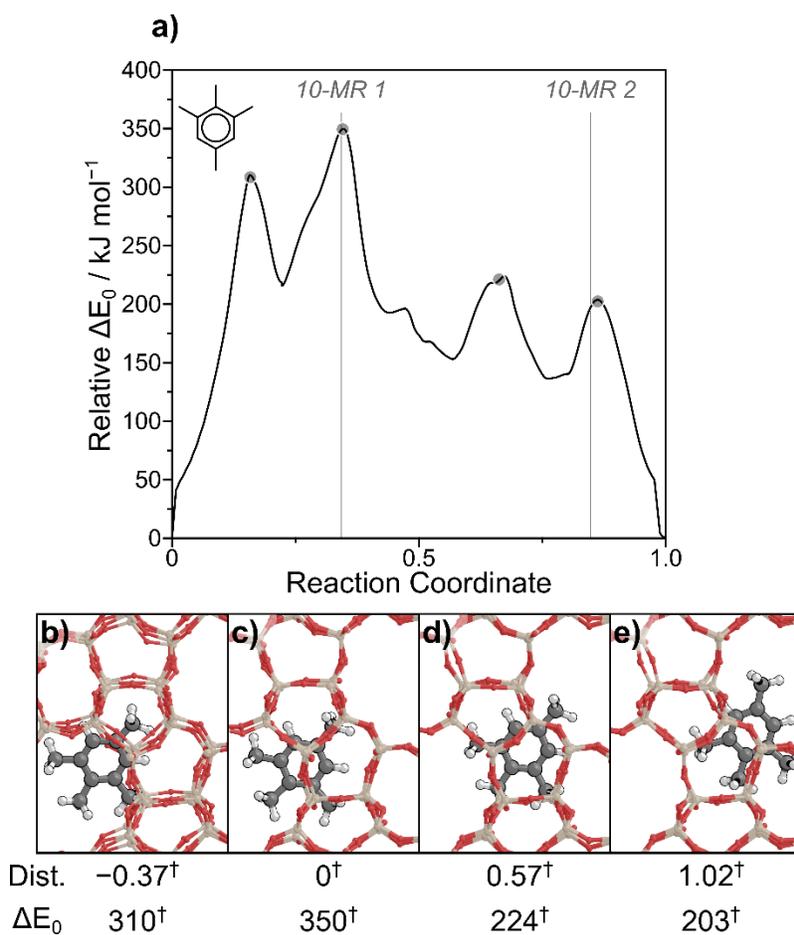


Figure S9. a) Potential energy surface and b–e) transition states of 1,2,3,5-tetramethylbenzene sinusoidal channel diffusion. The distance of the transition state relative to the two 10 MRs (gray lines) and potential energy of the transition states (kJ mol^{-1}) are also reported. Partially filled circles and [†] represents distances values estimated from the potential energy surface.

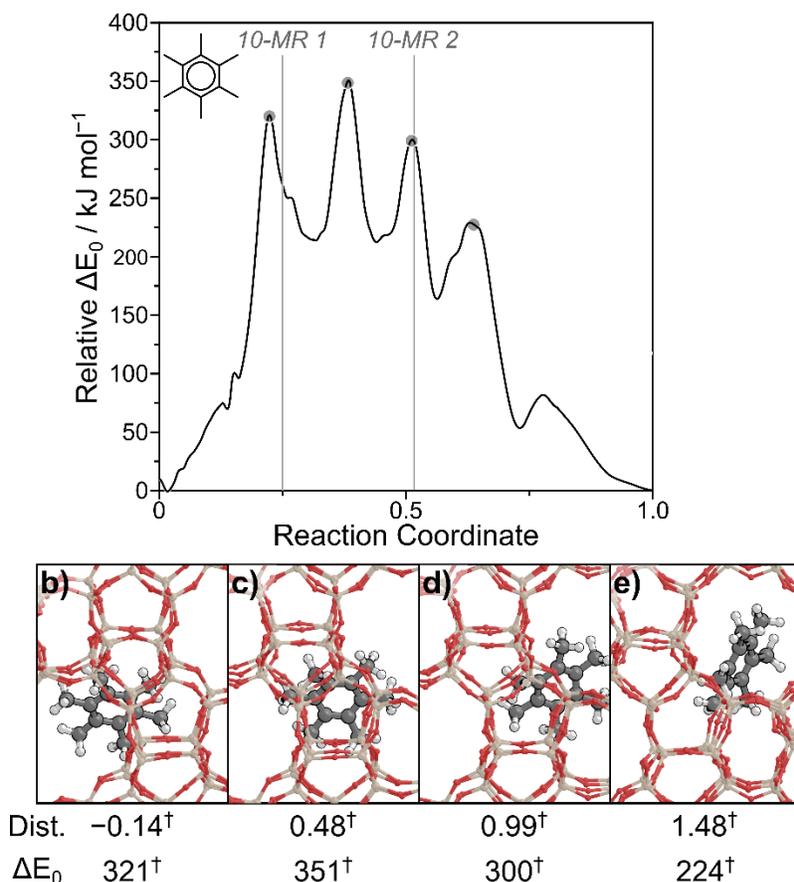


Figure S10. a) Potential energy surface and b–e) transition states of hexamethylbenzene sinusoidal channel diffusion. The distance of the transition state relative to the two 10 MRs (gray lines) and potential energy of the transition states (kJ mol^{-1}) are also reported. Partially filled circles and † represents distances values estimated from the potential energy surface.

S5. Details of 3N-dimensional distance calculations

3N-dimensional distance (Δx_{3N}) is used to quantify the distance between two frameworks with identical unit cell parameters. This distance is calculated here as

$$\Delta x_{3N} = \sqrt{\sum_{i=1}^N (x_i - x'_i)^2 + (y - y'_i)^2 + (z - z'_i)^2}$$

where x_i , y_i , z_i are the coordinates in Å of an atom from one structure and x'_i , y'_i , z'_i are the coordinates in Å of the same atom from the second structure. Here, we take the distance between the initial silicalite-1 structure ($a = 20.090$ Å, $b = 19.738$ Å, $c = 13.142$ Å) and the structure of a given Dimer calculation with the methylbenzene removed (unit cell parameters were fixed during optimization) to obtain the reported 3N-dimensional distances.