

Supplementary Information

Solvent-Tuned Hydrophobicity for Faujasite-Catalyzed Cycloaddition of Biomass-derived Dimethylfuran for Renewable p-Xylene

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I. Simulation details

Adsorption isotherms were calculated using configurational-bias Monte Carlo (CBMC)^{1, 2} simulations in the grand-canonical ensemble, in which the volume, temperature, and fluid chemical potential are kept fixed during the simulation. The criterion for chemical equilibrium is that the chemical potentials for each adsorbate between the adsorbed and bulk phases should be equal. The same equation of state (EOS) used in the determination of the phase equilibria was used for the calculation of the fugacities (or chemical potentials) of the different substances in the reactor.

Lennard-Jones (LJ) 12-6 interaction plus a Coulombic point-charge interaction were used to describe adsorbate-adsorbate and adsorbate-adsorbent interactions. The intermolecular interactions were truncated at a fixed cutoff distance of 12.0 Å with the long-range tail correction applied. The electrostatic interactions were computed using the Ewald summation method³. Standard periodic boundary conditions and the minimum image convention were employed in all three dimensions. The energy-bias scheme devised by Snurr *et al.*⁴ was used to increase the insertion efficiency. A pretabulated potential map on the framework with a grid size of 0.2 Å was also used to speed up the simulations. The simulations were allowed to equilibrate for 2.5×10⁸ Monte Carlo (MC) steps before data production was done with another 2.5×10⁸ MC steps to sample the thermodynamic properties of interest.

Hard cores were assigned to the oxygen, the T atoms and protons in the zeolite lattices. In addition to these zeolite atoms, we also placed hard cores at the center of sodalite cages that are

present in faujasite zeolite structures. This effectively blocked the sodalite cages from adsorbing molecules as the interior of a sodalite cage is expected to be inaccessible by diffusion from the main channels due to the narrowness of the 4-T and 6-T ring apertures of the sodalite cages⁵.

II. Force fields

The force field parameters for the zeolite H-Y (Si/Al=2.6) are listed in Table S1. The zeolite H-Y is composed of silicon, aluminum, oxygen, and proton atoms. The transferrable TraPPE-zeo force field was used here, which was first developed for all-silica zeolites⁶ and then extended to faujasite-type zeolites with low and high Si/Al ratios⁷. The proton charge for the zeolite H-Y model was assigned to +0.4e, which is close to that obtained from the density functional theory (DFT) calculations in Brønsted acid site models for zeolites^{8,9}. The LJ well depth (ϵ) of proton was taken from the ion model of Dang¹⁰, in which the ϵ value for all different ions are assigned to the same value. The LJ collision diameter (σ) of proton was scaled from that of Na⁺ ion developed by Dang¹⁰ and was also close to the σ value of proton deduced from Jousse *et al.*¹¹ using the Lorentz–Berthelot (L-B) combining rules.

The molecular force field parameters are listed in Table S2. For hydrocarbon groups, such as CH₃ or CH₂, the hydrogen atoms are not explicitly represented, but instead a united-atom (UA) force field was used. The ethylene molecule was modeled with an explicit representation of the quadrupole moment via partial charges developed by Weitz and Potoff¹². [The one without the quadrupole moment developed by Jakobtorweihen *et al.*¹³ for alkene adsorption in zeolites was also good. We have compared the calculated ethylene adsorption results to the measured ethylene adsorption in silicalite-1 zeolite using both force field models. The calculated results from both are similar and in reasonably good agreement with experimental data, as shown in Fig. S1. The one with the quadrupole moment used in this work gives slightly better agreement at low loadings.] DMF and p-xylene were modeled using the OPLS parameters¹⁴⁻¹⁶, which have previously been used for the calculation of xylenes adsorbed in zeolites^{17,18}. The water molecules were modeled using the Tip4p model¹⁹, which is suitable for studying adsorption of water in zeolites^{20, 21}. The interactions of n-heptane were modeled using the TraPPE-UA force field²². The L-B combining mixing rules were used to calculate the cross-term interaction parameters for adsorbate-adsorbate and adsorbate-adsorbent interactions. It

has been demonstrated^{6,7} that, by simply combining bulk fluid potential with the TraPPE-zeo force field, the predicted adsorption isotherms for water and a number of hydrocarbons, such as alkanes and alcohols, are in reasonably good agreement with experimental data over a wide range of pressures and temperatures for various zeolites.

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Table S1. LJ parameters and partial charges of the H-Y (Si/Al=2.6) zeolite model in this work. O_{Si} are oxygen atoms bridging two Si atoms and O_{Al} are oxygen atoms bridging one Si and one Al atom. All-silica zeolite force fields are recovered when no Al atoms and cations exist.

Site	ϵ/k_B (K)	σ (Å)	q (e)	Ref.
O_{Si}	53	3.3	-0.75	[6, 7]
Si	22	2.3	1.5	[6, 7]
O_{Al}	58	3.6	-0.8	[7]
Al	24	2.5	1.3	[7]
H	50.3	2.1	0.4	[10]

Table S2. Interaction potential parameters for the fluid molecules used in this study. The water model Tip4p has one dummy atom, labeled as M; CoM is a dummy atom at the center-of-mass position of ethylene.

Interaction Site	ϵ/k_B (K)	σ (Å)	q (e)	Ref.	Site illustration
ethylene					
CH ₂	86	3.71	0.85	[12]	<chem>H2C=CH2</chem>
CH ₂	83	3.72	0.85	[12]	
CoM	0	0	-1.70	[12]	
p-xylene					
C	35.2	3.55	-0.115	[14, 15]	<chem>Cc1ccc(C)cc1</chem>
H	15.1	2.42	0.115	[14, 15]	
CH ₃	85.5	3.80	0.115	[14, 15]	
Water					
O	78.2	3.1536	0.0	[19]	<chem>O</chem>
H	0.0	0.0	0.52	[19]	
M	0.0	0.0	-1.04	[19]	
DMF					
C _s	35.2	3.55	-0.154	[15]	<chem>CN(C)C=O</chem>
C _w	35.2	3.55	-0.019	[15]	
O	70.5	2.90	-0.19	[15]	
H	15.1	2.42	0.126	[15]	
CH ₃	104.16	3.775	0.142	[15, 16]	
n-heptane					
CH ₃	98.0	3.75	0.0	[22]	<chem>CCCCCCC</chem>
CH ₂	46.0	3.95	0.0	[22]	

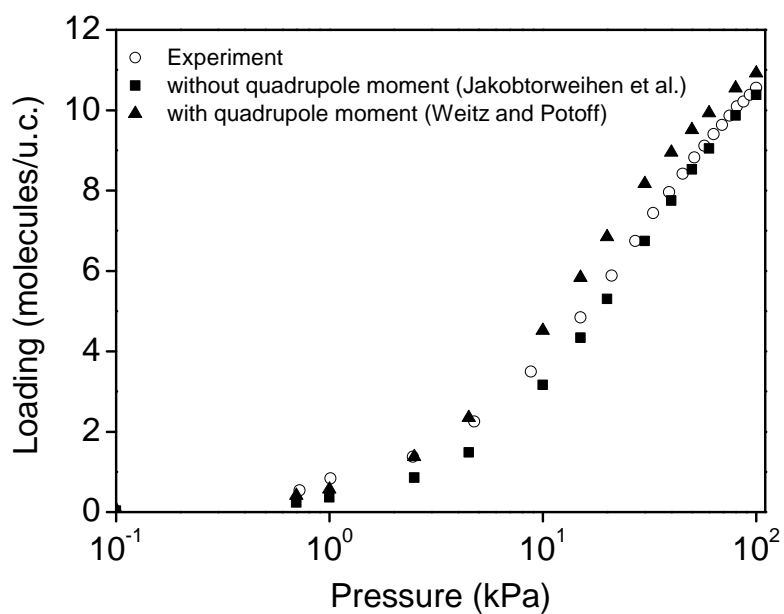


Fig. S1. The calculated ethylene adsorption in silicalite-1 zeolite at 303 K using ethylene force field models with¹² and without¹³ quadrupole moment compared with experimental data²³.