Supporting Information

Impacts of Ethanol and Water Adsorptions on Thermal Conductivity of ZIF-8

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1.Force field parameters

The force field of ZIF-8 with structural flexibility has been developed by Hu et al[1], which can accurately describe the crystalline, mechanical, and thermophysical properties of ZIF-8.[1] In this force field, the bonded interactions include stretching, bending and proper and improper torsional potentials as described by following equations.

$$U_{\text{stretching}} = \sum \frac{1}{2} k_r (r_{ij} - r_{ij}^0)^2 \quad (1)$$

$$U_{\text{bending}} = \sum \frac{1}{2} k_\theta (\theta_{ijk} - \theta_{ijk}^0)^2 \quad (2)$$

$$U_{\text{proper}} = \sum k_\phi [1 + \cos(m\phi_{ijkl} - \phi_{ijkl}^0)] \quad (3)$$

$$U_{\text{improper}} = \sum k_\xi [1 + \cos(m\xi_{ijkl} - \xi_{ijkl}^0)] \quad (4)$$

where k_r, k_θ, k_ϕ, and k_ξ are the force constants; r_{ij}, θ_{ijk}, ϕ_{ijkl}, and ξ_{ijkl} are bond lengths and angles, proper and improper dihedrals, respectively; r_{ij}^0, θ_{ij}^0, ϕ_{ijkl}^0, and ξ_{ijkl}^0 are the equilibrated bond length and angles; m is the multiplicity. The nonbonded interactions include Lennard-Jones (LJ) and Coulombic potentials.

$$U_{\text{LJ}} = \sum 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right] \quad (5)$$

$$U_{\text{Coulombic}} = \sum \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad (6)$$

where σ_{ij} and σ_{ij} are collision diameter and well depth, respectively; q_i is atomic charge; ε_0=8.8542 ×10^{-12} C^{2}N^{-1}m^{-2} is vacuum permittivity.

Ethanol is modeled by the TraPPE[2] force field, in which CH_x groups are treated as pseudoatoms located at the sites of the carbon atoms. Whereas the other atoms (e.g., hydroxyl O and H) are modeled explicitly. All bond lengths are fixed[2] (CH_3-CH_2 : 0.1540 nm ; CH_3-OH: 0.1430 nm; O-

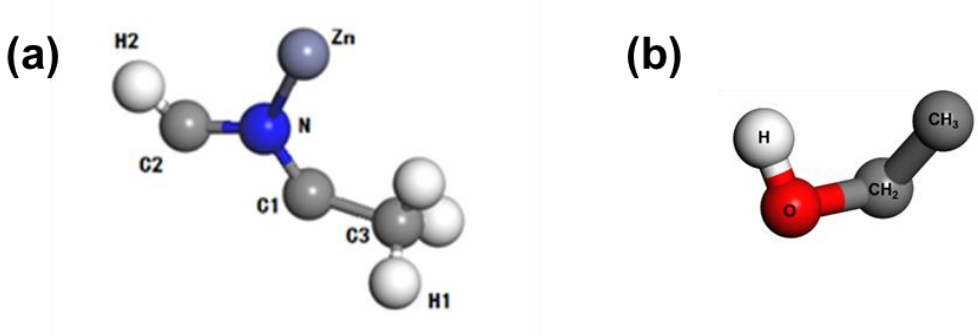

Fig. S1. (a) Atomic types in ZIF-8 and (b) ethanol model

H: 0.0945 nm). The torsional potentials used to restrict the dihedral from the OPLS-UA force field[3] with the Fourier coefficients. [2]

$$U_{\text{proper}} = c_0+c_1[1+\cos(\phi)]+c_2[1-\cos(2\phi)]+c_3[1+\cos(3\phi)] \quad (7)$$

In the TIP4P/2005 model[4], each water molecule has four interaction sites, including a massless M-site located coplanar with the oxygen (O) and hydrogen (H) sites on the bisector of the H–O–H bond angle. The O–H bond length and the H–O–H bond angle are fixed as 0.9572 Å and 104.52°, respectively. Detailed parameters were provided in Table S1-S4.

Table S1. Parameters for bond stretching in ZIF-8 and guest molecules.

Bond stretching			
Species	*i-j*	k_r (10^5 kJ/(mol nm^2))	r_0 (nm)
ZIF-8	Zn-N	0.7000	0.1987
	N-C1	4.0836	0.1340
	N-C2	3.4309	0.1371
	C1-C3	2.6527	0.1493
	C2-C2	4.3346	0.1346
	C2-H2	3.0710	0.0929
	C3-H1	2.8451	0.0960
Ethanol (fixed)	CH_3-CH_2	1.8628	0.1540
	CH_2-OH	3.5830	0.1430
	O-H	4.5626	0.0945
Water (fixed)	OW-HW	5.0264	0.0957

Table S2. Parameters for bond bending potentials in ZIF-8 and guest molecules

Bond bending			
Species	*i-j-k*	k_θ (10^2 kJ/mol)	θ_0 (degree)
ZIF-8	N-Zn-N	1.0000	109.47
	Zn-N-C1	1.7000	128.35
	Zn-N-C2	1.8000	126.40
	C1-N-C2	5.8576	105.24
	N-C1-N	5.8576	112.17
	N-C1-C3	5.8576	123.89
	N-C2-C2	5.8576	108.67
	N-C2-H2	4.1840	125.66
	C2-C2-H2	4.1840	125.67
	C1-C3-H1	4.1840	109.44
	H1-C3-H1	2.9288	109.50
Ethanol	CH_3-(CH_2)-OH	4.1922	109.50
	CH_2-(O)-H	4.6082	108.50
Water (fixed)	HW-OW-HW	6.2830	104.52

Table S3. Parameters for proper and improper torsional potentials in ZIF-8 and ethanol.

Proper torsional					
Species	*i-j-k-l*	k_ϕ (kJ/mol)	θ_0 (degree)		
ZIF-8	Zn–N–C1–N	0.5000	180		
	Zn–N–C1–C3	0.5000	180		
	C2–N–C1–N	20.0832	180		
	C2–N–C1–C3	20.0832	180		
	Zn–N–C2–C2	0.5000	180		
	Zn-N-C2-H2	0.5000	180		
	C1–N–C2–C2	20.0832	180		
	C1–N–C2–H2	20.0832	180		
	N–C2–C2–N	16.7360	180		
	N–C2–C2–H2	16.7360	180		
	H2–C2–C2–H2	16.7360	180		
Ethanol	*i-j-k-l*	C_0(kJ/mol)	C_1(kJ/mol)	C_2(kJ/mol)	C_3(kJ/mol)
	CH_3-(CH_2)-(O)-H	0	3.4906	-0.4853	3.1264
Improper torsional					
Species	*i-j-k-l*	k_ξ (kJ/mol)	ξ_0 (degree)		
ZIF-8	N–Zn–C1–C2	0.4000	180		
	C1–N–N–C3	4.6024	180		
	C2–N–C2–H2	4.6024	180		

Table S4. Lennard-Jones parameters and atomic charges in ZIF-8 and guest molecules.

Species	Atoms	σ (nm)	ε (kJ/mol)	q (e)
ZIF-8	Zn	0.1960	0.0523	+1.0
	N	0.3250	0.7113	-0.5
	C1	0.3400	0.3598	+0.5
	C2	0.3400	0.3598	-0.1
	C3	0.3400	0.4577	-0.3
	H1	0.2650	0.0657	+0.1
	H2	0.2421	0.0628	+0.1
Ethanol	CH_3	0.3750	0.8152	0
	CH_2	0.3950	0.3826	0.2650
	O	0.3020	0.7736	-0.7000
	H	0	0	0.4350
Water	OW	0.3159	0.1852	-1.1128
	HW	0	0	0.5564

2.The effect of different water models on the thermal conductivity and interaction of ZIF-8

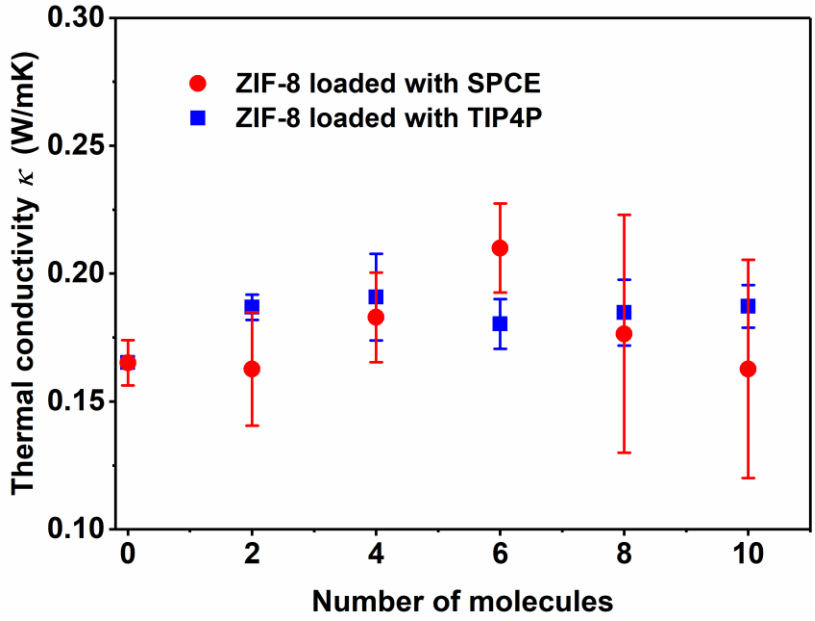

Fig. S2. The thermal conductivity of ZIF-8 loaded with water as a function of adsorbed number of water molecules. There are SPCE (red) and TIP4P (blue) water models, respectively.

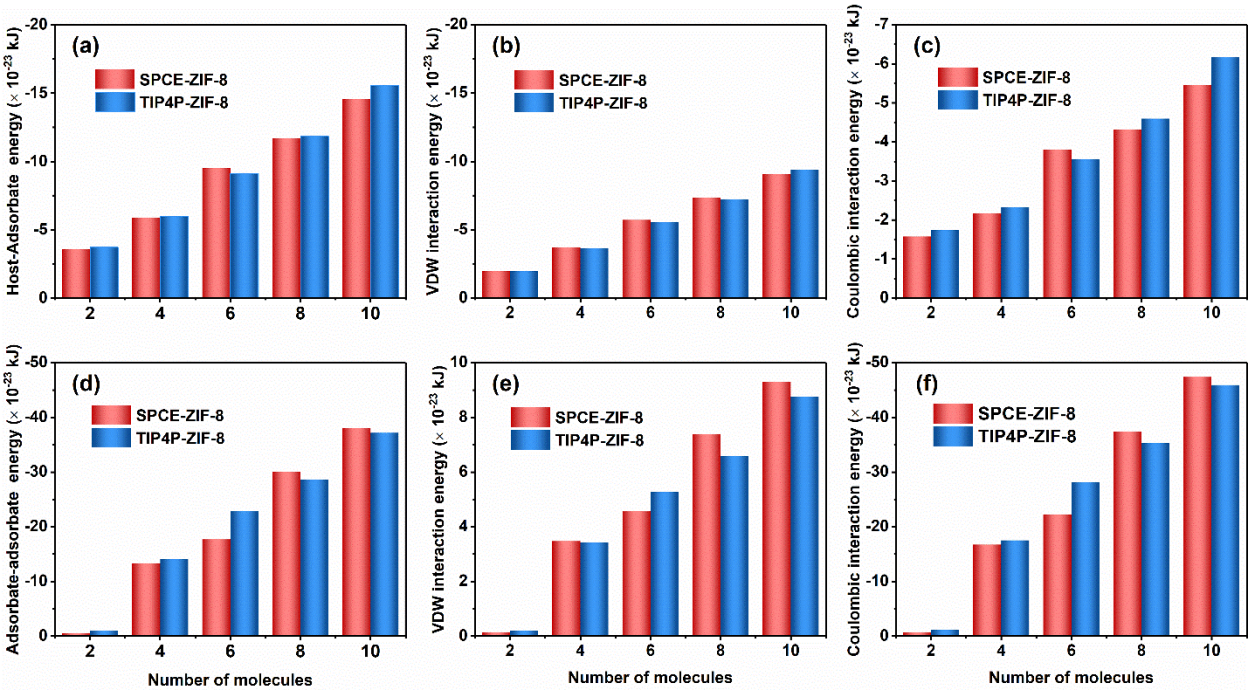

Fig. S3. (a) Host-adsorbate and (d) adsorbate-adsorbate interaction energy as well as the contributions from (b, e) van der Waals and (c,f) Coulombic interactions in ZIF-8 loaded with different water models (SPCE(red) and TIP4P(blue)).

REFERENCES

(1) Hu, Z.; Zhang, L.; Jiang, J. Development of a Force Field for Zeolitic Imidazolate Framework-8 with Structural Flexibility. *J. Chem. Phys.* **2012**, *136*, 244703.
(2) 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.
(3) Jorgensen, W. L. Optimized Intermolecular Potential Functions for Liquid Alcohols. *J. Phys. Chem.* **1986**, *90*, 1276-1284.
(4) Abascal, J. L.; Vega, C. A General Purpose Model for the Condensed Phases of Water: Tip4p/2005. *J. Chem. Phys.* **2005**, *123*, 234505.