Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Biofuel purification in zeolitic imidazolate frameworks: significant role of functional groups

Kang Zhang, Anjaiah Nalaparaju, Yifei Chen, and Jianwen Jiang*

Department of Chemical and Biomolecular Engineering, National University of Singapore, 117576, Singapore

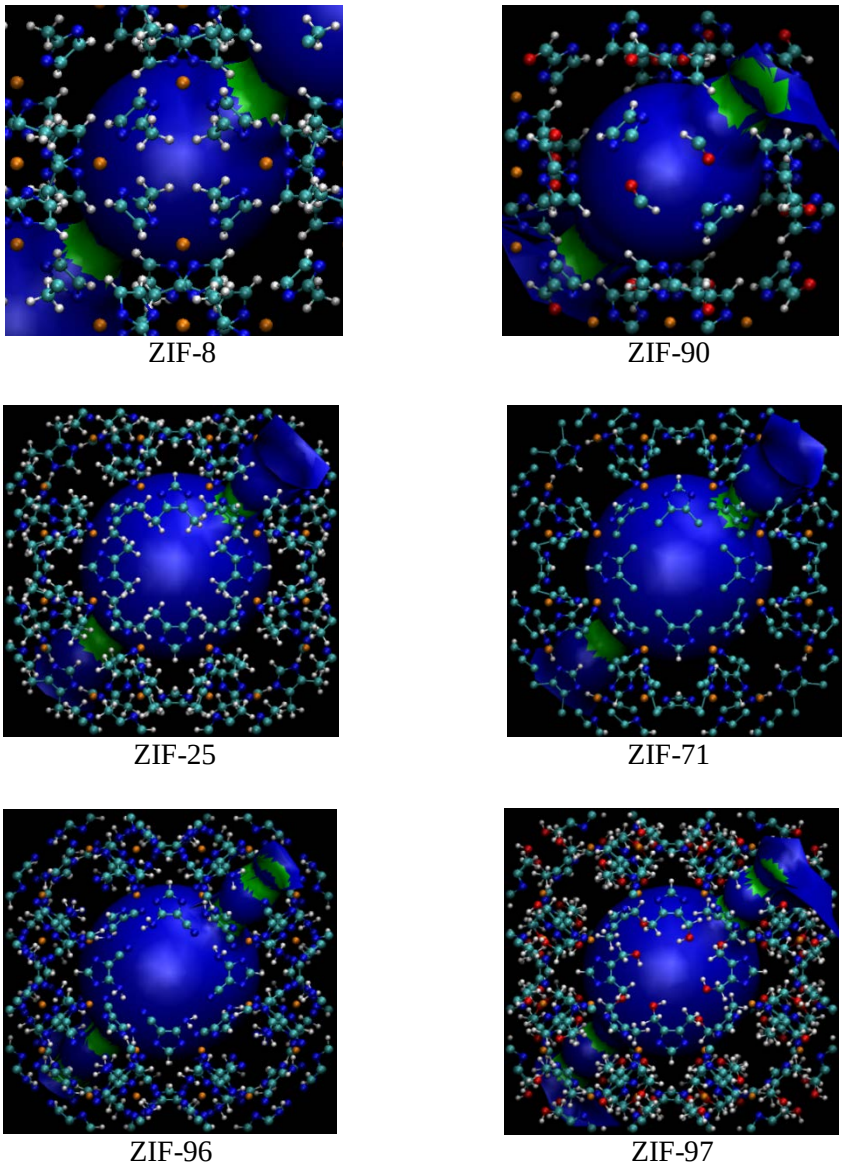

Fig. S1 Pores along the (111) direction in ZIF-8, -90, -25, -71, -96 and -97. The size is not in the same scale.

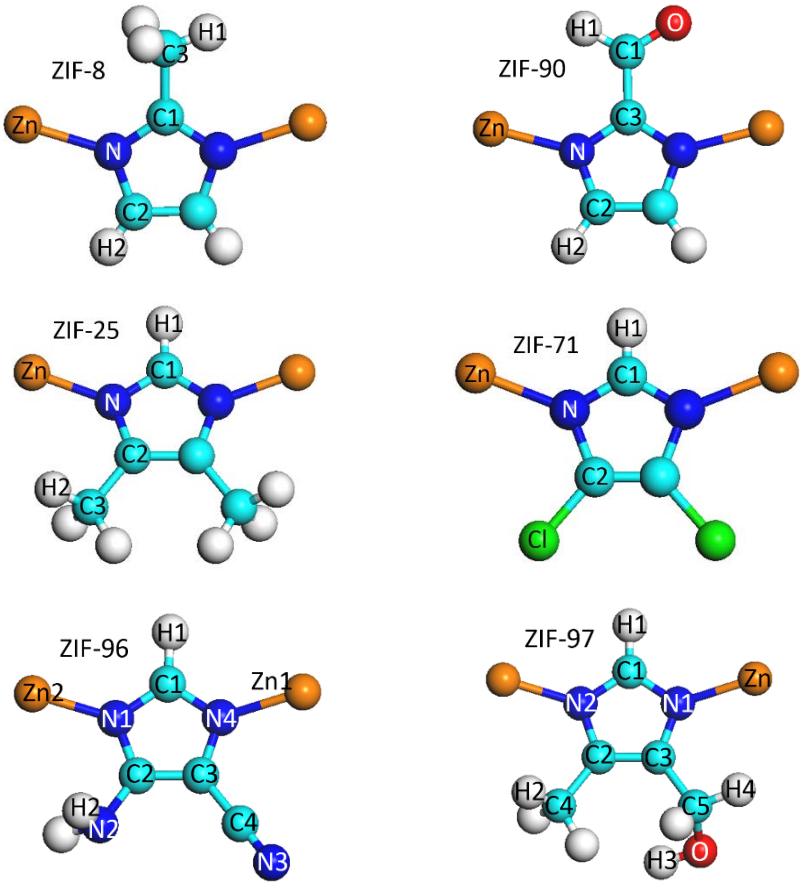

Fig. S2 Fragmental clusters of ZIF-8, -90, -25, -71, -96 and -97.

Table S1. Atomic charges of ZIFs.

ZIF-8	
Atom	Charge (*e*)
Zn	1.0219
N	–0.4973
C1	0.4958
C2	–0.0672
C3	–0.2720
H1	0.0632
H2	0.1023

ZIF-90	
Atom	Charge (*e*)
Zn	0.8311
N	–0.2964
O	–0.5150
C1	0.5118
C2	0.0844
C3	–0.0113
H1	–0.0452
H2	0.0341

ZIF-25	
Atom	Charge (*e*)
Zn	1.0678
N	–0.4356
C1	0.3009
C2	0.1248
C3	–0.1216
H1	–0.0507
H2	0.0134

ZIF-71	
Atom	Charge (*e*)
Zn	0.9553
N	–0.1611
C1	–0.4036
C2	0.1322
Cl	–0.1160
H1	0.2158

ZIF-96	
Atom	Charge (*e*)
Zn1	0.6342
Zn2	0.9203
N1	–0.4847
N2	–0.7835
N3	–0.5257
N4	–0.3627
C1	0.1640
C2	0.5131
C3	–0.1342
C4	0.4781
H1	0.1706
H2	0.2882

ZIF-97	
Atom	Charge (*e*)
Zn	0.7797
N1	–0.3800
N2	–0.2654
O	–0.6790
C1	–0.0008
C2	0.0700
C3	–0.0024
C4	–0.1805
C5	0.2866
H1	0.1882
H2	0.0592
H3	0.3927
H4	0.0011

Table S2. DREIDING force field parameters of ZIF atoms.

Atom	σ (Å)	ε/k_B (K)
Zn	4.045	27.652
N	3.263	38.914
C	3.473	47.813
O	3.033	48.115
Cl	3.519	142.434
H	2.846	7.642

Table S3. Potential parameters of ethanol and water.

	LJ parameters and charges				bond stretching	bond bending
	site	σ (Å)	ε/k_B (K)	charge (e)		
EtOH	CH_3	3.75	98	0	$r_{CH_3\text{-}CH_2}$ = 1.54 Å $r_{CH_2\text{-}O}$ = 1.43 Å $r_{O\text{-}H}$ = 0.945 Å	$\theta^0_{\angle CH_3\text{-}CH_2\text{-}O}$ = 109.47° k_θ/k_B = 50400 K $\theta^0_{\angle CH_2\text{-}O\text{-}H}$ = 108.5° k_θ/k_B = 55400 K
	CH_2	3.95	46	0.265		
	O	3.02	93	–0.7		
	H	0	0	0.435		
H_2O	O	3.151	76.42	–0.834	$r_{O\text{-}H}$ = 0.96 Å	$\theta^0_{\angle H\text{-}O\text{-}H}$ = 104.52°
	H	0	0	0.417		

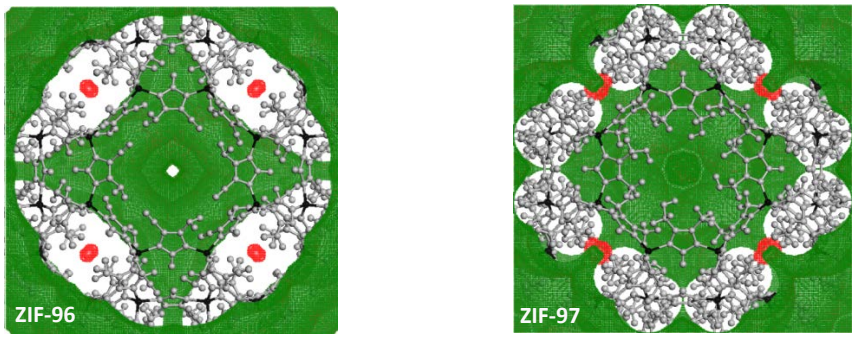

Fig. S3 Accessibility in ZIF-96 and ZIF-97. Green and red represent the accessible and inaccessible regions for ethanol, respectively.

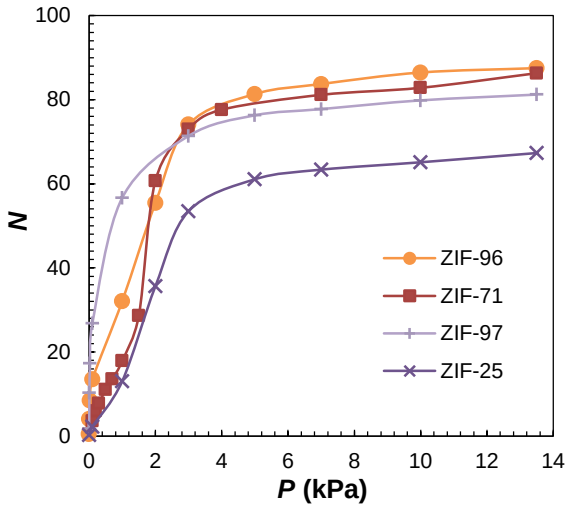

Fig. S4 Adsorption isotherms of EtOH in ZIF-25, -71, -96 and -97 based on the number of molecules in simulation box.

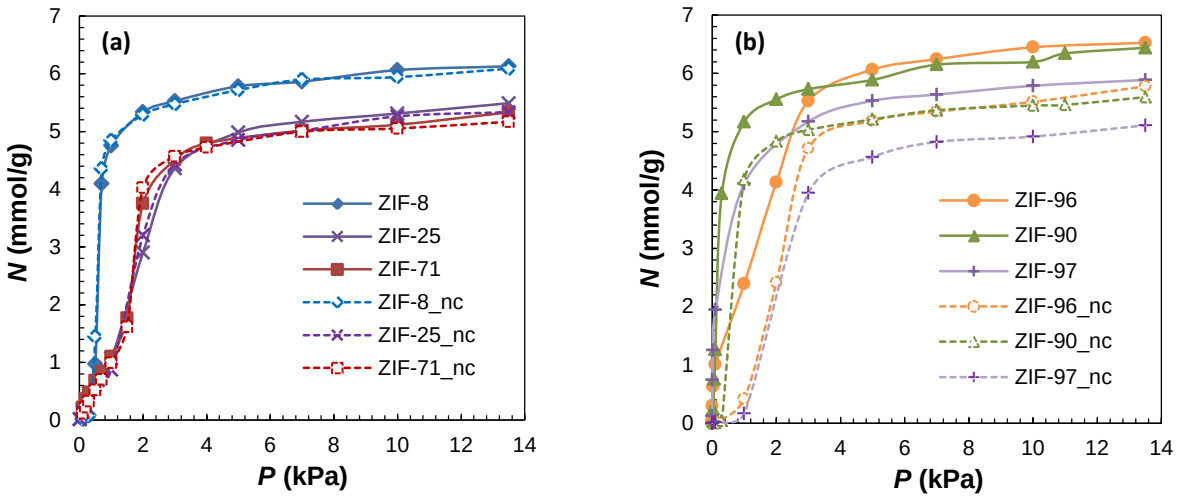

Fig. S5 Adsorption isotherms of EtOH in (a) ZIF-8, -25 and -71 (b) ZIF-90, -96 and -97. The solid and dotted lines denote simulation results with and without atomic charges in ZIFs.

Table S4. Antoine equation parameters of ethanol and water.

$$\log_{10} P(\text{kPa}) = A - \frac{B}{T(\text{K}) + C}$$

	A	B	C
Ethanol	7.24215	1596.044	–46.655
Water	7.11572	1684.123	–43.568

At 298 K, $P^{\text{sat}}_{\text{ethanol}} = 7.80$ kPa and $P^{\text{sat}}_{\text{H}_2\text{O}} = 3.14$ kPa.

At 308 K, $P^{\text{sat}}_{\text{ethanol}} = 13.65$ kPa and $P^{\text{sat}}_{\text{H}_2\text{O}} = 5.58$ kPa.

From Kurihara, K.; Minoura, T.; Takeda, K.; Kojima, K. Isothermal Vapor-Liquid Equilibria for Methanol + Ethanol + Water, Methanol + Water, and Ethanol + Water. *J. Chem. Eng. Data* **1995**, *40*, 679-684.

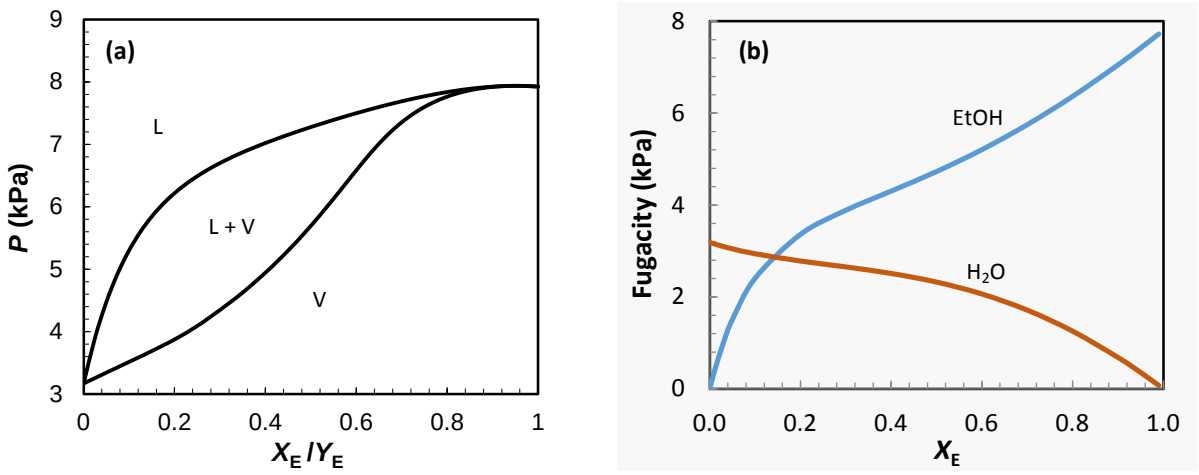

Fig. S6 (a) Vapor-liquid equilibria (b) fugacities of EtOH/H_2O mixtures at 298 K.

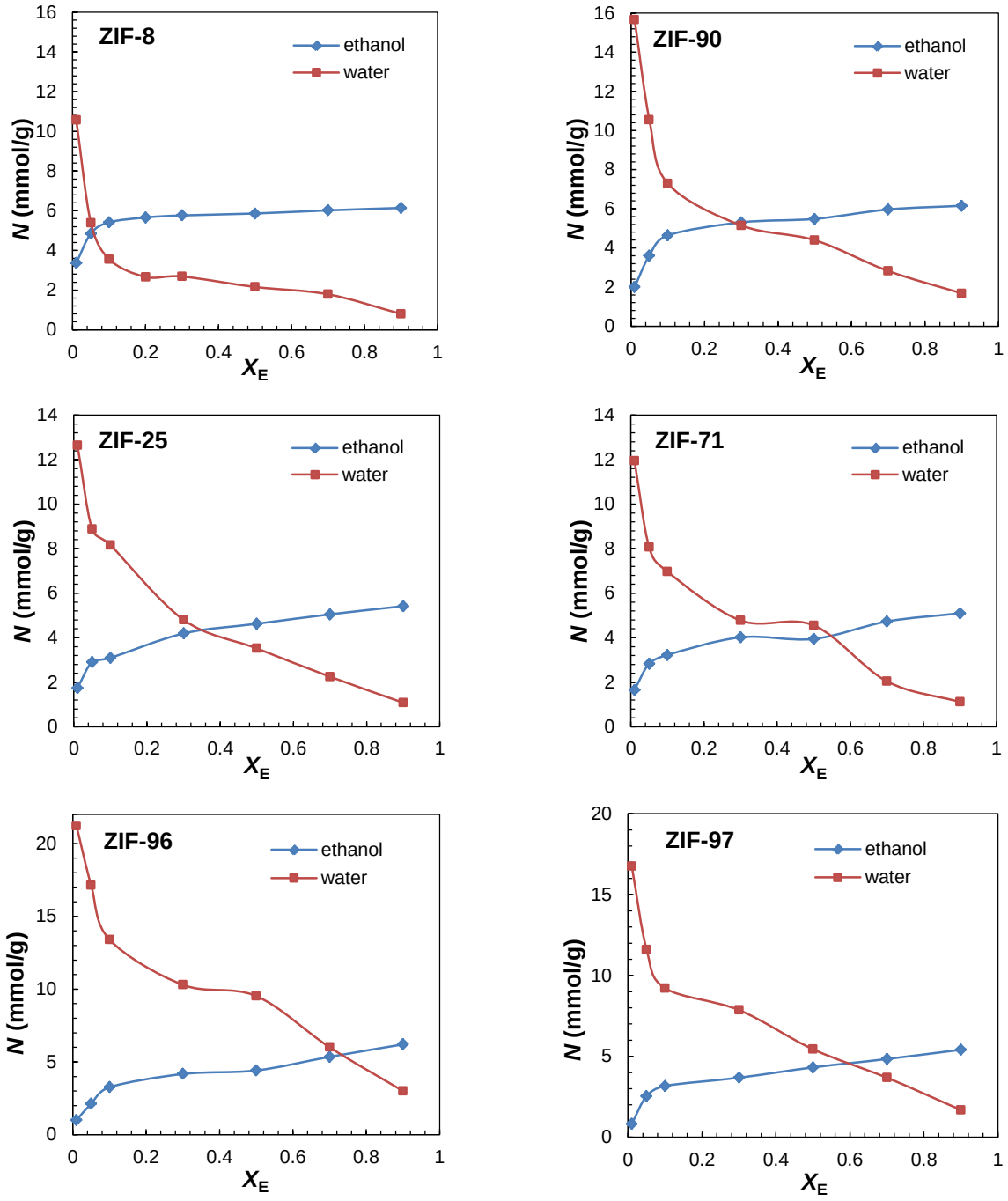

Fig. S7 Adsorption isotherms of EtOH/H_2O mixtures in ZIF-8, -90, -25, -71, -96 and -97 at 298 K.