Supporting Information – Roy. Soc. Chem. Adv. # rscadv-0000-00000z

Force Field for ZIF-8 Flexible Frameworks: Atomistic Simulation on Adsorption, Diffusion of Pure Gases as CH_4, H_2, CO_2 and N_2

Xuanjun Wu[†], Jin Huang[†], Weiquan Cai*[,†] and Mietek Jaroniec[‡]

[†]School of Chemical Engineering, Wuhan University of Technology, Luoshi Road 205#, Wuhan 430070, P. R. China

[‡]Department of Chemistry, Kent State University, Kent, Ohio, 44242, USA

Force field parameters for guest molecules and host framework of ZIF-8 used in this work and the lattice constants for four different initial structures of ZIF-8 are shown in Tables S1-S3.Their six-ring windows are shown in Figure S1.

Table S1. Force field parameters for ZIF-8 flexible framework.

Bond type	K_b *(kcal·mol^{-1}·Å^{-2})*	b_0 *(Å)*
C1-C3	317.000	1.492
C1-N	488.000	1.339
C2-N	410.000	1.371
C2-H2	367.000	0.929
C2-C2	518.000	1.346
C3-H3	340.000	0.959
Zn-N	86.000	1.987
Angle type	K_θ *(kcal·mol^{-1}·rad^{-2})*	θ_0 *(°)*
N-C1-N	70.000	112.17

N-C1-C3	70.000		123.89
C2-C2-N	70.000		108.67
C2-C2-H2	50.000		125.67
N-C2-H2	50.000		125.66
C1-C3-H3	50.000		109.44
C1-N-C2	70.000		105.24
C1-N-Zn	50.000		127.50
C2-N-Zn	35.000		128.00
N-Zn-N	10.500		109.47
H3-C3-H3	35.000		109.50
Dihedral type[a]	K_φ *(kcal·mol*$^{-1}$*)*	*n*	φ_0 (°)
C2-N-C1-N	4.800	2	180.0
C2-N-C1-C3	4.150	2	180.0
C1-N-C2-C2	4.800	2	180.0
C1-N-C2-H2	4.800	2	180.0
N-C2-C2-N	4.000	2	180.0
N-C2-C2-H2	4.000	2	180.0
H2-C2-C2-H2	4.000	2	180.0
Zn-N-C1-N	0.100	2	180.0
Zn-N-C1-C3	0.100	2	180.0
Zn-N-C2-C2	0.100	2	180.0
N-Zn-N-C1	0.174	3	0.0
N-Zn-N-C2	0.174	3	0.0
Improper type	K_ψ *(kcal·mol*$^{-1}$*·rad*$^{-2}$*)*	*n*	ψ_0 (°)

N-C3-C1-N	1.100	2	180.0
C2-H2-C2-N	1.100	2	180.0
Atom type	*E (kcal·mol^{-1})*	*Σ (Å)*	*q (e)*
Zn	0.0787	2.462	+0.6918
N	0.0438	3.261	-0.3879
C1	0.0667	3.431	+0.4291
C2	0.0667	3.431	-0.0839
C3	0.0667	3.431	-0.4526
H2	0.0279	2.571	+0.1128
H3	0.0279	2.571	+0.1325, +0.1306

Table S2. Interaction parameters for various gas molecules.

	CO_2		
Atom type	*ε (K)*	*σ (Å)*	*q (e)*
C	28.129	2.757	0.6512
O	80.507	3.033	-0.3256
d_{C-O} (Å)	1.149		
	N_2		
N	36.433	3.32	-0.482
COM			0.964
d_{COM-N} (Å)	0.55		
	CH_4		
CH_4	148.0	3.73	0.0
	H_2		

H_2	34.2	2.96	0.0

Table S3. Lattice parameters and the pore free volume of various ZIF-8 frameworks.

ZIF-8 frameworks type	$d_{aperture}$*(Å)*	d_{pore}*(Å)*	*lattice constant(Å)*	*pore volume(cm³/g)*
ZIF-8[1]	3.4	11.6	16.991	0.59
ZIF8HL[2]	3.4	11.6	17.070999	0.61
ZIF8_ja3[3]	3.4	11.6	17.107269	0.61
ZIF8_55CH4UC	3.4	11.6	16.991	0.59

d_{pore} is pore diameters, and $d_{aperture}$ is pore aperture.

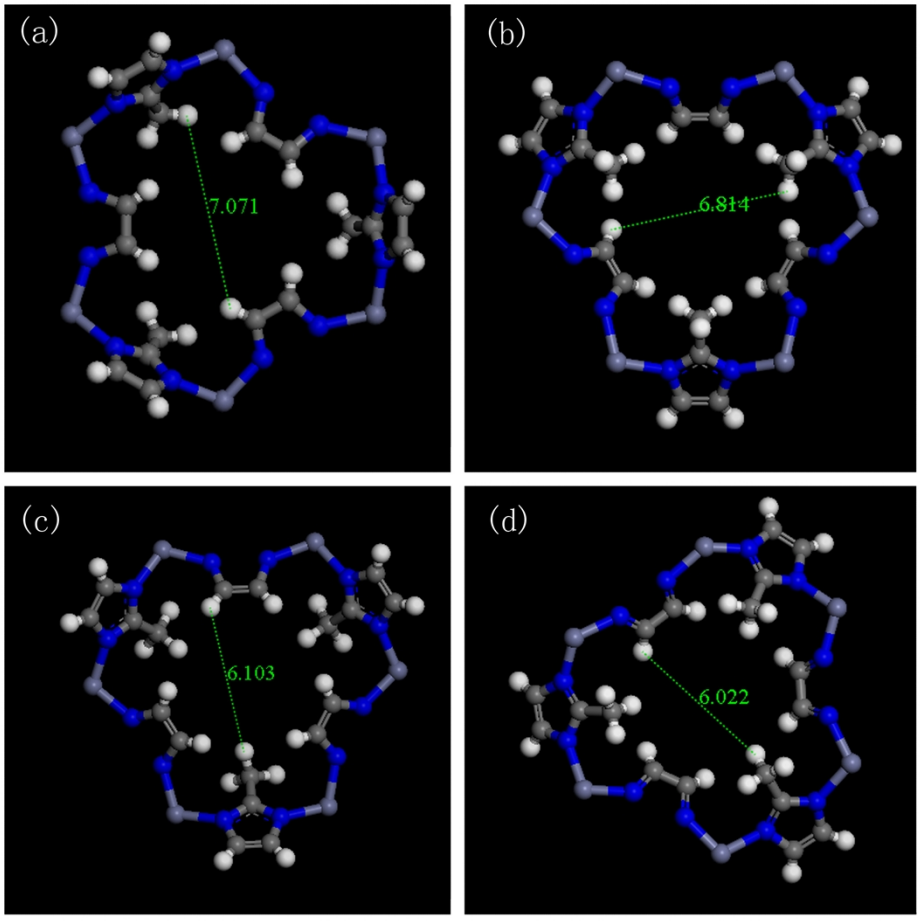

Figure S1. Six-ring windows of (a)ZIF-8 (b) ZIF8HL (c)ZIF8_ja3 (d)ZIF8_55CH4UC.

N_2 adsorption isotherms at 77 K and CH_4 adsorption isotherms at 240 K for ZIF-8 are shown in Figures S2-S3, computed by GCMC simulations using the proposed force field in this work and that of Zhang et al.[4] in comparison to the experimental data reported by Zhou et al.[5] and Park et al[1], respectively.

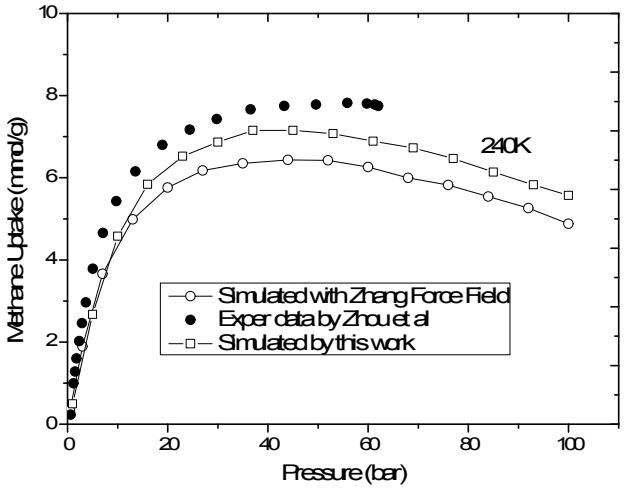

Figure S2. Adsorption isotherms for CH_4 on ZIF-8 at 240 K. The circles refer to the experimental data from Ref. (5)

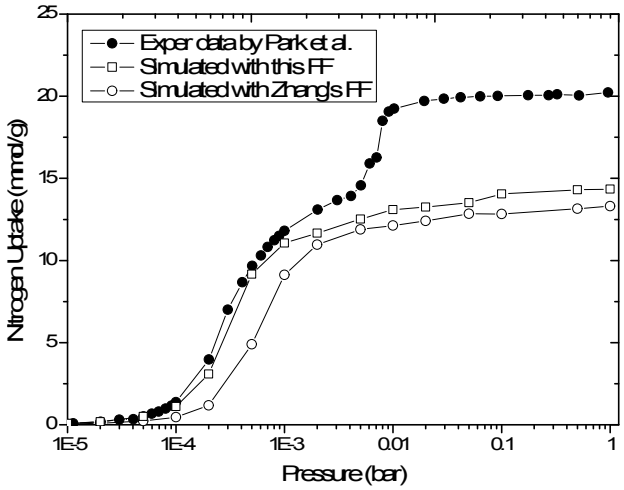

Figure S3. Adsorption isotherms for N_2 on ZIF-8 at 77 K. The circles refer to the experimental data from Ref. (1)

REFERENCES

1. K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, 103, 10186-10191.
2. S. A. Moggach, T. D. Bennett and A. K. Cheetham, *Angew. Chem. Int. Ed.*, 2009, 48, 7087-7089.
3. D. Fairen-Jimenez, S. A. Moggach, M. T. Wharmby, P. A. Wright, S. Parsons and T. Dueren, *J. Am. Chem. Soc.*, 2011, 133, 8900-8902.
4. L. Zhang, Z. Hu and J. Jiang, *J. Am. Chem. Soc.*, 2013, 135, 3722-3728.
5. W. Zhou, H. Wu, M. R. Hartman and T. Yildirim, *J. Phys. Chem. C*, 2007, 111, 16131-16137.