A comparative molecular simulation study of CO_2/N_2 and CH_4/N_2 separation in zeolites and metal-organic frameworks

Bei Liu and Berend Smit

Supporting Information

The force field parameters for zeolites and MOFs used in this work are given in Tables 1-5.

Table 1. Partial charges and LJ potential parameters for adsorbate-adsorbate and adsorbate-zeolites interactions. σ_{ij} (Å) value is in the Upper Left Corner and ε_{ij}/k_B (K) is in the Lower Right Corner of Each Field.

	O_{zeo}	Si_{zeo}	C_{co2}	O_{co2}	N	Dummy(N_2)
charge	-1.025	2.05	0.6512	-0.3256	-0.40484	0.80968

	O_{zeo}	CH_4	C_{co2}	O_{co2}	N
CH_4	3.47 115	3.72 158.5	3.24 66.77	3.38 112.96	3.52 75.96
C_{co2}	2.7815 50.2	3.24 66.77	2.76 28.129	2.89 47.59	3.04 32.0
O_{co2}	2.9195 84.93	3.38 112.96	2.89 47.59	3.033 80.507	3.18 54.13
N	3.062 58.25	3.52 75.96	3.04 32.0	3.18 54.13	3.32 36.4

Table 2. Partial charges and LJ potential parameters for adsorbate-adsorbate and adsorbate-Cu-BTC interactions.

	Cu	O	$C_{Carboxyl}$	$C^1_{Benzene}$	$C^2_{Benzene}$	H	C_{co2}	O_{co2}	N	Dummy(N_2)
charge	1.098	-0.665	0.778	-0.092	-0.014	0.109	0.7	-0.35	-0.482	0.964

	CH_4	C_{co2}	O_{co2}	N
atom-atom σ (Å)	3.73	2.8	3.05	3.31
atom-atom ε/k_B (K)	148.0	27.0	79.0	36.0

Atom	CH_4		CO_2		N_2	
	σ (Å)	ε/k_B (K)	σ (Å)	ε/k_B (K)	σ (Å)	ε/k_B (K)
Cu	3.11	2.52	3.11	2.52	3.11	2.52
O	2.96	61.29	2.96	73.98	2.96	63.41
$C_{Carboxyl}$	3.75	42.27	3.75	44.91	3.75	39.63
$C^1_{Benzene}$	3.55	35.23	3.55	35.23	3.55	35.23
$C^2_{Benzene}$	3.55	35.23	3.55	35.23	3.55	35.23
H	2.42	15.10	2.42	15.10	2.42	15.10

Table 3 . Partial charges and LJ potential parameters for adsorbate-adsorbate and adsorbate-IRMOF-1 interactions.

	Zn	$O_{Zn\text{-}O\text{-}Zn}$	$O_{Zn\text{-}O\text{-}C_{Carboxyl}}$	$C_{Carboxyl}$	$C^1_{Benzene}$	$C^2_{Benzene}$	H
charge	1.501	-1.846	-0.724	0.667	0.072	-0.132	0.140

	C_{co2}	O_{co2}	N	Dummy(N_2)
charge	0.7	-0.35	-0.482	0.964

	CH_4	C_{co2}	O_{co2}	N
atom-atom σ_{ij} (Å)	3.73	2.8	3.05	3.31
atom-atom ε_{ij}/k_B (K)	148.0	27.0	79.0	36.0

Atom	CH_4		CO_2		N_2	
	σ (Å)	ε / k_B (K)	σ (Å)	ε / k_B (K)	σ (Å)	ε / k_B (K)
Zn	2.46	62.4	2.46	62.4	2.46	62.4
$O_{Zn\text{-}O\text{-}Zn}$	3.12	30.19	3.12	30.19	3.12	30.19
$O_{Zn\text{-}O\text{-}C_{Carboxyl}}$	3.12	30.19	3.12	30.19	3.12	30.19
$C_{Carboxyl}$	3.43	52.84	3.43	52.84	3.43	52.84
$C^1_{Benzene}$	3.43	52.84	3.43	52.84	3.43	52.84
$C^2_{Benzene}$	3.43	52.84	3.43	52.84	3.43	52.84
H	2.57	22.14	2.57	22.14	2.57	22.14

Table 4 . Partial charges and LJ potential parameters for adsorbate-adsorbate and adsorbate-IRMOF-11/IRMOF-12 interactions.

	Zn	$O_{Zn\text{-}O\text{-}Zn}$	$O_{Zn\text{-}O\text{-}C_{Carboxyl}}$	H_1	H_2
charge	1.576	-1.924	-0.799	0.107	0.027

	$C_{Carboxyl}$	$C^1_{Benzene}$	$C^2_{Benzene}$	$C^3_{Benzene}$	$C^4_{Benzene}$	$C^5_{Benzene}$
charge	0.878	-0.045	-0.166	0.036	0.045	-0.036

	C_{co2}	O_{co2}	N	Dummy(N_2)
charge	0.7	-0.35	-0.482	0.964

	CH_4	C_{co2}	O_{co2}	N
atom-atom σ_{ij} (Å)	3.73	2.8	3.05	3.31
atom-atom ε_{ij}/k_B (K)	148.0	27.0	79.0	36.0

Atom	CH_4		CO_2		N_2	
	σ (Å)	ε/k_B (K)	σ (Å)	ε/k_B (K)	σ (Å)	ε/k_B (K)
Zn	2.46	62.4	2.46	62.4	2.46	62.4
$O_{Zn\text{-}O\text{-}Zn}$	3.12	30.19	3.12	30.19	3.12	30.19
$O_{Zn\text{-}O\text{-}C_{Carboxyl}}$	3.12	30.19	3.12	30.19	3.12	30.19
$C_{Carboxyl}$	3.43	52.84	3.43	52.84	3.43	52.84
$C^1_{Benzene}$	3.43	52.84	3.43	52.84	3.43	52.84
$C^2_{Benzene}$	3.43	52.84	3.43	52.84	3.43	52.84
$C^3_{Benzene}$	3.43	52.84	3.43	52.84	3.43	52.84
$C^4_{Benzene}$	3.43	52.84	3.43	52.84	3.43	52.84
$C^5_{Benzene}$	3.43	52.84	3.43	52.84	3.43	52.84
H_1	2.57	22.14	2.57	22.14	2.57	22.14
H_2	2.57	22.14	2.57	22.14	2.57	22.14

Table 5. Partial charges and LJ potential parameters for adsorbate-adsorbate and adsorbate-IRMOF-13/IRMOF-14 interactions.

	Zn	$O_{Zn\text{-}O\text{-}Zn}$	$O_{Zn\text{-}O\text{-}C_{Carboxyl}}$	H_1	H_2
charge	1.563	-1.950	-0.799	0.187	0.127

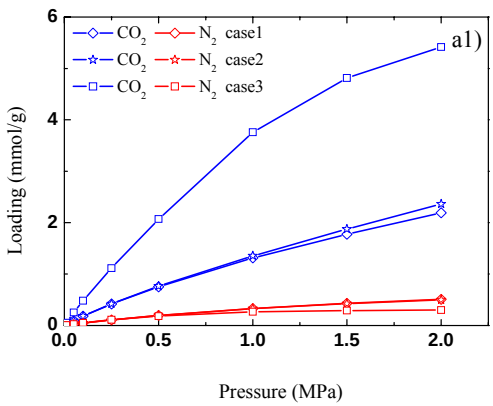
	$C_{Carboxyl}$	$C^1_{Benzene}$	$C^2_{Benzene}$	$C^3_{Benzene}$	$C^4_{Benzene}$	$C^5_{Benzene}$
charge	0.805	0.114	-0.307	0.176	-0.204	0.004

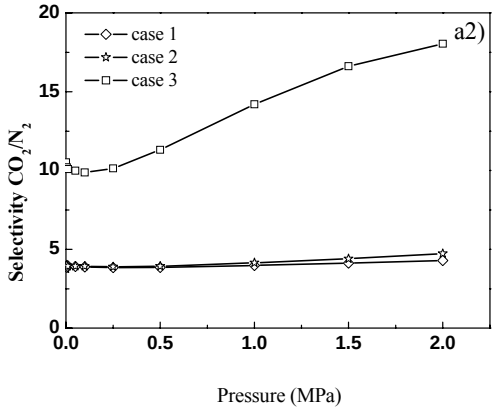
	C_{co2}	O_{co2}	N	Dummy(N_2)
charge	0.7	-0.35	-0.482	0.964

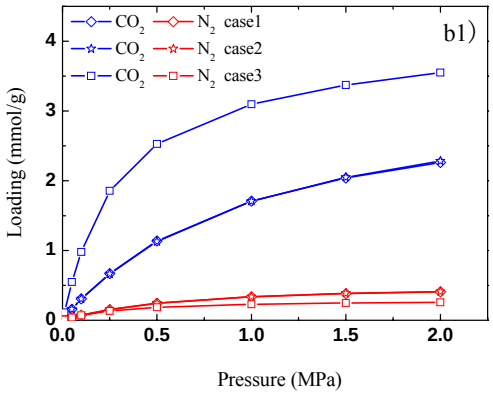
	CH_4	C_{co2}	O_{co2}	N
atom-atom σ_{ij} (Å)	3.73	2.8	3.05	3.31
atom-atom ε_{ij}/k_B (K)	148.0	27.0	79.0	36.0

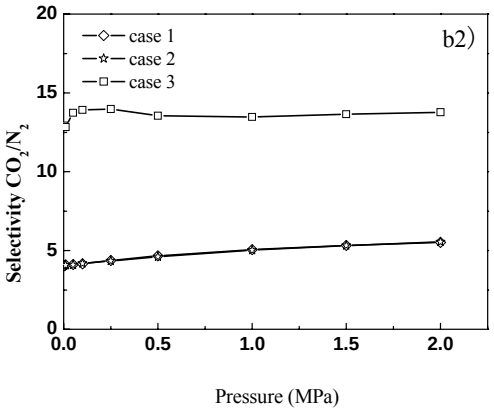
Atom	CH_4		CO_2		N_2	
	σ (Å)	ε/k_B (K)	σ (Å)	ε/k_B (K)	σ (Å)	ε/k_B (K)
Zn	2.46	62.4	2.46	62.4	2.46	62.4
$O_{Zn\text{-}O\text{-}Zn}$	3.12	30.19	3.12	30.19	3.12	30.19
$O_{Zn\text{-}O\text{-}C_{Carboxyl}}$	3.12	30.19	3.12	30.19	3.12	30.19
$C_{Carboxyl}$	3.43	52.84	3.43	52.84	3.43	52.84
$C^1_{Benzene}$	3.43	52.84	3.43	52.84	3.43	52.84
$C^2_{Benzene}$	3.43	52.84	3.43	52.84	3.43	52.84
$C^3_{Benzene}$	3.43	52.84	3.43	52.84	3.43	52.84
$C^4_{Benzene}$	3.43	52.84	3.43	52.84	3.43	52.84
$C^5_{Benzene}$	3.43	52.84	3.43	52.84	3.43	52.84
H_1	2.57	22.14	2.57	22.14	2.57	22.14
H_2	2.57	22.14	2.57	22.14	2.57	22.14

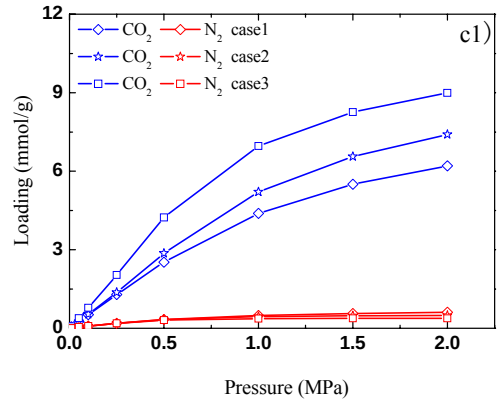
Figures 1a-1h show the effect of electrostatic interactions on the adsorption isotherms of CO_2/N_2 mixture and the adsorption selectivities for CO_2 from equimolar binary mixture simulations of CO_2/N_2 in a) LTA, b) DDR, c) MIL-47 (V), d) IRMOF-1, e) IRMOF-11, f) IRMOF-12, g) IRMOF-13, and h) IRMOF-14. In these figures, case 1 denotes the simulations by switching off all the electrostatic interactions involved by CO_2 and N_2 molecules; case 2 denotes the simulations by witching off only the electrostatic interactions of CO_2-adsorbents and N_2-adsorbents; case 3 denotes the simulations where the results with all the electrostatic interactions are considered.







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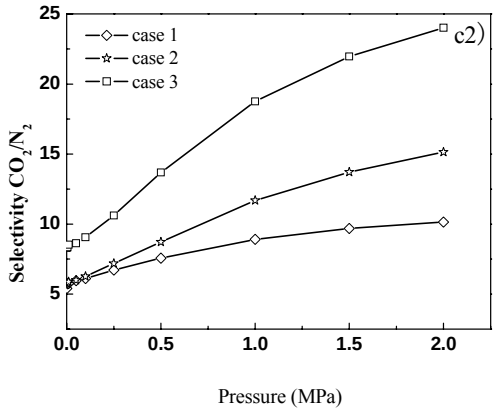
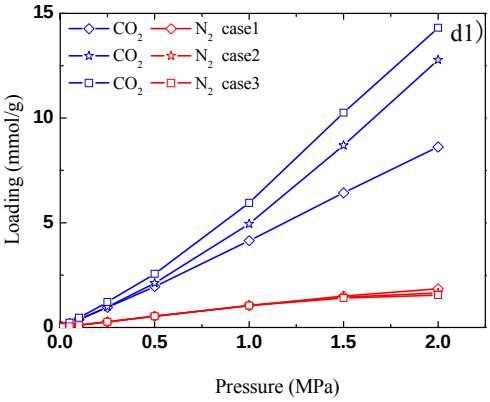
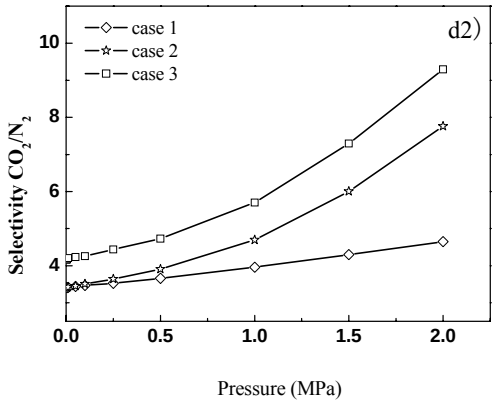
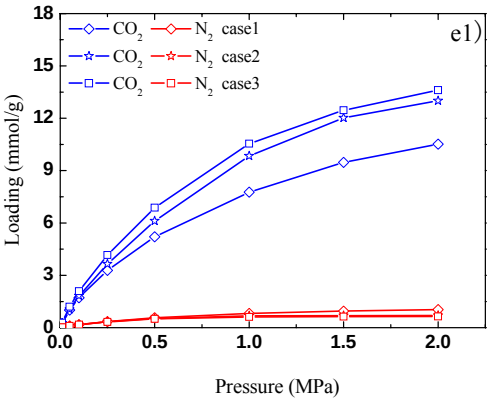
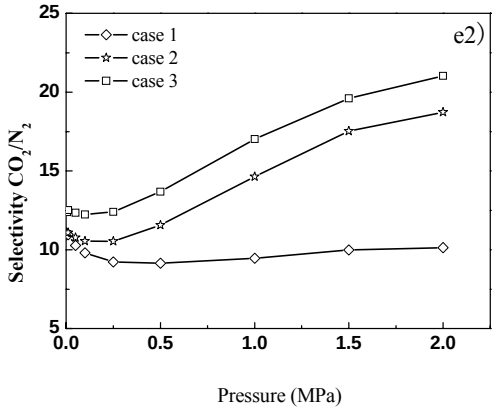
CO2 N2 case1
CO2 N2 case2
CO2 N2 case3
Loading (mmol/g)
Pressure (MPa)


c2)
case 1
case 2
case 3
Selectivity CO2/N2
Pressure (MPa)


d1)
CO2 N2 case1
CO2 N2 case2
CO2 N2 case3
Loading (mmol/g)
Pressure (MPa)


d2)
case 1
case 2
case 3
Selectivity CO2/N2
Pressure (MPa)


e1)
CO2 N2 case1
CO2 N2 case2
CO2 N2 case3
Loading (mmol/g)
Pressure (MPa)


e2)
case 1
case 2
case 3
Selectivity CO2/N2
Pressure (MPa)

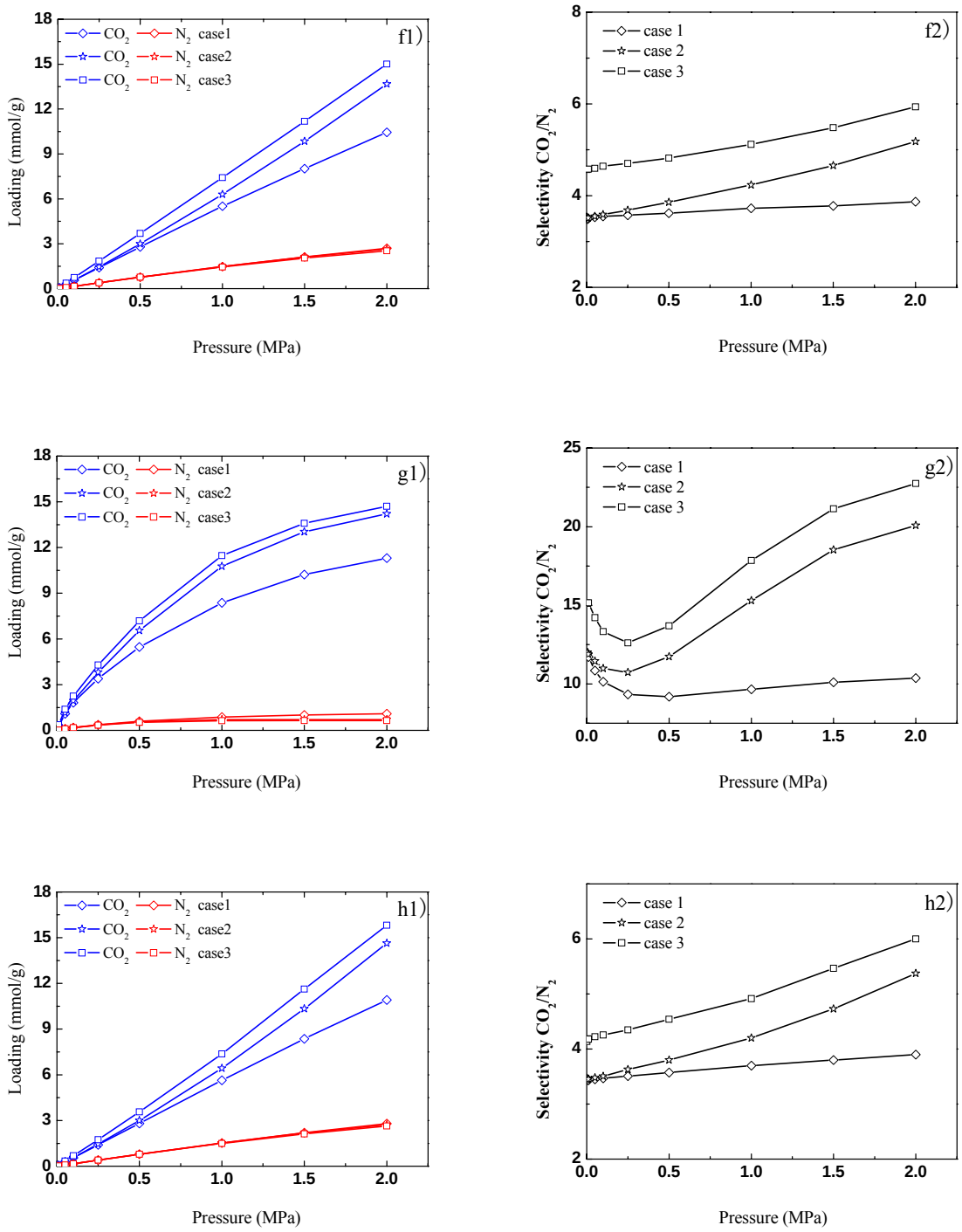
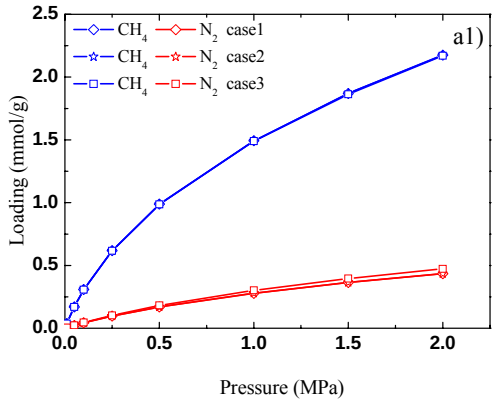
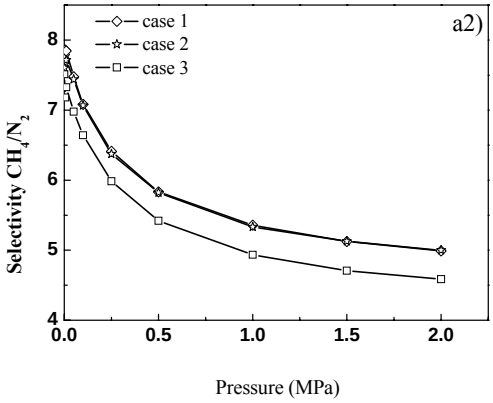
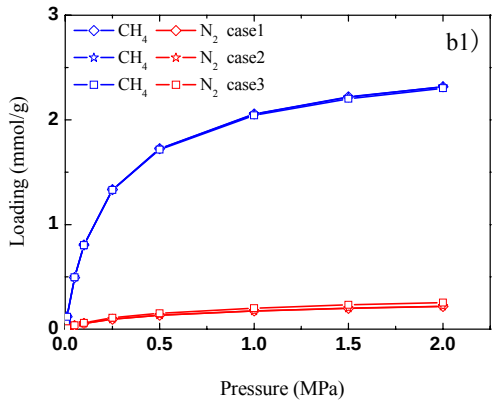


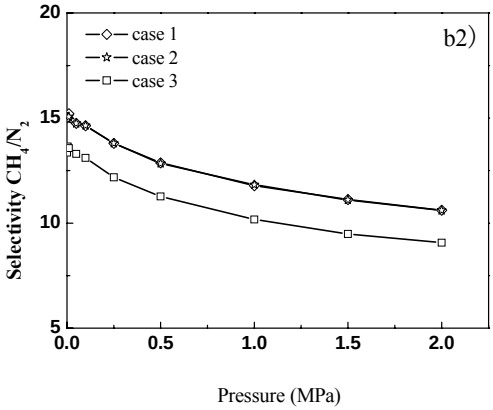
Figure 1. Effect of the electrostatic interactions on 1) the adsorption isotherms of CO_2/N_2 mixture and 2) the adsorption selectivities for CO_2 from equimolar binary mixture simulations of CO_2/N_2 in a) LTA, b) DDR, c) MIL-47 (V), d) IRMOF-1, e) IRMOF-11, f) IRMOF-12, g) IRMOF-13, and h) IRMOF-14.

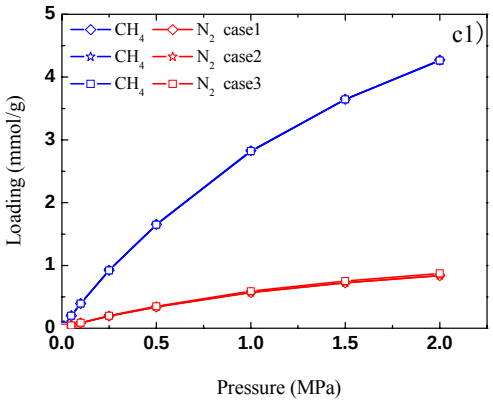
Figures 2a-2h show the effect of electrostatic interactions on the adsorption isotherms of CH_4/N_2 mixture and the adsorption selectivities for CH_4 from equimolar binary mixture simulations of CH_4/N_2 in a) LTA, b) DDR, c) MIL-47 (V), d) IRMOF-1, e) IRMOF-11, f) IRMOF-12, g) IRMOF-13, and h) IRMOF-14. Cases 1, 2, and 3 are same as the ones in Figure 1.







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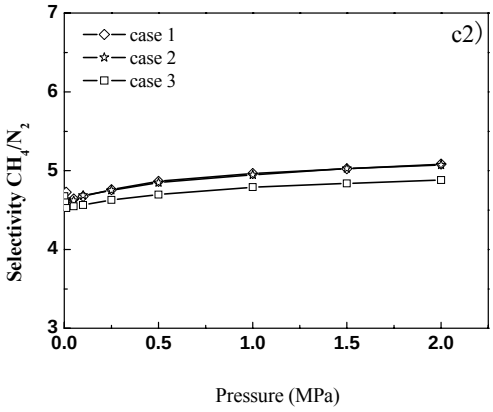
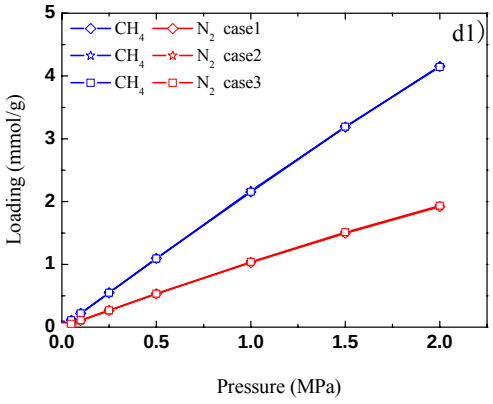
CH4 N2 case1
CH4 N2 case2
CH4 N2 case3
Loading (mmol/g)
Pressure (MPa)


c2)
case 1
case 2
case 3
Selectivity CH4/N2
Pressure (MPa)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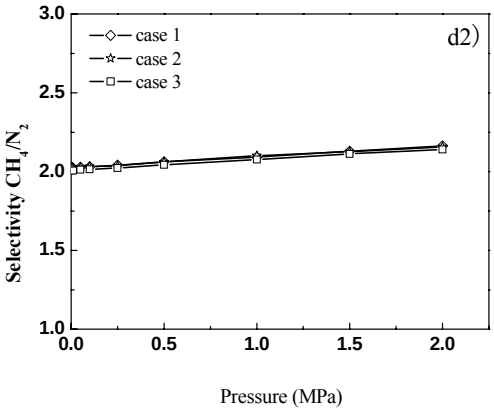
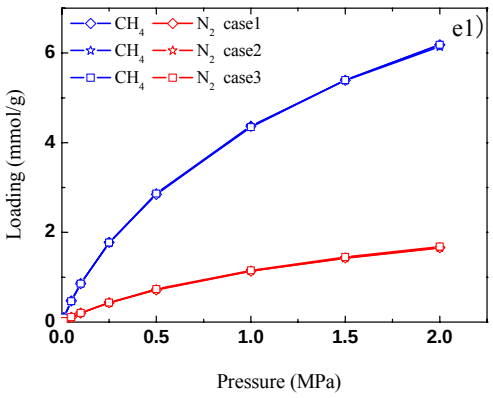
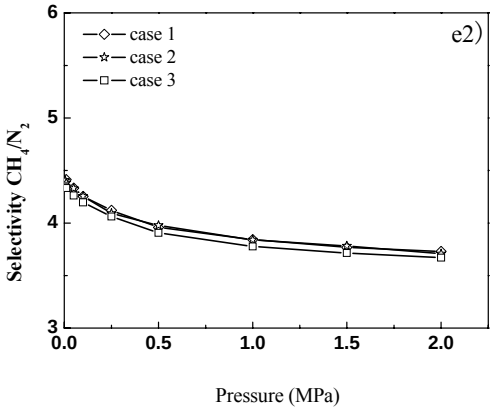
CH4 N2 case1
CH4 N2 case2
CH4 N2 case3
Loading (mmol/g)
Pressure (MPa)


d2)
case 1
case 2
case 3
Selectivity CH4/N2
Pressure (MPa)


e1)
CH4 N2 case1
CH4 N2 case2
CH4 N2 case3
Loading (mmol/g)
Pressure (MPa)


e2)
case 1
case 2
case 3
Selectivity CH4/N2
Pressure (MPa)

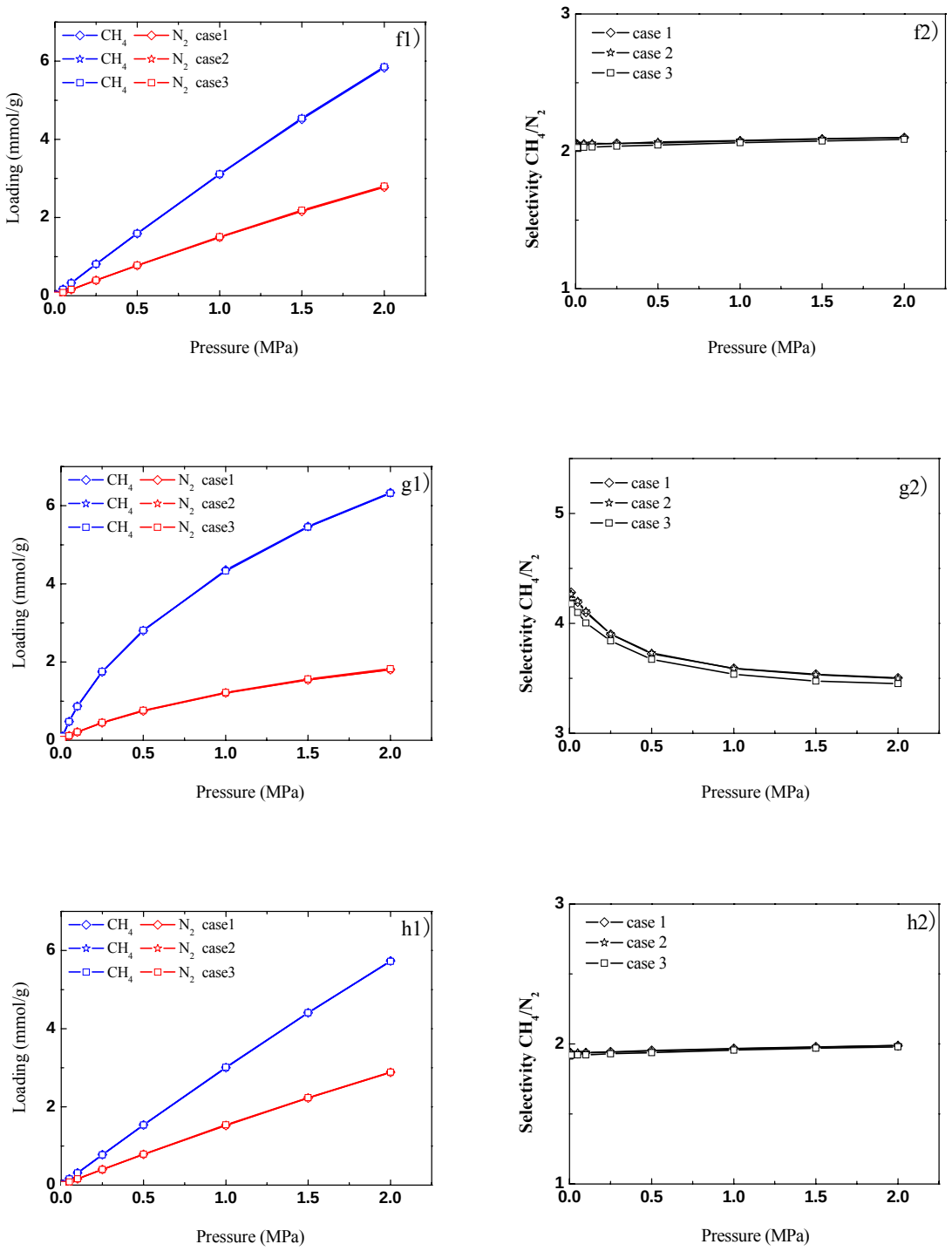


Figure 2. Effect of the electrostatic interactions on 1) the adsorption isotherms of CH_4/N_2 mixture and 2) the adsorption selectivities for CH_4 from equimolar binary mixture simulations of CH_4/N_2 in a) LTA, b) DDR, c) MIL-47 (V), d) IRMOF-1, e) IRMOF-11, f) IRMOF-12, g) IRMOF-13, and h) IRMOF-14.