

Coordinatively Unsaturated Metal Sites (Open Metal Sites) in Metal-Organic Frameworks: Design and Applications†

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Table S 1 Calculated binding energies $-\Delta E$ and isosteric heats of adsorption ($-\Delta H$, $-Q_{st}$) values for CO_2 in relation to the different OMS, using computational methods in comparison to $-Q_{st}^0$ values from experimental studies.

MOF	M-MOF-74								HKUST-1
OMS	Mg	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cu
Exp.	39.0-47.0 _{1,2,3,4,6,17}	/	31.7-31.9 ^{6,17}	33.2-34.3 ^{6,17}	33.6-37.0 ^{3,4,6,17}	38.6-41.0 ^{3,4,6,17}	22.1-24.0 ^{6,17}	26.8-30.6 ^{1,6,17}	29.0 ⁵
MP2	40.5 ⁶		30.3 ⁶	24.2 ⁶	29.7 ⁶	31.2 ⁶	16.2 ⁶	29.7 ⁶	
LDA	54.3 ⁶ (51.2) ⁷		38.4 ⁶	38.1 ⁶	42.5 ⁶ (36.6) ⁷	43.1 ⁶	31.0 ⁶	40.2 ⁶	(30.6) ⁷ 32.7 ⁸
GGA-PW91	23.9 ⁶		13.3 ⁶	9.4 ⁶	10.6 ⁶	12.5 ⁶	6.0 ⁶	12.6 ⁶	
GGA-PBE	(20.2) ⁷				(8.3) ⁷	(8.8) ⁷			(9.4) ⁷
Hybrid-GGA B3LYP	23.9 ⁶ 27.1 ⁹		12.1 ⁶	4.5 ⁶	7.0 ⁶	11.6 ⁶	3.5 ⁶	11.8 ⁶	
DFT-D2	(39.7) ⁷				(29.0) ⁷	(30.6) ⁷			(18.5) ⁷
PBE-D2	40.5 ¹⁰		33.8 ¹⁰	33.9 ¹⁰	33.7 ¹⁰	36.9 ¹⁰	27.1 ¹⁰	30.5 ¹⁰	21.0 ¹¹
PBE-D3	39.7 ¹⁰		34.6 ¹⁰ 32.4 ¹²	34.5 ¹⁰	33.9 ¹⁰ 29.5 ¹²	36.7 ¹⁰ 32.3 ¹²	28.0 ¹⁰ 21.5 ¹²	31.8 ¹⁰	21.0 ¹¹
PBE-D3 BJ	40.5 ¹⁰		35.5 ¹⁰	35.3 ¹⁰	34.5 ¹⁰	37.4 ¹⁰	27.8 ¹⁰	31.0 ¹⁰	
B3LYP-D*	(37.9) ^{13,14}					(35.5) ¹⁴		(31.7) ¹⁴	
ω B97X-D	(44.9) ⁹								
optB88-vdW	(52.8) ⁷ 53.1 ¹⁰	46.2 ¹⁰		46.5 ¹⁰	(39.9) ⁷ 46.7 ¹⁰	(43.1) ⁷ 51.0 ¹⁰	37.9 ^{10**}	41.6 ¹⁰	
optB86b-vdW	52.5 ¹⁰ (53.9) ⁷	45.9 ¹⁰		46.1 ¹⁰	46.6 ¹⁰ (40.4) ⁷	50.7 ¹⁰ (45.6) ⁷	37.5 ¹⁰	41.3 ¹⁰	28.0 ¹¹ (25.4) ⁷
vdW-DF	(40.5) ¹⁵								
PBE-vdW	(58.3) ¹⁵								
optPBE-vdW	(57.2) ⁷				(43.7) ⁷	(46.6) ⁷			(27.7) ⁷
revPBE-vdW	(47.3) ⁷				(37.2) ⁷	(37.8) ⁷			(23.3) ⁷
rPW86-vdW	(46.2) ⁷				(32.5) ⁷	(34.5) ⁷			(21.5) ⁷

vdW-DF2	(37.4) ¹⁵ (44.7) ¹⁶	38.1 ¹⁰		38.1 ¹⁰	37.7 ¹⁰	41.5 ¹⁰	30.9 ¹⁰	34.0 ¹⁰	22.0 ¹¹
vdW-DF2 + U	(40.9) ¹⁷ (41.0) ²⁹		(33.9) ¹⁷ (27.0) ²⁹	(34.1) ¹⁷ (34.0) ²⁹	(33.8) ¹⁷ (34.0) ²⁹	(37.3) ¹⁷ (34.0) ²⁹	(27.1) ¹⁷ (37.0) ²⁹	(30.2) ¹⁷ (27.0) ²⁹	(30.0) ²⁹
rev-vdW-DF2	43.6 ¹⁰		37.0 ¹⁰	37.3 ¹⁰	37.4 ¹⁰	41.3 ¹⁰	28.2 ¹⁰	32.1 ¹⁰	
B3LYP+D*/MP2	(42.7) ¹⁴					(40.5) ¹⁴		(39.0) ¹⁴	
DFT/CC									28.0 ¹¹
QM/MM DFT/MP2	48.2 ⁶		37.2 ⁶	32.2 ⁶	37.0 ⁶	39.1 ⁶	23.9 ⁶	37.0 ⁶	
GCMC PHAST*									30 ¹⁸
MOF	M-btt								
Exp.		36.7 ¹⁹		51.2 ¹⁹			30.7 ¹⁹		
vdW-DF+ U		(36.6) ¹⁹		(51.7) ¹⁹			(29.4) ¹⁹		

Table S 2 Calculated $-\Delta E$ and $(-\Delta H, -Q_{st})$ values for H₂ in relation to the different OMS, using computational methods in comparison to $-Q_{st}^0$ from experimental studies.

MOF	M-MOF-74							
OMS	Mg	Cr	Mn	Fe	Co	Ni	Cu	Zn
Exp.	10.1-10.7 ^{20,24}		8.8 ^{21,24}	9.7 ²¹	10.7 ^{21,24}	12.9-13.5 ^{22,23,24}	6.1 ²⁸	8.5-8.8 ^{24, 25}
DL	(6.5) ²⁰							
BSS	(6.0) ²⁰							
BSSP	(10.9) ²⁰				(12.4) ²⁶	(14.0) ²⁶	(6.5) ²⁷	(8.7) ²⁶
LDA	24.8 ²⁴		22.4 ²⁴		35.6 ²⁴	39.0 ²⁴		22.0 ²⁴
GGA-PBE	12.4 ²⁴		11.1 ²⁴		12.8 ²⁴	15.0 ²⁴		10.5 ²⁴
PBE+D			13.9 ²⁸				11.3 ²⁸	
vdW-DF2	(10.0) ²⁹	(6.0) ²⁹	(8.0) ²⁹	(9.0) ²⁹	(9.0) ²⁹	(10.0) ²⁹	(6.0) ²⁹	(8.0) ²⁹
MOF	MOF-505							
Exp.							6.1 ^{24,30}	
PBE							13.4 ³¹	

Table S 3 Calculated $-\Delta E$ and $(-\Delta H, -Q_{st})$ values for C_2H_2 , CO, CH_4 in relation to the different OMS, using computational methods in comparison to $-Q_{st}^0$ from experimental studies.

C_2H_2									
MOF	M-MOF-74								
OMS	Mg	Cr	Mn	Fe	Co	Ni	Cu	Zn	
Exp.	41.0 ³²			45.0-46.5 ^{32,33}	45.0 ³²				30.4-39.0 ^{32,34}
DFT-PBE									(30.0) ³⁵
vdW-DF2	(38.0) ²⁹	(31.0) ²⁹	(38.0) ²⁹	(37.0) ²⁹	(36.0) ²⁹	(37.0) ²⁹	(20.0) ²⁹	(35.0) ²⁹	
Cu-paddle-wheel-MOFs									
MOF	MOF-505	PCN-46	NJU-Bai12	ZJU-40	NOT-101	NOT-102	NOT-103	NOT-106	NOT-108
Exp.	24.7 ^{38,36}			34.5 ^{38,37}	37.1 ^{38,36}	22.0 ^{38,37}	30.8 ^{38,36}		
GCMC	(27.7) ³⁸	(24.1) ³⁸	(22.9) ³⁸	(23.9) ³⁸	(23.8) ³⁸	(24.7) ³⁸	(23.3) ³⁸	(25.5) ³⁸	(26.2) ³⁸
PBE	33.6 ³⁸	34.8 ³⁸	31.4 ³⁸	30.8 ³⁸	30.7 ³⁸	33.7 ³⁸	31.2 ³⁸	31.8 ³⁸	30.8 ³⁸
CO									
MOF	M-MOF-74								
OMS	Mg	Cr	Mn	Fe	Co	Ni	Cu	Zn	
Exp.	38.0 ³				55.5 ³	59.7 ³			
B3LYP-D*	(30.0) ¹⁴					(41.9) ¹⁴		(24.8) ¹⁴	
vdW-DF2	(35.0) ²⁹	(20.0) ²⁹	(29.0) ²⁹	(30.0) ²⁹	(30.0) ²⁹	(34.0) ²⁹	(16.0) ²⁹	(25.0) ²⁹	
B3LYP+D*/MP 2	(41.2) ¹⁴					(50.3) ¹⁴		(39.8)	
MOF	MIL-101								
Exp.									
ω B97X-D		(37.4) ⁹							
CH_4									
MOF	M-MOF-74								
OMS	Mg	Cr	Mn	Fe	Co	Ni	Cu	Zn	
Exp.	18.2 ⁶		18.2 ⁶		19.2 ⁶	19.0 ⁶		18.3 ³⁹	
vdW-DF2+U	(19.0) ²⁹	(14.0) ²⁹	(19.0) ²⁹	(19.0) ²⁹	(18.0) ²⁹	(19.0) ²⁹	(14.0) ²⁹	(19.0) ²⁹	
MOF	HKUST-1								
DFT/CC-PES							13.23 ⁴⁰		

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