Electronic Supplementary Information

Metal-organic frameworks and related materials for hydrogen purification: Interplay of pore size and pore wall polarity

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(1) Models and parameters

1.1 Fluid molecules



Figure S-1. Models of the H_2 and the O_2 molecule used in the calculations, Q_{com} = dummy site at the center of mass. The corresponding Lennard-Jones parameters and partial charges are given in table S-1.

Table S-1. Force-field parameters used for hydrogen [1, 2] and oxygen [3].

	<i>r₀</i> /Å	D_0 / kJ mol ⁻¹	<i>q /</i> e
a) H ₂			
Н	_	-	0.4705
Q _{com}	3.3225	0.2844	-0.9410
<i>b)</i> O ₂			
0	3.3898	0.4074	-0.1336
Q _{com}	_	-	0.2672

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Figure S-2. Different models for the CO molecule [4-6]. The model of Gu *et al.* uses only one Lennard-Jones site at the center of mass [7]. In this work, it is combined with the point charge model proposed by Straub and Karplus. For all four models, the Lennard-Jones parameters and charges are reported in table S-2.

Table S-2.	Force-field	parameters	used for	carbon	monoxide	[4-7].
						r

	<i>r</i> ₀ / Å	D_0 / kJ mol ⁻¹	<i>q /</i> e
a) Stoll et al.			
С	3.7051	0.3068	-0.1347
0	3.7051	0.3068	0.1347
b) Straub & Karplus			
С	4.2990	0.1096	-0.75
Q _{com}	_	_	1.60
0	3.5021	0.6657	-0.85
c) Piper et al.			
Q _{ext1}	_	_	-0.636
С	3.7995	0.3316	0.831
Q _{ext2}	-	-	-0.195
0	3.2383	0.5117	_
d) Gu et al. (LJ) + Straub & Karplus (charges)			
С	-	_	-0.75
Q _{com}	4.2238	0.8330	1.60
0	-	_	-0.85

1.3 Adsorbents: Structural models and pore volumes

I. Silicalite



Figure S-3. *a)* Schematic and atomistic representation of one pentasil unit, consisting of eight five-membered rings. *b)* 2 x 2 array of unit cells, displayed along the *b*-axis. *c, d)* Visualization of the two types of channels present in the structure, using the accessible surface area calculated from crystal structure data (light blue). Colour scheme: Yellow = silicon, red = oxygen.

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II. Mg-formate



Figure S-4. *a*) Chain of octahedrally coordinated Mg atoms running in the direction of the *b*-axis. The syn-syn/anti-bridging mode of the formate linkers is apparent. MgO₆ octahedra connecting the chains are also displayed, with the Mg atoms shown in dark blue to distinguish them from those atoms constituting the chains, which are shown in green. *b*) 2×2 array of unit cells, displayed along the *b*-axis. Colour scheme: Dark green = magnesium, red = oxygen, grey = carbon, white = hydrogen.

III. Zn(dtp)



Figure S-5. *a*) Coordination of one dtp linker to three Zn centers. *b*) 2×2 array of unit cells, displayed along the *c*-axis. More than one cell is shown to visualize the helical channels, which are centered around the cell edge. Colour scheme: Green = zinc, blue = nitrogen, grey = carbon, white = hydrogen.

IV. Cu₃(btc)₂



Figure S-6. *a*) Unit cell, displayed along the *c*-axis. *b*) Small pore (diameter ~ 5 Å), octahedrally surrounded by Cu₂ paddle wheels. Phenyl rings span four of the eight faces of the octahedron. *c*) Large pore (diameter ~ 11 Å), cuboctahedrally surrounded by Cu₂ paddle wheels. The unsaturated copper centers point into the pore. *d*) Large pore (diameter ~ 11 Å), cuboctahedrally surrounded by Cu₂ paddle wheels which lie tangentially. The Cu₂ paddle wheels are connected to highlight the pore topology. Colour scheme: Light blue = copper, red = oxygen, grey = carbon, white = hydrogen.

V. Cucurbit[6]uril



Figure S-7. *a)* Single CB[6] macrocycle. *b)* Unit cell of crystalline, microporous cucurbit[6]uril, displayed along the *c*-axis. Colour scheme: Red = oxygen, blue = nitrogen, grey = carbon, white = hydrogen.

Pore volumes of adsorbents

Table S-3: Free pore volumes of adsorbent materials, obtained from simulations of Helium adsorption at T = 298 K (see [2] for further details). Experimental values are given for comparison.

	V_p (sim) / cm ³ g ⁻¹	$V_{ ho}$ (exp) / cm ³ g ⁻¹
Silicalite	0.19	0.19
Mg-formate	0.18	0.14
Zn(dtp)	0.25	0.16
Cu ₃ (btc) ₂	0.70	0.75
Cucurbit[6]uril	0.12	0.13

1.3 Adsorbents: Lennard-Jones parameters

Table S-4: Lennard-Jones parameters used for the representation of framework atoms. With the exception of the O_z parameters representing the oxygen atoms of Silicalite, all parameters were taken from the Universal Force Field [8]. For Silicalite, the O_z parameters were taken from the work of Dubbeldam *et al.*, and the silicon atoms were treated as non-interacting sites [9].

	<i>r</i> ₀ /Å	D_0 / kJ mol ⁻¹	Description
H_	2.886	0.1841	Hydrogen
C_2, C_3, C_R	3.851	0.4393	Carbon
N_R	3.660	0.2887	Nitrogen
O_2, O_R	3.500	0.2510	Oxygen in MOFs and CB[6]
O_z	3.614	0.6937	Oxygen in Silicalite
Mg3+2	3.021	0.4644	Magnesium
Cu3+1	3.495	0.0209	Copper
Zn3+2	2.763	0.5188	Zinc

1.4 Adsorbents: ESP charges

Computational details of ESP charge calculations

ESP charges were obtained from DFT calculations for representative fragments of the adsorbents. In each case, the geometry was optimized prior to the partial charge calculation. The all-electron DFT calculations were carried out using the DMol³ code [10, 11] included in the Accelrys "Materials Studio" package [12]. A DNP basis set was employed in all calculations, and the PBE exchange-correlation functional was used [13]. The DMol³ code uses the ESP method as proposed by Singh and Kollman [14]. This method relies on a least-squares fit of the partial charges to the DFT electrostatic potential for a set of grid points located on shells around the nuclei. These shells are generated for a range of distances lying between the van der Waals radius and an upper limiting value. The quality of the calculation depends mainly on the distance between the grid points. In the DMol³ code, the default grid spacing corresponds to 0.5 Å. Default settings were used in all calculations.

The actual partial charges used in the GCMC simulations were extracted from the DFT results obtained for the non-periodic fragments. In the case of Silicalite, Zn(dtp), and $Cu_3(btc)_2$, only the atoms from the central area of the fragment were taken into account. This leads to a necessity of adjusting at least one of the charge values to obtain a neutral framework. In these cases, both the original ESP charge and the adjusted value used in the GCMC simulations are given.

Model systems and results

I. Silicalite, Mg-formate



Figure S-8. *a*) $Si_{12}O_{16}(OH)_{16}$ cluster used for the ESP charge calculation for Silicalite. The average value of the individual ESP charges obtained for the silicon and bridging oxygen atoms is given in the table below. *b*) $Mg_2(OOCH)_4$ paddle wheel used for the ESP charge calculation for Mg-formate.

Table S-5. Resulting ESP charges for Silicalite and Mg-formate, atom labels assigned according to figure S-8.

a) Silicalite		b) Mg-formate	
Atom label	<i>q /</i> e	Atom label	<i>q /</i> e
Si	1.206	Mg	1.636
0	-0.603	0	-0.766
		С	0.671
		Н	0.043

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Figure S-9. *a)* $[Zn_3(dtp)(tetrazolate)_6]^{2-}$ cluster used in the ESP charge calculation for Zn(dtp). *b)* $(Cu_2)_3(btc)(benzoate)_9$ cluster used in the ESP charge calculation for Cu₃(btc)₂. Phenyl rings of the benzoate moieties are omitted for clarity.

Table S-6. Resulting ESP charges for Zn(dtp) and $Cu_3(btc)_2$, atom labels assigned according to figure S-9. In the case of Zn(dtp), the charge assigned to the Zn atom is the weighted average of the ESP charges obtained for the two non-equivalent Zn atoms of the cluster. The charges of N_{t4} in Zn(dtp), and of the Cu atom in $Cu_3(btc)_2$ were adjusted to ensure charge neutrality. Original values from DFT calculation are given in brackets, adjusted values without brackets.

a) Zn(dtp)		b) Cu ₃ (btc) ₂	
Atom label	<i>q /</i> e	Atom label	<i>q</i> / e
Zn	0.6490	Cu	1.030 (1.015)
N _p	-0.3840	0	-0.574
C _{p1}	-0.0220	C _{carb}	0.573
C _{p2}	0.2240	C _{r1}	0.215
н	0.0750	C _{r2}	-0.364
Ct	0.6670	н	0.209
N _{t1}	-0.1780		
N _{t2}	-0.2130		
N _{t3}	-0.0710		
N _{t4}	-0.4225 (-0.5150)		



Figure S-10. Cucurbit[6]uril macrocycle used in the ESP charge calculation.

Table S-7. Resulting ESP charges for cucurbit[6]uril, atom labels assigned according to figure S-10.

Atom label	<i>q /</i> e
Ν	-0.0030
C _{carb}	0.4070
0	-0.4200
C _{port}	-0.2240
H _{port1}	0.1470
H _{port2}	0.1400
C _{equ}	-0.2035
H _{equ}	0.1595

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(2) Additional results

2.1 Comparison with experimental low-pressure isotherms



Figure S-11. Mg-formate: Comparison of simulated oxygen adsorption isotherm with experimental data [15].



Figure S-12. Cucurbit[6]uril: Comparison of simulated carbon monoxide adsorption isotherm with experimental data [16].

2.2 Silicalite – Adsorption isotherms



Figure S-13. Mixture adsorption isotherms. *a*) CO/H₂ mixture. *b*) O₂/H₂ mixture.



Figure S-14. Adsorption isotherms for mixtures of varying composition, p = 1 bar. The x-axis corresponds to the content of the more strongly adsorbed component in relation to the total pressure. The hydrogen uptakes from both mixtures are virtually identical.

2.3 Mg-formate – Adsorption isotherms



Figure S-15. Mixture adsorption isotherms. *a*) CO/H₂ mixture. *b*) O_2/H_2 mixture. The same colour scheme as in figure S-13 is used.



Figure S-16. Adsorption isotherms for mixtures of varying composition, p = 1 bar. The same colour scheme as in figure S-14 is used.





Figure S-17. Mixture adsorption isotherms. *a*) CO/H₂ mixture. *b*) O_2/H_2 mixture. The same colour scheme as in figure S-13 is used.



Figure S-18. Adsorption isotherms for mixtures of varying composition, p = 1 bar. The same colour scheme as in figure S-14 is used.

2.5 Cu₃(btc)₂ – Adsorption isotherms

Figure S-19. Mixture adsorption isotherms. *a*) CO/H₂ mixture. *b*) O_2/H_2 mixture. The same colour scheme as in figure S-13 is used.

Figure S-20. Adsorption isotherms for mixtures of varying composition, p = 1 bar. The same colour scheme as in figure S-14 is used.

2.6 Cucurbit[6]uril – Adsorption isotherms

Figure S-21. Mixture adsorption isotherms. *a*) CO/H₂ mixture. *b*) O_2/H_2 mixture. The same colour scheme as in figure S-13 is used.

Figure S-22. Adsorption isotherms for mixtures of varying composition, p = 1 bar. The same colour scheme as in figure S-14 is used.

2.7 Henry constants

Figure S-23. Henry constants obtained for Silicalite. The values of K_{H} , which are displayed on a logarithmic scale, are given in molality *vs.* partial pressure.

Figure S-24. Henry constants obtained for Mg-formate.

Figure S-25. Henry constants obtained for Zn(dtp).

Figure S-26. Henry constants obtained for Cu₃(btc)₂.

Figure S-27. Henry constants obtained for cucurbit[6]uril.

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