

Supporting Information

Guest dependent pressure behavior of the flexible MIL-53(Cr) : A computational exploration

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1. Charge distribution for the framework of MIL-53 (Cr)

The periodic model of the MIL-53 (Cr) material was first geometry optimized, using the crystallographic coordinates of the atoms as starting configurations.¹ The partial charges for all the atoms of the framework were then extracted using periodic density functional theory (DFT) calculations and Mulliken charge partitioning method as previously reported.² The Accelrys DMol3 code³ was used for these calculations, which were performed using the PW91 GGA functional,⁴ and the double numerical basis set containing polarization functions on hydrogen atoms (DNP).⁵ The resulting charges carried by all the atoms are reported in Table S1, the location of each atom type on the framework being detailed in Fig. S1.

Table S1 Atomic partial charges carried by the MIL-53(Cr) framework atoms

Atoms	h_c	cg1	cg2	c_c	o_c	Cr	μ_2_o	h_o
Charges (e)	0.1393	-0.0739	-0.0739	0.6126	-0.506	1.031	-0.637	0.291

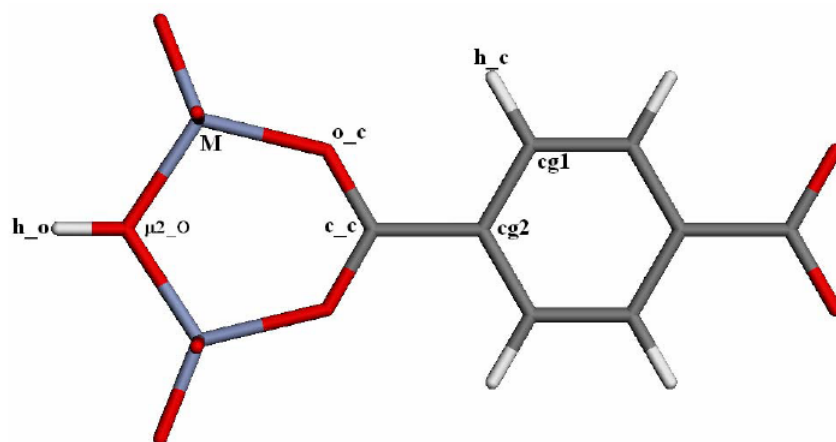


Fig. S1 Labels of the atoms for the organic and inorganic parts in MIL-53 (Cr), corresponding to the force field atom types, to allow the easy reading of Tables S1-S3. M represents the Cr atom.

2. Flexible force field used for the MIL-53(Cr)

In the recently refined force field,⁶ the intramolecular force constants for the organic moiety were extracted from the widely used Consistent Valence Force Field (CVFF)⁷ with a slight adjustment (see Table S2). The bond stretching, angle bending and torsion potentials are described by the following terms:

$$E_{ij}^{bond} = \frac{1}{2}k_{ij}(r_{ij} - r_0)^2 \quad (1)$$

$$E_{ijk}^{bending} = \frac{1}{2}k_{ijk}(\theta_{ijk} - \theta_0)^2$$

$$E_{ijkl}^{torsion} = k_{ijkl}[1 + \cos(n\phi_{ijkl} - \phi_0)]$$

where k_{ij} , k_{ijk} and k_{ijkl} are the force constants for the different interactions, r_{ij} is the distance separating two atoms i and j , θ_{ijk} and θ_0 are the angle involving three atoms i , j , k and the equilibrium angle respectively, n is the periodicity, ϕ is the dihedral angle and ϕ_0 is the factor phase. The non-bonded Lennard-Jones (LJ) parameters (Eq. 2) for describing the interactions between the organic parts are given in Table S2.

$$E_{ij}^{LJ} = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2)$$

One can note that the parameters for o_c have been modified to reproduce accurately the distance between Cr and O atoms. The cross LJ potential parameters were calculated by the Lorentz-Berthelot rules (Eq. 3)

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad \text{and} \quad \sigma_{ij} = \left(\frac{\sigma_{ii} + \sigma_{jj}}{2} \right) \quad (3)$$

Table S2 Force field parameters for the intramolecular and non-bonded interactions of the organic moiety.

<i>Bond potential</i>			
Bond Type	k_{ij} (kJ·mol ⁻¹ ·Å ⁻²)	r_0 (Å)	
cg1-cg1	4015.045	1.34	
cg1-cg2	4015.045	1.34	
c_c-cg2	2943.723	1.47	
c_c-o_c	4516.925	1.25	
<i>Bending potential</i>			
Angle type	k_{ijk} (kJ·mol ⁻¹ ·rad ⁻²)	θ_0 (°)	
cg1-cg2-cg1 / cg2-cg1-cg1	753.3034	120.0	
cg1-cg1-h_c / cg2-cg1-h_c	309.7182	120.0	
cg1-cg2-c_c	290.3186	120.0	
cg2-c_c-o_c	569.2484	120.0	
o_c-c_c-o_c	114.1649	123.0	
<i>Torsion potential</i>			
Dihedral type	k_{ijkl} (kJ·mol ⁻¹)	N	ϕ_0 (°)
cg1-cg2-c_c-o_c	5.0000	2	180.0
<i>Lennard-Jones potential</i>			
Atom type	σ_{ii} (Å)	ε_{ii} (kJ·mol ⁻¹)	
o_c	3.1200	0.2495	
c_c / cg1 / cg2	3.8068	0.2478	
h_c	2.4483	0.1602	

For the inorganic part, the Cr-O intramolecular and non bonded interactions were adjusted by our own starting with the parameters defined in the DREIDING force field.⁸ In addition, the torsion term between the inorganic and the organic parts, cg2-c_c-o_c-Cr, were refined to reproduce the key structural features of the MIL-53(Cr) upon CO₂ adsorption. It has to be mentioned that in the MIL framework, the nonbonded interactions concern atoms separated by exactly three bonds usually

described as 1-4 van der Waals interactions with LJ potentials.

Table S3 Force field parameters for the intramolecular and non-bonded interactions of the inorganic part.

<i>Bond potential</i>			
Bond Type	k_{ij} (kJ·mol ⁻¹ ·Å ⁻²)	r_0 (Å)	
Cr-o_c	2928.2800	1.95	
Cr-μ ₂ _o	2928.2800	1.95	
<i>Bending potential</i>			
Angle type	k_{ijk} (kJ·mol ⁻¹ ·rad ⁻²)	θ_0 (°)	
c_c-o_c-Cr	115.8186	136.0	
<i>Torsion potential</i>			
Dihedral type	k_{ijkl} (kJ·mol ⁻¹)	n	ϕ_0 (°)
cg2-c_c-o_c-Cr	20.0000	2	180.0
<i>Lennard Jones potential</i>			
Atom type	σ_{ii} (Å)	ε_{ii} (kJ·mol ⁻¹)	
Cr	2.6901	0.0627	
μ ₂ _o	3.1200	0.2495	
h_o	0.0000	0.0000	

3. Flexible force field used for CO₂ molecule

CO₂ molecule was described by the flexible EPM2 potential as reported by Harris and Yung,⁹ where all the three atoms were treated as the LJ interaction sites with the partial charges centered at each atom ($q_C = 0.6512 e$, $q_O = -0.3256 e$). In this model, the C–O bond length is fixed at 1.149 Å, and the O–C–O bond angle is described by an harmonic bending potential shown in Eq. 1. The corresponding potential parameters are given in Table S4. The Lorentz-Berthelot mixing rules were applied to describe the LJ interactions between the CO₂ molecules and the framework atoms of the MIL-53(Cr) except for the interaction between the oxygen atoms of the CO₂ molecule and the o_c of the MIL-53(Cr) framework where the LJ parameters have been adjusted by our own to capture the re-opening of the structure at high concentration of CO₂. The Jorgensen mixing rules (Eq. 4) were used to describe the LJ interactions between the CO₂ molecules, as required by the EPM2 potential.⁹

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}, \quad \sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}} \quad (4)$$

Table S4 Intramolecular and non-bonded potential parameters used for CO₂. The LJ parameters for the CO₂/o_c interactions are also reported.

<i>Bending potential</i>		
Angle type	k_{ijk} (kJ·mol ⁻¹ ·rad ⁻²)	θ_0 (°)
o-c-o	1236.0	180.0
<i>Lennard Jones potential</i>		
Atom type	σ_{ii} (Å)	ϵ_{ii} (kJ·mol ⁻¹)
c_CO ₂	2.7570	0.2339
o_CO ₂	3.0330	0.6694
o_CO ₂ – o_c	3.0765	0.7087

4. Calculation method for the order parameter

The order parameter S was extracted from the analysis of the whole MD simulation runs. In this work, S was calculated using eq 5,

$$S = \frac{3}{2} \left\langle \cos^2 \theta_i - \frac{1}{3} \right\rangle \quad (5)$$

where θ_i is the angle between the long axis of molecule i (the directional unit vector) and the mean orientation (the director). In general, this director cannot be found by a simple averaging method, but is always the average of the largest eigenvalue of the ordering $Q_{\alpha\beta}$ tensor¹⁰ which corresponds to the components of the unit vectors along the principal axis of the molecules (Our simulations showed that all the flexible CO₂ molecules almost remain in a linear shape). $Q_{\alpha\beta}$ was calculated by,

$$Q_{\varepsilon\beta} = \frac{3}{2N} \left(\sum_{i=1}^N e_{i\alpha} e_{i\beta} - \frac{1}{3} \delta_{\alpha\beta} \right) \quad (6)$$

where N is the total number of adsorbed molecules, e_i is the unit vector of the molecule i , and $\delta_{\alpha\beta}$ is the delta of Kronecker ($\delta_{\alpha\beta}=1$ if $\alpha=\beta$ or 0 if else). The order parameter S is specifically used to characterize the degree of the orientational order, and its value can vary from 0 (fully orientationally disordered fluid) to 1 (perfectly oriented system).

5. Radial distribution functions

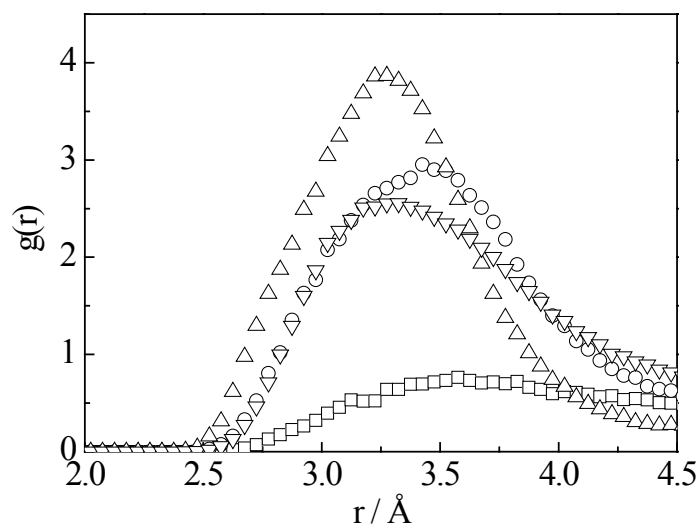


Fig. S2 Radial distribution functions (RDFs) between the C atoms of CO₂ and O atoms of the μ_2 -OH

in the MIL-53(Cr) for a loading of 1 CO₂/u.c at: 0.1 MPa (square symbols), 20 MPa (circle symbols) and 300 MPa (up triangle symbols) and for 3 CO₂/u.c. at 0.1 MPa (down triangle symbols).

6. Cif files of the simulated structures

The structures of MIL-53(Cr) at 53.5 MPa and 300 MPa as well as of MIL-53(Cr) with 1 CO₂/u.c. under the applied pressure of 20 MPa and 300 MPa are provided as cif files with the labels: MIL-53(Cr)-NP53.5MPa, MIL-53(Cr)-NP300MPa, MIL-53(Cr)with1CO2uc-NP20MPa, and MIL-53(Cr)with1CO2uc-NP300MPa respectively.

7. Summary of the Bulk Modulus for different MOFs recently reported in the literature.

Table S5 Bulk Modulus of some MOFs

Structure	Bulk modulus (GPa)	Temperature (K)	Method	Reference
MIL-53(Cr) ^a	~1.8	300	Simulation	Our work
	~2.0	~300	Experiment	11
MOF-5	~17.02	0	Simulation	12
	~18.2	0	Simulation	13
	~18.5	0	Simulation	14
	~16.3	0	Simulation	15
	~20.0	0	Simulation	16
	~4.0	300	Simulation	16
	~14.4	0	Simulation	17
	~15.34	0	Simulation	18
	~16.66	300	Simulation	19
IRMOF-8 (MOF-C10)	~11.28	300	Simulation	19
IRMOF-14 (MOF-C16)	~10.05	300	Simulation	19
MOF-C22	~6.88	300	Simulation	19
MOF-C30	~4.11	300	Simulation	19
MOF-177	~10.10	0	Simulation	18
DUT-6	~10.73	0	Simulation	18
MOF-14 (interpenetrated)	~14.8	0	Simulation	20
MOF-14 (non-interpenetrated)	~5.5	0	Simulation	20
DUT-34	~9.1	0	Simulation	20
DUT-23	~13.2	0	Simulation	20
HKUST-1	~30.7	~300	Experiment	21
	~25	~300	Simulation	22
	~35.2	300	Simulation	23
Zn(Im) ₂	~14	~300	Experiment	24
LiB(Im) ₄	~16.6	~300	Experiment	25
ZIF-8	~6.5	~300	Experiment	26

^aLarge-pore form

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