COMPLEX ADSORPTION OF SHORT LINEAR ALKANES IN THE FLEXIBLE METAL-ORGANIC-FRAMEWORK MIL-53(Fe)

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The Supplementary information contains :

- Various images of the experimental set-up at the ESRF
- Partial charges for both alkanes and MIL-53(Fe) and interatomic potentials used for the molecular simulation
- CIF images obtained from the molecular simulation study.

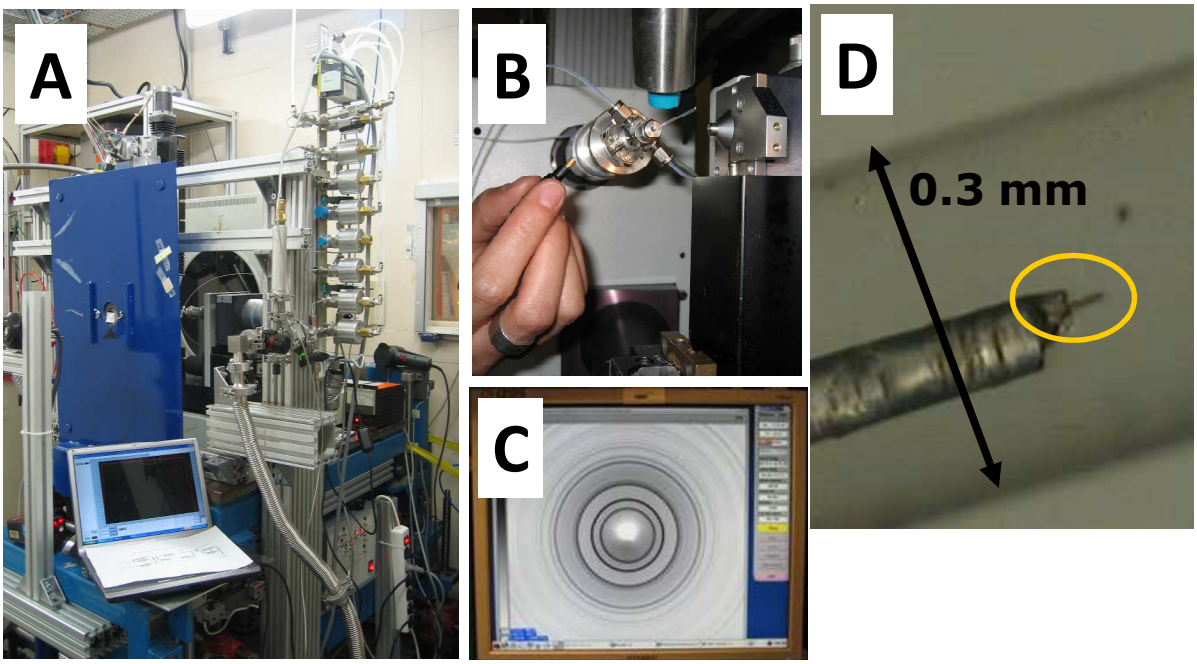

Figure S1 : Various images of the set-up at the ESRF.

(A) set-up showing the 8 electrovalves, the computer controlling the system which follows the pressure and in the background the MAR detector.

(B) a close up of the capillary in front of the X-ray beam and the tubes leading into and out from the capillary.

(C) Typical pattern obtained on the monitor of a powder sample.

(D) single crystal inside a 0.3 mm capillary which can enable studies of molecule localisation.

Charge distributions

The partial charges for the hybrid porous systems MIL-53(Fe) were then extracted using periodic Density Functional Theory calculations and Mulliken charge partitioning method as previously reported for MIL-53(Cr).[1] The Accelrys DMol[3] code was used for these calculations which were performed using the PW91 GGA density functional, and the double numerical basis set containing polarisation functions on hydrogen atoms (DNP).[2] The resulting charges carried by all the atoms are reported in Table S1, the position of each atom type on the framework being shown in Figure S1.

MIL Atoms	h_c	cg1	cg2	c_c	o_c	M	o_h	h_o
MIL-53(Fe)	0.145	-0.073	-0.077	0.572	-0.530	1.210	-0.676	0.308

Hydrocarbon atoms	C	H	$C(CH_3)$	$H(CH_3)$	$C(CH_2)$	$H(CH_2)$
Methane Charges	-0.4720	-0.1180	-	-	-	-
Ethane Charges	-	-	-0.3150	0.1050	-	-
Propane Charges	-	-	-0.3100	-0.1000	-0.1720	-0.0960
Butane Charges	-	-	-0.3170	-0.1000	-0.1650	-0.0910

Table S1: Atomic partial charges (in electron units) carried by the different atoms within the hydrocarbons and MIL-53(Fe) frameworks, the labels of the atoms are described in Figure S1.

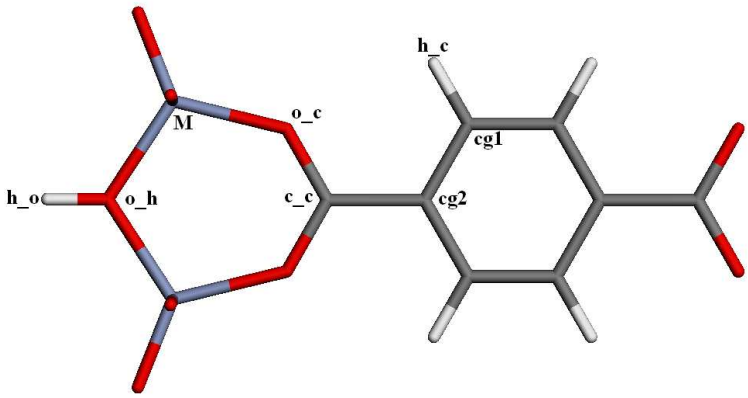

Figure S2 - Labels of the atoms for the organic and inorganic parts for MIL-53 (Fe=M) materials corresponding to the forcefield atom types, to allow the easy reading of Tables S1 and S2.

Interatomic potentials

The hydrocarbons were represented by an explicit atomic model where each atom provides a contribution to the adsorbate/adsorbate and adsorbate/adsorbent interactions which are described via a repulsion-dispersion 12-6 Lennard Jones (LJ) or Buckingham potentials and a Coulombic term. The hydrocarbon/hydrocarbon and hydrocarbon/MILs interatomic potential parameters were taken from our previous investigations which successfully capture the adsorption of C1-C4 in MIL-53(Cr) compared to Microcalorimetry measurements.[3]

The dispersion-repulsion interactions between the alkane molecules and the metal centers of the inorganic part, i.e. Fe(OH), were not taken in account, as the polarisabilities of this center is much lower than those of the oxygen atoms. Indeed, the repulsion-dispersion contribution of the inorganic part can be assigned only to the oxygen atoms as well as the protons of the μ_2-OH groups of the MIL-53 (Fe) material. All the interatomic potential parameters are listed in Table S2.

(a) Nonbonded Lennard-Jones potentials		
Atom pairs	**σ (Å)**	**ε (eV)**
$C(CH_4)$ / $C(CH_4)$	3.473	0.00309
$C(CH_3, CH_2)$/ $C(CH_3, CH_2)$	3.473	0.00309
$H(CH_4)$ / $H(CH_4)$	2.846	0.00066
$H(CH_3, CH_2)$/ $H(CH_3, CH_2)$	2.846	0.00066
$C(CH_4)$ / $H(CH_4)$	3.293	0.00136
$C(CH_3, CH_2)$/ $H(CH_3, CH_2)$	3.293	0.00136
$C(CH_4)$ / h_c	3.160	0.00143
$C(CH_3)$ / h_c	3.239	0.00143
$C(CH_2)$ / h_c	3.320	0.00143
$H(CH_4)$ / h_c	2.846	0.00066
$H(CH_3, CH_2)$/ h_c	2.846	0.00066
$C(CH_4)$ / cg1, cg2 or c_c	3.473	0.00357
$C(CH_3)$ / cg1, cg2 or c_c	3.560	0.00357
$C(CH_2)$ / cg1, cg2 or c_c	3.649	0.00357
$H(CH_4)$ / cg1, cg2 or c_c	3.160	0.00165
H (CH_3, CH_2) / cg1, cg2 or c_c	3.160	0.00165
$C(CH_4)$ / o_c or o_h	3.200	0.00599
$C(CH_3)$ / o_c or o_h	3.280	0.00599
$C(CH_2)$ / o_c or o_h	3.362	0.00599

$H(CH_4)$ / o_c or o_h	2.899	0.00362	
$H(CH_3, CH_2)$ / o_c or o_h	2.899	0.00362	
(b) Nonbonded Buckingham potentials			
Atom pairs	***ρ* (Å)**	***A* (eV)**	***C* (eV)**
$C(CH_4)$ / h_o	3.950	1020.41055	20.86350
$C(CH_3)$ / h_o	4.049	1020.41055	20.86350
$C(CH_2)$ / h_o	4.150	1020.41055	20.86350
$H(CH_4)$ / h_o	3.860	35.35799	0.00000
$H(CH_3, CH_2)$ / h_o	3.860	35.35799	0.00000

Table S2 – Interatomic pair potential parameters for both hydrocarbon/hydrocarbon and hydrocarbon/hybrid porous framework used in the GCMC.

1. N.A. Ramsahye, G. Maurin, S. Bourrelly, P.L. Llewellyn, T. Loiseau, G. Férey, *Phys. Chem. Chem. Phys*. **2007**, 9, 1059.

2. Dmol[3]. Accelrys Inc., San Diego, **1999**.

3. P.L. Llewellyn, G. Maurin, S. Loera-Serna, N. Rosenbach, T. Devic, C. Serre, S. Bourrelly, P. Horcajada, Y. Filinchuk & G. Férey**,** *J. Am. Chem. Soc.*, **2008,** 130, 38, 12808.