

Synthesis procedure and structural characterization of the different MIL materials

MIL-47(V) or $V^{IV}O(O_2C-C_6H_4-CO_2)$ [$V_4O_4(O_2C-C_6H_4-CO_2)_4$ per unit-cell]

$V^{IV}O(O_2C-C_6H_4-CO_2)$ was synthesized according to the published procedure.¹ VCl_3 and terephthalic acid were reacted in water at 200°C for 3 days. The resulting solid was washed with water, DMF, acetone and dried in air, and is formulated $V^{III}OH(O_2C-C_6H_4-CO_2).(HO_2C-C_6H_4-CO_2H)_x$ ($x \sim 0.75$). The solid was further placed in DMF at 150°C overnight (1g of solid for 50 ml of DMF), to afford after cooling down to room temperature and additional washing (DMF and acetone) the $V^{III}OH(O_2C-C_6H_4-CO_2).(DMF)_x$ ($x \sim 0.8$) solid.² Eventually, $V^{IV}O(O_2C-C_6H_4-CO_2)$ was obtained by heating the above-mentioned solid under primary vacuum at 250°C for 2 days. Nitrogen sorption measurement at 77K indicates a Langmuir surface area of about 1450 $m^2.g^{-1}$.

Table S1: Unit-cell of the different forms of MIL-47(V)

Solid	a (Å)	b (Å)	c (Å)	V (Å ³)	Space Group	Reference
$V^{III}OH(O_2C-C_6H_4-CO_2).(HO_2C-C_6H_4-CO_2H)_{0.75}$ MIL-47 as	17.519(1)	12.168(1)	6.875(1)	1465.5(1)	P n a m	1
$V^{IV}O(O_2C-C_6H_4-CO_2)$ MIL-47 (V)	16.143(1)	13.939(1)	6.818(1)	1534.1(1)	P n a m	1

MIL-53(Cr) or $Cr^{III}OH(O_2C-C_6H_4-CO_2)$ [$Cr_4(OH)_4(O_2C-C_6H_4-CO_2)_4$ per unit-cell]

$Cr^{III}(OH)(O_2C-C_6H_4-CO_2)$ was synthesized according to the published procedure.³ $Cr(NO_3)_3 \cdot 9H_2O$, terephthalic acid and hydrofluoric acid were reacted in water at 220°C for 3 days. The resulting solid was washed with water, DMF, acetone and dried in air, and is formulated $CrOH(O_2C-C_6H_4-CO_2).(HO_2C-C_6H_4-CO_2H)_x$ ($x \sim 0.75$). The solid was further placed in DMF at 150°C overnight (1g of solid for 50 ml of DMF), to afford after cooling down to room temperature and additional washing (DMF and acetone) $CrOH(O_2C-C_6H_4-CO_2).(DMF)_x$ ($x \sim 0.8$).² Eventually, $CrOH(O_2C-C_6H_4-CO_2)$ was obtained by heating the above-mentioned solid under primary vacuum at 250°C for 2 days. Nitrogen sorption measurement at 77K indicates a Langmuir surface area of about 1400 $m^2.g^{-1}$. The solid let in air afforded $Cr^{III}(OH)(O_2C-C_6H_4-CO_2).(H_2O)$, while redispersed in water, this leads to $Cr^{III}(OH)(O_2C-C_6H_4-CO_2).n(H_2O)$ ($n \sim 4$) or MIL-53(Cr)(H₂O)open.

Table S2: Unit-cell of the different forms of MIL-53(Cr):

Solid	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	Space Group	Reference
Cr ^{III} OH(O ₂ C-C ₆ H ₄ -CO ₂).(HO ₂ C-C ₆ H ₄ -CO ₂ H) _{0.75} MIL-53 as	17.340(1)	12.178(1)	6.822(1)	-	1440.6(1)	P n a m	3
Cr ^{III} (OH)(O ₂ C-C ₆ H ₄ -CO ₂) MIL-53ht labelled MIL-53 _{lp} (Cr)	16.733(1)	13.038(1)	6.812	-	1486.1(1)	I m c m	3
Cr ^{III} (OH)(O ₂ C-C ₆ H ₄ -CO ₂).(H ₂ O) MIL-53lt labelled MIL-53 _{np} (Cr)	19.685(1)	7.849(1)	6.782	104.9(1)	1012.0(1)	C 2/c	3
Cr ^{III} (OH)(O ₂ C-C ₆ H ₄ -CO ₂).n(H ₂ O) MIL-53(H ₂ O)open labelled MIL-53 _{lp} (Cr)	15.80(1)	14.15(1)	6.83(1)	-	1527.2(1)	I m c m	unpublished results

lp = large pore, np = narrow pore

MIL-53(Fe) or Fe^{III}(OH)(O₂C-C₆H₄-CO₂) [Fe₄(OH)(O₂C-C₆H₄-CO₂)₄ per unit-cell]

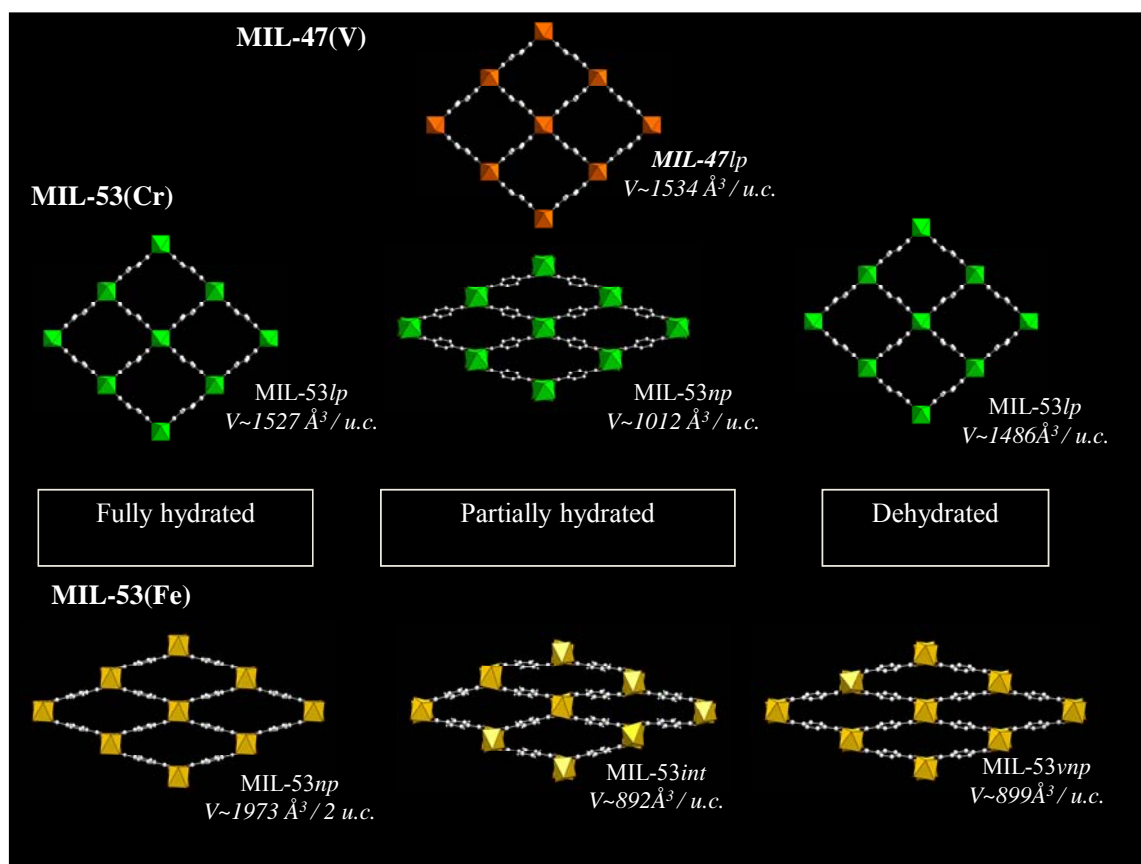
Fe^{III}(OH)(O₂C-C₆H₄-CO₂) was synthesized according to the published procedure.⁴ FeCl₃·xH₂O and terephthalic acid (1, 1 mmol of each in 5 ml of DMF) were reacted in DMF at 150°C for 1 days. The resulting solid was washed with water, DMF, acetone and dried in air, and is formulated Fe^{III}(OH)(O₂C-C₆H₄-CO₂)(DMF)_x (x ~ 0.8). DMF was exchanged by deionised water at room temperature (1 g of the solid in 0.5 l of water) to afford Fe^{III}(OH)(O₂C-C₆H₄-CO₂)·(H₂O). Eventually, Fe^{III}(OH)(O₂C-C₆H₄-CO₂)·x(H₂O) (0<x<0.5) and Fe^{III}(OH)(O₂C-C₆H₄-CO₂) was obtained by heating the above-mentioned solid in air at 50°C and 150°C, respectively. Nitrogen sorption measurement at 77K indicates no permanent microporosity.

Table S3: Unit cell parameters of the different forms of MIL-53(Fe)

Solid	a (Å)	b (Å)	c (Å)	α (°)	β (°)	V (Å ³)	Space Group	Ref.
Fe ^{III} (OH)(O ₂ C-C ₆ H ₄ -CO ₂) MIL-53(Fe)ht labelled MIL-53 <i>vnp</i> (Fe)	21.269(1)	6.760(1)	6.884(2)	-	114.62(1)	899.6(1)	C2/c	5
Fe ^{III} (OH)(O ₂ C-C ₆ H ₄ -CO ₂). x(H ₂ O) (0 < x < 0.5) labelled MIL-53 <i>int</i> (Fe)	6.886(5)	10.557(9)	13.466(2)	109.85(6)	88.05(6)	892.4(1)	P-1	5
Fe ^{III} (OH)(O ₂ C-C ₆ H ₄ -CO ₂).(H ₂ O) MIL-53(Fe)lt labelled MIL-53 <i>np</i> (Fe)	19.320(1)	15.036(1)	6.835(1)	-	96.30(1)	1973.5(1)*	C2/c	5

np = narrow pore, *int* = intermediate pore, *vnp* = very narrow pore
* for a 1x2x1 unit cell

Figure S1: Crystal structures of the MIL-47(V), MIL-53(Cr) (*lp* and *np* versions) and MIL-53(Fe) (*np*, *int* and *vnp* versions) upon water desorption.



- ¹ K. Barthelet, J. Marrot, D. Riou and G. Férey, *Angew. Chem. Int. Ed.*, 2002, **41**, 281.
- ² C. Serre, S. Bourrelly, A. Vimont, N. A. Ramsahye, G. Maurin, P.L. Llewellyn, M. Daturi, Y. Filinchuk, O. Leynaud, P. Barnes and G. Férey, *Adv. Mater.*, 2007, **19**, 2246.
- ³ C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër and G. Férey, *J. Am. Chem. Soc.*, 2002, **124**, 13519.
- ⁴ G. Férey, F. Millange, M. Morcrette, C. Serre, M.-L. Doublet, J.-M. Grenèche, J.-M. Tarascon, *Angew. Chem. Int. Ed.*, 2007, **46**, 3259.
- ⁵ F. Millange, N. Guillou, R. I. Walton, J.-M. Grenèche, G. Férey, *Chem. Commun.*, 2008, 4732.