Tuning the breathing behaviour of MIL-53 by cation mixing

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Experimental procedure

A mixture of 250 mg of terephthalic acid (1.5 mmol), 28 mg of Iron powder (0.5 mmol) and 200 mg of Chromium nitrate (0.5 mmol) in 3.5 mL distilled H_2O was prepared. 1.5 mL of HF solution (0.15 mmol) was then added. The whole mixture was then transferred to a Teflon lined vessel and heated to 453 K (at a rate of 0.2 °C/min) for 96 hours. After cooling to room temperature (rate of 0.1 °C/min), the solution was filtrated and the obtained powder washed with water. The solid was then dispersed in 10 mL of dimethylformamide and heated to 423 K for 12 hours. After cooling to room temperature, the resulting exchanged compound was recovered by filtration.

Activation

The narrow pore form (low temperature form) was obtained after heating the as-synthesized compound to 473 K under air for about 18 hours.

Energy-Dispersive X-Ray spectroscopy (EDX)

A JSM-5800LV Scanning Microscope equipped with an integrated EDX system was used to evaluate the ratio between Iron and Chromium. The Cr/Fe molar ratio does not vary significantly depending on the position the measurement is taken which suggests the sample is homogeneous. On average 60 molar% Cr/40 molar% Fe was found in the sample.

Elemental Analysis

The analysis was performed at CNRS Service Central d'Analyse (SCA), Solaize, France.

The following mass percentages were obtained:

C: 38.68%; H: 2.47%; Cr: 12.51%; Fe: 8.87%; F: 2.29% (Theoretical: C: 37.94%; H: 2.67%; Cr: 12.31%; Fe: 8.82%; F: 2.25; O: 36.00%)

Proposed formula: $Cr_{0.6}Fe_{0.4}(OH)_{0.7}F_{0.3}(OOC\text{-}C_6H_4\text{-}COO).(H_2O)$; Mw= 253.27 g.mol^{-1}

Thermogravimetric Analysis (TGA)

A PerkinElmer STA 6000 apparatus was used for thermogravimetric analyses under O_2. A heating rate of 1°C.min^{-1} was used. The experiment was done on the MIL-53(Cr-Fe) compound free of unreacted terephthalic acid after a DMF soaking step. The weigh losses are well within the expected range i.e., 21% for the DMF molecules (20.8% calc. considering 0.85 DMF molecules) and 53% for the bound terephthalates (55.2% calc. considering the formation of Cr_2O_3 and Fe_2O_3).

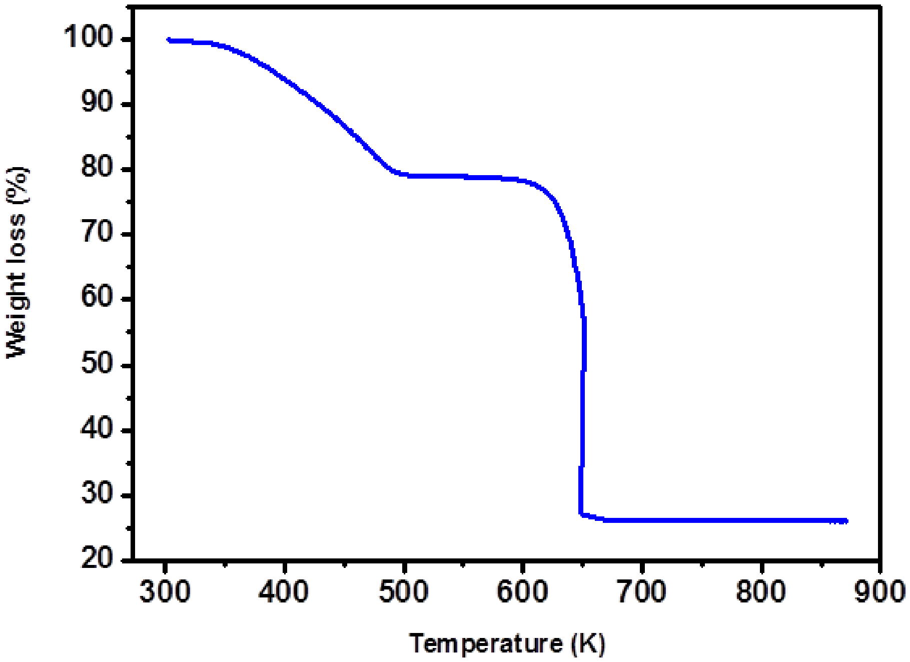

Figure S1: Thermogravimetric analysis for the MIL-53(Cr-Fe) (DMF)

X-Ray powder diffraction

Data were collected on a Bruker D8 Advance diffractometer with a Debye-Scherrer geometry, in the range 7-60°(2*θ*) with a step length of 0.01°(2*θ*) . The D8 system is equipped with a Ge(111) monochromator producing CuKα1 radiation (λ = 1.540598 Å) and a LynxEye detector. Indexing and Rietveld refinement were performed using Topas software.[i] The structural models of MIL-53-Cr narrow pore (NP) and large pore (LP) forms were used for the Rietveld refinement. Indeed, presence of a small fraction of (LP) form was detected.

	Narrow pore (NP)	Large pore (LP)
Space group	*C*2/*c*	*Imcm*
Cell Volume (Å^3)	1001.2(3)	1573(20)
Wt% - Rietveld	94.5(2)	5.5(2)
a (Å)	19.752(5)	16.9(2)
b (Å)	7.705(1)	13.4(9)
c (Å)	6.798(1)	6.92(3)
β (°)	104.60(3)	
R_{Bragg}	0.015	0.007
R_{wp}	0.029	

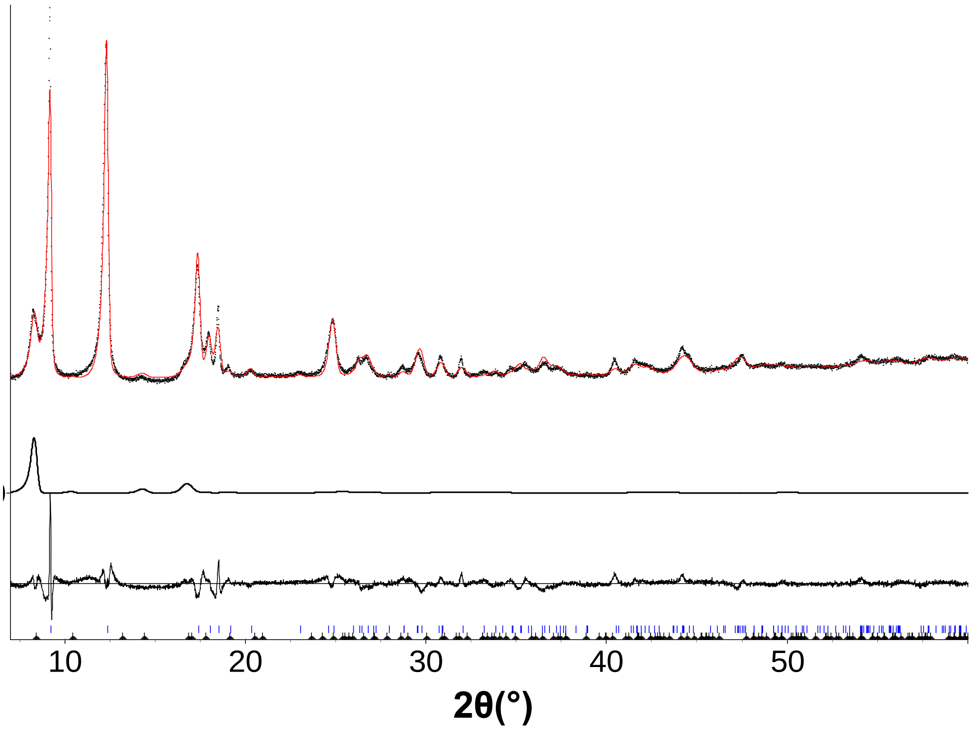

Figure S2: Final Rietveld plot for MIL-53(Cr-Fe) sample showing the mixture of (NP) and (LP) forms

Infra-red Spectroscopy

The sample was dispersed in water (1_2 mg of powder) and deposited on a silicium plate. Samples were placed in a quartz cell equipped with KBr windows. A movable quartz sample holder allowed both activation in situ under vacuum and the acquisition of IR spectra at rt.

Transmission IR spectra were recorded in the 500_5500 cm^{-1} range, with 4 cm^{-1} resolution on a Nicolet Nexus spectrometer equipped with an extended KBr beam splitter device and, depending on the case, either a MCT or a DTGS detector.

Activation was carried out in situ under a secondary vacuum (~10^{-5} mbar). The sample was heated at 473K (ramp 3.75 K/ min) for 1 h. H/D exchange experiments were done by repeated introductions of 13.3 mbar of D_2O at room temperature and further evacuation at 473 K.

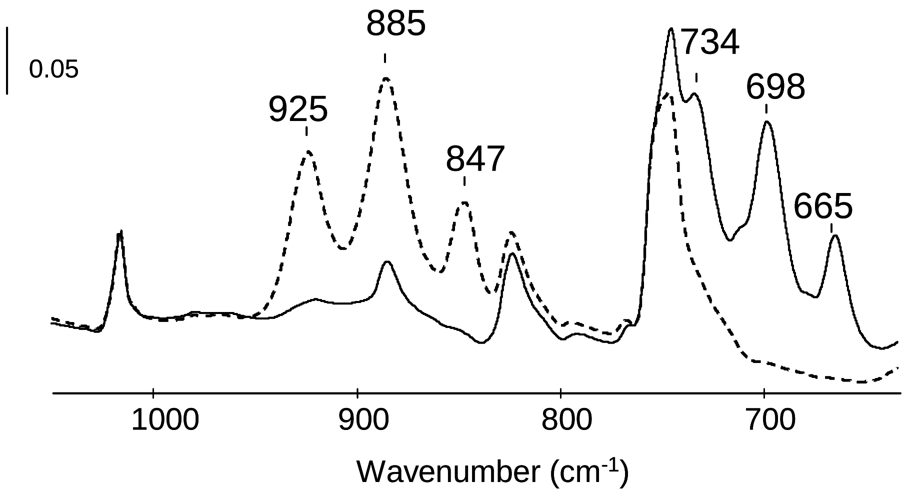

Figure S3: Spectra of MIL-53(Fe, Cr) outgassed at 473 K (dotted line) followed by introduction of D_2O vapor into the cell and evacuation at the same temperature (full line)

Nitrogen Sorption

N_2 sorption analysis was performed on a BelsorpII mini BEL apparatus on MIL-53 (Cr-Fe) in narrow pore form. The sample was degassed at 473 K for 12 hours.

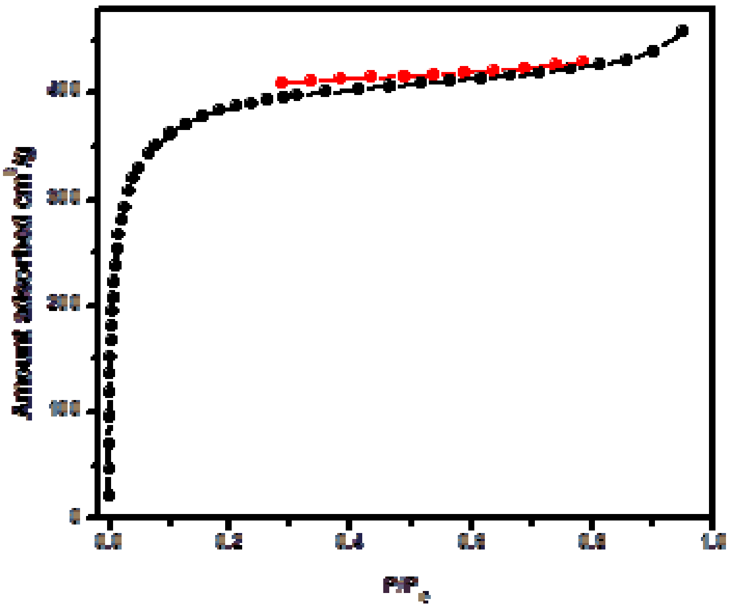

Figure S4: Nitrogen sorption isotherm for MIL-53 (Cr-Fe)

CO_2 sorption

CO_2 sorption was evaluated with an IGA Hiden Isochema system. A sample of MIL-53 (Cr-Fe) in a narrow pore form was degassed at 473 K and the data was collected at 283 K.

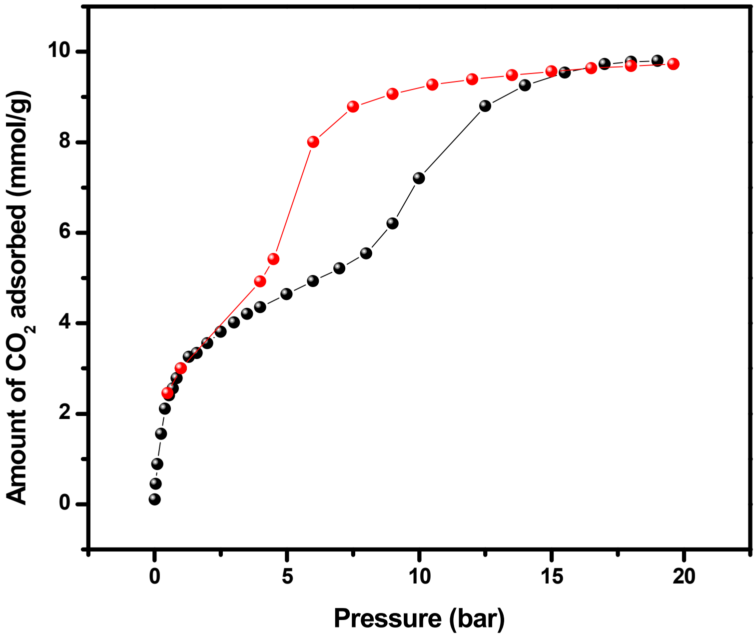

Figure S5: CO_2 sorption isotherm for MIL-53 (Cr-Fe) at 283 K (adsorption in black and desorption in red)

In situ X Ray Powder Diffraction (XRPD) Studies

XRPD patterns under gas pressure were collected at the BM01A station at the Swiss Norwegian Beam Line of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The powdered sample was introduced in a 1 mm quartz capillary and connected to a home-made gas dosing system.[ii] Prior to the experiments, the sample was outgassed under vacuum (pressure of about 10^{-3} mbar) at 473 K for a few hours. The temperature was then adjusted to 303 K, and doses of CO_2 were introduced. XRPD patterns were collected using a MAR345 imaging plate with a sample-to-detector distance of 400 mm and $\lambda = 0.709622$ Å and, were collected one minute after the gas introduction, with an acquisition time of 60 seconds (rotation rate 1° s^{-1}). New XRPD patterns were recorded at the same pressure every five minutes, and equilibrium (at a given pressure) was assumed when no change was observed between the successive patterns. The data were integrated using the Fit2D program (Dr. A. Hammersley, ESRF) and a calibration measurement of a NIST LaB_6 standard sample. The patterns were indexed using the Dicvol software;[iii] Le Bail fits were then performed with the Fullprof2k software package[iv] via the Winplotr interface.[v]

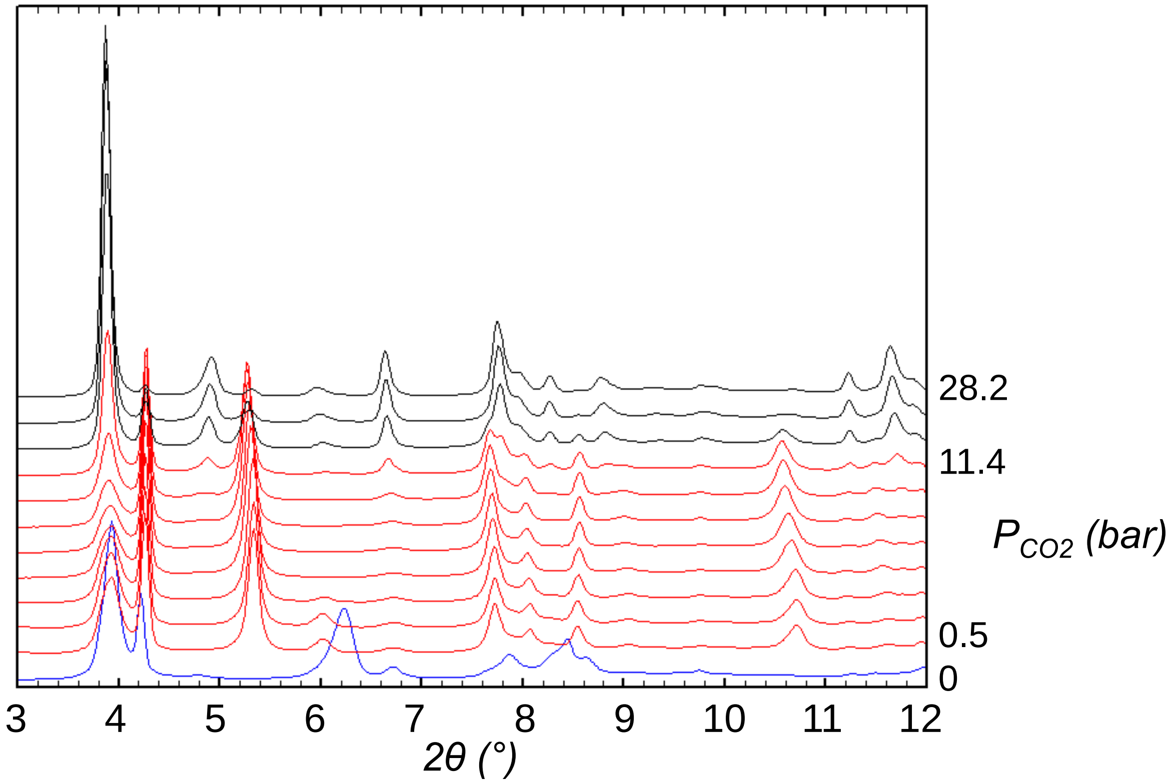

Figure S6: In situ XRPD plots for MIL-53 (Cr-Fe). The colors correspond to the major form. Blue: CP, red: NP, black: LP.

Extended X-ray Absorption Fine Structure (EXAFS) Analysis

EXAFS experiments were performed using beamline B18 of the Diamond Light Source, UK[vi] This beamline provides X-ray energies in the range 2.05 - 35 keV using a fixed-exit, double-crystal Si (111) monochromator, which provided an energy resolution of 2×10^4. The optics of the beamline include a collimating mirror and a toroidal focussing mirror before and after the monochromator, respectively and the measurements were carried out using the Cr coating of these two optical elements. Under this configuration, the expected flux on the sample is of the order of 5×10^{11} photons s^{-1} and the size of the beam at that position is approximately 200 µm in the vertical direction by 150 µm in the horizontal one. In our experiments small samples (~20 mg) of materials to be studied were ground finely with polyethylene powder (~ 80 mg) under acetone and after evaporation of the solvent pressed into 13 mm diameter pellets of ~1 mm thickness under a pressure of 5 Tonnes. EXAFS data were collected at the Fe K and Cr K edges in transmission mode with ion chambers before and behind the sample filled with appropriate mixtures of inert gases to optimise sensitivity. The spectra were measured with a step size equivalent to less than 0.5 eV in the near-edge and with a count time weighted to be proportional to k^2 at high energy. Data were normalised using the program Athena[vii] with a linear pre-edge and polynomial post-edge background subtracted from the raw $\ln(I_t/I_0)$ data, and then analysed using the Artemis software, [vii] which makes use of the FFEF code.[viii]

- The procedure for analysing the EXAFS data and the definition of the terms involved is given below: The crystal structures of hydrated MIL-53(Fe) and its chromium analogue were used to find initial guesses for the metal-scatterer distances (R_{eff}).
- The coordination number of atoms (N) is assumed to be known and hence is fixed
- S_0^2 is a parameter describing the relaxation of electrons around the core hole (only dependent on absorbing atom).
- ΔE_o aligns the data with the theory (constant for a given FEFF calculation on a single data set)
- Fits were performed over a R range of 1-5 and k range between 3 and around 12 (10 for MIL-53(Cr-Fe) at the Fe K edge).

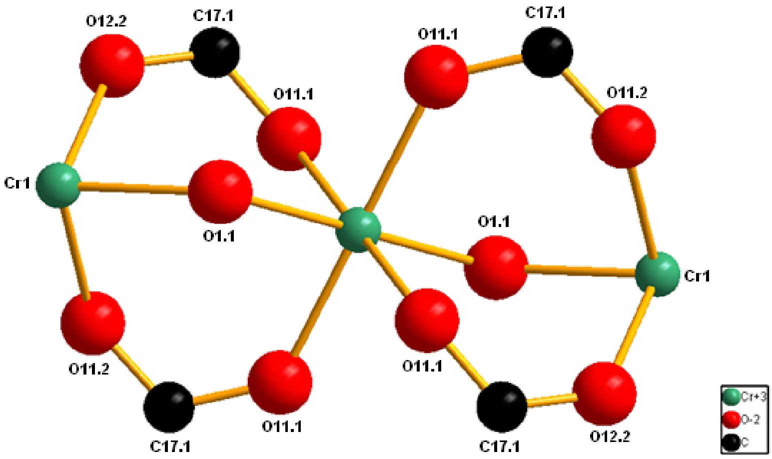

Figure S7: The cluster used to fit the EXAFS data

Figure S7 shows the model used to fit the data for Cr EXAFS. For Fe EXAFS, a similar model was used. Very weak scattering was observed from 2nd shell oxygens (O11.1 and O12.2) so they were not included in the fit (physically unreasonable parameters were produced). This also reduced the overall number of parameters refined.

Note that Fe and Cr are almost impossible to distinguish as back-scatters by EXAFS, differing by only one atomic number so we have used an analysis of interatomic distances to examine the possibility of mixed Fe/Cr chains in the mixed-metal material.

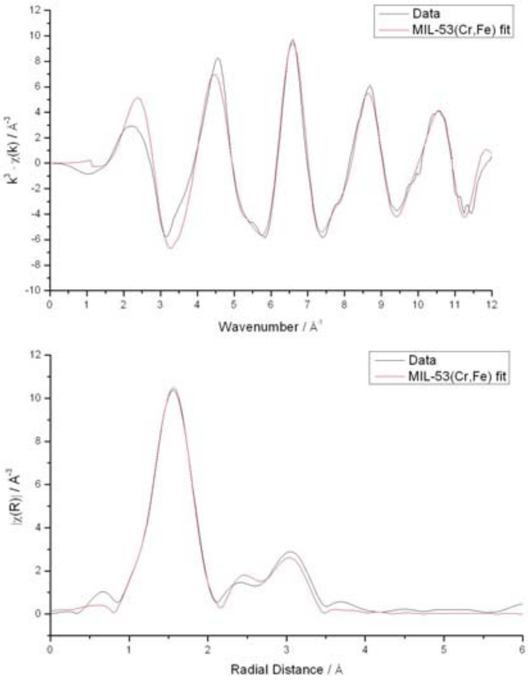

Figure S8: Cr K-edge EXAFS of MIL-53(Fe,Cr): top k^3-weighted EXAFS and bottom the Fourier transform.

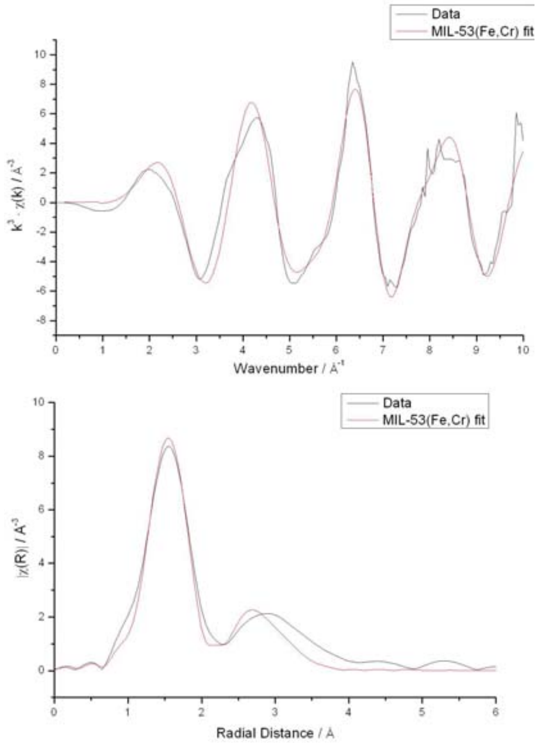

Figure S9: Fe K-edge EXAFS of MIL-53(Fe,Cr): top k^3-weighted EXAFS and bottom the Fourier transform.

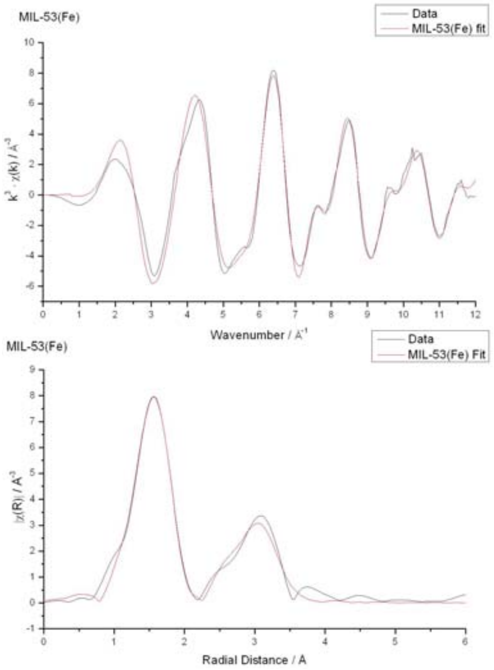

Figure S10: Fe K-edge EXAFS of MIL-53(Fe): top k^3-weighted EXAFS and bottom the Fourier transform.

Table S1: Refined parameters resulting from the EXAFS analysis

Material	**Edge Studied**	**Shell**	**N**	**σ^2 / Å^2**	**R/ Å**
MIL-53(Fe,Cr)	Cr	O	6	0.0036 ± 0.0009	1.973 ± 0.0070
		C	4	0.0055 ± 0.0034	2.960 ± 0.0271
		Fe/Cr	2	0.0054 ± 0.0017	3.419 ± 0.0161
MIL-53(Fe,Cr)	Fe	O	6	0.0036 ± 0.0022	1.997 ± 0.0130
		C	4	0.0049 ± 0.0055	2.948 ± 0.0372
		Fe/Cr	2	0.0056 ± 0.0033	3.419 ± 0.0300
MIL-53(Fe)	Fe	O	6	0.0062 ± 0.0011	1.998 ± 0.0076
		C	4	0.0075 ± 0.0031	2.978 ± 0.0241
		Fe	2	0.0476 ± 0.0012	3.429 ± 0.0120

The errors are statistical errors and the true error on refined interatomic distances is +/- 0.02 Å.

The M--M distance along chain depends on choice of M as shown for the published crystal data for the pure Fe and pure Cr materials:

in MIL-53(Fe) Fe--Fe = 3.416 Å[ix]

in MIL-53(Cr) Cr--Cr = 3.389 Å[x]

For the mixed MIL-53(Fe/Cr) at the Cr K-edge, the refined Cr--M distance (3.429Å) is longer than expected for MIL-53(Cr) (3.389 Å)and matches more closely the Fe--Fe distance in MIL-53(Fe) (3.416 Å from crystallography and 3.429 Å from EXAFS). This provides direct evidence for the presence of mixed-metal chains.

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[i] TOPAS V4.2: General Profile and Structure Analysis Software for Powder Diffraction Data, Bruker AXS Ltd, 2004

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