

## Synthesis and catalytic properties of MIL-100(Fe), an iron(III) carboxylate with large pores

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### Structure Determination.

Powder X-ray diffraction data were collected at the high resolution beamline ID31 of the ESRF, from a sample contained in a 1 mm diameter capillary. ID31 beamline receives X-rays from the synchrotron source (which operates with an average energy of 6 GeV and a current beam of typically 200 mA) from an undulator device. The incident X-ray wavelength was 0.80098(5) Å using an incident beam size of 2.0 mm [2.0 mm (horizontally) × 1.0 mm (vertically)]. Owing to the rapid data collection performance of this beamline (data collection times for a whole pattern of a few minutes), high-speed spinning of the sample is necessary in order to ensure reasonable powder averaging. Hence, samples were mounted (by robot) on a new generation translating fast capillary spinner situated on the axis of the diffractometer, and equipped with an auto-centring and a magnetic coupling for the sample holder. Powder diffraction measurements of particularly high resolution, in terms of minimum instrumental contribution to the widths of the diffraction lines, were carried out over the angular range of 0.915-60° 2θ, with a step of 0.003°. The sample was cooled to 80 K using an Oxford Cryosystems 700 series nitrogen cryostream and data collection was performed at this temperature. Using positions extracted for the first 20 diffraction lines, a cubic unit cell with dimension of  $a = 72.34(1)$  Å was found using the DICVOL program (Boultif & Louer, 1991) with figure of merit  $F(20) = 150$ , a value which indicates that the indexing is substantially correct. Systematic absences were consistent with the space group  $Fd\bar{3}m$  ( $n^{\circ}227$ ).

Based on previous results obtained with the porous chromium trimesate MIL-100(Cr) and considering that **MIL-100(Fe)**, after a pattern matching performed using Fullprof<sup>2</sup> and its Winplotr interface,<sup>3</sup> the structure refinement was initiated using the atomic positions obtained from the structure of MIL-100(Cr). The structure of **MIL-100(Fe)** was first refined using also Fullprof and in a second step, several successive Fourier differences were performed, using the Shelxtl97 program<sup>4</sup> to locate the missing water molecule atoms present within the pores. Please note that the solid was heated a few hours at 120°C in an oven prior to the data collection in order to minimize the amount of free water in the pores. Some of the water molecules were found occupying disordered crystallographical sites and partial occupations were applied. Fluorine counter anions present in MIL-100, are probably located in terminal position bounded to iron atoms.

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The whole structure of **MIL-100(Fe)** was finally refined using Fullprof. Experimental points were used to adjust the background with a Pseudo-Voigt function to determine the peak profile. Two asymmetry parameters, one overall thermal parameter were also applied during refinements. Distance and angle constraints were used during the refinement especially to refine the trimesate anion as a rigid body. Despite the large number of parameters (68 independent framework atoms (~170 parameters) in a cell volume of 394,400 Å<sup>3</sup>), the refinement converges toward good R values<sup>5</sup> ( $R_p=12.0\%$ , and  $R_{\text{Bragg}}=12.9\%$ ). Some discrepancies are however still present because of an excessive peak anisotropy due to the very low peak width. Crystal data and structure refinement parameters are reported in the crystallographic Table. The refinement correctly converged towards the general formula  $\text{Fe}_3\text{F}_3\text{O}[\text{C}_6\text{H}_3-(\text{CO}_2)_2]_3 \cdot n\text{H}_2\text{O}$  ( $n \sim 14.5$ ) which is in agreement with the chemical analysis.

## Crystallographic Table.

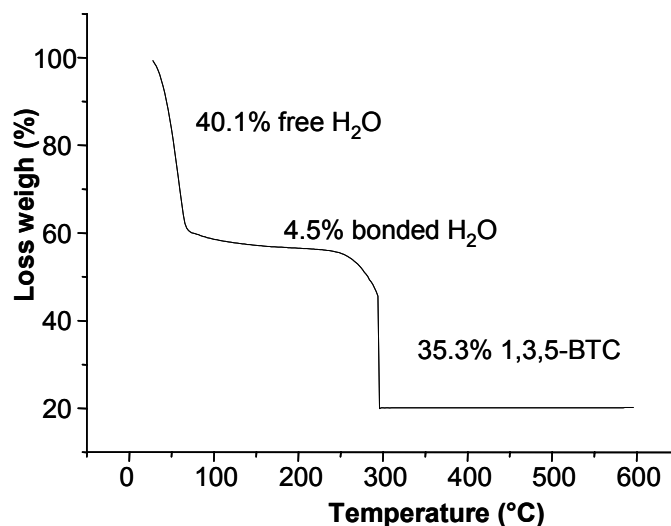
**Table S1** : Crystal data and structure refinement parameters for **MIL-100(Fe)**.

Formula	$\text{Fe}_3\text{X}(\text{H}_2\text{O})_2\text{O}[(\text{C}_6\text{H}_3)-(\text{CO}_2)_3]_2 \cdot n\text{H}_2\text{O}$ X=F,OH; n~14.5
Molar mass ( $\text{g mol}^{-1}$ )	878 (X=F)
System	cubic
Calculated density ( $\text{g.cm}^{-3}$ ) (hydrated phase)	0.98
Calculated density ( $\text{g.cm}^{-3}$ ) (anhydrous phase)	0.69
Space group	<i>Fd-3m</i> (n°227, origin choice n°2)
Cell parameters	a = 73.340 Å (1) V= 394481.1(1) Å <sup>3</sup> (1)
Figures of merit	$M_{20}=30$ $F_{20}=150$ (0.0011, 73)
Synchrotron radiation (Å)	0.801682
Data collection (°)	1.5- 30
Number of independent reflections	2636
Number of independant atoms	97
N. intensity-dependent parameters	231
N. profile parameters	9
N. Distance constraints	97
Profile function	Pearson VII
Background	Experimental (73 points)
Overall Thermal parameter	1.6(1)
N. asymetry parameters	3
R <sub>p</sub>	12.0
R <sub>wp</sub>	16.1
R <sub>B</sub>	12.9

$$(R1 = \Sigma(|F_o| - |F_c|) / \Sigma |F_o| \text{ et } wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2})$$

### Thermogravimetric analysis.

Thermogravimetric analysis (Figure S1) were carried out in a TGA2050 TA equipment from 25 to 600°C, using a heating rate of 3°C.min<sup>-1</sup> under a oxygen flow (100 mL.min<sup>-1</sup>).



**Figure S1.** Thermogravimetric analysis of MIL-100(Fe)

### Adsorption.

Nitrogen sorption experiment was performed at 77 K using a ASAP2010 Micromeritics apparatus with nitrogen as the adsorbed gas. The MIL-100(Fe) sample was activated during 16 hours at 150°C under primary vacuum prior to the experiment.

### Mössbauer.

Transmission Mössbauer experiments were carried out using a constant acceleration spectrometer and a <sup>57</sup>Co source diffused into a Rh matrix. The Mössbauer spectra were recorded at 300K and at 77 K using a bath cryostat. Velocity calibrations were made using an <sup>57</sup>Fe foil at room temperature (300K) while the isomer shift values are quoted relative to that of <sup>57</sup>Fe at 300K. The hyperfine parameters were refined using a least square fitting procedure in MOSFIT program.<sup>[1]</sup>

### Catalysis.

The liquid phase benzylation reaction of benzene with benzyl chloride was carried out in a magnetically stirred glass reactor (50 ml) fitted with a reflux condenser and a mercury thermometer. (Reaction conditions: reaction temperature 70°C, 7.8 ml benzene, benzene/benzyl chloride = 10 (molar ratio), 0.1g catalyst) During the reaction, inert He gas (50 ml/min) was continuously bubbled through the liquid reaction mixture. Prior to the reaction, MIL-100(Fe) and MIL-100(Cr) were dehydrated overnight at 150°C and the zeolite catalysts were dried in a flow of moisture-free N<sub>2</sub> at 450°C for 1 h. The reaction was started by injecting benzyl chloride in the reaction mixture, containing catalyst and benzene, after attaining the reaction temperature. The conversion of benzyl chloride as well as the selectivity to diphenylmethane was calculated by analyzing samples of the reaction mixture collected at regular intervals by a gas chromatograph equipped with a flame ionization detector FID and a capillary column SE-54. In order to confirm the induction period and initial reactivity, the HCl evolved during the reaction was transferred to an Erlenmeyer flask by He gas and was measured by acid-base titration with a 0.1 M NaOH solution containing phenolphthalein indicator.

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[1] J. Teillet, F. Varret, unpublished ed.