Effect of the Nature of the Metal on the Breathing Steps in MOFs with Dynamic Frameworks

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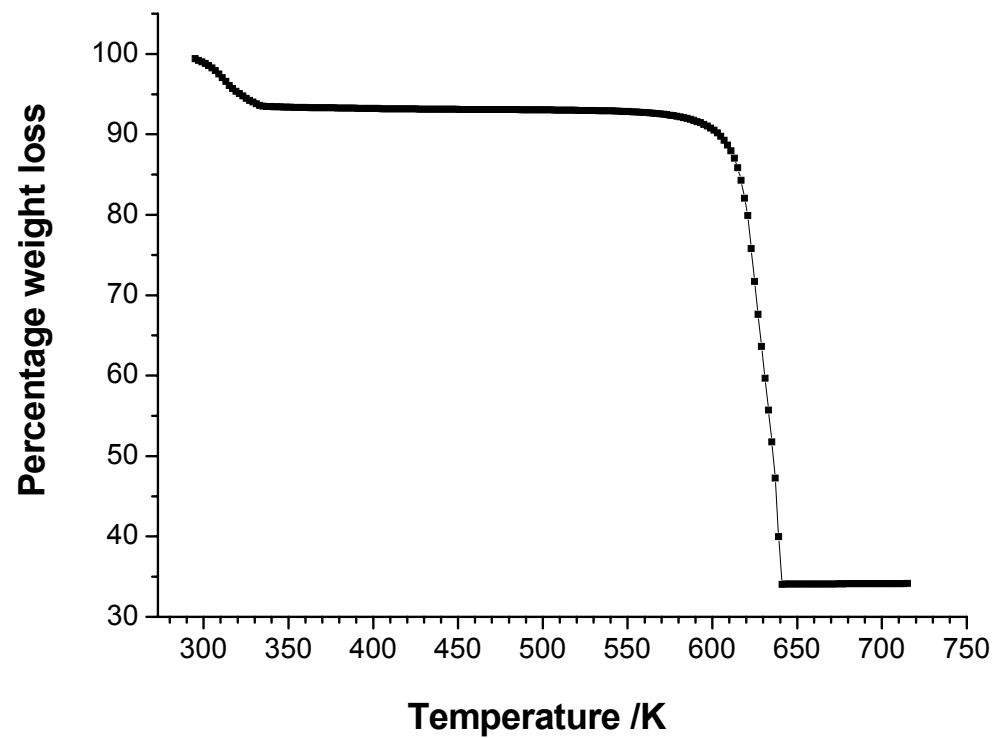


Fig. S1 : Thermogravimetric analysis

Structure solution

Unit cells and space groups were found unambiguously with satisfactory figures of merit [M_{20} = 50 for **MIL-53(Fe)_lt,** M_{20} = 86 for **MIL-53(Fe)_int** and M_{20} = 208 for **MIL-53(Fe)_ht**]. For **MIL-53(Fe)_ht**, the atomic coordinates of the MIL-53(Cr) skeleton were used as a starting model in the Rietveld refinement. For **MIL-53(Fe)_lt** and **MIL-53(Fe)_int**, first calculations were performed with the EXPO package,[1] using EXTRA for extracting integrated intensities and SIR*97* for direct methods structure solution. Lists of 476 and 431 reflections were extracted in the angular range 2 – 48° (2θ), respectively. According to the degree of diffraction overlap, 21.99 % and 21.73 % of these reflections were statistically considered as independent. For **MIL-53(Fe)_lt,** the whole structural model (three independent Fe atoms and their environments, two organic moieties and two occluded water molecules) was found unambiguously from the E-map with the highest figure of merit. The atomic coordinates were then used as a starting model in the Rietveld refinement and the two independent terephthalate ions were treated as rigid bodies. At the final stage, Rietveld refinement of **MIL-53(Fe)_lt** involved the following structural parameters : 15 atomic coordinates (Fe$_1$, OH$_1$, OH$_2$, Ow$_1$ and Ow$_2$) , 6 translation and 6 rotation parameters of terephthalate ions, 4 thermal factors and 1 scale factor in comparison with 87 atomic coordinates corresponding to 31 non-hydrogen independent atoms. The anisotropic line broadening effect was corrected by using spherical harmonics series. The final Rietveld plot corresponds to satisfactory crystal structure model indicator (R_B = 0.040) and profile factors (R_P = 0.072 and R_{WP} = 0.089). For **MIL-53(Fe)_int,** two independent Fe atoms and their environments were found unambiguously from the E-map with the highest figure of merit. According to the MIL-53(Cr) topology, three independent

organic moieties (with two located on symmetry centres) have been considered. Their positions were then determined by using the direct space strategy program TOPAS. The use of 5 objects (three organic molecules and two octahedra centered on starting positions found by SIR*97*) restricts the number of parameters to 18 (3 for the orientation of each object and 3 for the translation of the organic moiety in general position) in the simulated annealing process. The atomic coordinates were then used as a starting model in the Rietveld refinement and the three independent terephthalate ions were treated as rigid bodies. At the final stage, Rietveld refinement of **MIL-53(Fe)_int** involved the following structural parameters : 12 atomic coordinates (Fe_1, Fe_2, OH_1 and OH_2) , 3 translation and 9 rotation parameters of terephthalate ions 3 thermal factors and 1 scale factor in comparison with 84 atomic coordinates corresponding to 28 independent atoms. The anisotropic line broadening effect was corrected by using spherical harmonics series. The final Rietveld plot corresponds to satisfactory crystal structure model indicator (R_B = 0.034) and profile factors (R_P = 0.069 and R_{WP} = 0.083). The same strategy was used for the Rietveld refinement of **MIL-53(Fe)_ht.** It also corresponds to satisfactory crystal structure model indicator (R_B =0.051) and profile factors (R_P = 0.0728 and R_{WP} = 0.093).

1. A. Altomare, M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, and R. Rizzi, *J. Appl. Crystallogr.*, 1999, **32**, 339
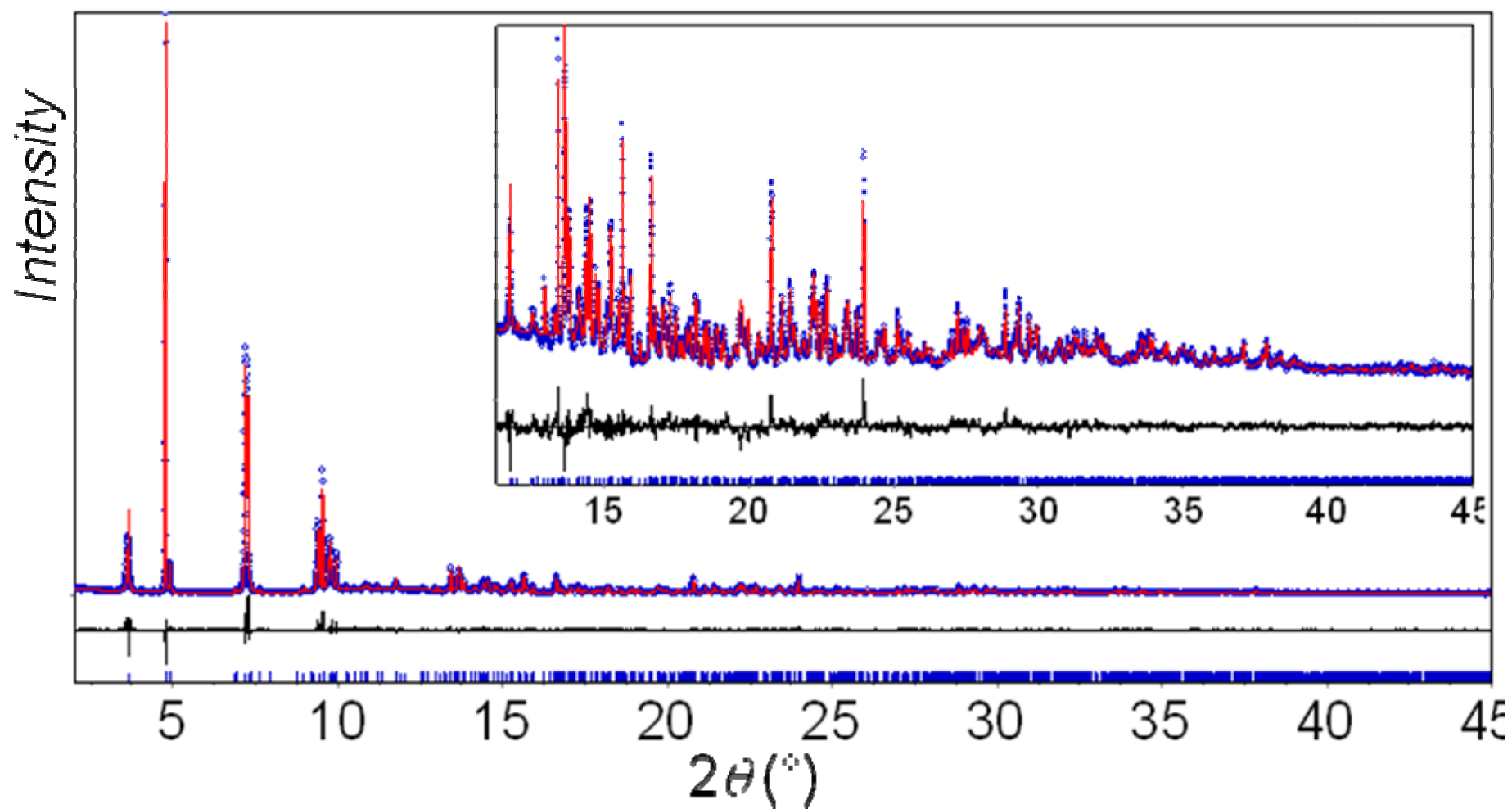
MIL-53(Fe)_lt

$a = 19.3197(2)$ Å, $b = 15.0362(2)$ Å, $c = 6.83508(6)$ Å, $\beta = 96.305(1)°$ and $V = 1973.55(3)$ Å^3; SG: $C\,2/c$
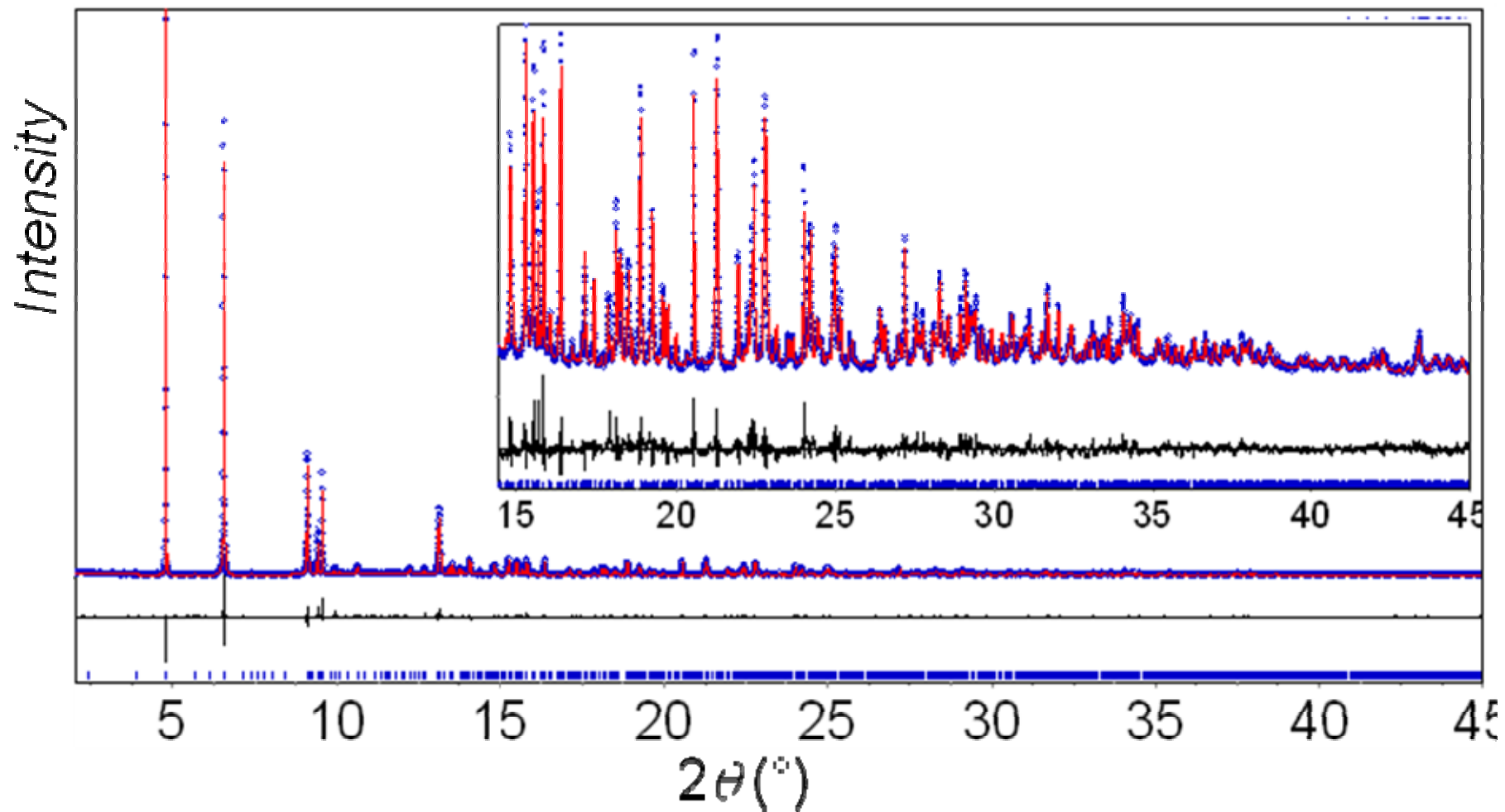
MIL-53(Fe)_int

a = 6.8865(2), b = 10.5579(2), c = 13.4662(3) Å, α = 109.856(2), β = 88.058(2), γ = 103.967(2)° and V = 892.41(3) Å^3; SG: P-1

MIL-53(Fe)_ht

$a = 21.2693(3)$, $b = 6.7589(1)$, $c = 6.8838(2)$ Å, $\beta = 114.625(2)°$ and $V = 899.59(3)$ Å^3; SG: $C\ 2/c$