



	Experiment title: Powder X-ray diffraction studies of nanoporous Metal-Organic Frameworks (MOFs) with various encapsulated guest molecules.	Experiment number: CH-2707
Beamline: ID31	Date of experiment: from: 28 January 2009 to: 31 January 2009	Date of report: August 2009
Shifts: 9	Local contact(s): I. Margiolaki	<i>Received at ESRF:</i>
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Report:

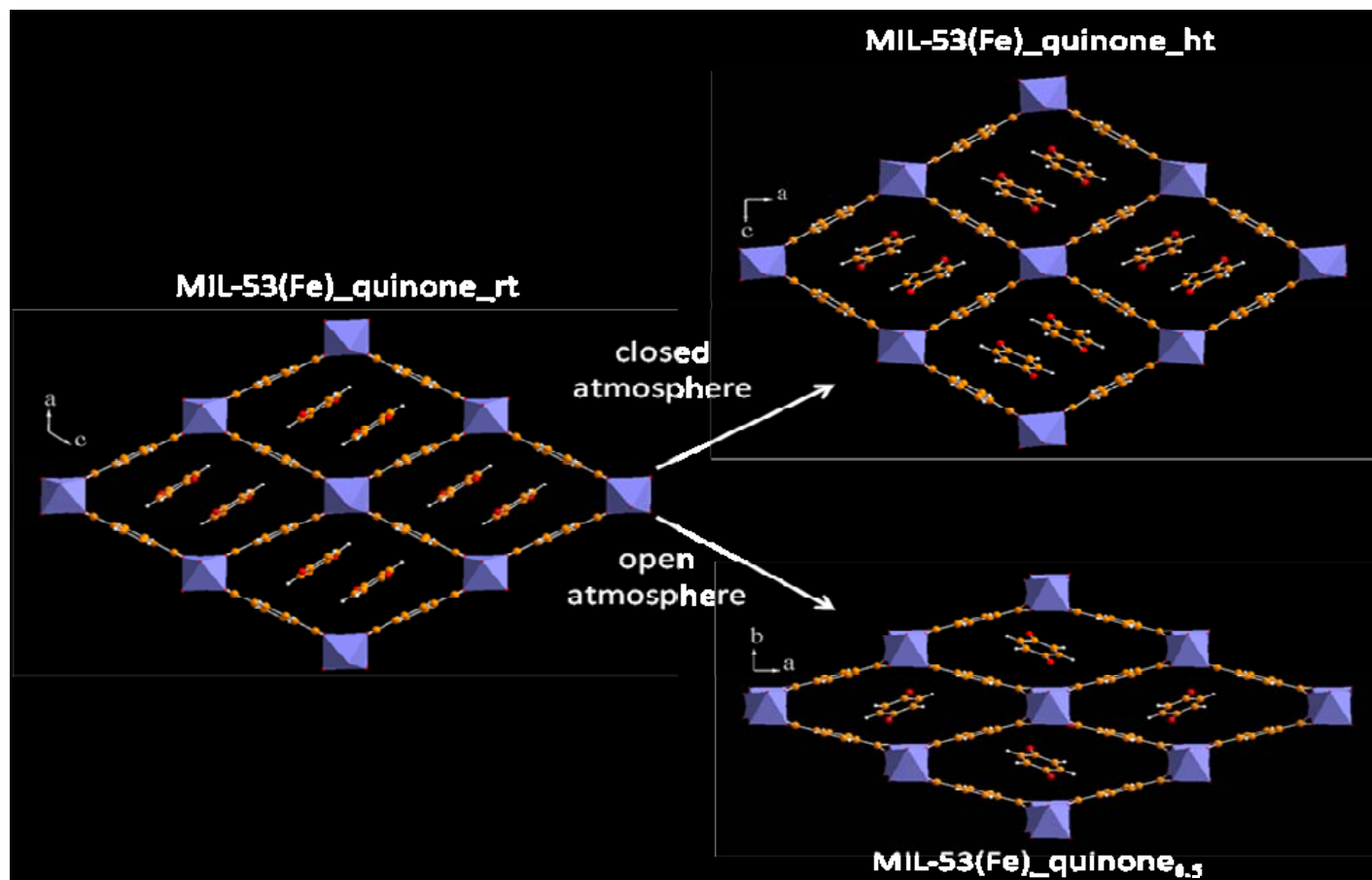
The wide-ranging properties and applications of nanoporous zeolites in ion-exchange, molecular separation and shape-selective molecular catalysis are well known but the continued drive for the optimisation of properties of such materials for practical application has lead to the intensive study of other classes of solids. Among the most striking materials that have been developed in the past few years are the Metal-Organic Framework materials. These solids are constructed from metal-oxy clusters link by organic moieties, and thus are described as organic-inorganic hybrid solids. This, now extensive, family of materials, differs in chemistry from traditional zeotype solids whose open nanoporous frameworks are purely inorganic, and this offers unprecedented opportunities for the rational synthesis of novel porous solids whose channel dimensions and connectivity are controlled by the choice of organic linkers and whose chemistry (such as active sites for catalysis or sorption) are tuned by choice of inorganic cluster unit. The MIL-n family of solids is one example of the new hybrid inorganic solids and these have been developed using a combination of targeted synthesis and computational prediction such that novel solids have been prepared by linking well-defined transition-metal oxide clusters (secondary building units) with carboxylate linkers of choice. Some of these materials possess the largest surface areas known for crystalline solids, and offer new possibilities in the sorption and separation of large entities such as biomolecules and nanoparticles.

Our initial focus was to characterise properly the host material MIL-53, an iron (III) carboxylate $\text{Fe}^{\text{III}}(\text{OH})\{\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\}$ in the presence of 1,4-benzoquinone. This work has now been published in *Chemistry of Materials* [1] and is illustrated in the figure below.

In order to prepare the quinone-loaded samples, **MIL-53(Fe)_H₂O** was first dehydrated by heating at 373 K under vacuum to get **MIL-53(Fe)_vac**. As soon as the 1,4-benzoquinone molecule is introduced, the peaks of **MIL-53(Fe)_vac** decrease and completely disappear for $y=1$ leading to the new phase **MIL-53(Fe)_quinone_rt**. Unit cell and space group were found unambiguously from synchrotron X-ray powder diffraction with satisfactory figure of merit ($M_{20} = 25$). **MIL-53(Fe)_quinone_rt** crystallizes at room temperature in the $P2_1/c$ space group [$a = 11.9140(2) \text{ \AA}$, $b = 6.8775(2) \text{ \AA}$, $c = 21.3414(3) \text{ \AA}$, $\beta = 123.67(2)^\circ$ and $V = 1455.33(4) \text{ \AA}^3$]. The final Rietveld plot corresponds to satisfactory crystal structure model indicator ($R_B = 0.031$) and profile factors ($R_P = 0.070$ and $R_{WP} = 0.096$). In this compound, the Fe^{3+} cation is six-fold coordinated in distorted octahedral geometry and the octahedral M-O centres are linked by sharing *trans*-hydroxyl groups forming bent M-(OH/F)-M chains. Bond valence calculations and infra-red spectroscopy gave further evidence for the presence of this μ_2 -hydroxyl group. The oxygen atoms of the BDC moieties occupy the equatorial positions of the $\text{MO}_4(\text{OH/F})_2$ octahedra while the OH/F groups occupy the shared positions between adjacent octahedra along the chain. The axial oxygen atom corners are shared by neighbouring octahedra to form a zigzag ---OH/F- Fe^{3+} -OH/F- Fe^{3+} --- backbone. The metal oxide chains in these compounds are parallel to each other and are cross-linked by the di-anions to form a framework with an array of 1-D diamond-shaped channels. Each channel is delimited by four walls of benzyl units and four chains of corner-shared octahedra. At room temperature, **MIL-53(Fe)_quinone_rt** contains guest molecules lying inside the channels that are nearly parallel to half of the four organic walls. Double chains of quinone molecules are aligned along the metal oxide chains, with a shift of half of the b axis between organic moieties of two adjacent chains. In contrast to what it is observed with pyridine the quinone molecules are not hydrogen-bonded to the hydrophilic part of the octahedral chain but interact through π - π interactions both (i) between equivalent neighbouring quinone molecules of two adjacent chains and (ii) between quinone molecules and the benzyl units of the dicarboxylate linkers.

At this stage, high resolution synchrotron XRD data were collected to obtain better insights into the structural changes of the temperature driven **MIL-53(Fe)_quinone_rt**. First, heating the **MIL-53(Fe)_quinone_rt** phase in a sealed capillary at 140°C led to the new phase labelled **MIL-53(Fe)_quinone_ht**. It crystallizes in an orthorhombic unit cell [$a=17.3814(3)$, $b= 6.8888(2)$, $c=12.4796(2) \text{ \AA}$, $V=1494.3(4) \text{ \AA}^3$; SG: $Pn2_1a$, $M_{20} = 254$]. The final Rietveld plot corresponds to satisfactory crystal structure model indicator ($R_B = 0.044$) and profile factors ($R_P = 0.073$ and $R_{WP} = 0.098$). It is obvious under these conditions that the guest molecules cannot leave the pores, and only a reorganization of half of the quinone double chains is clearly observed. Within the same tunnel, the double chain is still nearly parallel to half of the four organic walls, while the double chain is tilted in order to be nearly parallel to the second half of the four organic walls in the nearest neighbouring tunnels. This phenomenon can be described as a “flip flop effect”. On the other hand, under open atmosphere, a different thermal behaviour appears. A new phase has been isolated which crystallizes in a monoclinic unit cell [$a=19.767(1) \text{ \AA}$, $b= 9.0697(7) \text{ \AA}$, $c=6.8753(3) \text{ \AA}$, $\beta = 106.814(5)^\circ$ and $V=1179.9(1) \text{ \AA}^3$; SG: Cc , $M_{20} = 50$]. The decrease in volume ($\sim 21\%$) is correlated to the departure of half of the quinone guest molecules from the pores leading to **MIL-53(Fe)_quinone_{0.5}**. The final Rietveld plot corresponds to satisfactory crystal structure model indicator ($R_B = 0.041$) and profile factors ($R_P = 0.079$ and $R_{WP} = 0.098$). Due to the departure of half of the quinone molecules, single chains are now present at the centre of the

tunnels with 50% occupancy. Within one tunnel, the single chain can be nearly parallel either to half of the four organic walls or to the second half. This new orientation of the organic moieties allows now both (i) π - π interactions between quinone molecules and the benzyl units of the dicarboxylate linkers and (ii) hydrogen bonds to the hydrophilic part of the octahedral chain. It is interesting to note that one oxygen in the quinone molecule is now hydrogen bonded to the OH group of the chains of corner-shared octahedra.



[1] Influence of the Benzoquinone Sorption on the Structure and Electrochemical Performance of the MIL-53(Fe) Hybrid Porous Material in a Lithium-Ion Battery, De Combarieu A., Morcrette M., Millange F., Guillou N., Cabana J., Grey C.P., Margiolaki I., Férey G., Tarascon J.M., Chemistry of Materials, vol.21, p.1602-1611, 2009.