



	Experiment title: Structural Flexibility of Functional Metal Carboxylate MOFs for Sorption	Experiment number: CH-3031
Beamline: ID31	Date of experiment: from: 18 Dec 2009 to: 21 Dec 2009	Date of report:
Shifts: 9	Local contact(s): Adrian Hill	<i>Received at ESRF:</i>
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Report:

We have been studying the interaction of porous metal-organic framework materials^[1] with guest molecules with the aim of understanding how the solids might be used in the separation of small molecules for various practical applications. These solids have the potential to offer distinct advantages over conventional inorganic porous materials, one reason being their structural flexibility where dramatic changes in pore volume are seen, involving displacements of atoms of several Ångströms whilst crystallinity is maintained.^[2] A good example is the group of materials MIL-53(M) (M = Cr, Al, Ga and Fe) (MIL = Material from Institut Lavoisier) or $M^{III}(\text{OH})\cdot[\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2]$, which are built up from chains of M(III) octahedra linked *via* terephthalate linkers to form a three-dimensional ordered structure with a one-dimensional channel system along the *c* axis.^[3] Materials with the MIL-53 structure have now been studied extensively for their vapour phase sorption properties, and they show high capacity for a variety of small molecules including CO₂, H₂, H₂S and hydrocarbons, where in some cases an evolution of structure with guest concentration has been observed.^[4]

In this experiment on ID31 we studied the interaction of iron(III) containing MIL-53 solids with a series of simple alcohols, methanol, ethanol, propan-1-ol and propan-2-ol, in the liquid phase. This work follows from a preliminary communication in which we reported the observation of a crystalline intermediate in the case of methanol sorption from the liquid phase,^[5] suggesting that the pore-opening associated with breathing may be a complex process involving several steps. We have now extended our study to a range of other alcohols and also at the same time investigated the simplest modification of the MIL-53 structure: the partial replacement of framework hydroxide by fluoride. The work on ID31 was complemented by a comprehensive time-resolved EDXRD study using the HASYLAB facility in Germany.

Data were measured from MIL-53 that has been immersed in alcohol or mixtures of alcohol and water within the capillary. Figure 1 shows the relationship between the various crystal symmetries encountered and the basic MIL-53 structure type: the topology of the framework is identical in each case, but small structural distortions result in various crystal symmetries. In most cases the effect of framework fluorination is subtle, but detectable in small changes in unit cell volume: in general the fluorinated host material has a slightly smaller unit cell volume than the fully hydroxylated material for a given guest.

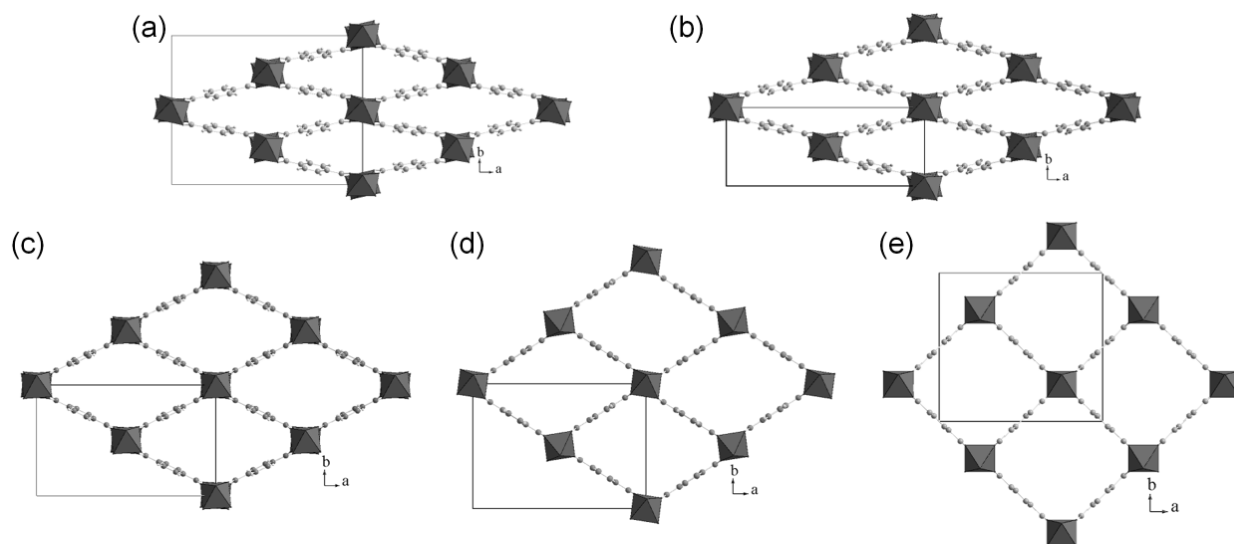


Figure 1: The structure of MIL-53(Fe) in various expanded forms showing the relationship of unit cell volume to the framework topology (a) closed $P2_1/c$ form seen for MIL-53(Fe,OH)[H₂O]^[3c] (b) closed $C2/c$ form seen for MIL-53(Fe,F,OH)[H₂O]^[6] (c) partially open $C2/c$ form seen for MIL-53(Fe,F,OH)[propan-2-ol] and for the case where diluted alcohols are added (d) open $Pnam$ form seen in the presence of excess propan-1-ol and (e) fully open $Imcm$ form seen in the presence of excess methanol or ethanol. Guest molecules are omitted. See Table 1 for unit cell parameters of the materials studied in the present work.

The alcohol molecules are disordered in these host:guest systems and only in two cases could we obtain a structure solution: these involved partial occupancy of several sites showing considerable static disorder. Nevertheless, the results from ID31 have been crucial in understanding the time-resolved EDXRD data and a paper describing the complete study has been accepted for publication in *Chemistry a European Journal*.^[7]

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