Metal–Organic Frameworks

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Structural Effects of Solvents on the Breathing of Metal–Organic Frameworks: An In Situ Diffraction Study**

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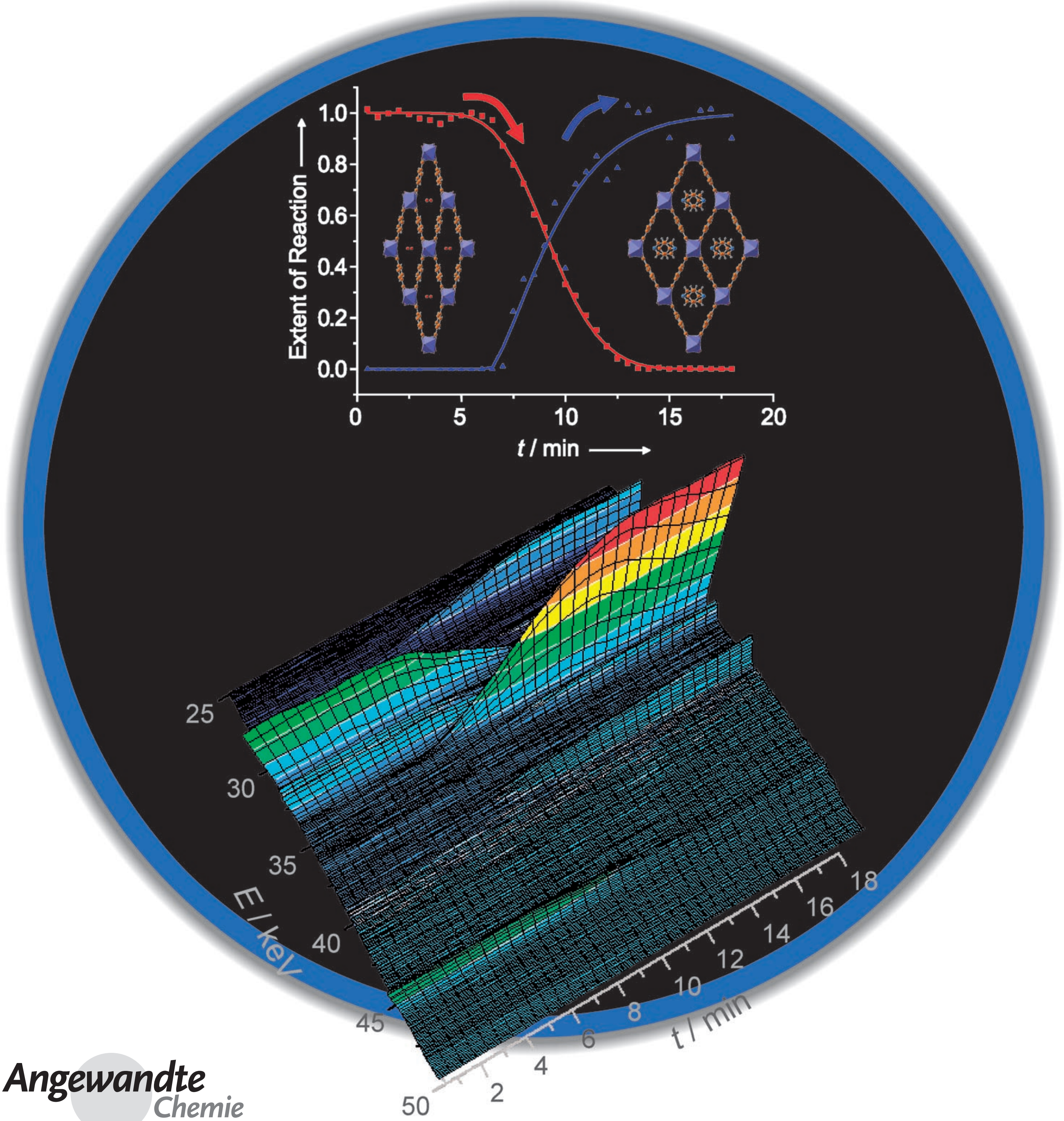

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Research on metal–organic frameworks (MOFs) is currently very topical.[1–4] The combination of inorganic and organic moieties linked by strong covalent bonds generates a huge number of three-dimensional open-framework structures, with porosities that span those exhibited by the well-known microporous zeolites and the mesoporous silicas; they also present some of the highest surface areas seen for crystalline inorganic solids.[5,6] Currently, study of the materials is focused on their applications in the sorption and separation of gases, mainly hydrogen for energy purposes[7–11] and carbon dioxide for environmental concerns,[12,13] but other applications have recently emerged, for example, in the domains of drug delivery,[14] catalysis,[15] and electrode materials.[16]

The synthesis of MOFs occurs in solvothermal media (water, organic solvents, or their mixtures), yet none of the recipes described in the literature[1] explains the reasoning behind solvent choice, despite it being an important parameter in the phase-pure synthesis of a desired phase. The interaction of MOF materials with organic solvent after synthesis is also important, because many materials show selective uptake of guest molecules, which is highly desirable for use in the separation or purification of organics. Herein, we describe work aimed at understanding the influence of solvent properties on structural changes in MOFs in terms of host–guest interactions.

We chose to study the metal(III) carboxylate family MIL-*n* (MIL = material of Institut Lavoisier) that shows a unique and interesting structural feature of MOFs: the "breathing" effect.[17,18] In these solids the introduction of guest molecules, such as water or CO_2,[19–21] gives rise to reversible atomic displacements of several Å, considerably larger than those observed in traditional zeolite materials. The MIL-*n* compounds can thus potentially act as tunable, selective molecular filters.[20,22]

The time-resolved energy-dispersive X-ray diffraction (EDXRD) technique at the Daresbury SRS was used for the study reported here. For over a decade, it has proved its efficiency in looking at the crystallization of a variety of microporous materials including zeolites and phosphates,[23–25] the behavior of minerals[26] and cements[27] under hydrothermal conditions, and the investigation of the intercalation of molecules and ions into layered solids.[28,29] The main advantage of EDXRD over other time-resolved diffraction techniques lies in the use of intense, white-beam X-rays over a wide energy range. This permits penetration of laboratory-sized reaction vessels (constructed from a variety of materials ranging from teflon-lined steel to glass), which allows diffraction data to be recorded rapidly (of the order of seconds) by a fixed, three-element detector[30] from stirred reaction mixtures in real time. This is particularly advantageous in the case of solid–liquid mixtures, for which the difficulties in measuring data from inhomogeneous samples, including movement of the sample during data collection, are ruled out.

The study concerns the exchange of water with a variety of solvents in the hydrated iron(III) 1,4-benzene dicarboxylate $Fe^{III}(OH,F)\{O_2C\text{-}C_6H_4\text{-}CO_2\}\cdot H_2O$ (labeled MIL-53(Fe),H_2O). This structure type[21] consists of chains of *trans* corner-shared iron octahedra linked in the two other directions by the dicarboxylate. The guests are localized in lozenge-shaped tunnels of the structure (Figure 1). A powder diffraction study on fully exchanged MIL-53(Fe),guest samples provided the cell parameters of each material and therefore a signature of the solvated solids (Table S1, Supporting Information).

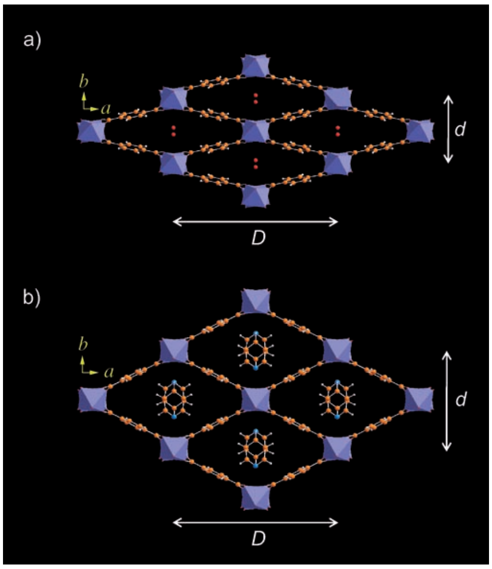

Figure 1. Structures of a) MIL-53(Fe),H_2O and b) MIL-53(Fe),pyridine. *D* and *d* = lozenge diagonals.

Depending on the nature of the guest, and with an invariant topology, the volume changes with an associated change in space group (initially *C*2/*c*, then *Pnam* and *Imcm*). It is possible that the smaller guest molecules (for example, methanol or acetonitrile) are present in larger concentrations within the pores of the various solvated MIL-53(Fe),guest materials: the unit cell parameters were obtained from fully exchanged materials immersed in organic solvent, and as soon as they were removed from the solvent the volatile guest molecules were readily lost, thus making thermogravimetric analysis problematic. Even bearing this in mind, there is no clear correlation between guest molecular dimension and unit

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cell volume, and so it is most probable that factors such as host–guest and guest–guest interactions are of equal importance for explaining the swelling effect.

To follow the evolution of the Bragg reflections in situ and the cell parameters of phases produced during replacement of the initial water, the guest molecules were introduced dropwise in liquid form by a syringe pump into a stirred suspension of hydrated MIL-53(Fe) and EDXRD data were obtained at 30 s per diffraction pattern. Although this addition of reagents during data collection precludes the measurement of true kinetic parameters, for processes that occur rapidly it does allow the acquisition of time-resolved diffraction data from reacting solid phases.[28] Depending on the nature of the guest, two types of situation occur, illustrated by the examples of lutidine (2,6-dimethylpyridine) and methanol. In each case, the exchange reaction is extremely fast (a matter of seconds), and diluted solutions (10 % in water) must be added dropwise to observe the decay of the starting phase and growth of product on a reasonable timescale.

Figure 2 shows three-dimensional plots of diffraction data measured during the introduction of a solution of 10 % lutidine in water to a suspension of MIL-53(Fe) in water. By using two detector elements, two Bragg peaks of the initial MIL-53(Fe),H_2O and four peaks of the final product could be resolved and integrated to yield decay and growth curves for each phase. The same experiment was performed with solutions of pyridine (10 % in water) and *m*-xylene (1,3-dimethylbenzene, pure; see Figure 3 a–c). The time of exchange, just a few minutes for pyridine, increases with lutidine and *m*-xylene: differences in solubility and molecular size could be argued for such a trend.

The second type of exchange process concerns the introduction of alcohols. As an example, Figure 4 a shows the results obtained from a study of methanol uptake by MIL-53(Fe),H_2O. This contour plot of the diffraction data clearly shows evidence for the presence of a transient crystalline phase whose Bragg peak positions shift continually during the time they are present. The decay of the initial hydrated phase is rapid (Figure 4 b), and after a short period the intermediate Bragg peaks appear along with some weak ones belonging to the final phase. For the intermediate phase, a monoclinic unit cell was extracted from the data collected after 25 min ($C2/c$, $a = 20.55$, $b = 9.32$, and $c = 6.92$ Å, $\beta = 113°$, $V = 1220$ Å^3). The values of the increasing unit cell volume obtained as a function of time over the period in which the intermediate phase is observed are given in the Supporting Information. One explanation for the intermediate phase is that it contains a mixture of water and methanol, as its volume lies between that of the water phase and the methanol phase. Alternatively, one guest molecule per tunnel is present, and in fact the volume is close to the value seen for the adsorption of methanol vapor at low pressure in MIL-53(Cr).[31]

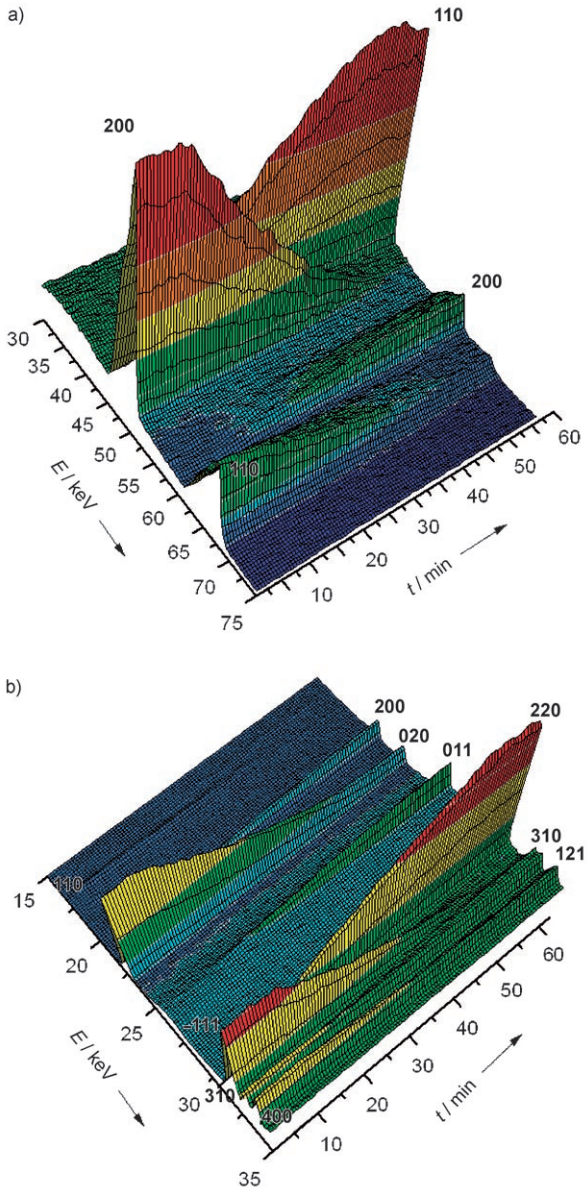

Figure 2. Contour plots of diffraction data measured during the uptake of lutidine by MIL-53,H_2O from the detector at a) $2\theta = 1.495°$ and b) $2\theta = 4.340°$. The *d* spacing (Å) is related to the energy *E* (keV) by $E = 6.11926/(d\sin\theta)$.

Before discussing these results in detail, several remarks must be made. 1) Introduction of the guests dropwise shows that the structural changes occur even for the very smallest added amounts of guests. 2) Despite the different space groups adopted when the cell volume increases ($C2/c$, $Pnam$, or $Imcm$), the topology of the structure of MIL-53(Fe) remains invariant and can be described in all cases by a reduced unit cell corresponding to a lozenge-based prism (see Figure 5). Its height is constant whatever the situation, as it corresponds to the cell parameter along the chains of octahedra. The edge of the lozenge describes the distance between two chains, linked by the dicarboxylate. The ratio *d*/*D* of the two lozenge diagonals therefore characterizes the extent of breathing. Small ratios relate to the shrunken form of MIL-53(Fe) and large ones to the expanded varieties. *d* is the signature of the strength of the host–guest interactions, and a strong shrinkage of hydrated MIL-53(Fe) indicates the strength of the hydrogen bonds that link the inserted water molecules to the OH groups.[32] 3) For exchange with pyridine, lutidine, and *m*-xylene, one only observes the Bragg reflec-

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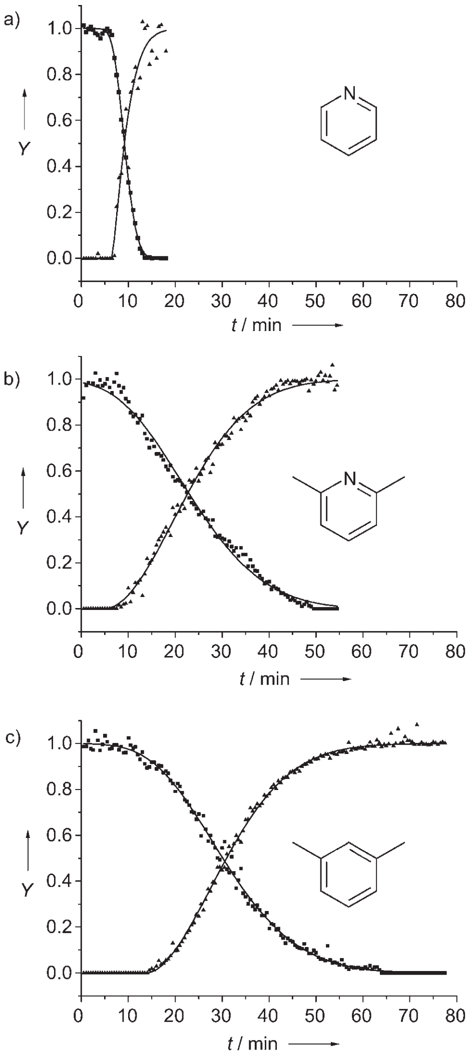

Figure 3. Extent of exchange (*Y*) obtained from the integration of Bragg peak areas during the reaction between MIL-53,H_2O and a) pyridine, b) lutidine, and c) *m*-xylene. The Bragg peaks of each phase used for integration are: the $(\bar{1}11)$ peak (at 31.9 keV in the detector at $2\theta = 4.34°$) for the starting material, the $(00\bar{2})$ peak (at 17.1 keV in the detector at $2\theta = 4.34°$) for the pyridine phase, and the (110) peak (at ca. 44.4 keV in the detector at $2\theta = 1.495°$) for the lutidine and *m*-xylene materials. The same timescale was used on all of the plots to emphasize the difference in reaction kinetics, and the lines are guides for the eye.

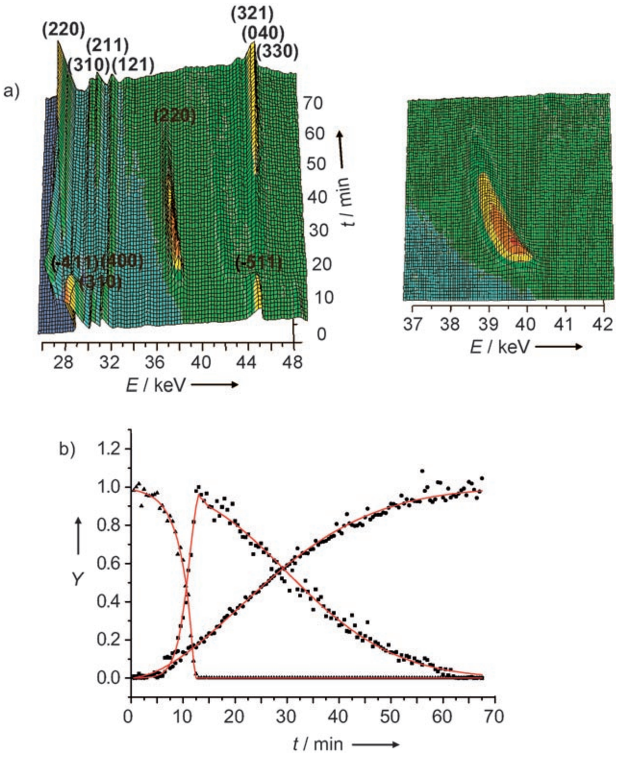

Figure 4. a) Left: 3D contour plot of EDXRD data measured during the reaction of MIL-53(Fe),H_2O with MeOH (detector angle $2\theta = 1.495°$); right: the shift in *d* spacing of the intermediate (220) peak with time. b) Integrated peak areas showing the extent of reaction (*Y*) using the (110) starting material peak, the (220) intermediate peak, and the (110) product peak. ■, intermediate phase; ◆, MIL-53(MeOH); ▲, MIL-53(H_2O).

tions of the starting and final phases without any evolution of their position (on the timescale of the experiment), which implies a dramatic stepwise expansion of the material even in the presence of minute amounts of guests.

With this in mind, some tentative explanations can be provided to explain the observations. Figure 5 illustrates the evolution of the volume of fully exchanged samples as a function of *d*/*D*, which may be considered a measure of the strength of host–guest interactions. The values are in good agreement with the theoretical values of the evolution of the volume of a prism with *d*/*D*, despite some deviations which show the influence of guests on the space group of the resulting solid, and therefore on the distortions they induce along the chains of OH-linked metal octahedra.

Considering the first exchange behavior, which concerns pyridine, lutidine, and *m*-xylene, as soon as a few guest molecules penetrate the tunnels, they weaken the water–host hydrogen bonds and the volume adopted by all cells in the grains of MIL-53(Fe) that are in contact with the added solvent is the volume of the fully exchanged sample, despite the fact that the majority of guest molecules in the tunnels must still be water molecules. This striking structural effect resembles the operation of forceps: as soon as the entrance of the tunnel is opened, the rigidity of the chains of octahedra obliges the whole structure to adapt and follow the effect of the stimulus. This finding is in agreement with the curves describing the decay of the hydrated material and the growth of the final phase because they cross at very close to 50%, which suggests a direct conversion of one phase to the other without the formation of any significant amount of an intermediate, disordered phase.

Although full structural models are not yet available for most of these phases, except for the pyridine-containing material[33] and for lutidine to a lesser extent,[34] it is interesting to compare the effect of these two molecules on MIL-53(Fe). Pyridine leads to a small increase in unit cell volume, whereas lutidine corresponds to one of the largest swellings of the series (Figure 5). The structure of MIL-

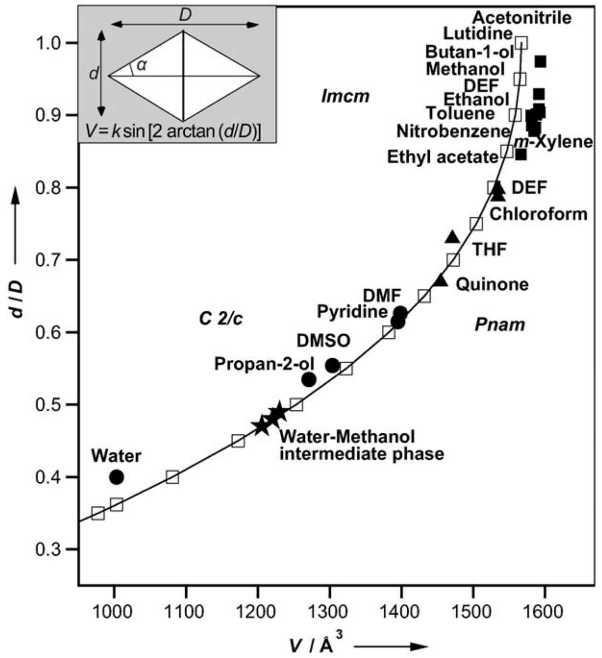

Figure 5. Comparison of the theoretical evolution of the cell volume versus *d*/*D* (□ and ——) with the experimental volumes associated with the changes of symmetry and space groups during swelling (●, *C*2/*c*; ▲, *Pnam*; ■, *Imcm*). The discontinuities and small deviations from the theoretical curve illustrate the influence of host–guest interactions in the phenomenon. The increase of swelling of the transient *C*2/*c* water–methanol phase at 10, 25, and 40 min is shown as stars. Inset: calculation of the volume of the lozenge-shaped structural motif from its edge length *k*. DEF = *N*,*N'*-diethylformamide, DMF = *N*,*N'*-dimethylformamide, DMSO = dimethyl sulfoxide, THF = tetrahydrofuran.

53(Fe),pyridine[33] (Figure 1 b) can be used to explain this result, as the main interactions between pyridine (which lies in the lozenge plane) and the framework occur through N···OH hydrogen-bonding interactions which, despite being weaker than those for H_2O, maintain rather strong host–guest interactions, thus explaining the relatively small extension of the cell.

On the contrary, with lutidine the N···OH interaction is weakened by the steric effect of the two methyl groups. Therefore, a larger swelling results. The same is seen for *m*-xylene, which possesses a similar molecular volume and shape to lutidine, but in this case with no donor for hydrogen bonding. The short guest–guest distances (3.6 Å for pyridine) imply strong π–π bonding between them. For comparison, in solid pyridine, in which the strongest interactions are CH···π, the corresponding distances are 4.7 Å.[35] This result shows that the encapsulation of the guests within the tunnels dramatically modifies their mutual interactions: confinement effects must clearly be responsible for the modification.

Even with presence of an intermediate crystalline phase during exchange, such as in the case of methanol (Figure 4 a), it is clear that the same "forceps" effect occurs when introducing minute amounts of guests, with a stepwise transition from one phase to the next. In this case, however, once the transient phase has formed, further addition of methanol is associated with an increase of the cell volume (and therefore a decrease of host–alcohol interactions), at variance to what is observed with pyridine and lutidine. This finding indicates that within a certain range of compositions that stabilizes the intermediate phase, the water–alcohol mixture within the tunnels plays a structural role. Strong hydrogen-bonding interaction between the water and alcohols might be invoked for explaining this behavior, but further complete ex situ structural studies are required for a deeper explanation.

In conclusion, the reversible spongelike properties of MIL-53(Fe) when exposed to a variety of simple liquid-phase organic molecules, including both protic and nonprotic species, and polar and nonpolar molecules, have revealed important information concerning the host–guest and guest–guest interactions. Beyond these fundamentals, the extreme sensitivity and selectivity of the solid host towards organic molecules may find applications in the fields of separation, sensors, and purification.

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