Selective Adsorption and Separation of Xylene Isomers and Ethylbenzene with the Microporous Vanadium(IV) Terephthalate MIL-47 — Source link ⧉

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Supporting Information

Selective Adsorption and Separation of Xylene Isomers and Ethylbenzene with the Microporous Vanadium(IV) Terephthalate MIL-47

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Batch experiments

For each batch experiment, a 1.8 ml vial with 0.025 g of pretreated adsorbent and an empty reference vial were filled with a solution of C_8-alkylaromatics in hexane. Uptake from solution was detected after 2 h by GC. Selectivities α_{ij} were calculated using Equation (1)

$$\alpha_{ij} = \left(\frac{q_i}{q_j}\right) \times \left(\frac{c_j}{c_i}\right) \tag{1}$$

with q_i and q_j the amount (mol/g) of C_8 aromatic isomers i and j adsorbed and c_j and c_i the amount (mol/l) of isomers j and i present in the external liquid phase.

Liquid phase experiments in a continuous flow setup

Pulse and breakthrough experiments were performed on a 5 cm stainless steel column with an internal diameter of 4 mm placed in an HPLC apparatus. For pulse experiments, an RI detector was connected to the column outlet. Selectivities α_{ij} were calculated from pulse experiments using Equation (2)

$$\alpha_{ij} = \frac{(\mu_i - \mu_{tc})}{(\mu_j - \mu_{tc})} \tag{2}$$

with μ_i and μ_j the first moments of isomers i and j and μ_{tc} the first moment of 1,3,5-triisopropylbenzene, a tracer compound. For breakthrough experiments, 1 ml samples were taken directly at the column outlet. Selectivities were calculated from breakthrough experiments using Equation (1) in which the adsorbed amount q of each isomer was calculated using Equation (3)

$$q = \int_0^t u \times (C_{in} - C_{out})dt \tag{3}$$

with u the volumetric flow rate of the feed (l/s) and C_{in} and C_{out} the concentration (mol/l) of the adsorbate in the liquid feed and effluent, respectively. Regeneration of the MIL-47 column was accomplished using a 4 ml min^{-1} flow of hexane.

Gas phase adsorption experiments

Gas phase adsorption at low degree of pore filling was studied using the pulse chromatographic technique with a 15 cm column (0.22 cm internal diameter) packed with pellets (500 – 630 µm) of MIL-47 (see also R. A. Ocakoglu, J. Denayer, G. Marin, J. Martens, G. Baron, *J. Phys. Chem. B* **2003**, *207*, 398). Adsorption equilibrium Henry constants were calculated from the first moment of the chromatographic response curves. Adsorption enthalpies were obtained from the temperature dependence of the Henry adsorption constants.
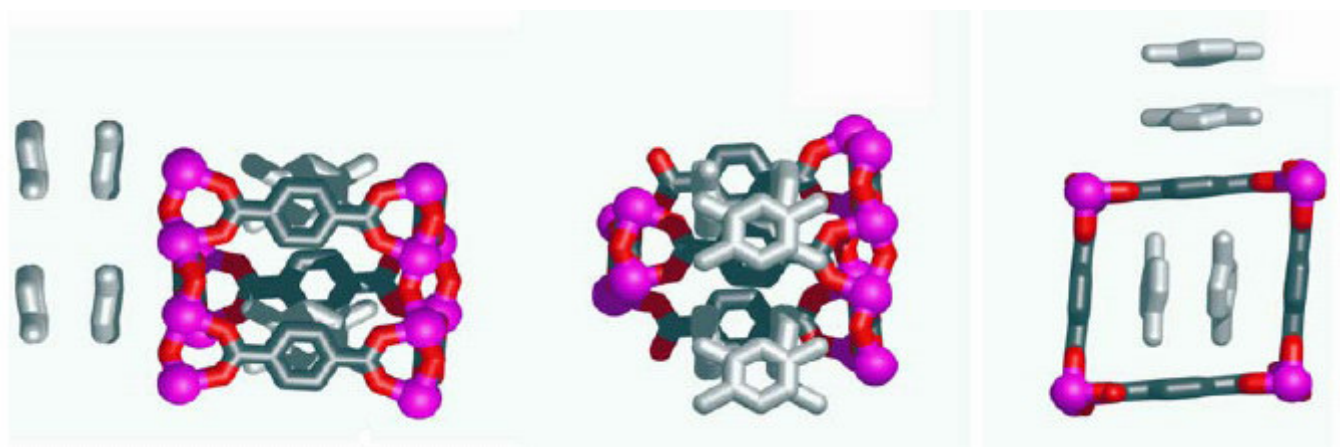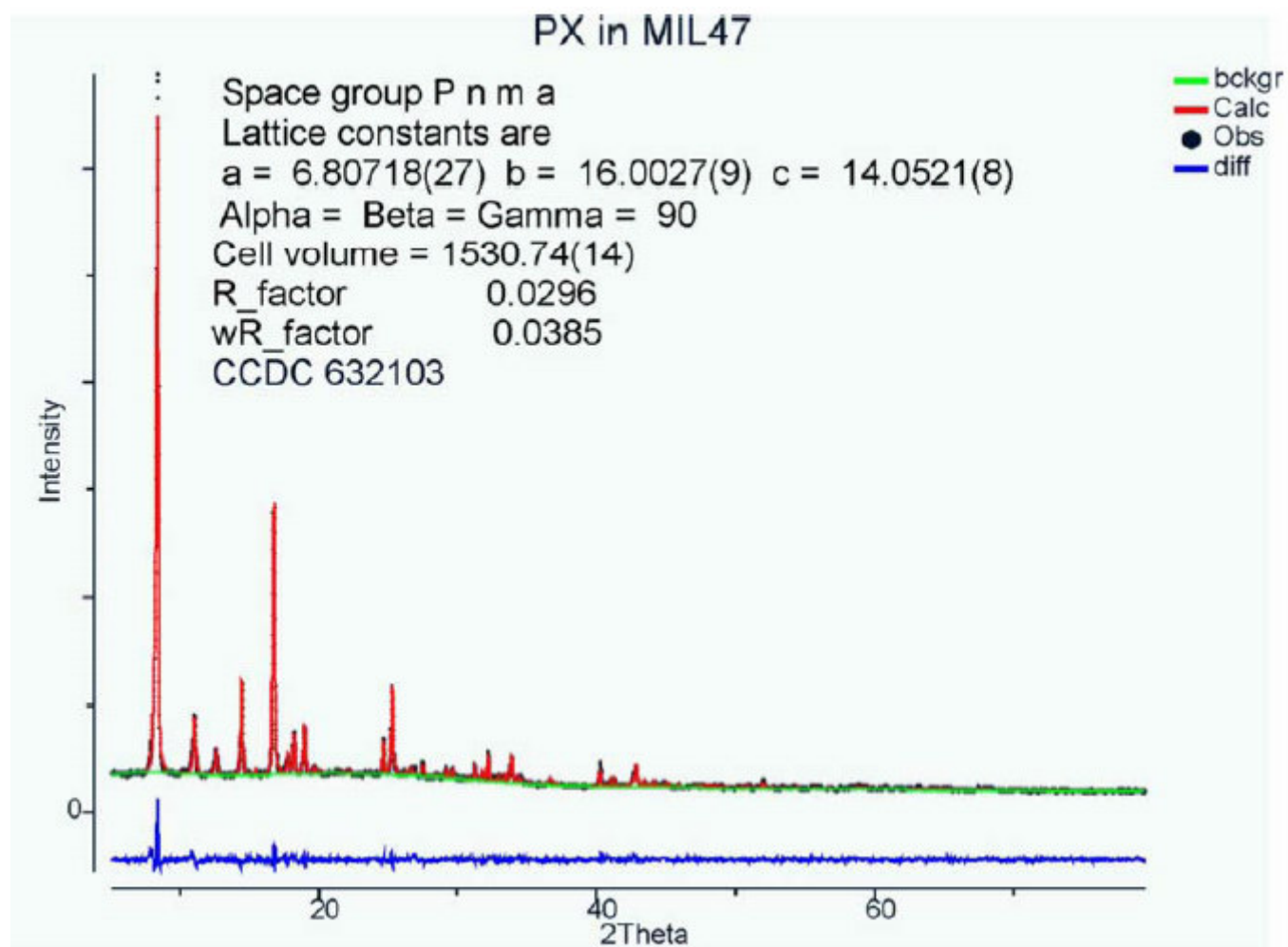
Table 1'. Henry adsorption constants, K', at 523 K and zero coverage adsorption enthalpies, $-\Delta H$, of C_8 alkylaromatics on MIL-47.

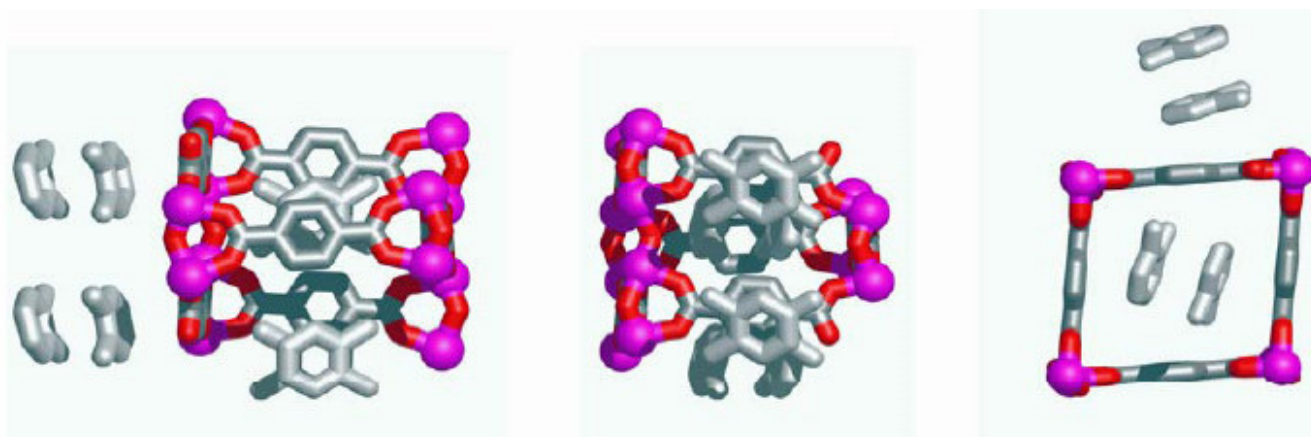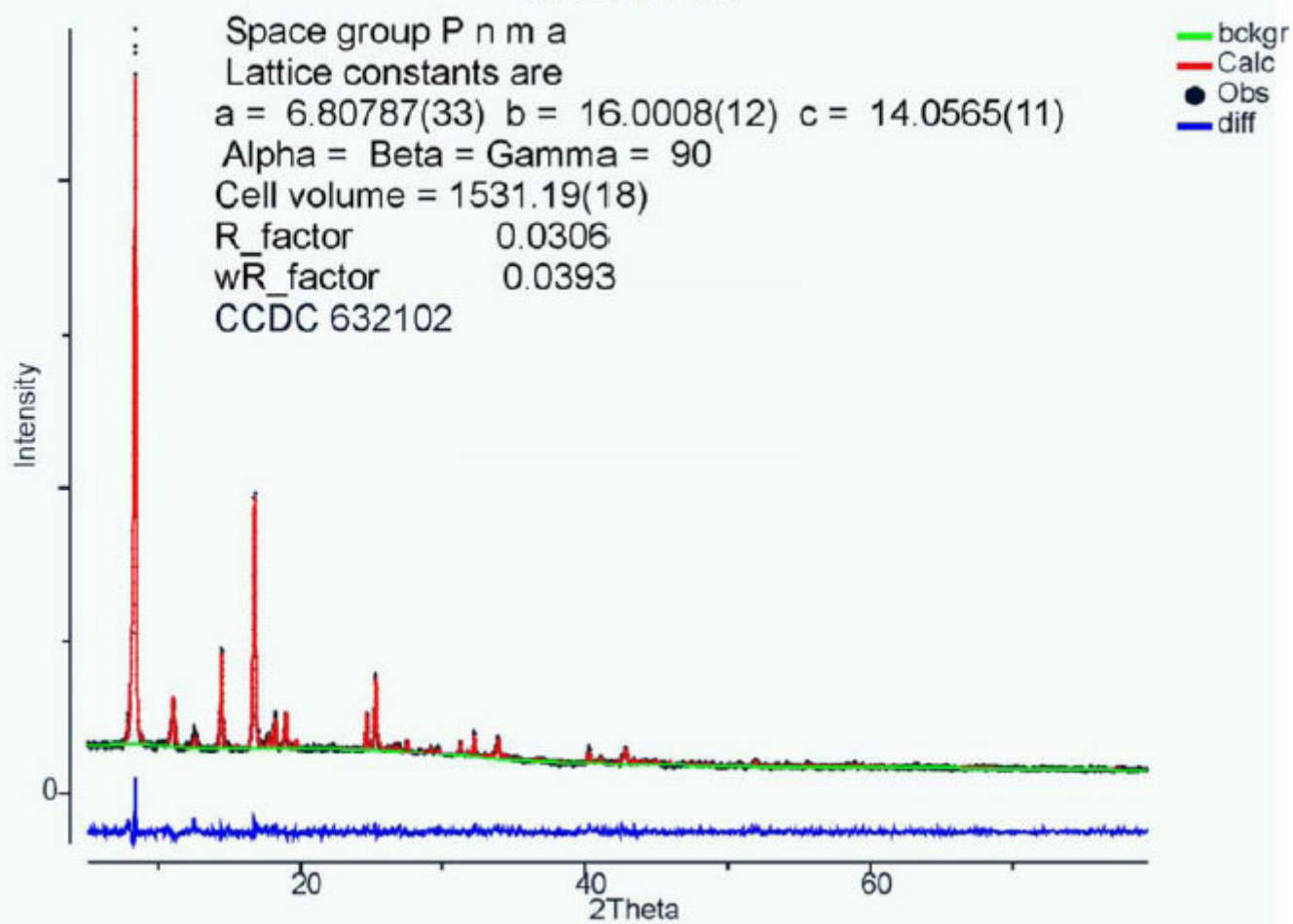|	$K'_{523\,K}$ (mmol/kg.Pa)	$-\Delta H$ (kJ/mol)
EB	0.421	59.7 ± 0.5
oX	0.475	59.6 ± 0.7
mX	0.353	59.7 ± 0.7
pX	0.375	61.2 ± 0.4

Crystal structure analysis

Each sample for X-ray powder diffraction (XRPD) was prepared by immersing MIL-47 crystallites in a pentane solution of C_8 alkylaromatics. After evaporation of pentane, the loaded MIL-47 crystallites were sealed in a capillary. Capillaries were measured on a Stoe Stadi MP with focusing monochromator (CuK$_{\alpha 1}$) in transmission geometry with a position sensitive detector (6°2θ) in a range between 3 and 80 and a resolution of 0.01°2θ. Measurement occurred at room temperature. Rietveld refinement was performed with the GSAS software (see: A. Larson, R. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR **2004**, 86-748). As starting parameters the published structure data of Barthelet et al. (K. Barthelet, J. Marrot, D. Riou, G. Férey, *Angew. Chem.* **2002**, *114*, 291; *Angew. Chem. Int. Ed.* **2002**, *41*, 281) were used. Overall parameters, like lattice constants, background or profile parameters were freely refined. The framework structure itself was not issue of refinement. Adsorbed molecules were first searched for by analysis of observed and difference electron density and then inserted as rigid bodies (RGB). Position and occupation numbers of the RGBs were at first freely refined. At later stages it turned out that linking the occupation numbers of the xylene molecule positions had a favorable effect on the refinement. All xylene containing samples could only be described using 2 molecular positions opposite to each other. EB was at first refined using an RGB of toluene. Finally the missing methyl group was localized by electron density analysis, constrained to the appropriate bond-length of the toluene fragment and then left to refine freely. Only one molecule position of EB was necessary to describe the structure. As can be expected for room temperature conditions, the refined temperature factors of the guest molecules were rather large due to thermal motion and/or disorder. However, fixation of the framework and the good refinement results indicate the refined average molecule positions to be reliable.

Refined XRD-patterns of C$_8$ alkylaromatics in MIL-47

PX in MIL47

Space group P n m a
Lattice constants are
a = 6.80718(27) b = 16.0027(9) c = 14.0521(8)
Alpha = Beta = Gamma = 90
Cell volume = 1530.74(14)
R_factor   0.0296
wR_factor   0.0385
CCDC 632103

- bckgr
- Calc
- Obs
- diff

Intensity

0-

20   40   60
2Theta

OX in MIL47

Space group P n m a
Lattice constants are
a = 6.80787(33) b = 16.0008(12) c = 14.0565(11)
Alpha = Beta = Gamma = 90
Cell volume = 1531.19(18)
R_factor   0.0306
wR_factor   0.0393
CCDC 632102

MX in MIL47

Space group P n m a
Lattice constants are
a = 6.80899(30) b = 16.0618(12) c = 13.9913(11)
Alpha = Beta =Gamma = 90
Cell volume = 1530.16(18)
R_factor   0.0302
wR_factor   0.0401
CCDC 632101

— bckgr
— Calc
● Obs
— diff

Intensity

2Theta

EB in MIL47

Space group P n m a
Lattice constants are
 a = 6.8091(4) b = 16.4128(15) c = 13.5674(11)
 Alpha = Beta = Gamma = 90
 Cell volume = 1516.25(21)
R_factor   0.0370
wR_factor   0.0516
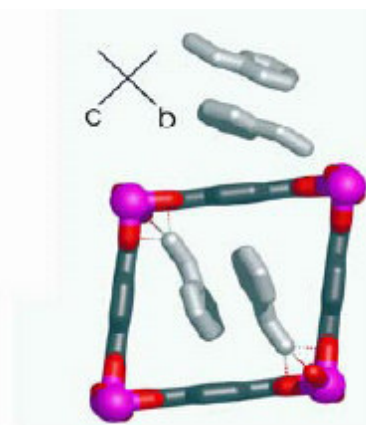CCDC 632104

bckgr
Calc
Obs
diff

Table 2'. Lattice constants for MIL-47 with different C_8 alkylaromatics as guests.

	a / Å	b / Å	c / Å
MIL-47	6.8197(4)	16.1012(16)	13.9424(13)
MIL-47 loaded with pX	6.80718(27)	16.0027(9)	14.0521(8)
MIL-47 loaded with oX	6.80787(33)	16.0008(12)	14.0565(11)
MIL-47 loaded with mX	6.80899(30)	16.0618(12)	13.9913(11)
MIL-47 loaded with EB	6.8091(4)	16.4128(15)	13.5674(11)

Notes on the disorder of xylene and ethylbenzene molecules in the MIL-47 framework

Introduction

Like many zeolites, the metal-organic framework MIL-47 contains more symmetry-related adsorption sites than can be simultaneously occupied. In zeolites, for example, this is observed when the loading with guest molecules or cations is below the maximum loading capacity, or when structural considerations exclude the simultaneous occupation of neighbouring or overlapping sites. In most cases this leads to a local lowering of the symmetry of the average spacegroup that is defined by the porous host. However, statistical occupation of the adsorption sites in different asymmetric units cancels this effect and the high symmetry spacegroup still adequately describes the system as a whole [Zhen and Seff, Microporous Mesoporous Mat. 39 (2000) 1-18, and references therein]. In these cases the localization of the guest molecules is no trivial task. Analysis of the Fourier patterns, especially from powder samples, usually shows a complex electron density pattern, generated by the various symmetry elements of the host's spacegroup. One big help in finding the adequate molecule positions is to assume rigidity of the guest molecule structure, as can be done for small aromatic molecules. Using a rigid body refinement, in which the molecule as a whole can shift and rotate freely through the pore structure, often reveals the molecular orientations and positions that give the best fit with the measured electron densities. However, one still has to check whether the refined molecule positions can be consistent with chemical and structural integrity. Flexibility of guest molecules or thermal mobility can cloud the picture even more. Molecule positions obtained in such a way have to be treated with care and seen as what they are: the best fit of the diffraction data which makes sense in a physico-chemical context.

Even though in most cases the spacegroup of a guest-host system is preserved, some cases are known in which guest molecules actively change the symmetry of the loaded porous framework. One famous example is the zeolite Silicalite with different p-xylene loadings: at low loadings the space group is Pnma, but ordering of the guests at high loadings induces a change to $P2_12_12_1$ [Long *et al*., J. Incl. Phen. and Mol. Rec. Chem. 28 (1997) 1-15 and references therein].

Changes in the symmetry of a guest-host system may be difficult to observe without a high-resolution single crystal refinement. Even if a large single crystal and small powder crystallites do not necessarily present the same adsorption behaviour, disorder phenomena are best studied on single crystals, because the splitting of diffraction lines that sometimes is caused by symmetry reduction is often obscured by pattern broadening due to a small particle size. However, indications for (dis)order of guest molecules in a porous host can be obtained by systematic variation of the used spacegroup or by variation of the lattice constants. This approach is illustrated in the present study for aromatic molecules adsorbed on MIL-47 powder.

Xylenes

Xylenes adsorbed in MIL-47 were found to occur pairwise, their aromatic planes facing each other. Such an arrangement is not compatible with the symmetry imposed by the MOF structure. Therefore, each pair of guests has to be described by two distinct molecule positions. The structure of the empty MIL-47 is described by the spacegroup Pnma. Including the guest molecules in this symmetry generates 8 fully equivalent positions for each xylene pair in the unit cell; these 8 positions are all identical in terms of interaction with the framework. However, as soon as one of these 8 positions is occupied, steric restrictions arise for occupation of neighbouring pair-positions within one channel:

1. along the channel (*a*-direction; figure 1'): the combination of the glide-mirror plane with the inversion operation acts as a 2_1 screw axis along the channel, generating a neighbouring xylene pair displaced by 1/2 *a*. The simultaneous occupation of these two sites by xylene pairs is impossible: the molecules' position overlaps after application of the screw axis with the joined partner of the original pair. This is schematically represented in figure 1' (ii). However, if occupation falls below full, occupation of such a site becomes possible by skipping 1.5 times *a* in the channel direction (figure 1' (iii)).
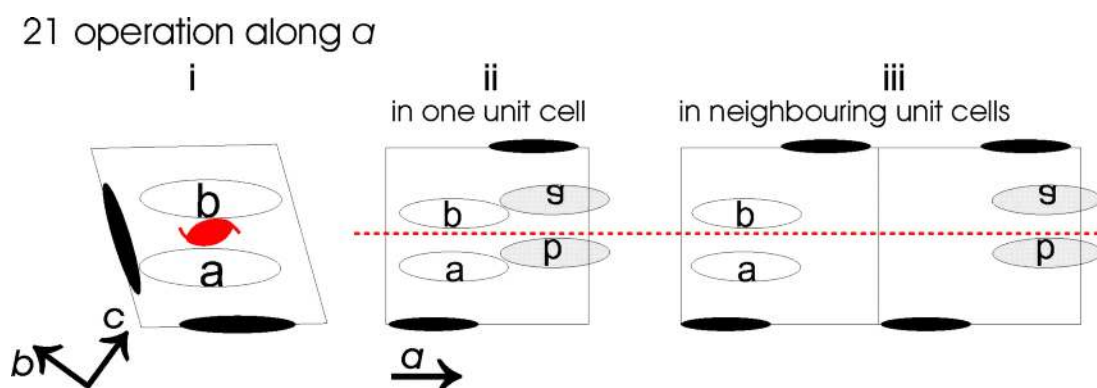

Figure 1': Combination of the glide-mirror operation with the inversion centre in Pnma generates a 2-fold screw axis along the channel centres of MIL-47. White ellipses a and b: molecules in a xylene pair; grey ellipses: molecule pair generated by the screw axis; black ellipses: aromatic rings of terephthalate in the pore walls. (i) the screw axis seen along the *a* direction. (ii) Application of the screw axis on molecule a(white) creates overlap between the new position a(grey) and the joined partner of the original pair b(white). (iii) If occupation falls below full, occupation of a site generated by the 2-fold screw axis becomes possible by skipping 1.5 times *a* in the channel direction.

2. around the channel-centre axis (*ac*-mirror planes on *b* = 0.25 and *b* = 0.75): In the same unit cell (constant x) the equivalent position generated by the mirror plane bisecting the channel in the *ac* plane through the channel corners is impossible (figure 2'). However, occupation of such a site is possible further down the channel.
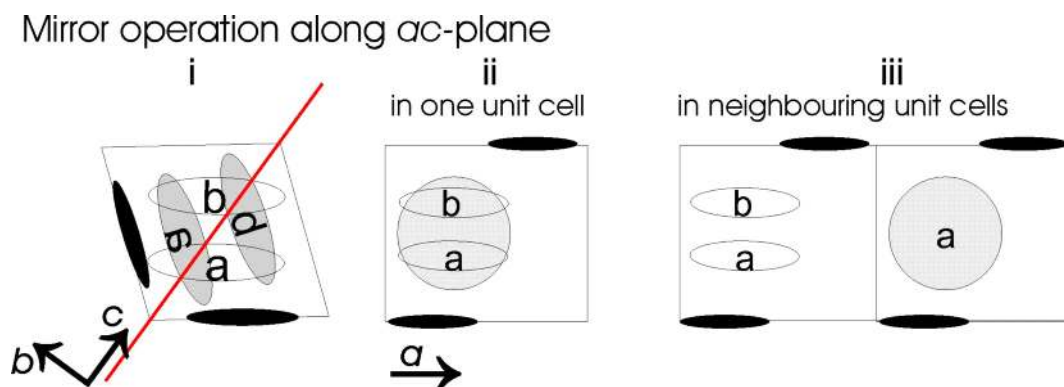
Figure 2': The mirror operation bisecting the channels of MIL-47 in the *ac* plane. White ellipses a and b: original position of the molecules in a xylene pair; grey ellipses: position of the molecule pair generated by the mirror operation; black ellipses: aromatic rings of terephthalate in the pore walls. (i) position of the mirror plane; (ii) overlap generated within the same unit cell; (iii) the different positions can be occupied in adjacent unit cells.

In total there are 4 possible sites for xylene pairs within one channel, while for steric reasons locally only one can be occupied (figures 1' and 2'). As the unit cell contains two channels, only two of the in total 8 symmetry-related sites can be occupied simultaneously, when the above-derived exclusion rules concerning the 2_1 axis and the mirror plane are obeyed. If in the material ordering from channel to channel and within the channel would occur, the overall symmetry of the structure would be even lower than $P2_12_12_1$ or $Pnm2_1$. If, however, occupation of the 4 possible molecule sites is statistical over and along the channels, any structure analysis would inevitably return the high symmetry spacegroup Pnma as a result.

To check for the presence of ordering, the refinement of the data has to be repeated for a lower symmetry spacegroup or using multiplied lattice constants. As the physicochemical behavior of *o*-xylene is highly similar to that of *p*-xylene, the current analysis was restricted to *p*-xylene, *m*-xylene and ethylbenzene. Several choices for subgroups of Pnma are possible.

$P2_12_12_1$ removes the mirror plane (see point 2 above) but keeps the 2_1 screw along the channel axis. **$Pnm2_1$** on the other hand keeps the two possible mirrored orientations in the channel but the screw axis along the channel axis is removed. Both reductions of symmetry also remove the inversion symmetry in the structure.

Refinement of the experimental data for *meta*- and *para*-xylene in MIL-47 has been carried out in the spacegroups $P2_12_12_1$ and $Pnm2_1$. The atomic parameters, including guest molecule positions, derived from the initial localisation in Pnma have accordingly been doubled to account for the removed symmetry element. Free refinement of the occupation numbers of the two guest molecule pairs allowed to probe for a preferred type of ordering in the two lowered symmetries. If partial or full ordering is present in the material, the occupation by the two pairs should be markedly different. Such a deviation of occupation numbers could not be observed. However, refinement in the spacegroup $Pnm2_1$ resulted in slightly better

refinement factors than in $P2_12_12_1$. This is most probably due to the better description of the electron density distribution in an individual channel: $Pnm2_1$ creates non-overlapping, alternating regions of electron density within one channel.

In summary, the refinement of the structures in lower symmetry spacegroups shows an absence of significant ordering of the xylene molecules within the pores of MIL-47. Even then, without a careful single crystal structure analysis we refrain from claiming that there is no order, not even on a small scale.

In fact, in a further analysis of possible disorder, the spacegroup symmetry should be further lowered to avoid generation of conflicting molecule positions even in the two probed spacegroups $P2_12_12_1$ and $Pnm2_1$. Considering that the diffraction study of the material was performed at room temperature and only on a powder, a further symmetry reduction was not carried out, especially in view of the observation that the initial symmetry reductions had no beneficial effect on the refinement quality.

Ethylbenzene

Loading of the MIL-47 framework with ethylbenzene has a marked effect on the lattice parameters of the host structure. This in itself already suggests a strong guest-host interaction at specific adsorption sites. As preferred adsorption sites, we identified 2 of the 4 corners of the channels. No pair formation as for the xylenes was observed. A single position for ethylbenzene therefore accurately describes the system and the 2_1 screw axis element of the high symmetry spacegroup Pnma can be obeyed without steric obstruction (symmetry argument 1 in section above). However, due to the mirror operation (see symmetry argument 2 in section above) two possible symmetrically equivalent orientations for a molecule on this site still exist, which mutually exclude each other (Figure 3'). Simultaneous occupation of these two molecule positions is impossible. Probing for possible order therefore was done in the spacegroup $P2_12_12_1$, in which the conflicting mirror operation is removed. However, fits with $P2_12_12_1$ did not improve the refinements in comparison with the analysis using Pnma. Even if some orientations of neighbouring molecules may be suppressed by previously occupied sites, it is clear that on the average all orientations can be assumed in the sample.
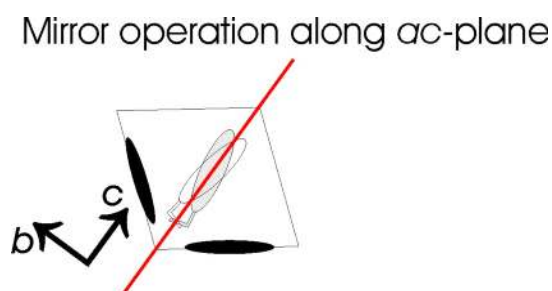

Figure 3': Effect of the mirror operation around the *ac* plane on an ethylbenzene molecule docked in the corner of the MIL-47 channel.

Further studies may focus on the mobility of the guests, in order to elucidate if a switch of orientation occurs for isolated molecules or in a concerted fashion, involving several molecules along the channel axis. The same comments concerning room temperature measurement and the analysis of powder data as in the case of the xylene molecules apply here.

Conclusion

The variation of spacegroups for MIL-47 containing xylenes or ethylbenzene revealed that the guest molecules are evenly distributed over the possible symmetrically equivalent orientations/positions. We found no evidence for long range organization of the organic molecules within or between the pores at room temperature.