《解　説》

STRUCTURAL PROPERTIES OF
SOME MFI/SORBATE COMPLEXES

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Molecular sieves and zeolites are microporous materials widely used for their shape-selective (1), adsorptive and/or catalytic properties (2), which are closely related to their framework structure (cavities, cages, 1D-, 2D- or 3D-channel-systems). Among the wide variety of synthetic crystalline microporous materials, those corresponding to the MFI topology (3) are of great industrial importance. Their framework structure is composed of two types of intersecting channels, both limited by 10-membered oxygen rings : the *straight* channels (slightly elliptical ≈5.7 x 5.3 Å) run parallel to the [0 1 0] direction (*b*-axis), whereas the *zig-zag* channels (nearly circular ≈ 5.5 Å) run parallel to the [1 0 0] direction (*a*-axis).
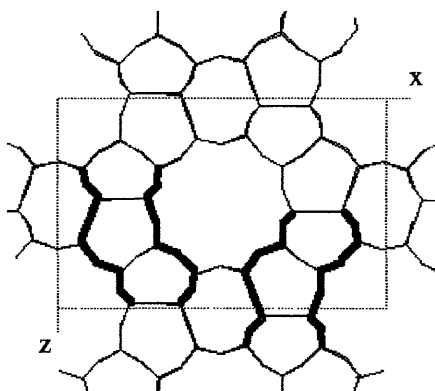

Figure 1 - Projection of the MFI framework down the *b*-axis. The origin is shifted by 1/2,0,0.
The 10-ring pore openings of the zig-zag channel sections centered at y = *1/4* are outlined by bold lines.

A projection of the structure down the *b*-axis, limited to a unit-cell (*uc*), is represented in figure 1, where the 10-rings of the zig-zag channels at y = *1/4* are outlined (bold lines). Presently, the 3D-framework of these zeolitic materials presents three known crystal symmetries, corresponding to the Pnma (orthorhombic/O1), P2₁/n.1.1 (monoclinic/M) and P2₁2₁2₁ (orthorhombic/O2) space groups. Recently, single-crystal investigations led to the determination of accurate atomic parameters for these O1(1), M(2) and O2(3) polymorphs, the chemical formulation of which corresponds to a highly siliceous $H_{0.32}Al_{0.32}Si_{95.68}O_{192}$ framework composition (Si/Al ≈ **3 0 0**). When the Si/Al ratio is higher than about ≈ 500 (0.2 Al/*uc*), the solid is considered as a silica polymorph named *silicalite* (4). For lower Si/Al ratios, the MFI materials correspond to the so-called ZMS-5 phases. Some silicon atoms might be replaced *during* the synthesis (isomorphous substitution) by other elements than aluminum (*e.g.*, B, Ga, Fe, Ti) yielding thus a wide family of M(*metallo*)•MFI-type materials : boro-/gallo-/ferri-/titanosilicates. *After* synthesis and calcination, some of these materials may be further modified (*post-synthesis* treatments). In the case of ZSM-5, boro- and ferrisilicates, the extra electronic charge due to the trivalent framework element might be compensated by protons

(acidic H-form) or metallic cations (*e.g.*, Na, K, Rb, Cs, Ca, Ni, Pb). As a consequence, MFI type materials correspond to numerous microporous solids, the structurally related properties of which might be tailored at convenience during or after their synthesis. In the case of genuine ZSM-5 solids, the idealized formulation of such crystalline phases corresponds to $Cat_xAl_ySi_{96-y}O_{192} \cdot n$ads, where Cat and ads stand for cationic and adsorbed species respectively. It clearly appears now that the knowledge of the localizations of the cations and/or of the adsorbed molecular species is of paramount importance for the understanding of shape-selective, diffusive and catalytic properties. Since 1985, our group has been extensively involved in the elucidation of some sorbent/sorbate interactions and structure-related properties in MFI materials. Among several experimental direct-characterization methods yielding structural informations on *extra-framework* species (cations, water and organic sorbate molecules), we use X-ray or neutron diffraction on *powdered* polycrystalline solids. The present paper, which is *strictly* devoted to some structural aspects corresponding to MFI/sorbate complexes investigated by *conventional* X-ray powder diffraction (step-scanned XRD profiles, using filtered CuKα radiation, corrected for *fixed* divergence slit effects at lower angles), is divided into four main sections corresponding to *1*- the situation of the problem, *2* - the multi-phase problem, *3* - the localization of extra-framework species and *4* - the flexibility of the MFI framework.

1 - Situation of the problem.

It is known since the early eighties that the crystal structure of ZSM-5 materials undergoes some modifications which are in relation with the nature of the sorbed or entrapped species (5,6). At that time, the question arised whether localizing sorbed species in the zeolitic channels of such phases by powder diffraction was possible or not. Part of the answer has been given by Baerlocher in 1984, by proposing a configuration of the TPA (tetrapropylammonium) anion in the structure of a ZSM-5•4TPA complex (7). TPA is usually considered as being the structure-directing and/or templating agent which is *entrapped* during the synthesis. This bulky molecule occupies the *entire* channel system of the zeolite and accordingly it might be considered as being in very *tight* interaction with the framework oxygen atoms. Thereafter, it has been shown that the TPA species are actually in a *twofold positional disorder* at the channel-intersections (8). In the case of smaller molecules which can diffuse through the channel-system, the situation might be completely different, since *several* sites are now *intuitively* available for them. Figure **2** compares three XRD profiles (6-48°2θ domain) corresponding to the evacuated (H•form, monoclinic **M**), the 4p-xylene/*uc* loaded (orthorhombic **O1** polymorph) and the 8p-xylene/*uc* loaded (orthorhombic **O2** polymorph) phases respectively (Si/Al = 132). At low aluminum concentrations (Si/Al>≈90), the MFI/*p*-xylene system is very interesting since, depending on the sorbate loading, the three known **M, O1** and **O2** framework symmetries are encountered. In order to qualitatively *visualize* the profile modifications induced by sorbed species, three main diffraction domains have to be considered. *1* - the 22-25°2θ region (figure **3**) corresponding to a complex massif where the intense 501, 051(05-1), 151(1,5-1), 303 and 133(1,3-3) lines appear (*hkl* triplets in parenthesis correspond to the splitting of some peaks in case of a monoclinic **M** polymorph). *2* - the 9-23°2θ region (figure **4**), where modifications of the relative intensities are best detected. *3* - the 44-46.5°2θ region (figure **5**) where the medium intensity 10,0,0/0,10,0 doublet might give valuable informations on the aluminum-content, the symmetry and the multi-phase problem (see below, second section). From the structural point of view, the second diffraction domain (9-23°2θ) is the most important, since it corresponds to the peaks which are the most sensitive towards *short-range* sorbent/sorbate interactions. As will be detailed in the third section, the localizations of sorbed species mainly depend on the correct interpretation of this domain.
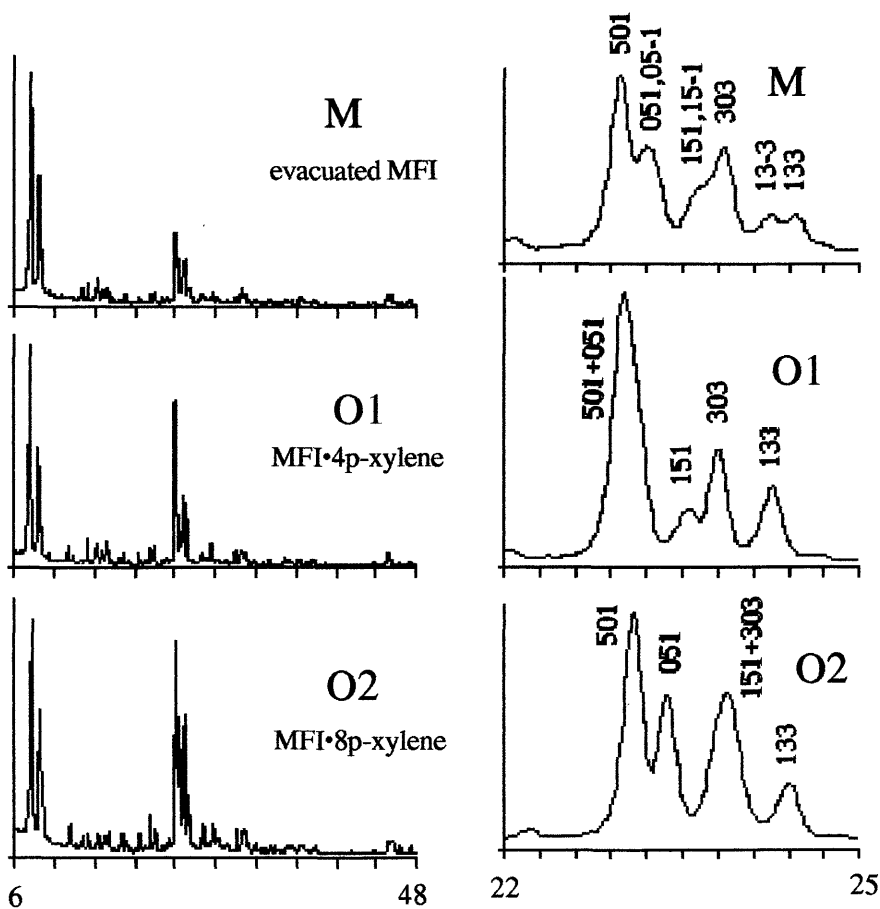
Figure 2 - the complete XRD profiles for the O1, M and O2 MFI polymorphs. All figures : Diffraction angles in 2θ°.

Figure 3 - Detail of the intense lines in the 22-25°2θ angular range

TABLE I

MFI/np-xylene system (Si/Al = 132) : *a/b* and *a/c* ratios for n = 0,4,8

composition	polymorph	a/b*	a/c*	ref. (8,13,14)
MFI (*bare*)	M	1.0113	1.5037	1.0115 - 1.5040
MFI·4XYL	O1	1.0050	1.4965	1.0052 - 1.4960
MFI·8XYL	O2	1.0146	1.4977	1.0152 - 1.4973

*see reference (12)

The *a/b* and *a/c* ratios between unit-cell parameters are characteristic of the MFI polymorph (Table I). In the case of **M**, the five strong peaks are very well resolved (fig. **3a**, the last peak is split). In the case of **O1**, the 501 and 051 lines are very close, and only four components are visible (fig.**3b**). Detailed analysis by peak-desummation techniques (9,10) reveals that the FWHM's (full width at half maximum) of the 501,051 doublet and of the 133 peak are significantly different; accordingly, the framework structure is not *tetragonal*, as it has recently been claimed in (11), on the basis of wrongly indexed diffraction lines (the invoked 332, 511 and 422 line-intensities are actually *several orders* of magnitude smaller than those of the strong 501, 051, 151, 303 and 133 lines in the same diffraction domain). In (ref.11, fig.4) the 501 peak is about 50% *broader* than the *isolated* 133 line : this is an evidence for *orthorhombic* symmetry. In the case of **O2** ($P2_12_12_1$ space group, fig.**3c**) the 151 and 303 peaks are merged. This latter diffraction profile is characteristic of **8** p-xylene/*uc* loaded MFI materials. It has been observed for a wide range of MFI materials (adsorption isotherms at room temperature, $0 < P/P_0 < 0.9$) corresponding to $1000 < Si/Al < 15$ ratios (15). The fact that an **H•MFI** material is saturated by *less* than eight p-xylene molecules, is a strong indication that some extra-framework material is present in the channels (residual cations, coke, six-coordinated aluminum, structure defects, impurities, faulty planes).
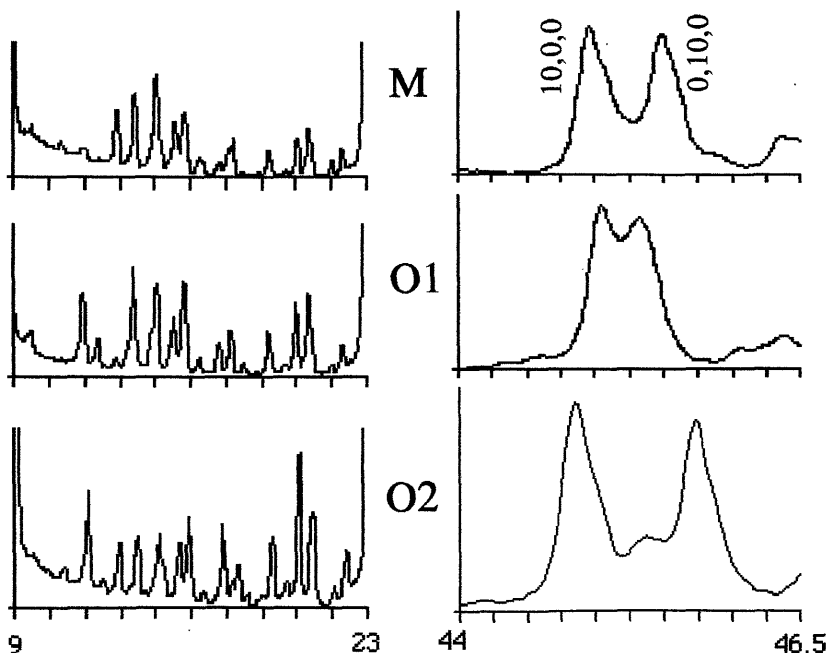

Figure **4** - Details of the XRD profiles where the structural modifications are the most visible.

Figure **5** - The 44-46.5°2θ region showing the medium intensity 10,0,0 and 0,10,0 peaks.

Two questions arise now : knowing that *all* the MFI materials corresponding to an evacuated H•form are *saturated* at **8** p-xylene/*uc* loadings (15). **Firstly** : what are the chemical compositions of the complexes. **Secondly** : what are the distributions of the sorbate molecules at *intermediate* loadings ? The answers to the first (qualitative and quantitative) and second (structural) questions will be given in the following second and third sections respectively.

2 - The multi-phase problem :

Prior to any structural investigation concerning a given zeolitic sorbent/sorbate complex, a precise knowledge on the corresponding *phase diagram* is prerequisite. Our group was first interested in the localization of the **p-xylene** molecule in MFI materials. In the early eighties, only some intuitive informations were available, and it was admitted without any experimental or structural support, that the molecule should be somewhere in the straight channels. In 1985, interpretation of some XRD profiles corresponding to several p-xylene loaded ZSM-5 phases, and obtained by high-resolution powder diffraction using a Guinier-type focussing camera, revealed that in the 4 to 8p-xylene/*uc* range, some multiplets at 22-25 and 44-46.5°2θ presented *ten* and *four* lines respectively (16). It has been established that for 4<p-xylene/*uc*<8 (Si/Al = 132), *all* the intermediate complexes were actually mixtures of the two limiting MFI•4p-XYL (orthorhombic **O1** form) and MFI•8p-XYL (orthorhombic **O2** form) phases (17).
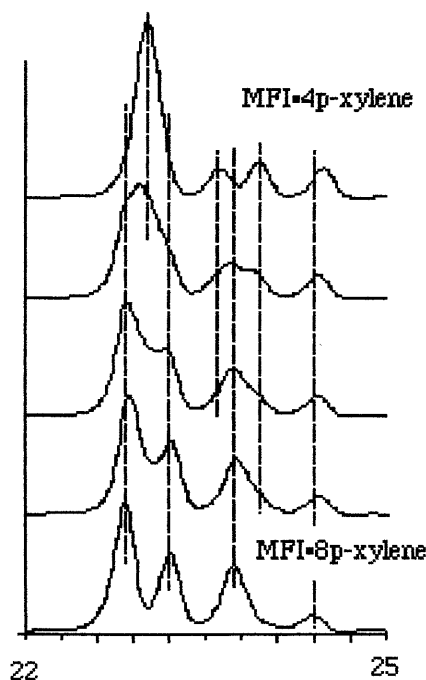

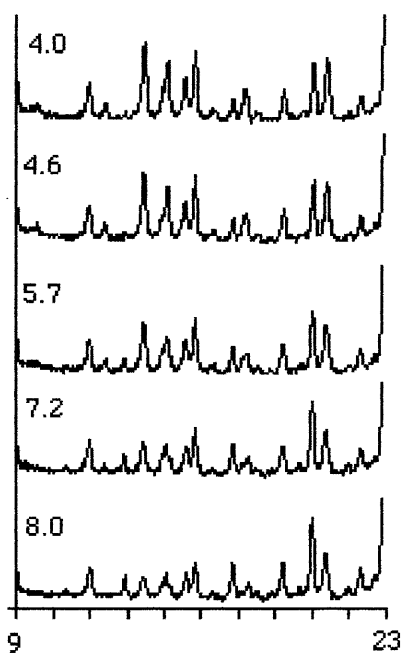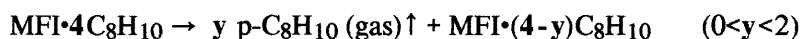Figure 6 - Modifications of the intense lines during the spontaneaous desorption of a MFI•8p-xylene complex.

Figure 7 - Modifications of the XRD peaks in the most sensitive region. Numbers represent the p-xylene loadings.

Further investigations in the 0<p-xylene/*uc*<4 range revealed that for 0-2 molecules/*uc* the system was actually *di-phased* (mixtures of the empty monoclinic **M** and the orthorhombic **O1** forms) and that for 2-4 molecules/uc the complexes correspond to a *solid solution* (18). Examples of structural modifications occuring in the 4<p-xylene/*uc*<8 concentration range during the spontaneous desorption of an MFI/p-xylene system are given in figures **6** and **7**. They represent *time-resolved X-ray diffraction* (TRXRD) profiles for two different angular ranges. Interpretation of these profiles by dessumation techniques (not *deconvolution*), shows that all the intermediate profiles are *linear combinations* of the two limiting profiles corresponding to the eight and the four molecules/*uc* loaded complexes respectively. Detailed informations on this subject are given in (9,10). The following reactions summarize the entire p-xylene *desorption* process for 0<p-xylene/*uc*<8 (complexes corresponding to p-xylene loaded MFI phases might be considered as genuine *xylenates*).
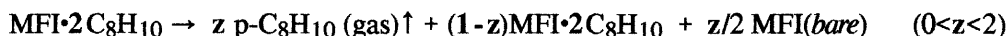
1 - the 4<p-xylene/*uc*<8 domain :

$$MFI \cdot 8\,C_8H_{10} \rightarrow x\ p\text{-}C_8H_{10}\ (gas)\uparrow + (1-x)MFI \cdot 8\,C_8H_{10} + x/4\ MFI \cdot 4\,C_8H_{10}\quad (0<x<4)$$

2 - the 2<p-xylene/*uc*<4 domain :

$$MFI \cdot 4\,C_8H_{10} \rightarrow y\ p\text{-}C_8H_{10}\ (gas)\uparrow + MFI \cdot (4-y)C_8H_{10}\quad (0<y<2)$$

3 - the 0<p-xylene/*uc*<2 domain :

$$MFI \cdot 2\,C_8H_{10} \rightarrow z\ p\text{-}C_8H_{10}\ (gas)\uparrow + (1-z)MFI \cdot 2\,C_8H_{10} + z/2\ MFI(bare)\quad (0<z<2)$$

Although this desorption process is represented by three reactions, it is among the *simplest* mechanisms encountered in zeolitic MFI/sorbate systems. In the case of MFI/benzene systems, the situation is much more complex : in the 4<benzene/*uc*<8 region at least *five* distinct benzenate phases and *three* multi-phased domains could be evidenced (19), whereas the 0<benzene/*uc*<4 domain is trivial and simply corresponds to a *solid-solution*. The multi-phase problem seems to be a general situation in MFI/sorbate systems. Some other systems are described in (9,10).

In a recent paper it has been shown that the MFI/nPCT, nPDCB and nPDBB systems (*para*-disubstituted benzene molecules : p-chlorotoluene, p-dichlorobenzene and p-dibromobenzene) present all exactly the same type of phase diagram as that described above for MFI/p-xylene (20). The same situation holds as well for *mono*-substituted halogeno-benzene (chloro-, bromo- and iodo-benzene) molecules (12).

The multi-phase problem has been confirmed by Fyfe's group, using very high-resolution solid-state *mas*NMR on highly siliceous MFI materials (21 and references therein). The authors conclude by stating that this phenomenon is generally present in almost all MFI/sorbate systems. Nevertheless, as shown in (19), in detecting multi-phase domains, X-ray diffraction is a more general technique than NMR, since for lower Si/Al ratios (Si/Al < 5000) all the fine details in the ^{29}Si peaks completely vanish (severe peak broadening due to the presence of Al in the framework), whereas at *all* Si/Al ratios, the XRD profiles corresponding to MFI materials remain well resolved. So far, time-resolved XRD (TRXRD) has proven to be a very efficient qualitative and quantitative investigation method for elucidating the multi-phase problem (9,10,16-19). Even correct diffusion coefficients corresponding to *spontaneaous* desorption mechanisms can be derived from such TRXRD experiments (9).

3 - Localization of extra-framework species:

As already mentioned above, our first interest in MFI/sorbate systems was the localization of *p-xylene* molecules in the channel-system. Structural and geometrical considerations show that there are mainly *three* possible active sites : site **I** at the channel intersection (x/y/z ≈ .00/.25/.50), site **II** in the zig-zag channel (x/y/z ≈ .18/.25/.85) and site **III** in the straight channel (x/y/z ≈ .00/.50/.50). Both the straight and zig-zag channel sections are limited by 10-ring openings. Using trial-and-error as well as structure refinements based on *full-profile fitting* techniques (the Rietveld method) a location for the p-xylene molecule at *lower* sorbate loadings (≈ 4 molecules/*uc*) has been proposed in a boron substituted (*boralite*) MFI material (22,23) : this molecule is located at the channel-intersection (site **I**), its long molecular axis being parallel to the *b*-axis. The distribution of the p-xylene molecules at *high* loadings (*saturation* corresponding to eight molecules/*uc*) has been described in (24,25) : two distinct molecules fill entirely the channel system, the first p-xylene being at the channel intersection and the second one in the zig-zag channel (site **II**). This latter result has been confirmed by single-crystal

investigations (13). Our *"butterfly hunting"* methodology described in (26) has been successfully applied in the case of other MFI/sorbate systems : TPA, n-hexane, benzene (27), toluene (28), pyridine (29).

Presently, we mainly use the Rietveld code (DBW) distributed by Wiles and Young (30), which has been improved by including geometrical constraints (restrained interatomic bond distances) and several file generation routines for the calculation of Fourier and difference-Fourier maps. Using this improvement, and as far as the *framework* structure is concerned, it has been verified that by starting with atomic positions rounded to the *nearest tenth*, it was possible to obtain crystallographic results very close to those published for M(14), O1(8) and O2(13). In the case of an MFI/naphthalene system, it has even been possible to describe a *novel* type of channel deformations (31). Accordingly, it must now be admitted that in the case of MFI type materials, powder diffraction compets effectively with single-crystal determinations. Nevertheless, locating and refining *sorbate* positions or other extra-framework species (water molecules, cations) is a more delicate problem, since only low-angle diffraction peaks are affected by the sorbed species (see *first* section).

In a recent paper it has been shown that the framework symmetry of MFI type zeolitic materials is intimately related to the nature and the amount of guest molecules sorbed in the channel-system (12). This paper relates some structural results corresponding to more than 30 distinct MFI/sorbate complexes, including *bulky* (aromatic C6-C8 derivatives) and *flexible* (linear α,ω-dibromo C1-C6 alkane derivatives) molecules. In our experimental conditions, it has been observed that in *all* cases the XRD profiles corresponding to the 22-48°2θ angular domain (CuKα radiation) are almost *unaffected* by the presence of sorbed species in the structure. In other terms, for this angular region, the refined profiles are almost similar *before* (*without* the sorbate) and *after* (*with* the sorbate) the complete structure refinement. Structure-factor calculations corresponding to well-elucidated examples (8,13), show that in the low-angle region (6-22°2θ) the contribution of the sorbed species might affect some intensities by *several orders* of magnitude, whereas for °2θ>22, the mean contribution of the sorbate molecules decrease progressively from 10 to almost 0%. It might then be *postulated* that the framework structure can be refined by neglecting the lower-angle reflections. In the case of zeolitic MFI framework/sorbate complexes and for a given F(hkl) structure factor *amplitude* the following general relations hold :

$$F(hkl)_{6-22°2\theta} = F(hkl)_{framework} + F(hkl)_{sorbate}$$

$$F(hkl) _{°2\theta>22} \approx F(hkl)_{framework}$$

This will now be illustrated by a detailed example corresponding to a MFI•4p-dichlorobenzene (PDCB) complex (Si/Al = 132). This phase crystallizes in the orthorhombic Pnma space group (O1) and presents the $H_{0.72}Al_{0.72}Si_{95.28}O_{192}•4C_6H_4Cl_2$ composition. The 6-22°2θ and 22-48°2θ angular domains correspond to 46 and 445 hkl triplets respectively. This means that the detection of the extra-framework species relies entirely on these 46 reflections. Knowing that some of the peaks recorded in step-scanned powder diffraction profiles correspond to multiplets, these 46 hkl triplets merge and correspond to about 24 *observable* intensities. Nevertheless, by using the Rietveld method (a *full-profile* refinement technique), this peak-overlap problem is to some extend avoided. But it still remains that from a mathematical point of view, the difference-Fourier synthesis will be severely hampered by serial-termination problems. Let us investigate now how this situation looks like in a *real* case.
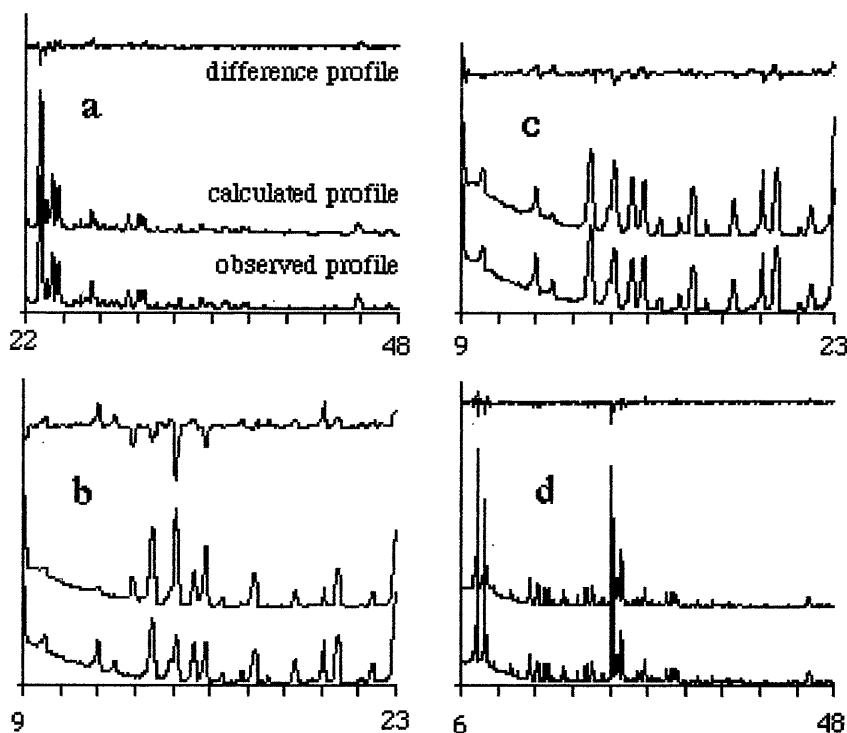
Figure 8 - Observed/calculated/difference profiles corresponding to different stages of the MFI•4-paradichlorobenzene structure refinement (*see text*).

The 22-48°2θ angular domain of the recorded XRD profile corresponding to the above mentioned complex has first been interpreted by constraining the framework atoms (Si,O). The starting atomic positions are those given in (8). After several refinement cycles (this might be a very time-consumming stage in the refinement), the unit-cell parameters are $a = 20.016(1)$, $b = 19.945(1)$, $c = 13.385(1)$Å. The a/b and a/c ratios are 1.0036 and 1.4954 respectively, and correspond to the *Pnma* framework symmetry (see Table **I** and ref.8,12). The observed (lower), calculated and difference (upper) profiles are given in figure **8a**. At this stage of the refinement, the *whole* diffraction range (6-48°2θ) is investigated, but *all* the profile and structure parameters are *fixed* (even the zero-shift and overall scale parameters). This corresponds to a run with *zero* variable parameters. A detail of the resulting observed, calculated and difference profiles are represented in figure **8b** (9-23°2θ range). The *missing* information appears on the calculated and difference profiles. Subsequent difference-Fourier maps are represented in figures **9a,b**. If we *trust* these drawings, it is clear that the *p-dichlorobenzene* sorbate molecule is located at the channel intersection and *not in the straight channel* as claimed in (32). Figure **9b** even indicates the *orientation* of the molecule. This orientation is comparable to that described for para-substituted benzene derivatives in the case of 2-3 molecules/*uc* loadings (12). The refinement process was continued by including the sorbate molecule. The resulting profiles are represented in figures **8c** (9-23°2θ) and **8d** (6-48°2θ). In the final stage of the refinements the framework *and* the sorbate are alternatively constrained. Complete structural results concerning the *whole* MFI/PDCB system (0<molecules/uc<8) will soon be published in conjunction with theoretical atom-atom potential calculations, high-resolution ^{29}Si *mas*NMR solid state spectroscopy and sorption capacity determinations. The location of the para-dichlorobenzene molecule in the MFI topology is represented in figure **1 0**.
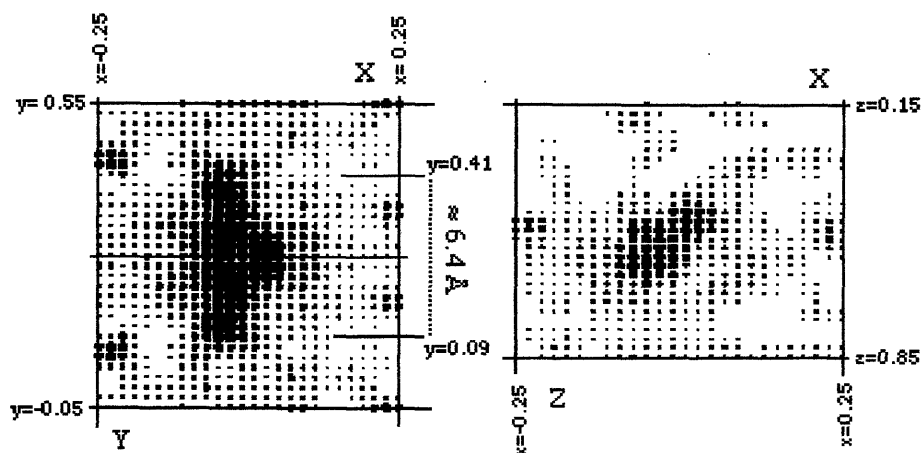
Figure 9 - Two difference-Fourier maps. Left : projection down the *c*-axis.
Right : projection down the *b*-axis.
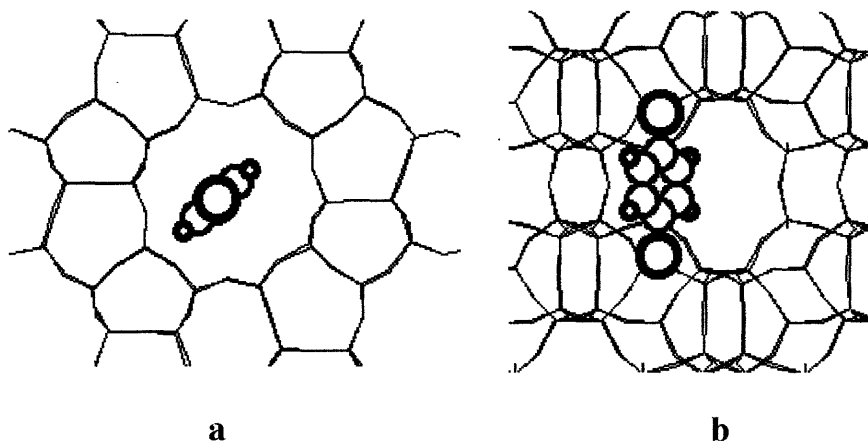

a   b

Figure 1 0 - The para-dichlorobenzene molecule in the MFI channel system.
Projection down the *b*-axis (a) and down the *a*-axis (b).

The above described methodology has been applied in the case of numerous MFI/sorbate systems including mono and di-substituted aromatic, benzyl (amine, alcohol, chloride, bromide), *n*-alkane (linear C1-C8 alcohols and α,ω-dibrominated hydrocarbons), naphthalene (normal and methyl or bromo- substituted naphthalene) and some diaryl (diphenyl-methane/ethane/ethylene/acetylene, biphenyl, benzil) derivatives. In the case of smaller molecules, as for instance MFI/dibromomethane complexes at lower loadings (0<molecules/uc<4), some other possible active sites (**II'**, **III'** and **IV**) have been evidenced (12). Recent results have also been obtained on the locations of exchanged cationic species (Na, Cs, Ni, Pb) in some ZSM-5 materials (33). Comparison of the informations obtained during these studies, allowed us to derive some structural correlations, existing *at room temperature* in MFI materials, between the framework symmetry and the location and/or the geometry of sorbed molecules (12). This illustrates the uniqueness of the intersecting channel system in the MFI topology (3), and explains why these materials are still so extensively investigated and widely proposed as *models* for experimental and theoretical calculations (33-41 *inter alia*). To the best of our knowledge, no other zeolitic framework presents such a versatile behaviour.

4 - Flexibility of the MFI framework :

It has already been mentioned that MFI materials crystallize in three different space groups. Figures 11a,b represent the projections of the orthorhombic O1 MFI framework down the *b*- and *a*-axis respectively. A prototype for this *Pnma* symmetry are the as-synthesized MFI/TPA and MFI/4p-xylene complexes (8, this work). The 10-ring openings corresponding to the straight and zig-zag channels are given in Table II. In this Table, the minimal and maximal van der Waals type oxygen...oxygen distances (Å) are shown and in the case of the straight channels the corresponding oxygen atoms have been labelled as in (8,13,14,31). Some other phases presenting the same symmetry are : calcined and evacuated H•MFI materials for Si/Al<≈90; as-synthesized MFI/TPA phases; sorbate loaded phases for Si/Al<≈90 at lower loadings (up to four molecules/*uc*).
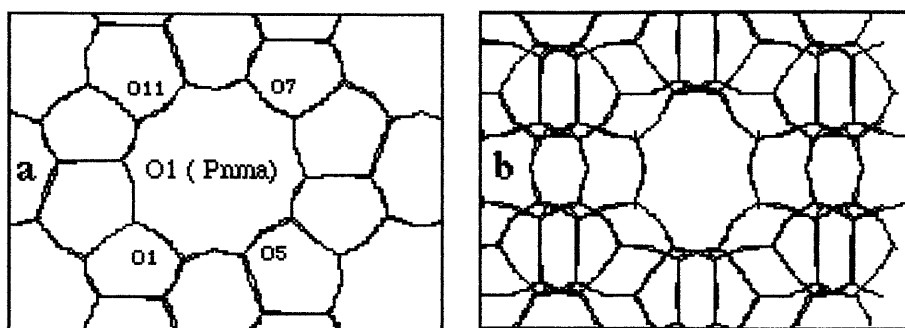

Figure 11 - projection of the orthorhombic O1 framework down the b-axis (a) and the a-axis (b).

Table II

MFI : 1 0-ring pore openings in the *O1*, *M*, *O2* and *NPH* framework deformations.

	ref.	space-group	10-ring in straight channel[a]		10-ring in zig-zag channel[b]	
			O5-O11	O1-O7		
			O31-O37[c]	O27-O33[c]		
O1	(8)	Pnma	5.22	5.75	5.29	5.55
					5.28	5.60
M	(14)	P2$_1$/n·1·1	5.18	5.78	5.89	5.35
			5.27	5.83	5.01	5.78
O2	(13)	P2$_1$2$_1$2$_1$	5.07	*6.06*	4.76	*6.37*
			4.80	*6.18*	4.58	*6.15*
NPH	(31)	Pnma	*6.30*	4.80	5.20	5.80
					5.30	5.70

[a] parallel to the b-axis, down the [0,y,1/2] direction ;

[b] parallel to the a-axis, down the [x,1/4,0.85] direction ;
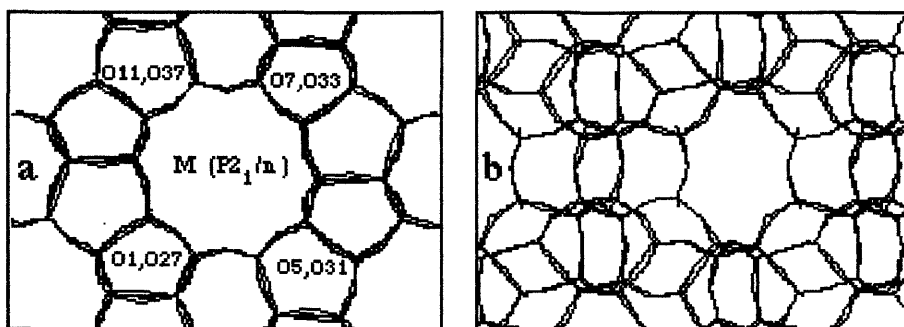
[c] in the monoclinic M and orthorhombic O2 polymorphs.

Figure 12 - projection of the orthorhombic M framework down the b-axis (a) and the a-axis (b).

Figures 12 a,b illustrate the same pojections in the case of the monoclinic (M) framework symmetry (14). It might be emphasized that in the M and O1 framework symmetries, the 10-ring pore openings are almost circular (Table II). This symmetry is usually observed for H·MFI materials presenting a Si/Al>≈90 ratio, as in silicalite and silicon rich phases. In this case, the symmetry of sorbent/sorbate complexes at lower loadings can usually not be predicted, and each MFI/sorbate system represents by itself an original problem, which has to be investigated for probable multi-phase domains and definite phases. Some examples are given in (12).
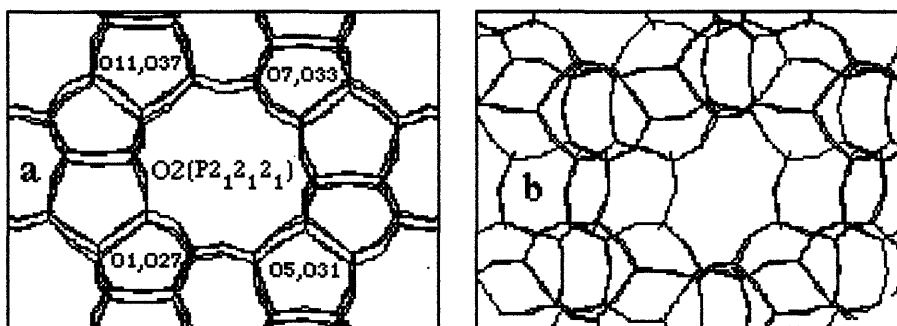
Figure 13 - projection of the orthorhombic O2 framework down the b-axis (a) and the a-axis (b).

At higher sorbate loadings (4<molecules/uc<8 to 12 and even more, *depending* on the sorbate), the third O2(13) framework symmetry might be observed. Some examples presenting this symmetry are given in section 2 (*e.g.*, mono and para-disubstituted C6-C8 aromatics). Figures 13 a,b represent two projections corresponding to this MFI polymorph. In order to accomodate the sorbate molecules, the 10-ring openings in both the straight and the zig-zag channels are now elliptical and almost comparable to those existing in the 1 D channel system of AEL (ALPO-11, SAPO-11) type materials, which also present a reversible Ima2/Pna2$_1$ polymorphism (42).

Recently, investigations on an MFI/4naphthalene complex have shown that at saturation (*four* molecules/uc) the a/b and a/c unit-cell parameter ratios are 0.9988 and 1.4924 respectively (12). This had never been observed before, and it was thought that we were in the presence of a new framework symmetry. Actually, structure refinements performed as described in the precedent section, show that the complex crystallizes in the orthorhombic Pnma space group and that the 10-ring pore openings in the straight channels present a *new* elliptical deformation (31), which has a *different* orientation than that observed in O2 (13). Accordingly, we propose the NPH label for this novel deformation (Table II). Figures 14 a,b represent two projections

corresponding to this complex. Work in progress shows that this unusual NPH framework deformation is also present in some MFI/diaryl complexes (*vide supra*). It must be emphasized that in NPH the zig-zag channel sections remain almost *circular.*
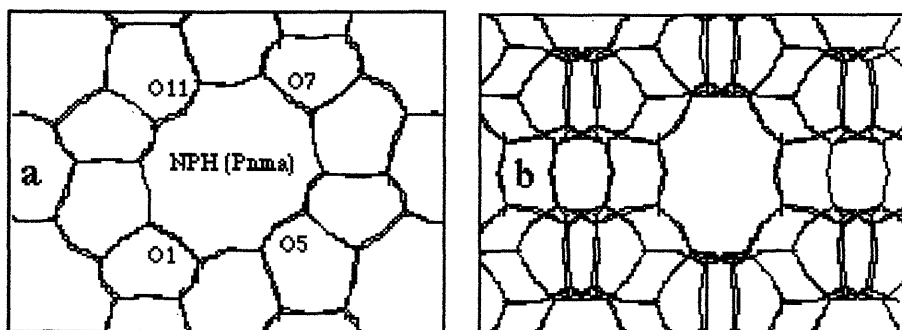

Figure 14 - projection of the orthorhombic NPH (Pnma) framework down the b-axis (a) and the a-axis (b).

To date, no other *original* channel deformations of the MFI framework have been observed by our group. Other deformations may exist as for instance the case where the straight channel sections are circular and the zig-zag channel sections strongly elliptical, *i.e.*, the *inverse* NPH form. Figures 1 0 to 1 4 illustrate the flexibility of the MFI framework. This gives an idea of some possible sorbate-induced structural modifications which are observed by several other experimental techniques (calorimetry and NMR), as for instance in MFI/benzene and MFI/pyridine systems (43).

Conclusion :

Some structural aspects concerning sorbent/sorbate complexes where the microporous zeolitic sorbent is an MFI material have been described in the present paper. It appears that, prior to any structure determination, one must get very precise information on the investigated MFI/sorbate *phase diagram.* Lack of information in this domain led sometimes to misinterpreted results. For instance, a structure determination on a single-crystal supposed to correspond to a *saturated* ZSM-5/dichlorobenzene complex led to unsatisfactory results : the final R = 14.9% residue is relatively high (usually 3 to 5%) and the second molecule in the zig-zag channel could not be detected (44). In our opinion this comes from the fact that the complex was *not saturated.* Consequently, the sample was no more a *monophasic* single-crystal, but actually the result of two *intergrown* structures where domains corresponding to MFI•4PDCB (Pnma) *and* MFI•8PDCB ($P2_12_12_1$) phases coexist, as already observed in the case of polycrystalline MFI•P-xylene complexes (16-18). Preliminary sorption capacity measurements show that in *all* the investigated H•MFI materials (15<Si/Al<≈5000) the saturation of para-dichlorobenzene was attained for *eight* molecules/unit-cell (45).

Of course XRD (or neutron powder diffraction) is not the sole investigation method which yields structural information on sorbent/sorbate systems. In conjunction with others groups, we are currently using theoretical modelling and energy-minimization calculations, determination of sorption capacities and isotherms, thermal analysis, thermogravimetry and high-resolution *mas*NMR (normal and cross-polarization) on highly dealuminated MFI samples. Nevertheless, the only technique which ensures a complete structure determination still remains X-ray and neutron powder diffraction. Single-crystals, when available, are also good starting samples, but as the molecular diffusion rate in such materials is *very slow*, one is never sure to be in the presence of the correct sorbate loadings.

Future prospects in the present field are already planned. Specially, investigations of structural modifications occuring during *real-time* sorption/desorption or reaction processes by neutron powder diffraction (D20 diffractometer at ILL, Grenoble) at the 15-50 μsec time-scale, and NMR cross-polarization experiments for the determination of Si...H interactions in sorbent/sorbate systems. Coupled with 2D high-resolution solid state NMR, this latter technique should give some valuable informations on the most probable anchoring sites of the sorbate molecules.

References

(1)   Csicsery, S.M., *Zeolites*, **4** , 202 (1984).
(2)   Breck, D.W., "Zeolite Molecular Sieves", Wiley, New York, 1974.
(3)   Meier, W.M., and Olson, D.H., "Atlas of Zeolite Structure Types", Butterworth, London, 1987.
(4)   Flanigen, E.M., Bennett, J.M., Grose, R.W., Cohen, J.P., Patton, R.L., Kirchner, R.M., and Smith, J.V., *Nature* (London), **271**, 512 (1978).
(5)   Olson, D.H., Kokotailo, G.T., Lawton, S.L., and Meier, W.M. *J. Phys. Chem.*, **85**, 2238 (1981).
(6)   Fyfe, C.A., Kennedy, G.J., DeSchutter, C.T., and Kokotailo, G.T., *J. Chem. Soc., Chem. Commun.*, 541 (1984).
(7)   Baerlocher, C., Proceedings of the 6th International Zeolite Conference, Reno, Nevada, 10-15 July 1983. Guildford, Buttherworth, p. 823 (1984).
(8)   van Koningsveld, H., van Bekkum, H., and Jansen, J.C., *Acta Cryst.*, **B43**, 127 (1987).
(9)   Mentzen, B.F., *J. Appl. Cryst.*, **21**, 266 (1988).
(10) Mentzen, B.F., International Symposium on Zeolites as Catalysts, Sorbents and Detergent Builders, Würzburg, FRG, September 4-8, 1988. Elsevier, Amsterdam, p.477 (1989).
(11) Alvarez, A.G., Viturro, H., and Bonetto, R.D., *Mat. Chem. Phys.*, **32**, 135 (1992).
(12) Mentzen, B.F., *Mater. Res. Bull.*, 27, 831 (1992).
(13) van KONINGSVELD, H., TUINSTRA, F., van BEKKUM, H., and JANSEN, J.C., *Acta Cryst.*, **B45**, 423-431 (1989).
(14) van KONINGSVELD, H., JANSEN, J.C., and van BEKKUM, H., *Zeolites*, **10**, 235-242 (1990).
(15) Gélin, P., and Mentzen, B.F., *in preparation*.
(16) Mentzen, B.F., and Védrine, J.C., *C.R.Acad.Sci., Paris*, **301**(II), 1017 (1985).
(17) Mentzen, B.F., Bosselet, F., and Bouix, J., *C.R.Acad.Sci., Paris*, **306**(II), 27 (1988).
(18) Mentzen, B.F., and Bosselet, F., *C.R.Acad.Sci., Paris*, **309**(II), 539 (1989).
(19) Sacerdote-Peronnet, M., Bosselet, F., and Mentzen, B.F., *C.R.Acad.Sci., Paris*, **312**(II), 1513 (1991).
(20) Mentzen, B.F., *Mater. Res. Bull.*, 27, 953 (1992).
(21) Fyfe, C.A., Feng, Y., Grondey, H., Kokotailo, G.T., and Gies, H., *Chem. Rev.*, **91**, 1525 (1991).
(22) Mentzen, B.F., *C.R.Acad.Sci., Paris*, **303**(II), 681 (1986).
(23) Mentzen, B.F., and Vigné-Maeder, F., *Mater.Res.Bull.*, **22**, 309 (1987).
(24) Mentzen, B.F., Bosselet, F., and Bouix, J., *C.R.Acad.Sci., Paris*, **305**(II), 581 (1987).
(25) Mentzen, B.F., and Bosselet, F., *Mater. Res. Bull.*, 23, 227 (1988).
(26) Mentzen, B.F., *Mater. Res. Bull.*, 22, 489 (1987).
(27) Mentzen, B.F., *C.R.Acad.Sci., Paris*, **303**(II), 1299 (1986).
(28) Mentzen, B.F., *C.R.Acad.Sci., Paris*, **307**(II), 59 (1988).
(29) Mentzen, B.F., *J. Appl. Cryst.*, **22**, 100 (1989).
(30) Wiles, D.B., and Young, R.A., *J. Appl. Cryst.*, **14**, 149 (1981).
(31) Mentzen, B.F., Sacerdote-Peronnet, M., Bérar, J.-F., and Lefebvre, F., *Zeolites*, *accepted for publication.*

(32) Gies, H., Marler, B., Fyfe, C., Kokotailo, G., Feng, Y., and Cox, D.E., *J. Phys.Chem. Solids*, **5 2**, 1235 (1991).

(33) Mentzen, B.F., Sacerdote-Peronnet, M., and Bouix, J., *C.R.Acad.Sci., Paris*, **3 1 5**(II), 59 (1992).

(34) Mentzen, B.F., and Bosselet, F., *C.R.Acad.Sci., Paris*, **3 0 9**(II), 539 (1989).

(35) Sacerdote-Peronnet, M., Bosselet, M., and Mentzen, B.F., *Mater. Res. Bull.*, **25**, 593 (1990).

(36) Bosselet, M., Sacerdote-Peronnet, M., Bouix, J., and Mentzen, B.F., *Mater. Res. Bull.*, **2 5**, 443 (1990).

(37) Titiloye, J.O., Parker, S.C., Stone, F.S., and Catlow, C.R.A., *J. Phys. Chem.*, **9 5**, 4038 (1991).

(38) June, R.L., Bell, A.T., and Theodorou, D.N., *J. Phys. Chem.*, **9 4**, 1508 (1990) and **9 6**, 1051 (1992).

(39) Goodbody, S.J., Watanabe, K., MacGowan, D., Watton, J.P.B., and Quirke, N., *J. Chem. Soc., Faraday Trans.*, **8 7**, 1951 (1991).

(40) Demontis, P., Suffritti, G.B., Fois, E.S., and Quartieri, S., *J. Phys. Chem.*, **9 6**, 1482 (1992).

(41) Catlow, C.R.A., Freeman, C.M., Vessal, B., Tomlinson, S.M., and Leslie, M., *J. Chem. Soc., Faraday Trans.*, **8 7**, 1947 (1991).

(42) Mentzen, B.F., Védrine, J.C., Khouzami, R., and Coudurier, G., *C. R. Acad. Sci., Paris*, **3 0 5**(II), 263 (1987); Mentzen, B.F., Védrine, J.C., and Khouzami, R., *C. R. Acad. Sci., Paris*, **3 0 4**(II), 11 (1987); Khouzami, R., Coudurier, G., Lefebvre, F., Védrine, J.C., and Mentzen, B.F., *Zeolites*, **1 0**, 183 (1990).

(43) Thamm, H., *J. Phys. Chem.*, **9 1**, 8 (1987) ; *ibib idem*, **9 2**, 193 (1988).

(44) van Koningsveld, H., Jansen, J.C. and van Bekkum, H., " in extended abstracts and program of the 9th International Zeolite Conference " (Ed. HIGGINS, J.B., von BALLMOOS, R. and TREACY, M.M.J.) Butterworth., Montreal, July 5-10, 1992, abstract RP 201.

(45) Mentzen, B.F., et al., *to be published*.