Structural evolution
of a Li$_{3.4}$ZSM-5(MFI)/benzene zeolitic host/guest system

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In order to understand the host/guest interactions taking place in a zeolitic Li$_{3.4}$ZSM-5(MFI)/benzene sorbent/sorbate system, complementary X-ray synchrotron and neutron (ND) diffraction patterns are analyzed for several benzene pore-fillings. It is shown that the locations of the sorbed molecules are strongly correlated with the Li...benzene interactions. Although it was not possible to detect by ND the Li atoms, these interactions are clearly visible on the calorimetric differential-heat curve (Fig.1)

Interest in host/guest interactions in zeolitic sorbent/sorbate systems has increased in recent years because of their potential applications in industrial petrochemistry and catalytic processes. In this regard the *ZSM5/ aromatics* systems have attracted a considerable interest (1,2). In the case of cation exchanged phases both the locations of the sorbed species and the sorptive properties are modified. Some examples of host/guest complexes are given in (3-7).

Recent results concerning ZSM5/benzene systems (8,9) show that the sorption heat curves can be correctly interpreted by considering their respective structural evolution. In the case of a Li exchanged ZSM5 sample the calorimetric heat curve exhibits some *unexpected* details (Fig.1) : (a) a very strong *heat change* occurs at ≈1.7 benzene/uc loading and (b) the total loading *exceeds* the usually observed one (8 mol/uc).
In order to get a better understanding on the host/guest interactions occuring in this system, synchrotron and ND diffraction experiments have been performed on *the same* LiZSM5 sample used by calorimetry, obtained by Li exchange on a *commercial* (Degussa) material.
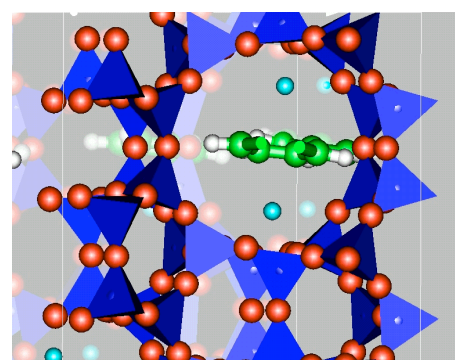

Figure 2: the *possible* Li$_2$C$_6$H$_6$ cluster in the Li$_{3.4}$ZSM-5/ 1.7C$_6$H$_6$ phase.

For the *ND* runs (D2B), the LiZSM5 sample in a *small* cylindrical V can has been dehydrated at 450°C and tightly closed with a silicon rubber septum. Successive benzene loadings are obtained by injecting *weighted* amounts of D$_2$O through the septum (homogenization at 80°C). For the *synchrotro*n runs a locally designed atmosphere controlled sample-holder has been used. The zeolite powder is packed in a 0.9mm quartz capillary. All the experimental diffraction profiles have been analysed by the Rieveld method by using the GSAS package and a modified DBW code. In all cases the locations of the benzene molecules are clearly revealed by the difference-Fourier maps but no negative residue could
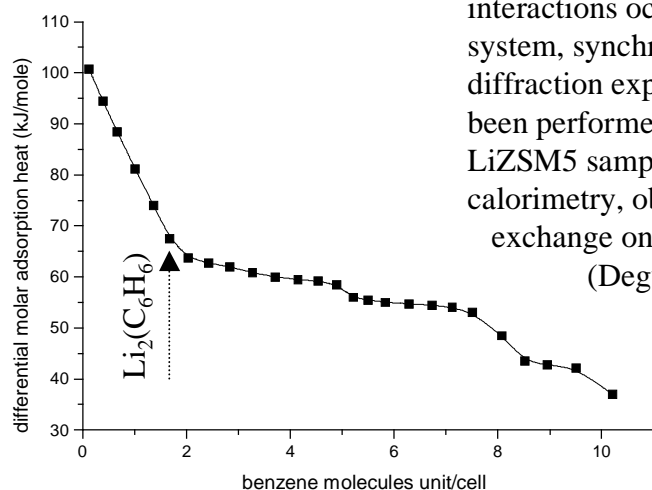

Figure 1: The Li 3.4 ZSM-5/benzene system : differential molar adsorption heats (kJ/mol)

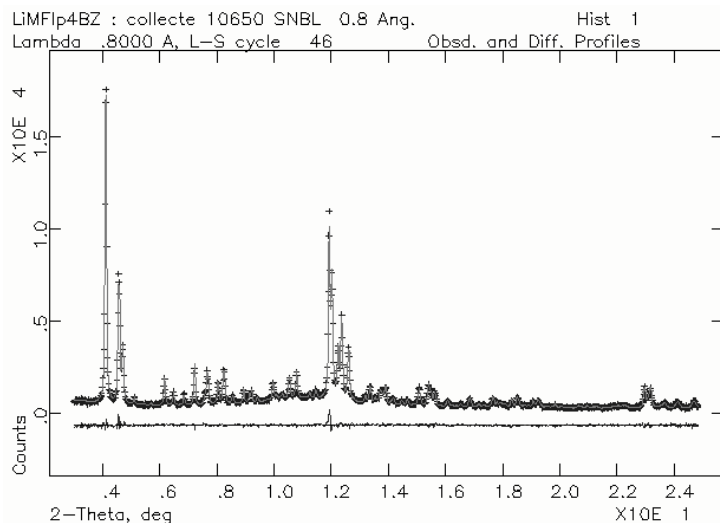Figure 3: Rietveld refinement of the synchrotron profile corresponding to the $Li_{3.4}ZSM-5/5.9C_6H_6$ sample at 303K.

unambiguously be attributed to Li species. The *sudden* adsorption heat change observed on the calorimetric curve (Fig.1) corresponds to the exact formation of $Li_2(C_6H_6)$ species. Knowing the location of the benzene molecule at this concentration (Fig.2), the *possible* sites for the π-interacting Li cations were also refined : surprisingly, their atomic coordinates and population factors are *not rejected* by the refinement. Carefull inspection of the experimental synchrotron profiles shows that for the 0-4.7 benzene/uc filling range the zeolitic framework symmetry is *monoclinic :* accordingly, the adsorbed benzene species are *ordered* in the ZSM5 channels. In the Table the progressive populations of the three adsorption sites are reported : I,II,III are for the channel intersection, the zig-zag channel and the straight channel respectively.

These results suggest several comments : (i) for the 0-3.5 mol/uc range only *one* sorbate species resides in site I. For higher loadings a *second* sorbate species appears in site II and finally close to the saturation capacity a *third* benzene species is located in the straight channel. (ii) the maximum benzene loading calculated for both the synchrotron and ND runs amounts to 7.3(3) mol/uc, which is significantly *lower* than the value observed on the calorimetric curve. (iii) in all cases the sorbed benzene molecules are *ordered* in the zeolitic channels. Nitrogen adsorption (BJH pore-distribution) shows that the ex-commercial LiZSM5 sample presents substantial *mesopores* : its micropore volume is 0.143 ml/g, which compared to an *ideal* ZSM-5 material (0.190 ml/g) should

correspond to a total amount of $10*0.143/0.190 \approx 7.5$ benzene/uc loaded in the zeolitic *micropores*, in good agreement with the highest loading refined for the *crystalline part* of the material. This work represents a good example of the structural information one might obtain by complementary neutron (ND), X-ray synchrotron diffraction and calorimetry on a zeolitic sorbent/sorbate system obtained by ion exchange on a *commercial* parent material : calorimetry yields the *total* amount sorbed in the zeolite (*micropore + mesopore*), whereas diffraction techniques only reveal the amount sorbed in its *crystalline* micropore part.

	adsorption site			
C6H6/uc	I	II	III	sp.gr*
0.2	0.20(5)			M
1.7	1.7(1)			M
2.3	2.3(1)			M
3.8	3.5(1)	0.3(1)		M
4.7	3.8(1)	0.9(1)		M
5.0	3.8(1)	1.2(1)		O
5.9	3.8(1)	2.1(1)		O
6.9	3.9(1)	2.5(1)	0.5(1)	O
7.3	3.9(1)	2.8(1)	0.6(1)	O

Table: locations of the adsorbed benzene molecules at increasing pore-filligs. **I** : intersection; **II** : zig-zag channels; **III** : straight channels. * space group - M : $P2_1/n.1.1$ - O : $P2_12_12_1$

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