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

In order to understand the host/guest interactions taking place in a zeolitic $\text{Li}_{3.4}\text{ZSM-5(MFI)}$ /benzene sorbent/sorbate system, complementary neutron diffraction and X-ray synchrotron diffraction patterns have been analysed for several benzene pore-fillings. It has been shown that the locations of the sorbed molecules are strongly correlated with the $\text{Li}\dots\text{benzene}$ interactions.

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 (figure 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 obtain a better understanding of the host/guest interactions occurring in this system, neutron diffraction and

synchrotron diffraction experiments have been performed on *the same* LiZSM5 sample used for calorimetry, obtained by Li exchange on a *commercial* (Degussa) material.

For the neutron diffraction 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. After cooling, successive benzene loadings have been obtained by

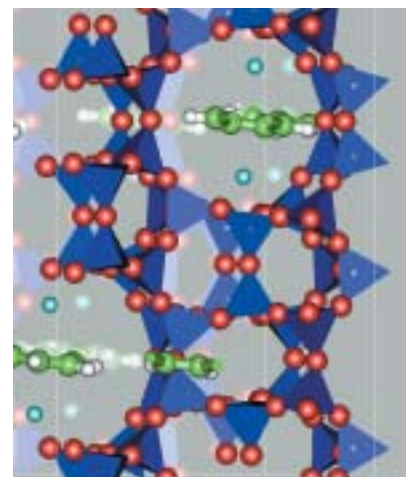


Figure 2: The possible $\text{Li}_2\text{C}_6\text{D}_6$ cluster in the $\text{Li}_{3.4}\text{ZSM-5/1.7C}_6\text{D}_6$ phase.

injecting *weighted* amounts of deuterio-benzene through the septum. Before each run the sample has been homogenized by heating at 80°C for ten minutes. All the experimental diffraction profiles have been analysed by the Rietveld method by using the GSAS

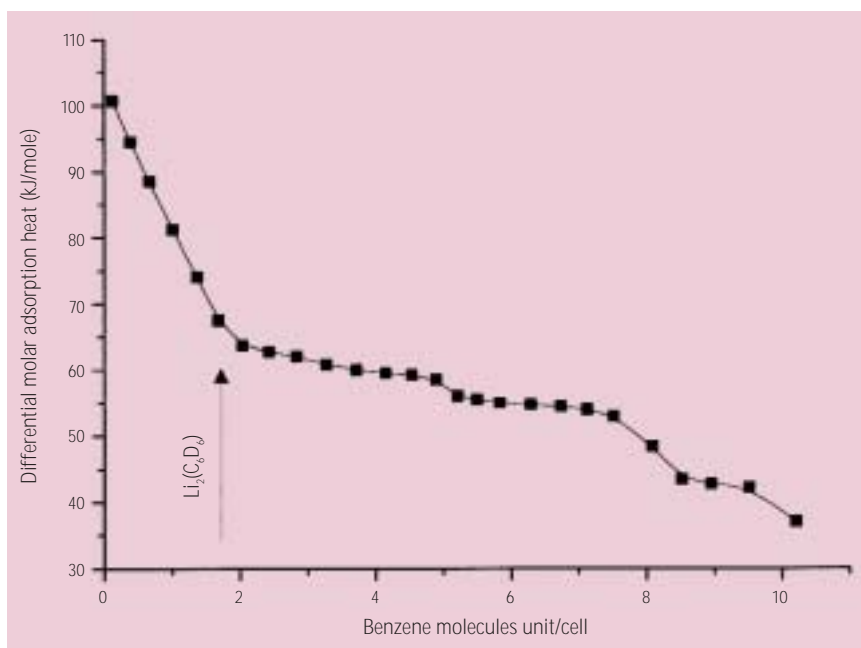


Figure 1: The $\text{Li}_{3.4}\text{ZSM-5/benzene}$ system : differential molar adsorption heats (kJ/mol).

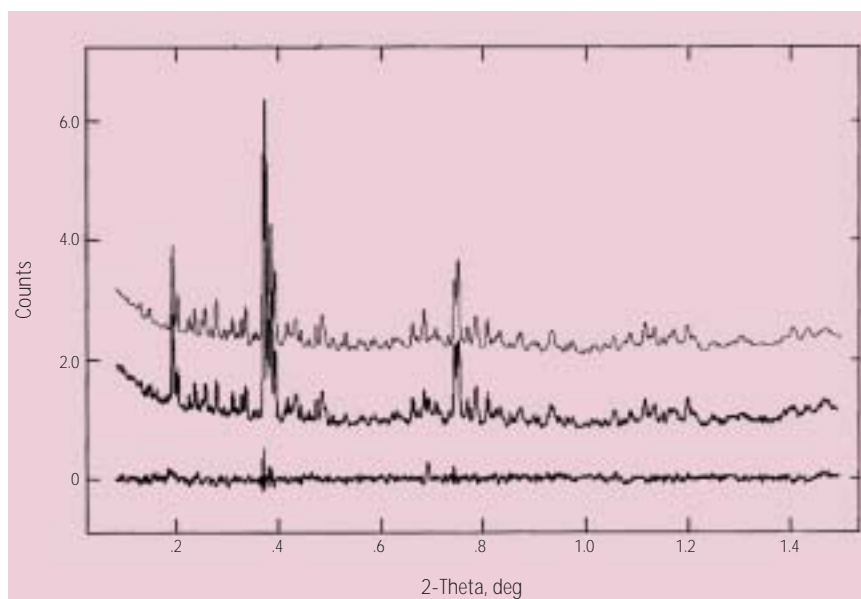


Figure 3: Rietveld refinement of the neutron diffraction profile corresponding to the $\text{Li}_{3.4}\text{ZSM-5}/5.9\text{C}_6\text{D}_6$ sample at 303K.

which compared to an *ideal* ZSM-5 material (0.190 ml/g) should correspond to a total amount of $10 \times 0.143 / 0.190 \approx 7.5$ 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.

$\text{C}_6\text{D}_6/\text{uc}$	Adsorption site			sp.gr*
	I	II	III	
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-fillings. I : intersection; II : zig-zag channels; III : straight channels. * space group - M : P₂/n - O : P₂,2₁.

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 unambiguously be attributed to Li species. The *sudden* adsorption heat change observed on the calorimetric curve (figure 1) corresponds to the exact formation of $\text{Li}_2(\text{C}_6\text{D}_6)$ species. Knowing the location of the benzene molecule at this concentration (figure 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. Careful 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 pop-

ulations 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 neutron diffraction and synchrotron 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,

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