	Experiment title: Localization of water sorbed in cesium exchanged ZSM-5 zeolitic materials at several loadings and temperatures. Evidence of Cs cation migration. I - Anhydrous phases.	Experiment number: CH-1838
Beamline: BM01B	Date of experiment: from: December 8 2004 to: December 13 2004	Date of report: 25 February 2005
Shifts: 15 (5 days)	Local contact(s): EMERICH Hermann	<i>Received at ESRF:</i>
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Report: Structural investigations concerning zeolitic host/guest complexes (*zeolates*) presenting the **MFI**(silicalite, ZSM-5 and cation substituted phases) framework type have been widely undertaken these last decades. Until now we have particularly studied the silicalite/sorbate systems involving genuine and substituted aromatic (p-xylene, benzene, naphthalene, p-nitroaniline ...) and aliphatic (C5-C18 n-alkanes, methanol, tetrachlorethylene ...) guest molecules (1-3). Very surprisingly, only a few structural studies concerning cation-exchanged ZSM-5 materials have been reported (4-6). The present study, devoted to the *structural evolution* (locations and migrations of the cation and water species) of a Cs_{6,6}-ZSM-5/water system versus *temperature* and *water fillings*, has been performed on the BM01B powder-diffraction equipment at the SNBL (ESRF). The chemical formula of the water saturated starting zeolite is Cs_{6,6}Al_{6,9}H_{0,3}Si_{89,1}O₁₉₂•28 H₂O (almost complete Cs exchange). The sample has been filled in a 0.8mm in-diameter quartz capillary and mounted on an atmosphere-controlled setup realized by the SNBL team. A first set of diffraction profiles (X-ray synchrotron radiation $\lambda = 0.69918$ Å) have been recorded at increasing temperatures (up to 450 °C) according to the experimental dehydration curve. A second set of diffraction profiles corresponds to anhydrous phases at several temperatures from 450°C down to 28.1°C in dynamic vacuum conditions. Interpretation of the collected profiles by the Rietveld method (modified DBW and GSAS codes) has been started on the second set (anhydrous phases). In fact, our structural study corresponds to three distinct steps : (1) determination of the MFI framework symmetry and structure, (2) location of the Cs cations and (3) location of the water molecules. The first step has been solved by investigating a restricted diffraction domain where the extra-framework species do not contribute too much to the structure factors : it appears that the space group is Pnma and that the straight-channel section of the MFI framework is **definitely elliptical**, which is a clue for the presence of **strong** cation-framework interactions (1). The second step has been

solved by interpreting the complete diffraction profile : several difference-Fourier maps reveal the presence of **five** distinct extra-framework species which might be attributed to Cs cations. Subsequent refinements confirm these sites. The total Cs content amounts to 6.6(2) Cs/uc ($U_{iso}=0.143(1)$). The Cs distribution at ambient T is $Cs1/2/2'/3/3' = 2.61(5)/0.81(5)/1.85(8)/0.86(2)/0.47(2)/uc$: Cs1 is located close to the intersection of the straight and zig-zag channels (site I-II), Cs2 and Cs2' are very close and located in the straight channels (site III), Cs3 and Cs3' are both located in the zig-zag channel (site II).

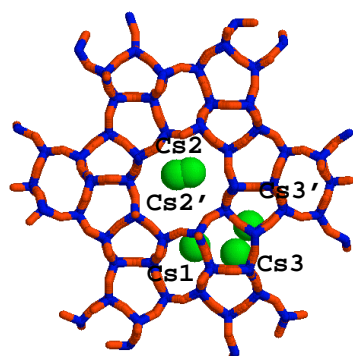


Figure 1. Cs cations in the MFI framework

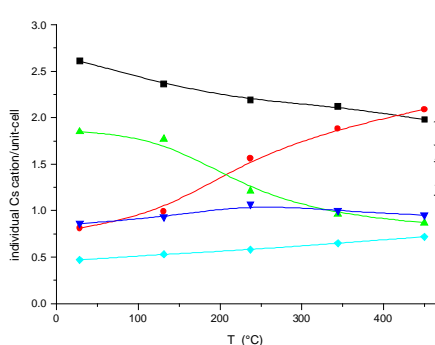


Figure 2. Migration of Cs cations versus T

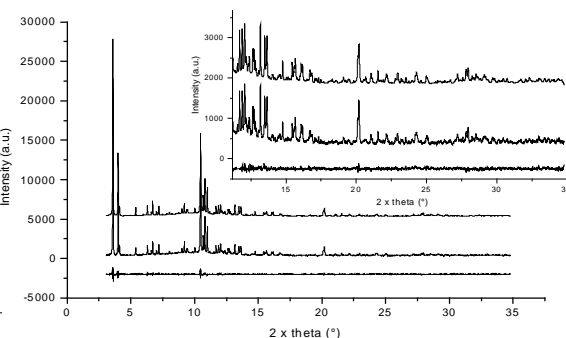


Figure 3. Rietveld plot : the anhydrous $Cs_{6.6}$ MFI zeolite.

A structural detail showing the locations of the Cs species in the MFI framework structure is given in figure 1 (view down the 010 direction). Cs cation migration versus T is represented in figure 2 and the Rietveld plot corresponding to the anhydrous Cs-exchanged MFI zeolite is represented in figure 3. Preliminary calculations based on **molecular mechanics** using the exp-6-1 type Buckingham model (7) show that it is possible to predict the five Cs sites found by structure refinements. An additional **sixth Cs site** predicted by computer simulations only appears at higher temperatures ($T > 340^\circ C$) where the Cs2-Cs2' contact increases from 0.4 **up to 2.4 Å**. Given the rather great amount of collected data (13 powder profiles) and the complexity of the structural study, specially in case of the hydrated phases at several temperatures, the results corresponding to the third step mentioned in this report will not be developed presently. Concerning the structural evolution of the anhydrous CsMFI zeolite versus temperature a first paper (5 detailed structures) is in progress (8). The present report relates the very **first complete structural study on a cation-exchanged MFI type material**. Concerning the structural evolution of the hydrated phases, many *site correlations* appear between the populations of the Cs and water sites. Knowing the *exact* Cs concentration in the investigated phases, the total Cs/uc variable has been *constrained to 6.6*. In these conditions the correlations between the site populations, the water locations and the framework atoms are greatly reduced. The first results concerning the hydrated phases show that among **nine possible** sites predicted by MM calculations for the water molecules, **only six** are characterized in the saturated CsMFI zeolite and that at $T > 100^\circ C$ **only two** water species are still present in the partially hydrated phases. **Complementary** data collections corresponding to partially dehydrated phases *equilibrated at room T* are already planned (part of the CH-1870 experiment, April 2005).

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