Report on Experiment n° CH1423 at the Swiss-Norwegian Beam Line of ESRF

Introduction

MCM-22 is a siliceous microporous material with the **MWW** topology.[1] The MCM-22 precursor is a lamellar material which contains hexametileneimine (HMI), as structural directing agent. The lamellar phase transforms into the three-dimensional zeolite at 250°C, still retaining HMI molecules inside the cages and the channels. The organic phase is removed from 350 to 550°C.

In this experiment we have studied, by X-ray powder diffraction, the structural modifications occurring during the calcination process of MCM-22 prepared following the recipe in ref. 2. Besides, a series of Cu-exchanged MCM-22 at different exchange level were examined, to locate the extra-framework sites more apt to host the Cu atoms. All the samples were treated in vacuum at 150°C (exploiting a suitably modified vacuum line) in capillary tubes, which were subsequently sealed to avoid the contact with air moisture and the re-hydration of the samples.

Aims of the experiment:

- follow the transformation from the lamellar phase (precursor) to the zeolitic phase (**MWW** structure) as a function of the thermal treatment under vacuum;
- evaluate the structural effects of the presence of HMI;
- localize the organic molecules inside the structure of MCM-22 precursor;
- study the structural changes upon dehydration/re-hydration cycles both in the presence and in the absence of HMI molecules within the **MWW** framework;
- evaluate the effect of the insertion of copper ions, and possibly localize them, within the **MWW** structure;
- evidenciate the presence of extra-phases.

Results

Figure 1 shows the XRPD pattern of three samples treated at increasing temperature, compared to the as made precursor. The as-synthesised sample (precursor in figure 1) presents a typical powder pattern of a lamellar structure, while also after a mild treatment at 250°C (red curve in figure 1 and 2), the zeolitic structure **MWW** is practically formed. The evolution of the diffraction patterns as a function of the temperature shows a substantial modification of the intensity ratio of peaks in the range 6.5-10° in comparison to the peaks in the 1.5-5° range. This behaviour is connected with the progressive elimination of the organic molecules from the channels. The peak at 1.05° due to the [001] reflection of the lamellar phase shows a net decrease as a function of the thermal treatments (Figure 2). Besides this peak is observed in different positions during the thermal treatment, passing from 27.3 Å in the as-synthesised sample, to 26.3 Å, in sample treated at 250°C, and to 25.8 Å (Figure 3 for the supposed structural modification during the thermal treatment), in the calcined sample. TGA analysis allows the evaluation of the number of HMI molecules within the structure of the differently treated samples and this is a relevant information

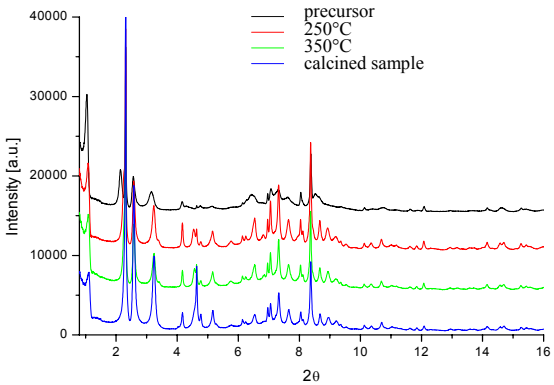

Figure 1: XRD patterns of MCM-22 samples

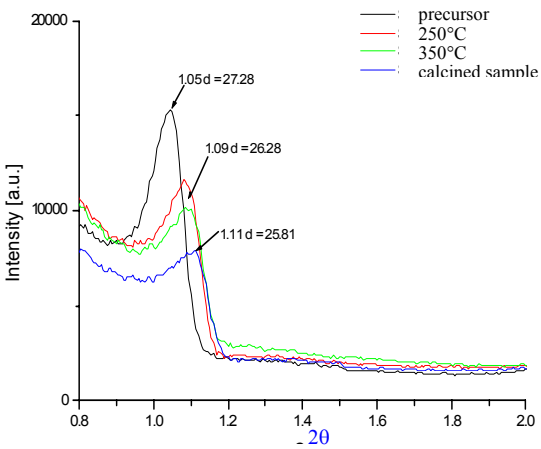

Figure 2: Low angles region

which should give us a good starting point for the structural refinement of the MCM-22 precursor structure.

The insertion of copper ions doesn't give drastic changes in the powder patterns; however, the Cu over-exchanged sample shows additional peaks due to a separate phase, which we identified as copper oxide.

Rietveld refinements

The Rietveld analysis of the collected XRPD powder profiles is currently in progress (employing the GSAS[3] software), employing as model only the siliceous **MWW** framework.[1] The anisotropic broadening of the peaks of these samples causes some complications in the Rietveld refinement, but the residual curve (violet in figure 4) is acceptable.

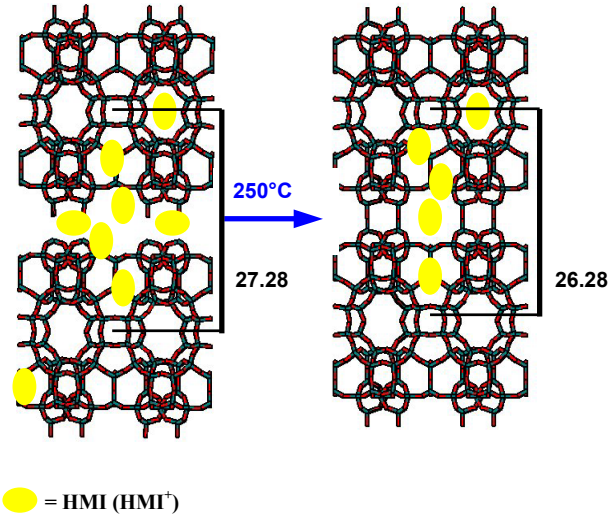

Figure 3: Structural modification during MCM-22 calcination

At first a calcined sample sealed in capillary under vacuum (figure 4) was compared to the calcined sample exposed to air (figure 5) to check if the sample preparation was successful. It is worth noting that calcined samples in vacuum (figure 4) present a good agreement between the calculated and observed pattern, indicating that no residual electron density is present in the MCM-22 channel and the sample preparation was correct. Conversely in figure 5 (sample exposed to air) the residual curve (violet) is rather irregular and some extraframework atoms (as suggested by Leonowicz et al. in ref. 4) must be added in the model to achieve a good agreement between calculated and observed pattern (data not shown).

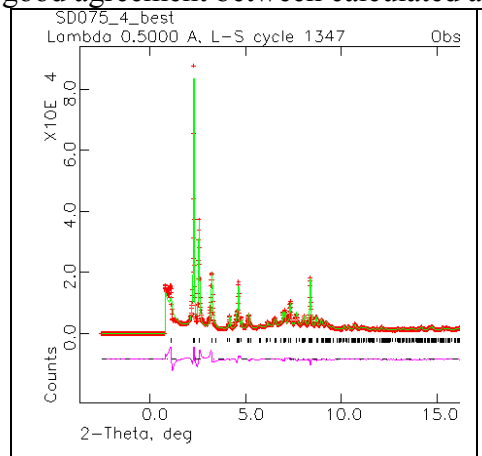

Figure 4: Rietveld analysis of the calcined samples in vacuum

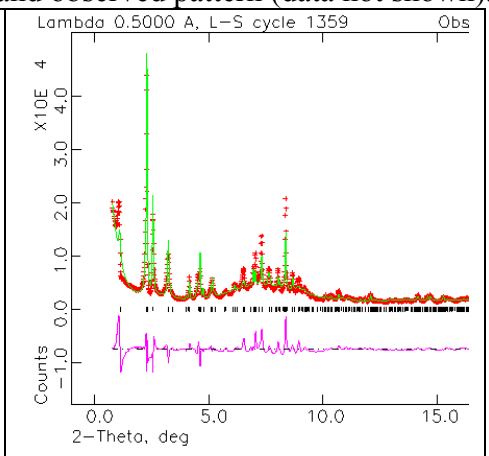

Figure 5: Rietveld analysis of calcined MCM-22 in air.

The Rietveld analysis of the MCM-22 precursor, containing the HMI molecules, and of the Cu-exchanged MCM-22 patterns is currently in progress. In these samples, the electron density, we observe in the channels, shows a different distribution from that observed by Leonowicz et al.[4] for MCM-22 in air. Currently we are trying to interpretate the extraframework peaks to locate the HMI and the Cu atoms present in the various samples.

References

[1] Meier, W.M.; Olson, D.H.; Baerlocher, Ch. *Atlas of Zeolite Structure Types*, Elsevier, **1996**, London.

[2] A.J.S. Mascarenhas, H.M.C. Andrade, H.O. Pastore, *Stud. Surf. Sci. Catal.*, *135*, (**2001**), 322.

[3] Larson A.C. and R.B. Von Dreele, "*General Structure Analysis System (GSAS)*", Los Alamos National Lab. Report LAUR **1994**, 86-748; (http://www.ccp14.ac.uk/solution/gsas/index.html).

[4] M. F. Leonowicz, J. A Lawton, S. L. Lawton, M. K. Rubin, *Science* 264 (1994) 1910.