ESRF	**Experiment title:** Structure determination of as-made and calcined zeolites	**Experiment number**: CH-3549
Beamline: BM25A	**Date of experiment**: from:02/02/2013 at 8:00 to: 05/02/2013 at 8:00	**Date of report**: April 2013
Shifts: 9	**Local contact(s)**: Dr. M.L. Corró Moyà/Dr. G. Castro	*Received at ESRF:*

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Report:

Introduction

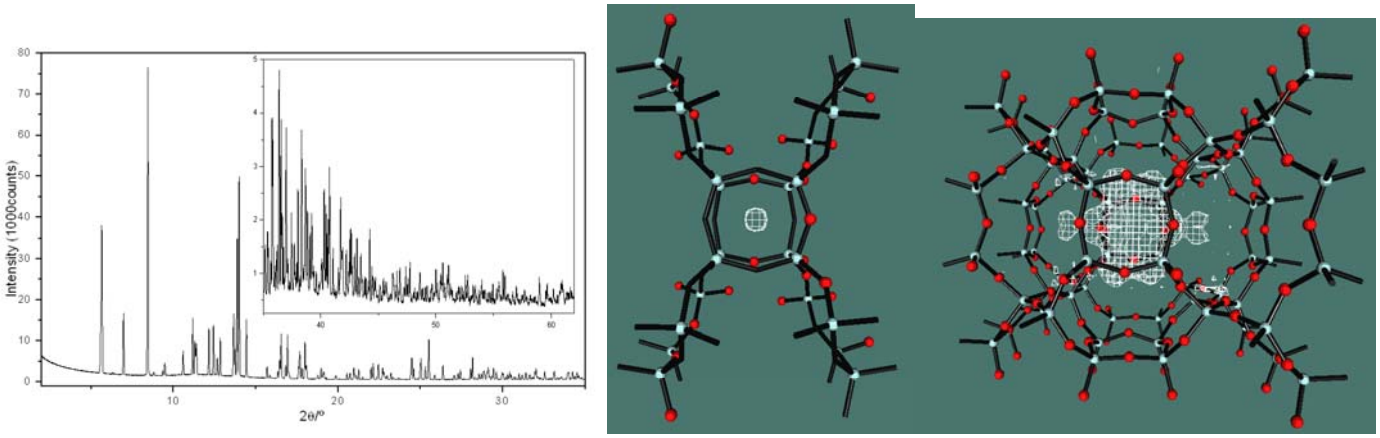
Structure-direction in zeolite science, i.e., the factors that ultimatelly determine the actual phase that crystallizes in a zeolite synthesis, is an important matter of research in the field. A deep understanding of this issue is essential not only for developing new materials for use as catalysts or adsorbents but, specially, for attaining the desired goal of targetting new structures for specific applications. In this respect, host-guest interactions between the zeolite framework and the species occluded in its pores and cavities are frequently some of the more important driving forces directing the crystallization. For neutral or nearly neutral framework compositions (such as those in pure silica and high silica zeolites or in zeolitic $AlPO_4$) the occluded species of the as-made materials are organic species (neutral or cationic) and, frequently, fluoride anions. The study of these interactions and of how it affects the zeolite framework and the zeolite stability requires of an accurate knowledge of the structure of the as-made material. Given that zeolites are difficult to crystallize as large crystals appropriate for single-crystal analysis, powder diffraction is more frequently used. Generally, data collected using conventional lab diffractometers don't have enough quality for an accurate structural analysis, specially at high angles. In this work we have collected data up to atomic resolution for 15 zeolitic samples using synchrotron radiation.

Experimental

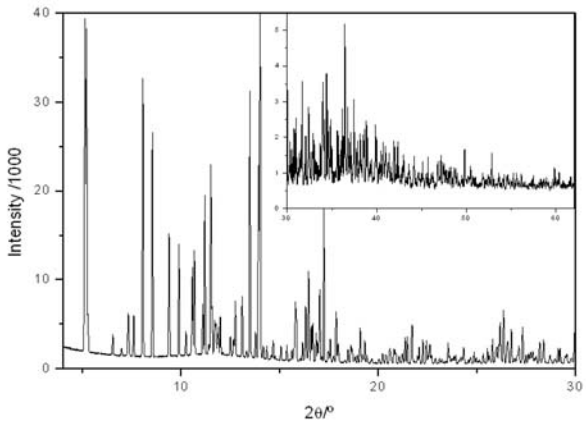
Data were collected in capillary mode (0.8mm internal diameter) using synchrotron radiation (λ=0.825480(11)Å) at room temperature. The 2 θ range was varied acording to the nature of the sample, but was generally 2-65º, (occasionally reaching 75º), with step size 0.01º and step time 2s.

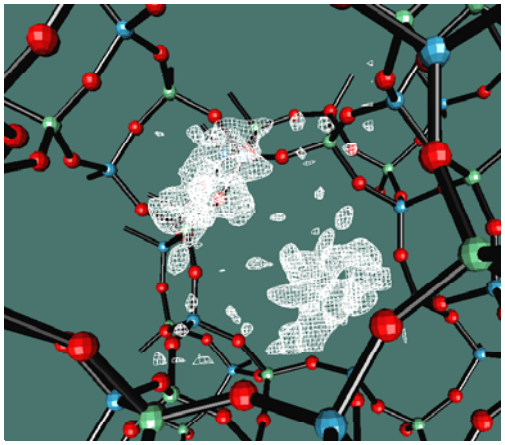
Results

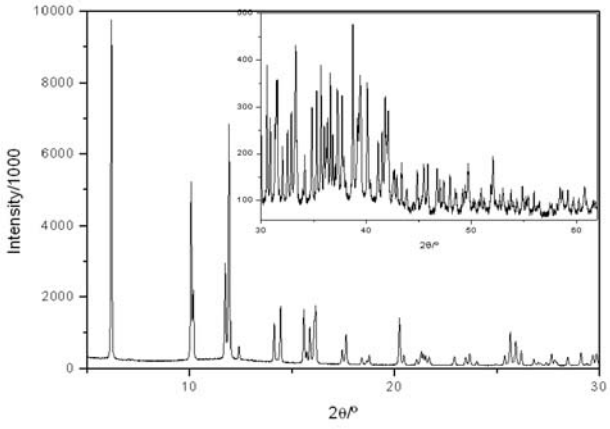
Preliminary analyses of the data look promising towards the goal of elucidating the exact position and orientation of the guests in the zeolite samples. Figure 1, left, shows the profile of an ITW zeolite synthesized with a new organic cation and fluoride anions, showing nice resolution still at d=0.8Å. These data were used in EXPO[1] for the structure solution by direct methods. The whole connectivity of the silica framework was found. A Fourier analysis under GSAS using only the silica framework provided a map of density missing in the center of double 4-rings (assigned to fluoride, proved by ^{19}F MAS NMR results) and in the equatorial plane of the larger [$4^4 5^4 6^4 8^4$] cavity, as seen in the Figure (middle and right, respectively).

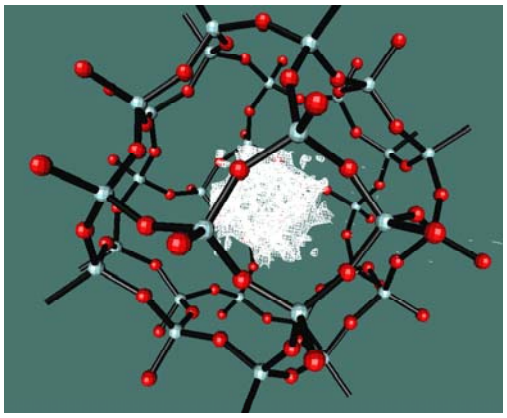


Other examples with good resolution up to around 0.8 Å and where the organic species are recognizable inside the zeolite voids are shown below:









Following these preliminary analyses, the location of the organic cation and fluoride anion will be determined by Rietveld refinement and Fourier analysis for each of the zeolites. The study of the deformation of the zeolite structure by comparison between the as-made and calcined materials and of the deviation from tetrahedrality will be undertaken, to get further insights on host-guest interactions in all the materials and, specifically on the proposed role of fluoride as enhancing the flexibility of the silica framework.[2]

References

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[2] C. M. Zicovich-Wilson, M. L. San-Román, M. A. Camblor, F. Pascale, J.S. Durand-Niconoff, *J. Am. Chem. Soc.*, 2007, 129, 11512; C.M. Zicovich-Wilson, F. Gándara, Á. Monge, M.A. Camblor, *J. Am. Chem. Soc.*, 2010, 132, 3461; A. Rojas, E. Martínez-Morales, C.M. Zicovich-Wilson, M.A. Camblor, *J. Am. Chem. Soc.*, 2012, 134, 2255; A. Rojas, M.L. San-Roman, C.M. Zicovich-Wilson, M.A. Camblor, *Chem. Mater.*, 2013, 25,729.