



Experiment title: CRYSTAL STRUCTURE OF THE AS-SYNTHESIZED AND CALCINED FORM OF ZEOLITE MATERIALS CR-1.

Experiment number:
CH-1537

Beamline: BM01B	Date of experiment: from: 05.09.2003 to: 08.09.2003	Date of report: 11 May 2005
Shifts: 9	Local contact(s): Mr. Wouter VAN BEEK	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Zanardi Stefano*, EniTecnologie S.p.A, Via F. Maritano 26, I-20097 San Donato Milanese, Italy.

Cruciani Giuseppe* Dipartimento di Scienze della Terra, Sez. di Mineralogia, Petrologia e Geofisica, Universita' degli Studi di Ferrara, Corso Ercole I D'Este, 32, I-44100.

Millini Roberto, EniTecnologie S.p.A, Via F. Maritano 26, I-20097 San Donato Milanese, Italy

Alberti Alberto, Dipartimento di Scienze della Terra, Sez. di Mineralogia, Petrologia e Geofisica, Universita' degli Studi di Ferrara, Corso Ercole I D'Este, 32, I-44100.

Report:

Zeolites are widely used as acid and oxidation catalysts, adsorbents and molecular sieves with the limitation that the molecules involved in these processes must be smaller than the pore openings. However, there are a large number of potential applications that involves bulky molecules, with dimensions much larger than the pore openings of the known zeolites. In this respect two options are available. The first one concerns the use of amorphous mesoporous molecular sieves, the second option involves the use of layered materials. In this paper, the crystal structure of layered material named CR-1 here after referred to as ERS-12 (EniRicerche molecular Sieve-12), are reported.

Experimental

Powder diffraction data were collected at the SNBL station B (BM1B) whose very high resolution powder diffractometer is equipped with six detectors and Si (111) analyzer crystals before them. The powder patterns were collected from 1 to 50° 2-theta; the wavelength employed was set to 0.79959 Å. An effective step size of 0.005 ° was used in rebinning the continuous –made-collected data. The counting time was optimized for each data collection in order to collect with good counting statistics the very weak reflection at high angle.

Results

In the case of the as-synthesized ERS-12, the XRD pattern has been fully indexed according a monoclinic unit cell with dimensions $a = 10.585(3)$, $b = 13.989(3)$, $c = 7.425(2)$ Å, $\beta = 98.03(2)^\circ$ and with a figure of merit $F_{20} = 186$. A careful inspection of the reflection indexes revealed the $0k0 = 2n + 1$ as the unique systematic absence. In the case of calcined ERS-12, the quality of the XRD pattern is lower with respect to that of the as-synthesized sample because of the contemporary presence of sharp and broad reflections indicative of a disordered structure. Crystal structure of as-synthesized ERS-12 was determined by an approach which combines experiments and modeling. Structural model in which a layers formed by $[\text{SiO}_4]$ and $[\text{SiO}_3\text{OH}]$ tetrahedra and resembling the ferrierite ones was easily identified by using the program SIRPOW [1]. On the contrary, no clear definition of the TMA cations present in the interlayer region was achieved. In order to develop a structural model with the TMA cations included the coordinates of the Si and O atoms were firstly transferred to the Cerius² graphical interface [2] and H atoms were added to the silanol oxygen atoms. The model obtained was used for searching the lowest energy location of TMA cations, by

using the docking procedure proposed by Freeman et al. [3]. The lowest energy conformation was selected and the atomic coordinates transferred to the GSAS program [4] for the Rietveld refinement of the structure. The refinement converged with Rietveld residual values: R^2F (%) = 12.6, R_p (%) = 9.2, R_{wp} (%) = 12.5, Red. χ^2 = 12.0 (figure 1).

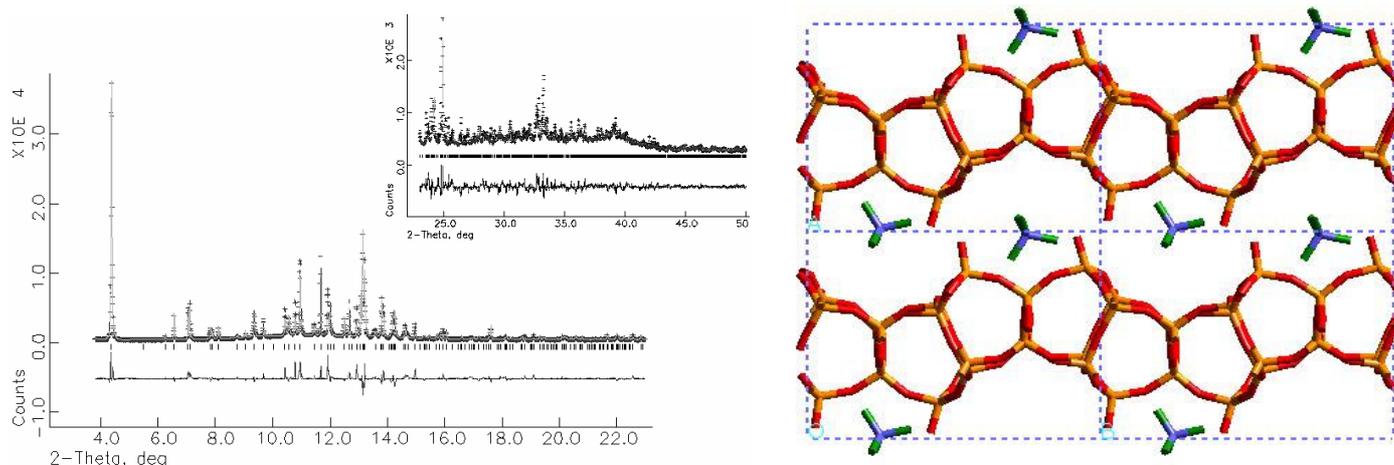


Figure 1. Observed (dotted upper line), calculated (solid upper line), and difference (solid lower line) SXPDP patterns of as-synthesized ERS-12 in $P2_1/m$ (left) and representation of the as-synthesized ERS-12 structure along [001] (right).

As showed in figure 1, in order to obtain a 3-D framework, analogous to that of zeolite ferrierite, the layer must be shift by and 1/2 of the unit cell. However, in figure 2 is possible to show that the high resolution XRD powder pattern collected for the calcined form of ERS-12 is very different respect to the ferrierite one. In order to analyses the possible disordered polymorphs an extensive study with the program DIFFaX [5] was carried out. The best fit between simulated and experimental X-ray diffraction pattern was obtained when a translation by 1/3 and 1/10 of the unit cell in a and b direction was introduced in the DIFFaX simulation. Translation of 1/10 of the unit cell in b direction involve that the neighboring silanol pair condense upon calcinations, but this implies that half of the pairs remain uncondensed precluding the formation of a fully connected framework. However, from figure 2 is possible to note that some differences between simulated and experimental diffraction pattern of ERS-12 still persist, these differences could be tentatively attributed to a more complex stacking sequences, rotations and/or a partially collapse of the ferrierite layers during calcination.

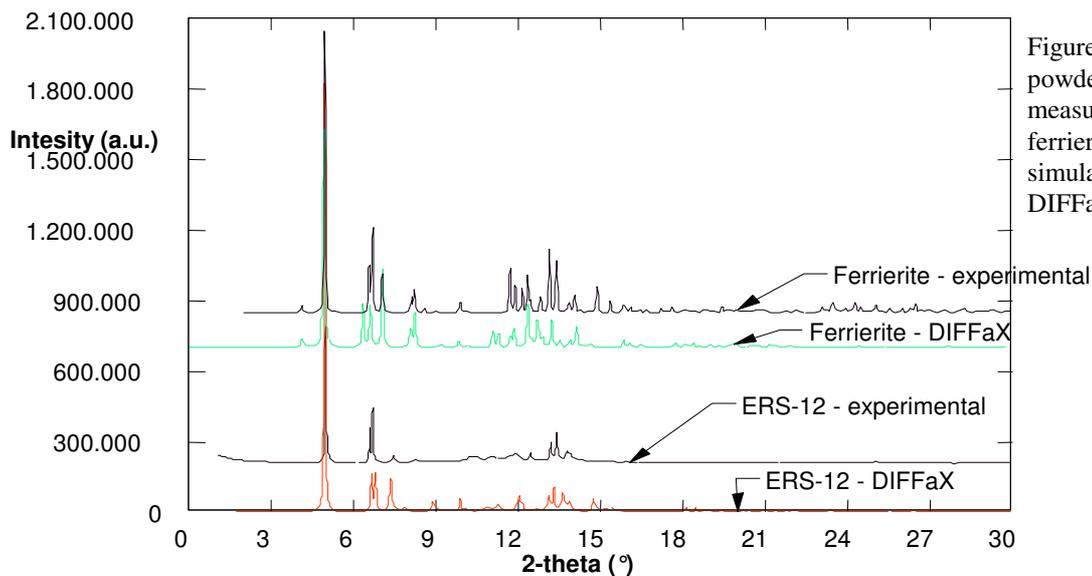


Figure 2. Comparison of X-ray powder diffraction patterns as measured on of pure silica ferrierite, and ERS-12, and as simulated using the program DIFFaX ($\lambda = 0.79982 \text{ \AA}$).

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