ESRF	**Experiment title: Template removal and water absorption in substituted silicalites: time resolved in-situ powder diffraction studies**	**Experiment number**: **CH-687**
Beamline: BM8 GILDA	**Date of experiment**: from: 04/10/1999 to: 09/10/1999	**Date of report**: 31/08/2003
Shifts: 12	Local contact(s)**: Carlo Meneghini**	*Received at ESRF:*

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Report: The high X-ray flux available at the ESRF, combined with the use of a suitably designed area detector setup[1] allowed to follow in real time the structural changes occurring during the template burning processes inside TS-1 and Fe-silicalite MFI zeolites with XRPD technique, see Fig. 1a. Rietveld analysis of the XRPD patterns collected in the 350-1000 K interval, integrated each 15 K, yields to the determination of the template overall occupancy factor vs. T (Figure 1b, solid squares, right axis) with an accuracy comparable with that obtained by thermo-gravimetric measurements, routinely employed for this purpose (continuous line, left axis). The agreement of the two curves is impressive. Let T_s and T_f be the temperatures where the refined value of the TPA occupancy (X_{TPA}) starts to be, within the experimental error, lower than 1.0 and equal to 0.0 respectively, see vertical lines in Fig. 1b. Let T_b be the starting temperature of the template burning process, indicated by the sharp change in the slope of the X_{TPA} vs. T curve. For $T_s < T < T_f$ the agreement between TGA and XRPD data is remarkable. For $T < T_s$ the TGA measures the desorption of physisorbed water molecules (not observed by XRPD). Also for $T > T_f$, where the residual electron density inside the zeolite channels is zero, TGA still shows sample loss due to: (i) burning of amorphous coke and (ii) saturation of framework silicon vacancies by creation of new Si-O-Si bond between two adjacent Si-OH groups by evacuation of one water molecule. By comparing the results obtained on TS-1 and Fe-MFI systems it emerges that the overall curve obtained for the Fe-MFI zeolite is shifted toward higher T by about 30 K. This holds also for the three key temperatures previously defined, which are: T_s = 550 K (580 K) T_b = 600 K (630 K) and T_f = 760 K (800 K) for TS-1 (Fe-MFI). This temperature shift of the whole template burning reaction can be interpreted in terms of an additional electrostatic interaction between positively charged TPA^+ and the framework, which is more negatively charged when trivalent Fe(III) ions are present.

Fig. 2 reports the evolution of the cell volume and of the cell parameters of both TS-1 and Fe-MFI in the 300-1000 K range. For both materials we observe first an increase of the lattice parameters, indicating that the thermal expansion is the physical mechanism dominating this stage of the experiment. The expansion trend stops at T_b. Above T_b template burning starts and the cell volume and lattice parameters decrease. The difference of about 30 K in T_b between TS-1 and Fe-MFI is observed in all parameters $V(T)/V_0$, $a(T)/a_0$, $b(T)/b_0$ and $c(T)/c_0$, being more visible in Figure 2a where the volumes are simultaneously reported. This difference does holds for the whole template burning reaction, according to the observed variation in the X_{TPA} factor (not reported). For $T < T_s$, the volume increase due to thermal expansion is isotropic for both samples within the experimental error. Between T_s and T_b however the observed volume increase is very anisotropic (see enlarged inset), the *a* axis having a substantially larger coefficient of thermal expansion. This is related to the decomposition of the tetrapropilammonium ion into tripropilamine, propene, and a huge variety of

secondary decomposition products. The anisotropy holds during the volume contraction too. At this stage we observe the effects of the expulsion of the secondary products outside the pores. During the whole process ($T > T_b$), for both TS-1 and Fe-MFI the following inequalities hold: $b(T)/b_0 < c(T)/c_0 << a(T)/a_0$. These results imply that the zeolite crystals are subjected to remarkable stress forces, which become dramatic when fast heating ramps are adopted. This strong anisotropic contraction certainly contributes to crack formation in zeolite crystals. These data allow us to have, for the first time, a complete view of the structural rearrangements induced by the template burning process on the zeolitic framework.

Also isothermal runs (not reported) have been performed. Kinetic analysis indicated that the template burning is a diffusion limited reaction with monodimensional advancement. The rate limiting step of the reaction is the diffusion of the volatile products of the template burning out of the crystal. Chemical and sterical considerations indicate that the straight channels along the *b* axis are the more favorable direction for the molecule removal. Corresponding Arrhenius plots result in an apparent activation energy of 151 ± 11 $kJmol^{-1}$ and of 159 ± 7 $kJmol^{-1}$ for TS-1 and Fe-MFI respectively. This study has recently been submitted.[2]

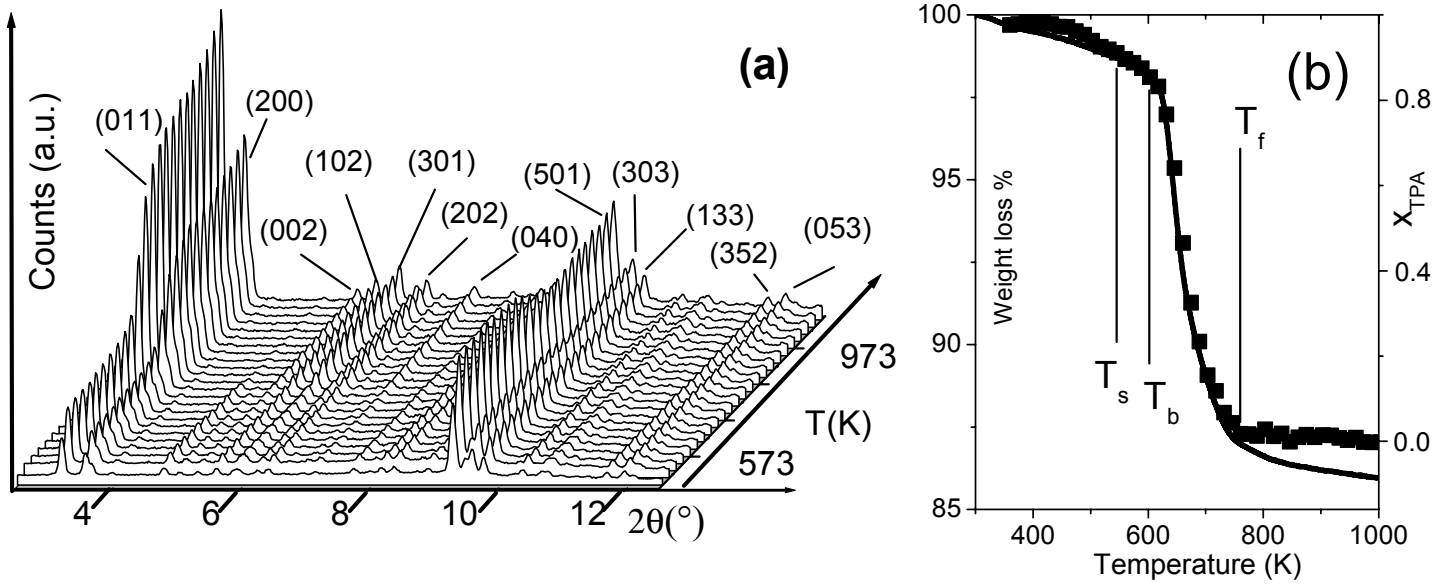

Figure 1. (a): Evolution of the XRPD patterns in the 2.5-12.5° 2θ-interval (corresponding to 14.2-2.8 Å d-spacing) as a function of the temperature during the *in situ* template burning. Main reflections have been indicated. Direct comparison between the refined TPA^+ occupancy factor (scattered squares, right axis) and the per cent loss of weight (continuous line, left axis) during the template burning process inside TS-1. Vertical lines show the positions of T_s, T_b, and T_f temperatures, see text. Data refers to TS-1

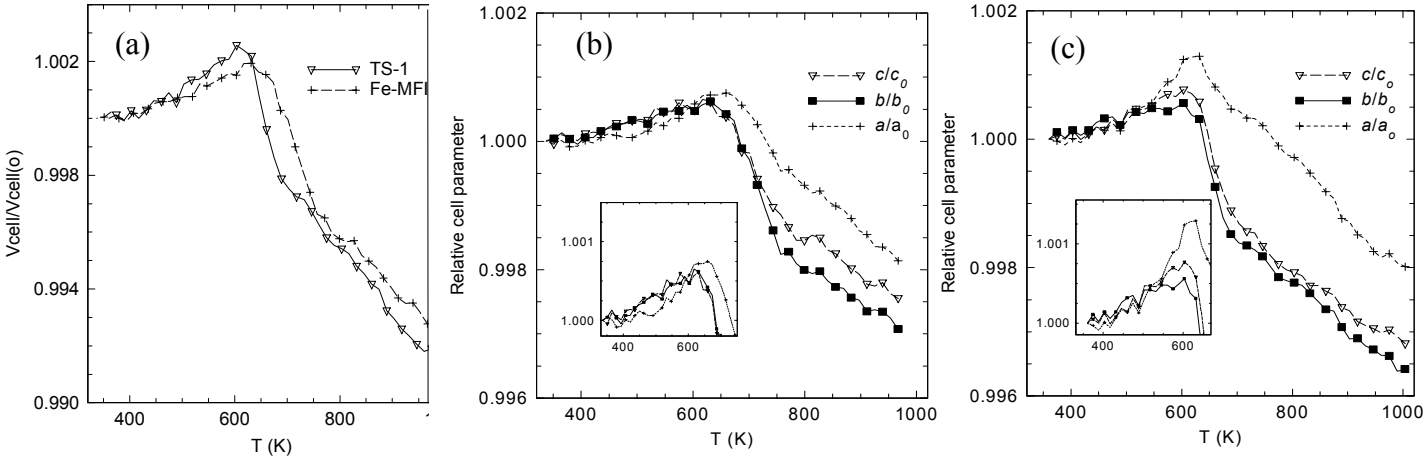

Figure 2. Evolution of the cell volume (part a) and the lattice parameters for both TS-1 (part b) and Fe-MFI (part c) during the *in situ* template burning in the 300-1000 K range plotted as $V(T)/V_0$, $a(T)/a_0$, $b(T)/b_0$ and $c(T)/c_0$ (being the reference values obtained at 350 and 340 K for TS-1 and Fe-MFI respectively). Only the data corresponding to one over two refinements are reported for clarity (the e.s.d.s on the absolute value of the cell volume and lattice parameters are almost constant and are equal to 7 on the 1st decimal digit and 1 on the 3rd decimal digit respectively).

References

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