ESRF	Experiment title: Structural study by XPD of the solid state cyclophotho-addition reaction of an N-acethylindolone derivative and structure analysis of Melam	**Experiment number:** CH-346
Beamline: MB16	**Date of experiment:** from: 02 July 1997 to: 07 July 1997	**Date of report:** 18 January 1999
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Report:

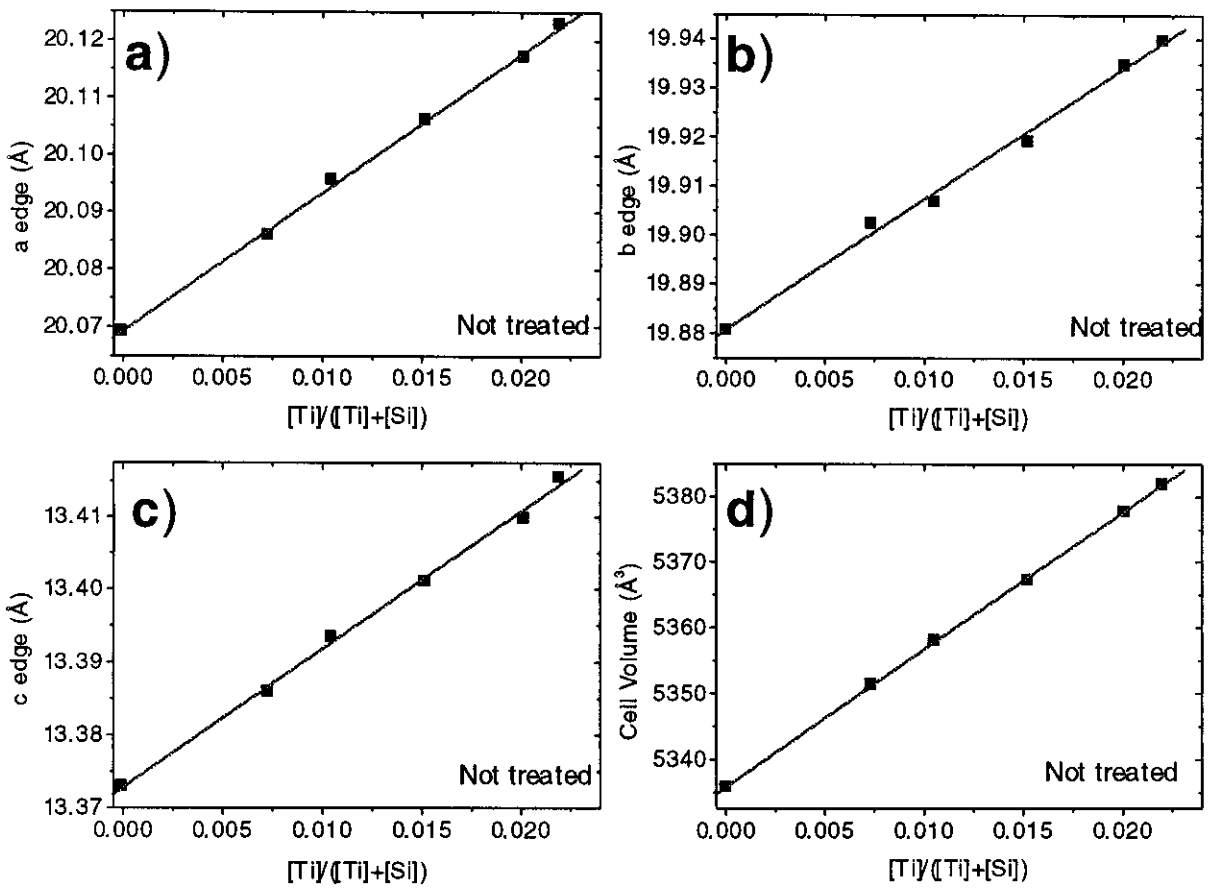
The powder samples were prepared in special glass capillaries in our laboratories and then taken to the XPD line for the measurement of the diffraction patterns. All measurements where made with radiation of wavelength 0.848836(3)Å and with a low temperature attachment at 100K. The 2θ range was from 1 to 60° and the data collection time was of 12 hours for each sample of the three measured organic compounds: trans-furil-N-acethylindolone dimer (as obtained phase), melam and melam hydrobromide.

From the structural study of the intermediate phase of the trans-furil-N-acethylindolone dimer we hoped to be able to gain some understanding of the mechanism of the cycloaddition reaction taking place in the solid state. The phase obtained by prolonged illumination, but no recrystallization, of trans-furil-N-acethylindolone constitutes an intermediate step of the reaction and from its structures it should be possible to obtain a more clear picture of the rearrangements needed in the reaction.

The solution of the structures of melam and melam hydrobromide would throw some light into the melamine condensation mechanism, which was originally studied by L. Pauling, but remains an open problem of great interest in macromolecular chemistry.

Unfortunately, so far, all our attempts, by a number of different approaches, to index the three diffraction patterns have failed. The patterns are of medium quality as expected for purely organic compounds and we suspect that our failures might be due to the presence of more than one crystalline phase in our samples.

Remaining beamtime has been successfully employed to terminate a set of measurements on Ti-Silicalite (TS-1) samples (Exp. CH-257) the complete set of dehydrated TS-1 samples having Ti content(molar ratio) x = [Ti]/([Ti]+[Si]) in the range 0 - 0.022 has so been measured. The cell volume values resulting from the Rietveld refinements of the powder diffraction data exhibit a very good linear correlation (r = 0.99994) with the Ti content: $V(x)$ = 2093.0 x + $V(0)$, (being $V(0)$ = 5335.8 Å^3), see Figure. This work represents a strong improvement of the important characterization work of the EniRicerche group [1] performed on TS-1 previously treated with ammonium acetate, calcined, and measured in atmosphere (*i.e.* under partially hydrous conditions). Our results indicate that when XRPD measurements are performed under carefully controlled vacuum conditions a highly linear correlation between V and x is obtained without any need of sample pre-treatment. Finally, the very high quality of our experimental data allows us to comment on the presence of some preferential framework T sites for Ti substitution. Such sites were recently proposed by two different groups on the basis of the results of molecular dynamics modeling [2]. This study has recently been accepted for publication [3].



References

[1] R. Millini, E. Previde Massara, G. Perego, and G. Bellussi, *J. Catal.* **137** (1992) 497.

[2] Y. Oumi, et al., *Microporous Materials,* **4** (1995) 53; S. L. Njo, et al. *J. Phys. Chem. B,* **101** (1997) 10065.

[3] C. Lamberti, et al. *J. Catal.,* **183** (1999) 222.