

## High pressure insertion and polymerization of hydrocarbons in VFI 1-D nanopores

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Dehydrated  $\text{AlPO}_4\text{-54}$  (hexagonal VFI structure, space group  $P6_3/mcm$ ,  $a=18.5457(3)$  Å and  $c=8.3992(1)$  Å), exhibits 12.7 Å diameter pores along the  $c$  direction, which are among the largest pores known for the zeolite group. Previous studies have shown this system to be ideal to probe the mechanism of insertion, reaction and ordering of guest molecules at the nanoscale<sup>[1,2]</sup>. High pressure (HP) can be used to insert unsaturated hydrocarbons in the

subnanometer pores of zeolites and to polymerize these molecules to form nanocomposites based on single polymer chains in the zeolite host matrix<sup>[3]</sup>. In the present work, very recent synchrotron X-ray diffraction (SXR) and synchrotron infrared (SY-IR) measurements, performed on Xpress and SISSI beamlines (Elettra Sincrotrone Trieste), were used to study the insertion and polymerization of phenylacetylene ( $\text{C}_8\text{H}_6\text{-PhA}$ ) in the nanopores of the VFI zeolite at HP and high temperature (HT) on powder and single crystals. A systematic study was performed on two different samples, partial dehydrated and strong dehydrated, and through two different  $P$ - $T$  paths: up to 0.2-1.0 GPa at 100-200 °C or up to 14 GPa at room  $T$ . Fig. 1 summarize the best results. Upon increasing pressure, the structural measurements indicate a slight pore collapse around the inserted PhA monomers. The PhA insertion hinders the pressure induced amorphization observed in the previous study<sup>[2]</sup>. A color change from the sample, together with structural and vibrational changes, were observed on both  $P$ - $T$  paths. A crystalline material is retained on pressure release, except on the sample treated above 200 °C, which shows phase transition on higher  $T$ . Preliminary refinements on the VFI powder loaded with PhA as pressure transmitting media (PTM) under 0.5 GPa at room  $T$  and 0.8 GPa at 114 °C shows a  $c/a$  lattice parameter ratio typical of a filled pore system (PhA instead of  $\text{H}_2\text{O}$ ). IR spectra of the recovered samples indicate that the C-H peaks of sp carbon of the acetylene moiety of PhA are replaced by those of  $\text{sp}^2$  carbon of the polymer. Two distinct colors were observed on the recovered samples: citron green and dark red, consistent with a conducting polymer in reflection. The evidence supports the polymerization of PhA in the nanopores of VFI structure, leading to the synthesis of a new conducting polymer based nanocomposite.

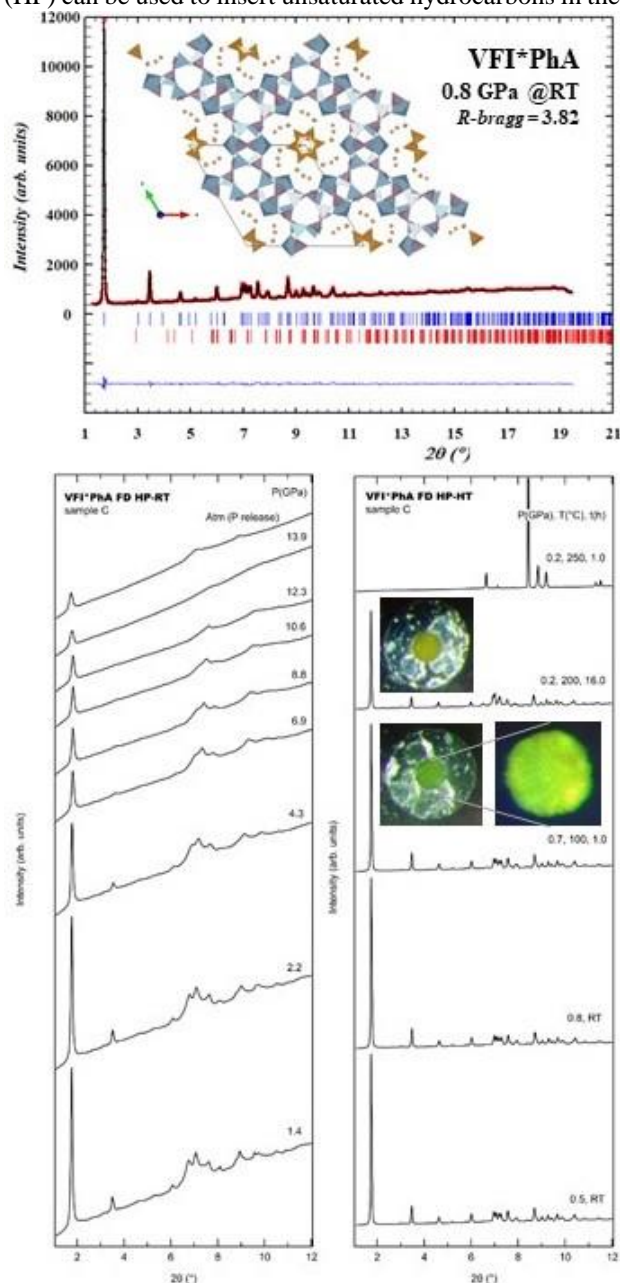


Figure 1: Bottom- in situ powder SXR patterns of VFI loaded with PhA as PTM at selected pressures and  $T$  for a run of samples strong dehydrated (FD, sample C). Insert: picture from the sample, inside the gasket hole, after the  $T$  treatment. Top- observed and calculated powder SXR pattern from VFI loaded with PhA PTM under 0.8 GPa at room  $T$ .  $R$ - $bragg=3.82$ . Insert: structure obtained from the Rietveld refinement, unit cell outlined in black. The light-blue and purple polyhedra are the  $\text{AlO}_4$ ,  $\text{AlO}_6$  and  $\text{PO}_4$  units of  $\text{AlPO}_4$  while the dark yellow on the pore indicating the inserted monomer.

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