



Experiment Report Form



	Experiment title: Unravelling the hydrocarbons polymerization mechanism in Sizeolite a new route for embedded conductive polymers formation	Experiment number: MA-4233
Beamline: ID22	Date of experiment: from: 05/12/2018 to: 08/12/2018	Date of report: 10/12/2019
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Report:

Scientific background:

Conductive polymers, coming from the polymerization of hydrocarbons, are of great interest for many technological applications. Indeed, they can be used in electronic devices exploitable in solar energy conversion, optoelectronic, or for gas sensing. Unfortunately, these types of conductive polymers, if exposed to the air, react losing their interesting properties. Therefore, their confinement is needed to enhance their stability. Hydrophobic zeolites, thanks to their structure, have been proved to be a very good host material, their hydrophobic nature allows to isolate and protect the resulting polymers, for example, from water vapor in air, a crucial point in the realization of gas sensing devices strongly affected by humidity. Zeolites present a microporous structure with channels and cages and can be considered as small chemical laboratories, where reactions can be induced and controlled. Pressure is certainly an ideal tool for implementing chemical reactions tuning the intermolecular/interatomic distances and inducing a rearrangement of chemical bonds. The nano-confinement deriving from combining pressure and the geometrical constraints imposed by the zeolitic framework has proven to be effective in driving the formation of arrays with the desired dimensionality, such as confined conjugated 1D-conductive polymers. The proposed composite materials feature a unique combination of properties, such as hydrophobicity, huge surface area joint with quantum confinement of the host material, which have strong potential in several technological applications. For example, in gas sensing field, the capability to fully exploit these properties means low cross-sensitivity to humidity and reaching high sensitivity.

Experimental technique:

Pure silica mordenite zeolite was selected as a host material taking into account the following specific needs: i) the dimensions of the pores allow the penetration of the molecules of interest. ii) framework has a mono-dimensional channel system which promote the synthesis of isolated 1D polymer chains. The composite material was prepared loading hydrocarbons through vapour pressure, in the selected mordenite. Specifically, two systems were prepared: all silica mordenite (Si-MOR) with phenylacetylene and all silica mordenite (Si-MOR) with hexadiene.

Data was collected through multianalyser detector, wavelength was set at 0.3543 Å. The empty zeolite was fully characterized *in situ* from ambient temperature to 800 °C using a hot-air blower to investigate the dehydration process.

In addition, the preloaded samples were heated in situ in order to induce a polymerization of the molecules into the porosities. In order to deeply characterized the polymer total scattering data were collected. The idea was to take advantage of the Differential Pair Distribution Function (d-PDF) approach using the total scattering data of empty zeolite as background.

Results and Discussion:

Results of the empty zeolite characterization are reported in the published article “Thermal behavior of high silica mordenite”, 2020, Microporous and Mesoporous Material, 294, 109982. The abstract is here reported:

“ This work studies the thermal stability, heat-induced structural deformations, and dehydration/rehydration dynamics of a synthetic high silica mordenite. It is of special interest because this particular phase has proven to be an ideal host for the encapsulation of several kinds of organic molecules making it a promising scaffold for drug delivery. The dehydration process was followed by thermal analysis, infrared spectroscopy in controlled atmosphere, in situ synchrotron XRPD, and structural refinement. Overall, all the results indicate weak interactions of H₂O molecules with the silicatic mordenite framework and evidence the presence of hydroxyl groups with different condensation responses at high temperature. Infrared characterization highlighted how the desorption of adsorbed H₂O molecules under degassing is already complete at rT . The unit cell parameters exhibit very slow and almost isotropic changes upon heating. Above 550 °C an increase in slope is observed for all parameters. This corresponds to the marked silanol condensation and consequent framework reassessment observed at this temperature by infrared characterization. Overall cell contractions are 0.67%, 1.18%, and 0.81% for a , b , c , respectively and 2.64% for cell volume. HS-MOR undergoes very moderate T induced deformations, indicating a very rigid and stable framework.”

The IR analysis performed on the mordenite preloaded with hexadiene show the formation a branched polymer of hexadiene molecules also at ambient condition, zeolite is thus proved to catalyze the reaction. This is confirmed also by the diffraction data collected in another synchrotron experiment performed after the submission of the present proposal experiment. However, high resolution data collected at room temperature at ID22 was useful to better define structure of the composite material. A clear framework modification was observed due to the hexadiene penetration. Polymers was localize into the mordenite channels, but it was possible to identify just a linear chain along the c direction. Due to the high disorder, we were not able to define better the polymer (i.e. the branches), despite the high-resolution data. Figure 1 shows the structure obtained.

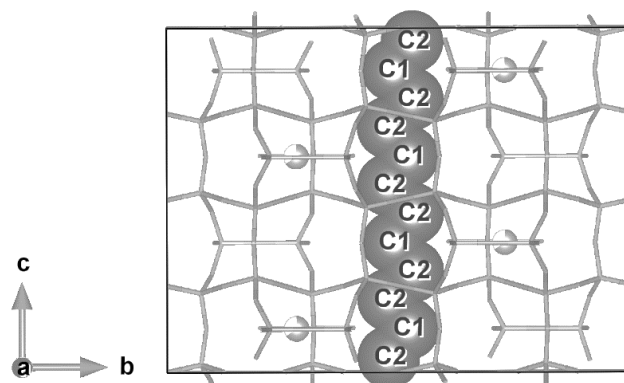


Figure 1. Structure details of HS-MOR preloaded with hexadiene at ambient condition.

In order to obtain a better description of formed polymer, Pair Distribution Function analysis was performed. Figure 2 shows the PDF of the empty zeolite and that of mordenite preloaded with hexadiene.

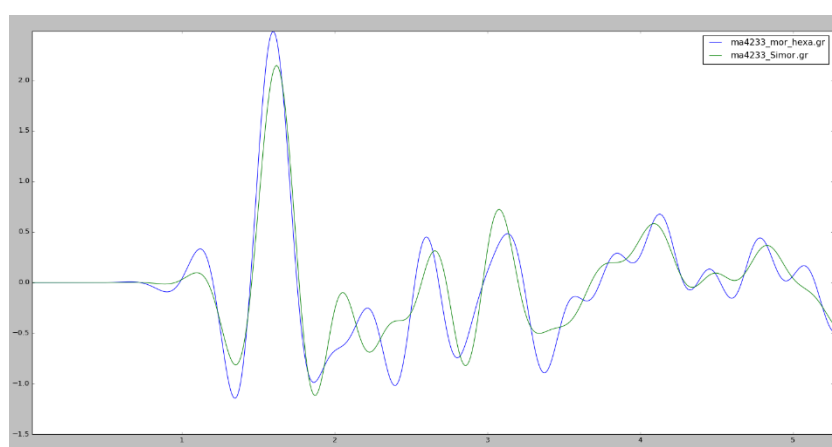


Figure 2. PDF of the empty zeolite (green line) and of mordenite preloaded with hexadiene (blue line).

As observed on the average structure, zeolite framework is deeply modified by the molecules introduction, cell parameters change as well as the tetrahedra rotate to accommodate the hexadiene polymer. This is also noticeable by the local structure, which presents differences in peak position and intensities. Unfortunately, this does not allow the use of Differential Pair Distribution Function (d-PDF) approach. In addition, the polymer characterization through the analysis of the data of the mordenite preloaded with the hexadiene by traditional PDF analysis was not possible due to the low signal of the hexadiene (caused by the form factor of the carbon and by the probably high disorder of the branched polymer).

Diffraction analysis was also performed *in situ*, the composite material seem to be stable up to 300 °C, however, due to the high thermal motion, it was difficult to perform reliable structural refinements of the polymer.

Structural analysis of the mordenite preloaded with phenylacetylene proved that just two molecules per unit cell were present at ambient temperature. The number of molecules was therefore not sufficient to obtain a polymer even using temperature. Despite this, IR analysis demonstrated a certain degree of reaction due to the catalytic property of the mordenite. Further analysis and deeper data treatment will be performed to characterized this system.