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Combined in situ EXAFS, PDF and PXRD study of the crystallization of metal-organic framework UiO-66

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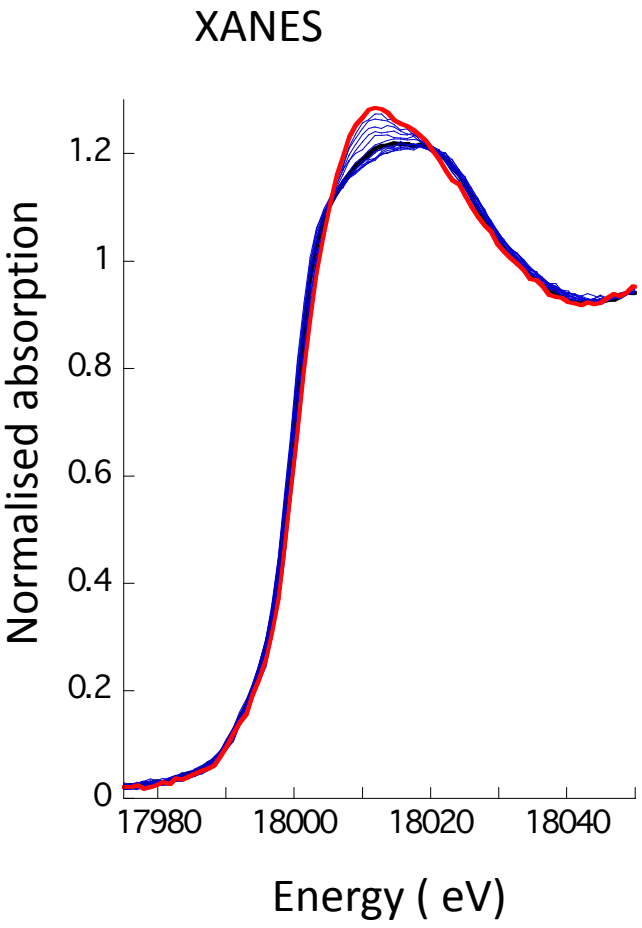
The experiments within this beam time were successful allowing to measure XAS at the Zr K-edge and scattering kinetics in the same samples and in an alternate way while switching automatically the X-ray energy of XAS conditions to PDF conditions. This was possible thanks to the design of a flat 3 mm thick quartz capillaries to measure XAS and PDF in the same synthesis mixture and to the great local support in developing the method to perform the measurement automatically. The results allowed monitoring of kinetics of nucleation and how it is related to the formation of the crystalline UiO-66. XAS and XRD data have been treated, but PDF analysis is still being evaluated due to the complexity of the data and of background acquisition.



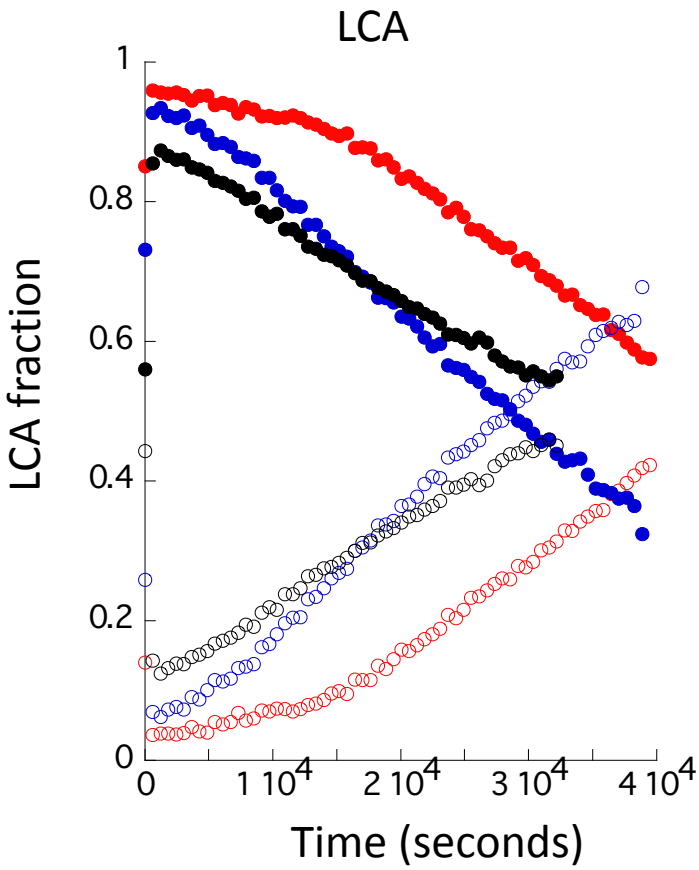


Fig. 1 XANES spectra of UiO-66 synthesis at different concentrations. Black 0.2M, blue 0.1 M, red 0.5 M. Filled points show the LCA fraction of $ZrCl_4$ and the empty ones the LCA of UiO-66.

We found that concentration has strong effects on nucleation rate and especially hydrolysis rate of $ZrCl_4$. The higher the concentration the faster the hydrolysis (Fig. 1). There seem to be two kinetic regimes at low concentrations suggesting an induction time and formation of an intermediate species. The modulator AcOH has no effect on the kinetics of the hydrolysis, but produces higher intensity of the Bragg peaks in the crystalline phase (Fig. 2). PDF analysis of the scattering patterns are underway to detect when the clusters are formed in the synthesis mixtures at different conditions.

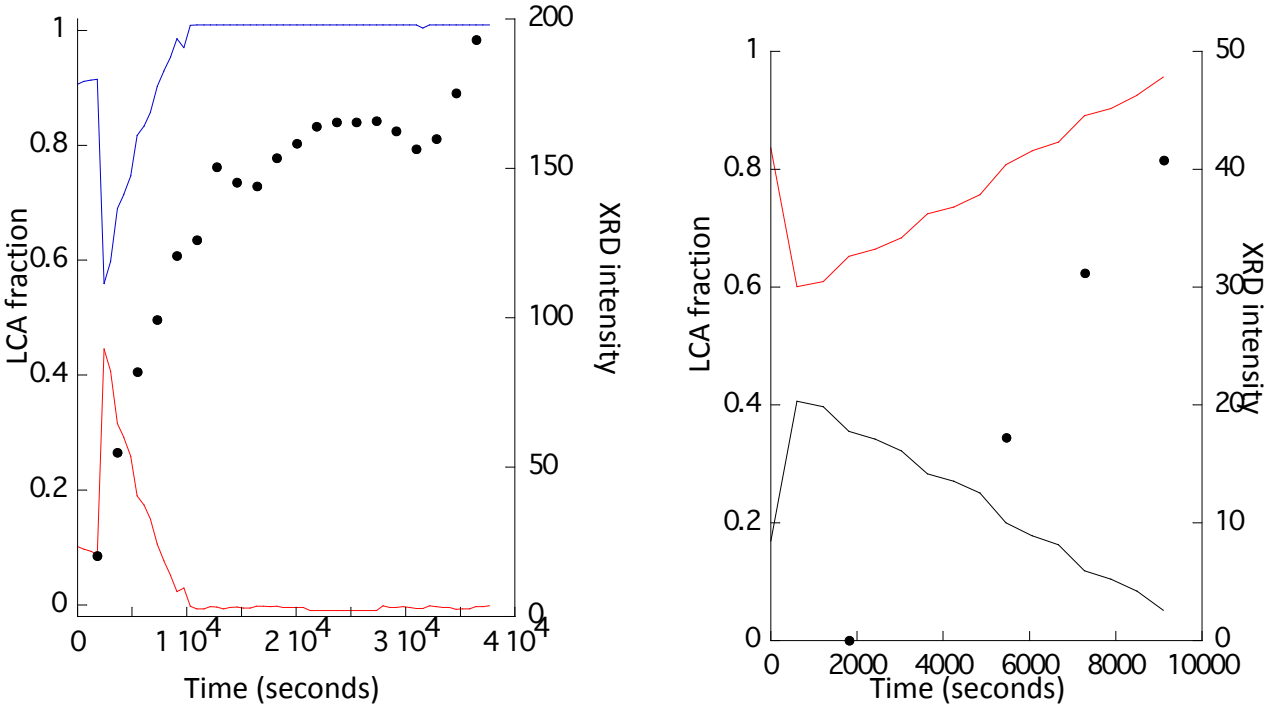


Fig. 2 LCA fraction and XRD intensity of UiO-66 synthesis mixture containing 15 equiv. Of AcOH (Left) and 0 equiv. Of AcOH (right).

The support from the local contact was exceptionally good for this challenging experiment.