


Experiment Report Form

 ESRF	Experiment title: XAS measurements disclose the details of the process of decomposition of Cu-carboxylate based MOF Basolite C300 upon exposure to air	Experiment number: MA-2949
Beamline: BM08	Date of experiment: from: 20/04/2016 to: 25/04/2016	Date of report:
Shifts: 15	Local contact(s): Alessandro Puri (email: alessandro.puri@esrf.fr)	<i>Received at ESRF:</i>
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Report:

The main purpose of our experiment has been that to study the stages of the decomposition process of a metal-organic framework (MOF) Basolite C300, produced by BASF, upon exposure to air. In this compound two copper ions are chelated by four carboxylate bridges to form a paddle-wheel unit; these carboxylate bridges are terminal groups of 1,3,5-benzene tricarboxylate (BTC) linker molecules. It is well known that a prolonged exposure to moisture damages the crystalline matrix of this compound by hydrolyzing the metal-to-linker bond. For this reason, we have investigated the local structural changes around a Cu ion in Basolite C300 material at different times of exposure to moisture.

We have performed absorption measurements on Cu K-edge (8979 eV) in transmission mode recording both XANES and EXAFS regions on samples of Basolite C300. In particular, we have measured 5 samples of Basolite C300 exposed to air for 0, 10, 20, 36 and 188 days previously prepared in our laboratory.

Furthermore, we have measured four reference compounds, that are Cu foil (provided by the local contact), Cu₂O, CuO and Copper Acetate Hydrate in powder form.

We have not prepared samples in pellets as usual, but we have performed XAFS measurements on packed powders into kapton tape. The reason is that recent studies on pressure effect on Basolite C300 have highlighted that the crystalline structure is easily damaged during the pellets preparation.

The XAFS measurements were performed in high vacuum at low temperature ($T=80$ K) using a cryostat to reduce effects of thermal disorder.

Different spectral regions were acquired with a different data pitch. In particular, for the energy ranges delimited by the following values: 8700, 8779, 8940, 9010, 9080, 8379, 10213 eV, we have used the energy step of 5, 2, 0.2, 1, 2, 4 eV respectively. The integration time was fixed at 3 s for each energy range. Furthermore, we have acquired two scans for sample.

The high quality of spectra acquired in these conditions is well visible in Figure 1.

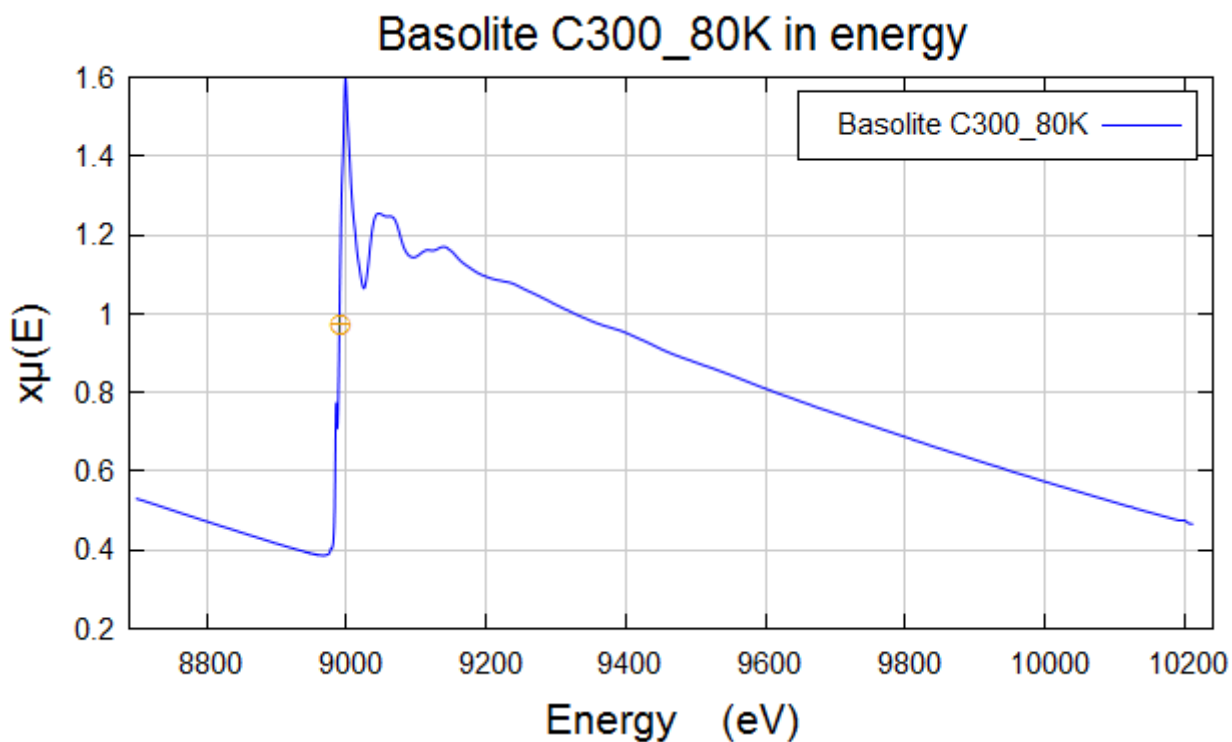


Figure 1: Absorption spectrum from 8700 eV to 10213 eV of a sample of Basolite C300 exposed to air for 0 days acquired at $T=80$ K.

Some of the samples were activated before the XAS measurement, so we have put them in the Microtomo Furnace available at the beamline overnight at $T=130$ °C and $P=5 \times 10^{-2}$ mbar.

We have also acquired some spectra at room temperature in ambient pressure condition to evaluate the temperature effect on the spectra.

The last part of the beamtime was dedicated to study the high temperature effect on the local environment of the Cu ion. For this reason we have put a sample of Basolite C300 in Microtomo Furnace and we have mounted it directly inside the EXAFS chamber, thus we have performed *in situ* measurements from 60 °C to 160 °C in 20 °C step, in condition of high vacuum.

A preliminary analysis of acquired measurements suggests that there are some differences in the local environment of the absorber atom, not in the change of its oxidation state, but in number of neighbours and bond distances.