ESRF	**Experiment title:** **Influence of ligand substitution on breathing mode of MOFs with MIL-53 type crystal structure**	**Experiment number**: 01-02-1076
Beamline: BM01A	**Date of experiment**: from: 22 Jul 2015 to: 27 Jul 2015	**Date of report**: 2.10.2015 *Received at ESRF:*
Shifts: 14	**Local contact(s)**: Alexey Mikheykin	

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Report:

Metal-organic framework (MOF) compounds are dimensionally extended structures consisting of metal or metal cluster centers that are linked by multidentate organic ligands. This interconnectivity can result in one-, two-, or three-dimensional networks. By smart choice of components, structures with large pore sizes and volumes can be achieved, and, as a result, MOFs are extremely promising materials in areas such as catalysis, gas storage and separation and ion exchange. As highly porous materials, MOFs can be sensitive towards changes in the pore volume content. Some of the most studied materials in this respect are the MIL-53 compounds which can be obtained with various trivalent cations, such as chromium, aluminum and indium, and linkers such as, terephthalic acid or 2-aminoterephthalic acid.[1] The MIL-53 reacts highly flexible by breathing of the crystal structure on variation in the pore content as functional groups or guest molecules. Especially the NH_2-group is of interest since it permits H-bonding interactions with guest molecules and can act as a catalytic active site.[2]

This work follows up previously experiments on BM01A (experiment 01-02-1019). Previously, we had synthesized a series of scandium MIL-53 compounds with terephthalate[3,4,5] and 2-aminoterephthalate as the organic linker in the MOF structure in order to study the effect increasing degrees of substitution have on the properties of the MIL-53 system. Now we continued these experiments using the 2,5-diaminoterephthalate substituted MOF, MIL-53(Sc)-$(NH_2)_2$.

Time resolved powder X-ray diffraction experiments at variable temperature show phase transitions from an open (*op-form*) -to a very-narrow-pore form (*vnp-form*) with significant changes in the lattice constants for all three “as synthesized” scandium MIL-53 compounds during the desolvation process. Variable temperature powder diffraction experiments under varying pressure of CO_2 show that the pore-opening of the *vnp*- “guest free” MIL-53(Sc)-NH_2 is fully reversible and proceeds in three steps via an intermediate (*int-form*) and narrow pore phase (*np-form*) (Fig. 1). The *np-form* could be observed for the first time in the MIL-53(Sc) system. However, the *op-form* of MIL-53(Sc)-NH_2 only occurs in a mixture with the *np-form*. Low temperatures (245 K) and high CO_2 pressures (13.5 bar) favor the *op-form*. For MIL-53(Sc)-$(NH_2)_2$ only the *np-form* can be observed at 13.5 bar/245 K indicating very strong NH_2-NH_2 interaction within the framework.

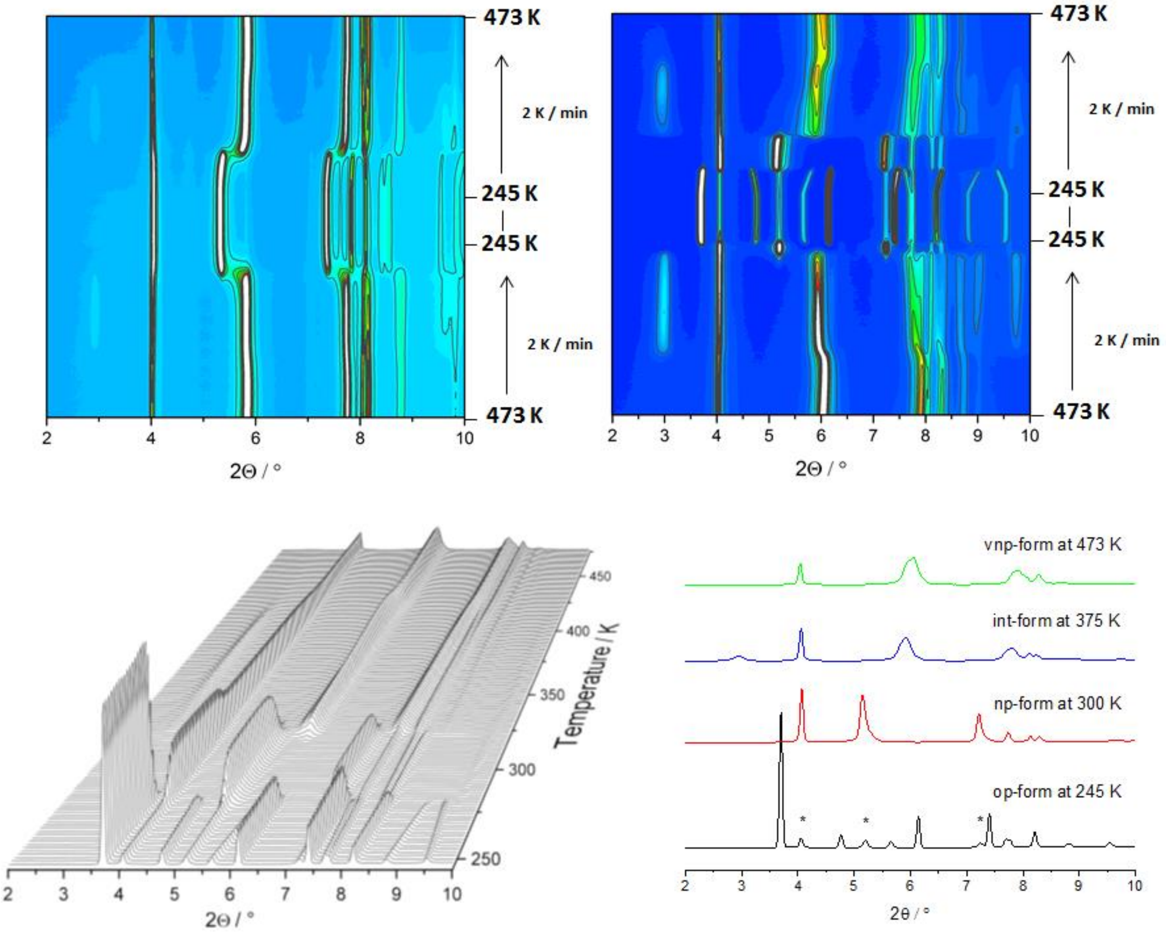

Figure 1*:up: Top-view of a temperature dependent powder diffraction experiment of Mil-53(Sc)-$(NH_2)_2$ (left) and Mil-53(Sc)-NH_2 (right) in CO_2 at 13.5 bar; down: zoom in on the temperature dependent powder diffraction experiment of Mil-53-NH_2(Sc)The diffraction peaks marked with black stars correspond to the np-form of and Mil-53(Sc)-NH_2.*

The additional experiments from BM01A have been crucial in understanding the amino-substitution on the flexibility of the MIL-53(Sc)-system and the results of this study will be complemented by high pressure CO_2 sorption studies and publish in the near future.

The original plan (and proposal) for this experiment included the use of simultaneous Raman spectroscopy to get additional information on a molecular level about the interaction of CO_2 with the various MIL-53(Sc)-$(NH_2)_x$ (x=0, 1, 2) frameworks during the in situ experiments, in which case the materials with x = 0 and 1 would have been measured again under this improved experimental setup. Regrettably, the Raman spectrometer was not available during the experiment. To make optimal use of the time that became available, we decided to use study the host-guest structures of CO_2 on several members of the **CPO-27 family**, a series of metal-organic frameworks which can be obtained by mixture of various divalent cations (e.g. Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and 2,5-dihydroxy-1,4-benzenedicarboxylic acid). These porous materials show promising applications in gas storage and catalysis thanks to the **presence of open metal sites** in their structure.[4]

CPO-27 samples were **exposed to several pressures of carbon dioxide** (in the range of 0.5 to 15 bar) at variable temperature (~195-500 K), using the gas dosing system setup available at SNBL and the cryostream for temperature control. Figure 2a shows the evolution for the powder patterns of CPO-27-Co in an atmosphere of CO_2 (1 bar) on decreasing the temperature from 453 K to 195 K and increasing it again.

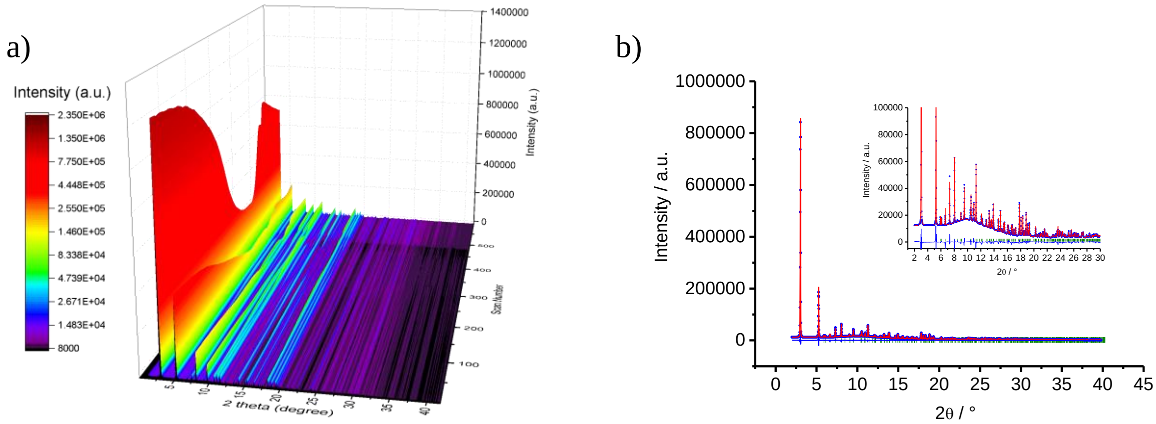

Figure 2. a) Temperature evolution for the powder diffraction patterns of CO_2-adsorbed-CPO-27 (Co^{2+}). b) Powder diffraction patter for CPO-27-Co as a function of the diffraction angle 2θ (blue dots: observed pattern; red line: best Rietveld-fit profile; line below pattern: difference curve; tick marks: reflection positions)

The obtained data enabled us to **solve by simulated annealing the crystal structure** of several CPO-27-M (M = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) materials with adsorbed CO_2 and perform **individual Rietveld refinements of each scan** obtained during the temperature program (figure 2b). As a result we significantly increase our knowledge on the host-guest interaction of these MOFs with the CO_2 molecules. The change on the adsorption capabilities of these porous materials in function of the temperature and the pressure was evaluated. The experimental parameter studied for such purpose was the occupancy of the adsorbed CO_2 molecules inside the framework structure (the CO_2 occupancy evolution for the cobalt CPO-27 sample can be seen in the figure 3a).

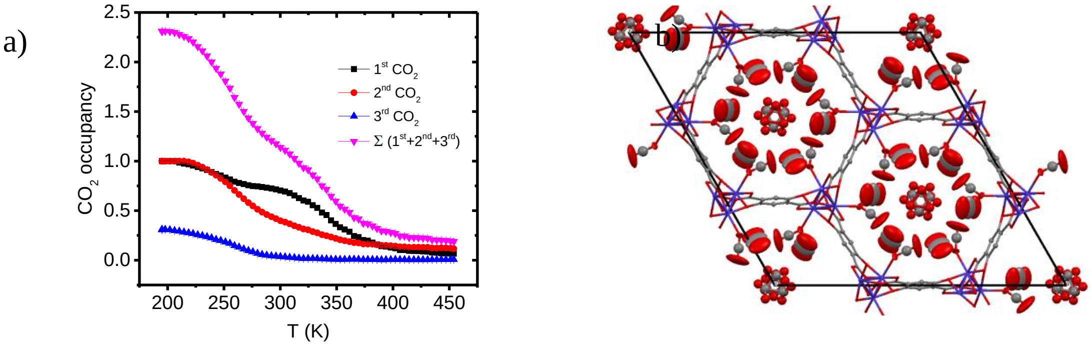

Figure 3. a) Evolution of the CO_2 occupancy with the temperature for CO_2-adsorbed-CPO-27 (Co^{2+}). b) Unit cell atoms (as ellipsoids) of the CO_2-adsorbed-CPO-27 (Co^{2+}) solved structure.

Additionally, thanks to the extraordinary quality of the obtained data we were able to perform an in depth analysis of these structures (including thermal parameters), and a correlation with the **CO_2 dynamics inside the cavities** (figure 3b) can be established. In this regard, a mention has to be done to the Pilatus detector system whose capabilities are in the cutting-edge of the X-ray detection. Thanks to that we were able to monitor minor changes which occur extremely rapidly with a sufficiently high time resolution to observe all relevant changes in the powder pattern.

The results presented herein are currently in submission for publication.

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