



	Experiment title: Influence of ligand substitution on breathing mode of MOFs with MIL-53 type crystal structure	Experiment number: 01-02-1019
Beamline: BM01A	Date of experiment: from: 10 Jul 2013 to: 13 Jul 2013	Date of report: 2.10.2015
Shifts: 9	Local contact(s): Vadim Diadkin	<i>Received at ESRF:</i>
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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 NH₂-group is of interest since it permits H-bonding interactions with guest molecules and can act as a catalytic active site.^[2]

In this experiment on BM01A we studied the breathing behavior of scandium-organic frameworks with MIL-53 type structure upon solvent removal and exposure to gas at various pressures. Therefore we have synthesized a series of scandium MIL-53 compounds with terephthalate^[3,4,5], 2-aminoterephthalate and 2,5-diaminoterephthalate as the organic linker in the MOF structure. Due to impurities in the prepared substance, only preliminary experiments were performed for the di-amino substituted member.

Both “as synthesized” scandium MIL-53 compounds, the pristine MIL-53(Sc)-H and amino-functionalized MIL-53(Sc)-NH₂, exhibit, upon heating under argon flow, phase transitions from an open- (op-Form) to a very narrow pore form (vnp-Form). In this desolvation process the orthorhombic “as synthesized” structures transform to monoclinic crystal structures with significant decrease of the cell volumes (over 35% for MIL-53(Sc)-NH₂). We have found that the temperature at which the phase transitions occurs increases with the introduction of amino groups on the ligand, while the thermal stability slightly decreases (Fig. 1).

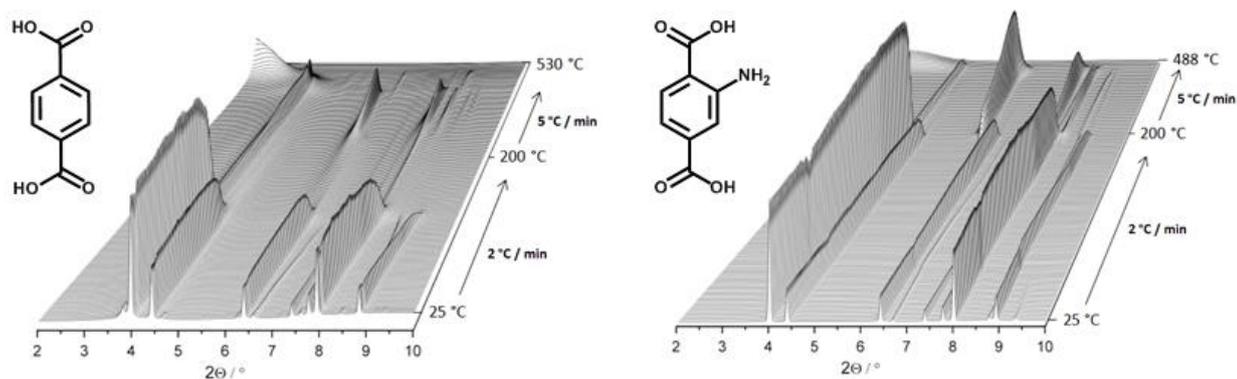


Figure 1: Breathing effect of MIL-53-NH₂(Sc) during the desolvation process. The measurements were performed by flowing an inert gas through an open capillary containing the “as synthesized” MOF.

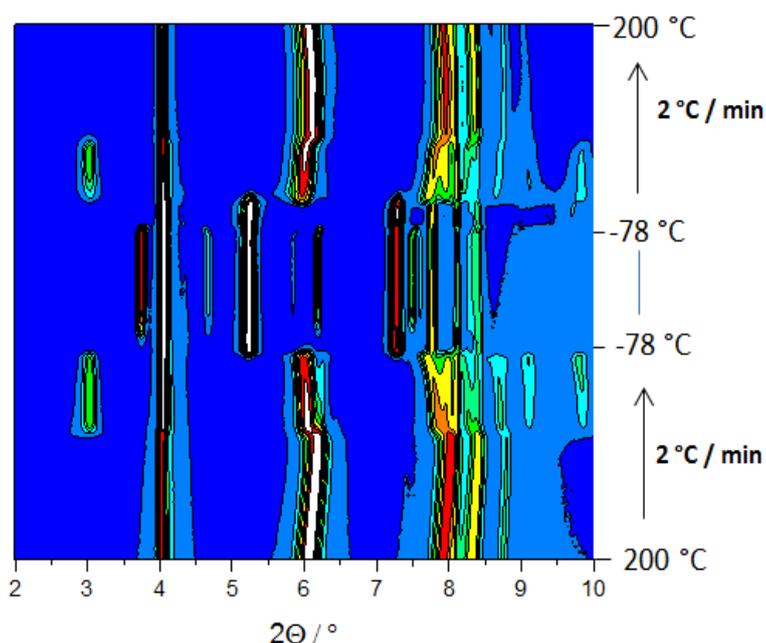


Figure 2: Top-view of a time resolved powder diffraction experiment of Mil-53(Sc)-NH₂ at -78 °C in CO₂ (1 bar) atmosphere.

pore forms are noticed at a temperature of -77°C (1bar) and -27°C (13.5bar). This is the first time *np-form* could be observed in the MIL-53(Sc) system. The results of this study will be complemented by the CO₂ sorption studies on MIL-53(Sc)-(NH₂)₂ on BM01A (this experiment was continued in experiment 01-02-1076). From the knowledge of these experiments we will hopefully improve our understanding on how the introduction of amino-groups into flexible MOFs of MIL-53 structure type influence their “breathing”-behavior and host-guest interaction towards CO₂.

In addition, variable temperature/pressure powder diffraction using CO₂ (during this experiment, we applied pressures from 1 to 13.5 bar) reveal that the pore-opening of the “guest free” MIL-53(Sc)-NH₂ is fully reversible and proceeds in three steps via an intermediate phase (*int-form*) and narrow pore phase (*np-form*) (Fig. 2). The Bragg peaks of the *vnp-forms* of these are observed at high temperatures (200 °C). With decrease in temperature, the Bragg reflections of the *vnp-forms* gradually disappear, and new reflections of an intermediate-phases start to appear at different temperatures (1bar: ~0°C 13.5bar: ~130°C) as a consequence of a partial opening of the pores. The formation into the *np-forms* was observed at temperatures of -43°C (1bar) and 17°C (13.5bar), respectively. The Bragg peaks of the open-

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