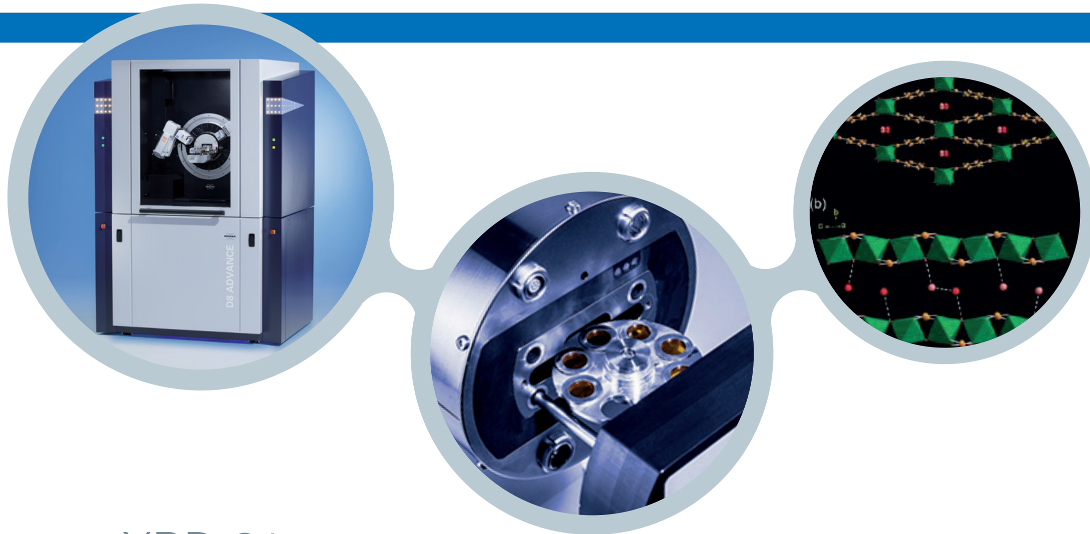

Lab Report XRD 81

Humidity induced phase transitions in MIL-53(Cr)

Metal-Organic Frameworks (MOFs) are a class of nano-porous materials which are formed of metallic centers linked to each other through organic chains. These materials have gained quite some interest because of their gas sorption/desorption properties with potential use for catalysis, sensing, gas storage, etc.

In this lab report the behavior of a typical MOF structure, MIL-53(Cr) metal-benzenedicarboxylate Cr(OH) (O_2C-C_6H_4-CO_2), is described as function of humidity.

XRD measurements were done in transmission mode on a D8 ADVANCE. Details on the instrument configuration are summarized in table 1.

The MHC-Trans in-situ chamber from Anton Paar enables temperature and humidity experiments on up to 8 powder samples simultaneously, while performing X-ray measurements in foil transmission geometry. Thanks to the thorough integration in DIFFRAC.SUITE even complex measurement strategies with varying temperature and humidity levels can be readily set up (Figure 1).

The superior energy resolution of the LYNXEYE XE allows completely discriminating Cr-fluorescence. Consequently, there is no need for a secondary monochromator and the LYNXEYE XE can be operated in 1D mode to speed up data collection.

Table 1. D8 ADVANCE Configuration
Cu radiation (40 kV, 40 mA)
Focusing Göbel mirror, 1mm exit slit, 5° primary Soller collimator, 4° secondary Soller collimator, LYNXEYE XE detector in 1D mode
Multi-sample Humidity Chamber MHC-Trans (Anton Paar)
Continuous scans from 7 to 50° 2Theta Step width 0.01° 2Theta Counting time 0.3 sec per step At different temperatures and humidity levels

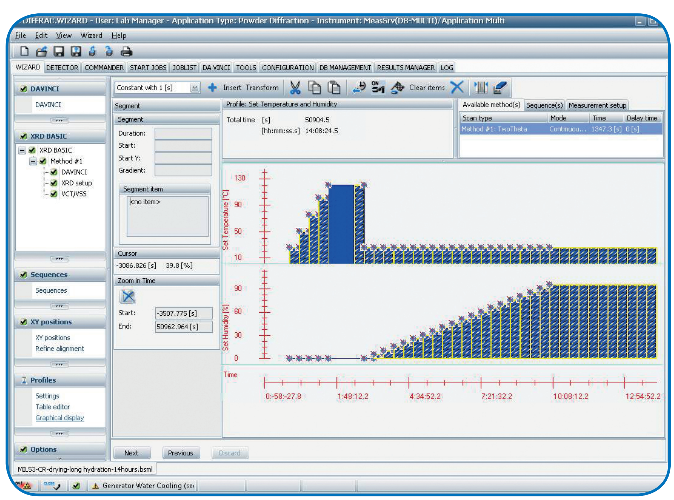

Figure 1: DIFFRAC.WIZARD for advanced measurement planning

The MIL-53(Cr) sample and the structural drawings were kindly provided by Dr. Guillou (Inst. Lavoisier, Versailles University, France)

Prior to the actual experiments, the sample was heated to 120°C in dry atmosphere. Upon full dehydration, the sample was cooled down again to room temperature in dry atmosphere. After these preparatory steps, MIL-53(Cr) has a large pore structure (form I).

In a first experiment, the humidity was gradually increased from 0% to 95% RH at room temperature. Every 5% RH a locked coupled scan was performed. After arriving at maximum humidity, the sample was immediately dried again at 120°C in dry air.

The corresponding iso-intensity plot (Figure 2) nicely shows 2 phase transitions. The first transition at about 20% RH corresponds to the formation of a narrow pore structure (form II, Figure 3), with water molecules being incorporated at well-defined crystallographic sites. The second transition happens while drying and demonstrates the reversible character of the form I-II phase transition. At the highest humidity levels, there is some indication for another phase transition.

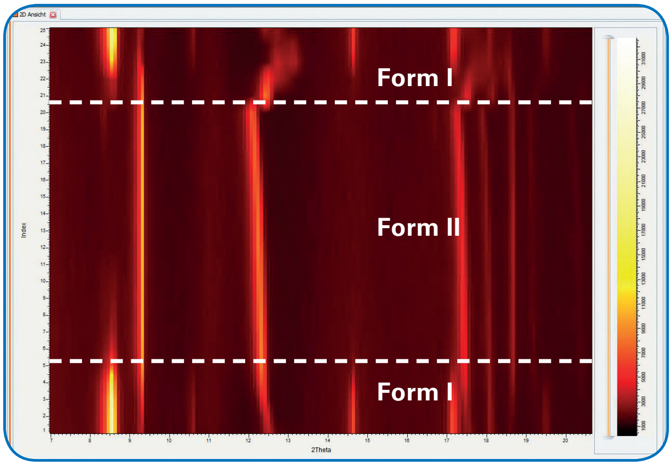

Figure 2: Reversible hydration/dehydration of MIL-53(Cr).

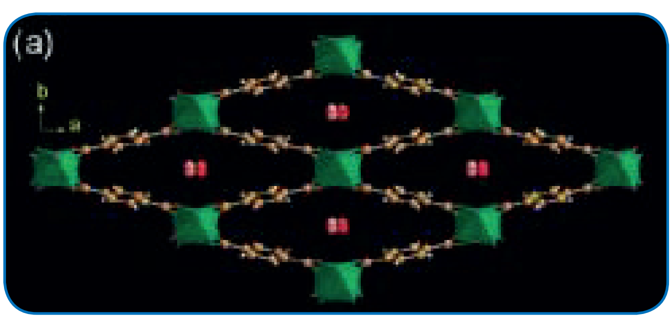

Figure 3: Form II structure.

Therefore a second experiment was done. Again the humidity was gradually increased from 0% to 95% RH at room temperature, starting from the form I structure. But instead of drying, the sample was kept for about 4 hours at 95% RH. The iso-intensity plot (Figure 4) also shows 2 phase transitions. The first one is the previously described form I-II phase transition at about 20% RH. The second transition indeed starts at about 90% RH, and results in a new large pore structure (superhydrated form III, Figure 5). During this form II-III phase transition the MIL-53(Cr) structure undergoes a big volume expansion to incorporate further water molecules. This second experiment confirms the existence of form III and its stability at high humidity.

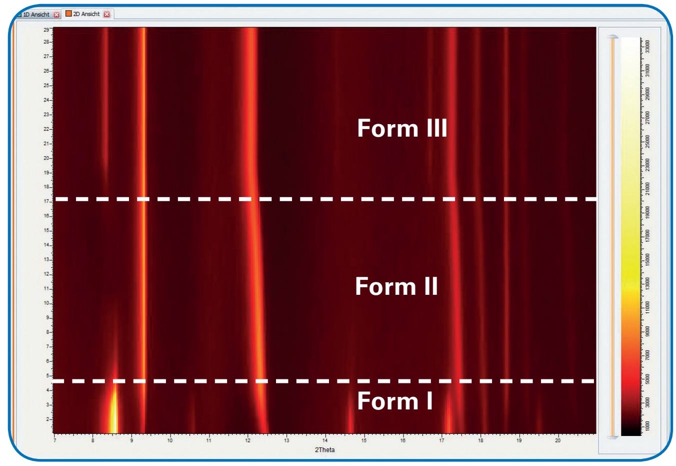

Figure 4: Formation of the superhydrated form III at high humidity.

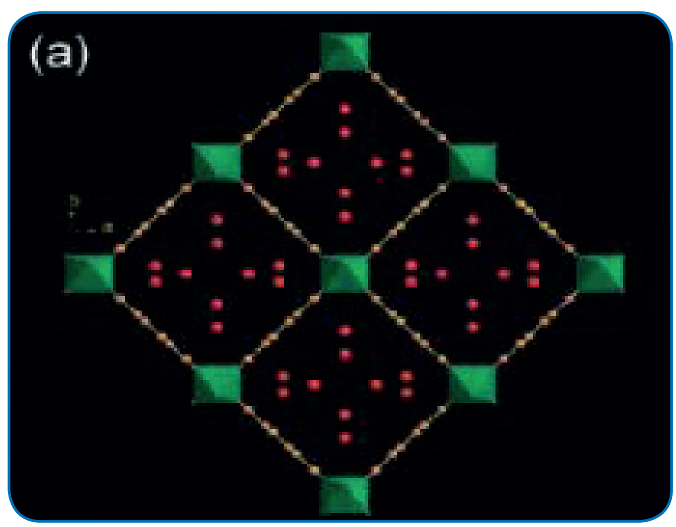

Figure 5: Superhydrated form III structure.

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