



In situ monitoring of structural changes during the adsorption on flexible porous coordination polymers by X-ray powder diffraction: Instrumentation and experimental results



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ABSTRACT

A new instrumentation for *in situ* X-ray powder diffraction allows to follow structural changes in the crystal structure of flexible coordination polymers during adsorption and desorption of gases. The system is based on closed cycle He-cryostat that ensures the high temperature stability in the range of 5.5–450 K. The automated gas dosing system facilitates the physisorption measurements in the pressure range of 0.01–130 kPa. The system is implemented on KMC-2 and MAGS beamlines at Helmholtz Zentrum Berlin für Materialien und Energie. Using new instrumentation, the adsorption of CO₂ and *n*-butane at 273 K on a flexible two-dimensional coordination polymer ELM-11 (ELM – Elastic Layer Material) was investigated.

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1. Introduction

Porous coordination polymers (PCP) or metal–organic frameworks (MOFs) represent a versatile class of porous materials fascinating scientists over and over again with their unique properties and functionality. A modular building concept of MOFs allows to synthesize ordered crystalline materials with ultra-high surface area and pore volume [1], that have high application potential for catalysis [2], for sensor technology [3], as well as for capture, [4] storage, [5] and separation [6] of almost all kinds of gases.

The most fascinating property of some MOF materials is the guest-induced flexibility of the framework, and the ability to adopt the pore size to the guest dimensions. This opens the potential for applications, which are not possible under use of conventional rigid adsorbents.

In order to classify all flexible MOF with respect to guest molecules removal/introduction, Kitagawa et al. discuss three generations of coordination polymers [7]. Materials belonging to the first generation do not show porosity because of the framework collapse after guests removal. Frameworks of the second

generation are robust possessing a rigid structure that remains intact after removal of guest molecules. Third generation frameworks show reversible structural changes during removal and insertion of solvent molecules. The latter also known as “gate pressure MOFs” or “breathable MOFs” that are the most exciting and at the same time less investigated class of crystalline porous materials.

Because of structural changes upon removal/insertion of guest molecules, the change in the powder X-ray diffraction would be an initial evidence regarding assignment of the compounds to this class of materials. Another fascinating phenomenon, commonly appeared by 3rd generations frameworks is characteristic hysteric loop in adsorption/desorption isotherms: the material starts to adsorb rapidly only above certain pressure, so called “gate opening pressure”, which is material and adsorptive dependent. The desorption branch of the isotherm does not exactly match the adsorption one and desorption take place primary at lower pressures (so called “gate closing pressure”) [8].

The main difficulty in understanding of processes and driving forces in “gate pressure” MOFs seems to be the tracking of structural changes during adsorption process. Taking the crystallinity of MOFs into account, the most suitable way to detect the structural changes should be concerted X-ray powder diffraction and

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gas physisorption experiments, coupling the findings provided by both techniques.

High intensity and monochromatic radiation of synchrotron facilities can provide high resolution diffraction data, collected in reasonable period of time, which make synchrotron facility highly attractive for such investigations. Up to date, a few instrumentations for “*in situ*” adsorption via X-ray powder diffraction are built worldwide: BLO2B2 (SPring-8) [9] and Swiss-Norwegian beamlines (ESRF) [10] propose the possibility to perform such experiments. Both of them use a glass capillary as a sample holder and cryostream gas flow cooler as a cryostat [11]. On the one hand, such set-up has several advantages, such as simple construction, rapid sample change, simple aligning in beam etc. On the another hand, the main drawback of such construction should be the complexity of introduction of sufficient amount of sample, which could be critical in some cases for the adsorption measurements, as well as inexactness in the temperature control. Another problem is the icing of the capillary during the experiment.

Despite the presence of such instrumentation, there are numerous publications that report flexible MOF materials without “*in situ*” investigation of their structural behavior [12–14]. Some of them also stress the lack of the facility [15].

Herein we describe a new instrumentation for “*in situ*” X-ray powder diffraction during the physisorption, which was developed and approved on KMC-2 or MAGS beamlines at Helmholtz Centre Berlin for Materials and Energy. The experimental setup allows the investigation of flexible porous materials by tracking the structural changes during adsorption of any non-corrosive gas in the pressure range 10 Pa–130 kPa and temperatures from 5.5 to 450 K. As a model compound, the flexible MOF material ELM-11 [16] was chosen.

2. Experimental section

2.1. Sample environment

To realize the concerted diffraction and adsorption measurements, the following requirements should be fulfilled: (i) precise temperature control of the sample and measuring cell, (ii) the sample holder (at the same time adsorption measuring cell) should be leakproof and permeable for X-ray; (iii) the dead volume of the adsorption system should be small; (iv) communication between adsorption and diffraction hardware should be feasible.

The sample environment developed involves the (i) close cycle cryostat fixed on the eulerian cradle. The cryostat DE-202AG is operated by the temperature controller LS-336 (Lake Shore). The heat, produced by cryostat is removed from the system by helium compressor ARS-2HW. (ii) The sample holder is made of aluminum (for improved thermal conductivity) with a Kapton[®] film window. The powdered sample can be placed between two Kapton[®] films (0.1 mm thickness). The volume of the sample holder can be varied by using aluminum gaskets of different sizes. Furthermore, an additional amount of the sample can be stored in a special reservoir in the sample holder at the adsorption temperature. This increases the accuracy of the adsorption measurements for materials with low uptake. The sample holder is enclosed in a small beryllium dome made of amorphous beryllium, brazed to stainless steel. The beryllium dome is fixed on the sample holder base with 8 screws. (iii) The copper gasket is used for sealing the construction. The sample holder base has two outlets with steel capillaries that can be connected to the gas inlet system. The sample holder base is made of copper and contains outer carving that allows to fix it on the cryostat. The large Be dome with simple fixation to the cryostat is also provided in order to achieve a satisfactory thermo isolation of the sample holder and to avoid

the icing of the cryostat part. The thermo isolation is realized by connecting the turbo-molecular vacuum pump to the cryostat.

In case of N₂ physisorption experiment, the system reaches the adsorption temperature of 77.35 ± 0.01 K approximately in 2 h.

The instrumentation was tested using two different beamlines, KMC-2 and MAGS at BESSY II, designed for diffraction experiments. Both beamlines are equipped with HUBER Euler cradles managed by SPEC software [17]. The KMC-2 beamline bending magnet is used as an insertion device which provides users with photon flux in range 10⁷–10¹⁰ photons/s/100 mA in energy region 4–15 keV. As detector a 2D VANTEC 2000 detector (Bruker) is installed.

MAGS beamline is equipped with insertion device based on superconducting Multipole Wiggler 7T-MPW providing users with monochromatic radiation with a wide range of photon energies (3.5–30 keV) and high photon flux (10¹¹–10¹³ photons/s/100 mA). Such a flux allows here to use a scintillation detector. Because of the cryostat dimensions, it is impossible to rotate the sample during the measurement imposing a restriction to the sample preparation.

Adsorption instrumentation of the equipment includes a commercially available automated gas dosing system BELSORP-max. The gas dosing system is connected to the gas inlet of the cryostat via 1/8 inch copper capillary. In order to trigger the adsorption and diffraction systems, the supplier company provides a special version of software, which allows to send the impulse to the diffraction system after the defined adsorption point is reached. The measurements can be performed fully automated and the intervention of operator is almost not needed during the measurement. The sample environment is established at BESSY-II and is available for users, whose proposals are approved by HZB user committee.

2.2. Structure refinement

Indexing of the powder XRDs, space group determination and Pawley refinement of the unit cells were performed using Reflex module in Material Studio 5.0 [18]. The same program was used for simulation of the *n*-butane@ELM-11 crystal structure that was refined using rigid body Rietveld with energy tool with 1% contribution of energy component. The Cu atoms, phenyl rings, and BF₄⁻ anions were treated as independent during the refinement. CCDC-974376 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge (Fig. 1) Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

3.1. Crystal structure of ELM-11(Cu)

ELM-11(Cu), one of the first and most investigated “gate pressure” MOFs was chosen as a model and reference compound [19–28].

The as made ELM-11 phase (also called preELM-11) consists of one-dimensional Cu-(4,4-bipy) (4,4'-bipyridine) chains that are linked to 3D framework by hydrogen bonds between coordinated H₂O, bridging guest 4,4'-bipy molecules, and BF₄⁻ anions. [29] After removal of solvent molecules, the as made compound transforms to the narrow pore structure, which is built up of [Cu(bipy)₂(BF₄)₂]_n layers, separated by interplanar distance of 4.5 Å (Fig. 2). The 4,4'-bipyridine molecules coordinate the copper atoms in square planar geometry, creating square meshes. Two BF₄⁻ anions fill residual sites in the octahedral copper coordination sphere coordinating in two axial positions, perpendicular to [Cu(bipy)₂]_∞²⁺ plane. The mutual orientation of the layers allows interdigitation of BF₄⁻ anions from one sheet into the square mesh of adjacent one. Such a close packing

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