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The importance of crystal size for breathing kinetics in MIL-53(Al)

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† N. Busov synthesized and characterized the samples by PXRD, nitrogen and *n*-butane physisorption and IR spectroscopy, and approved the submission of the original version of the manuscript. However, N. Busov did not respond to multiple requests during the revision process, therefore, does not take any responsibility for the published version.

1. Synthesis of MIL-53(Al)

1.1. Synthesis of Mil-53(Al)-1

$AlCl_3 \cdot 6H_2O$ (966 mg, 4 mmol) was added 30 mL of demineralized water and placed into a 45 ml Teflon liner, and oxalic acid dehydrate (4 mmol, 504 mg) was added to the solution, which was homogenized by stirring. Terephthalic acid (665 mg, 4 mmol) was added to the mixture and stirred again. The liner was sealed inside a steel autoclave and placed in an oven at 220 °C for 72 hours.

1.2. Synthesis of MIL-53(Al)-2

$AlCl_3 \cdot 6H_2O$ (966 mg, 4 mmol) was added to 30 mL of demineralized water and placed into a 45 mL Teflon liner. Terephthalic acid (665 mg, 4 mmol) was added to the mixture and stirred. The liner was sealed inside a steel autoclave and placed in an oven at 220 °C for 72 hours.

1.3. Synthesis of MIL-53(Al)-3

$AlCl_3 \cdot 6H_2O$ (966 mg, 4 mmol) was added 30 mL of DMF and placed inside a 45 ml Teflon liner. Terephthalic acid (665 mg, 4 mmol) was added to the mixture and stirred. The liner was sealed inside a steel autoclave and placed in an oven at 60°C for 24 hours.

1.4. Post-synthetic treatment

All samples were centrifuged, to separate crystals from the solution, and washed with Dimethylformamide several times. After washing all the remaining material from each synthesis was mixed in a Teflon liner with 30 mL of DMF and placed in an oven at 150 °C for 24 hours.

Before each measurement samples were calcined under dynamic vacuum at 200 °C overnight.

2. Physical characterization techniques

Powder X-ray diffraction (PXRD) patterns were recorded on a Malvern Panalytical Empyrean diffractometer in ω-2θ Bragg-Brentano geometry using Cu K-α1 ($\lambda = 1.5406$ Å) radiation, generated at 40 kV and 40 mA. The diffractograms were collected in the 2θ range of 5-50° at 0.0131 °θ step scan with exposure time of 97.920 s per step.

Nitrogen physisorption experiments were performed on QUADRASORB apparatus at 77 K. Nitrogen with a purity of 99.999% was used for all the measurements.

***n*-Butane physisorption** experiments were carried out in a pressure range up to 101.35 kPa at 298 K using a BELSORP-max instrument. Materials were loaded in the measurement cells and activated using heating up to 200 °C in dynamic vacuum.

SEM images SEM images were taken with secondary electrons in a HITACHI SU8020 microscope using 2.0 kV acceleration voltage and 8.2 / 8.3 mm working distance. The sample powders were prepared on a sticky carbon pad or a Si-wafer attached to an aluminum sample holder. All samples have been sputtered with gold to increase the conductivity.

Thermogravimetric analysis was performed under synthetic air flow in a temperature range of 298 – 700 K with a heating rate of 5 K/min using STA 409 PC (NETZSCH).

3. Powder X-ray Diffraction (PXRD)

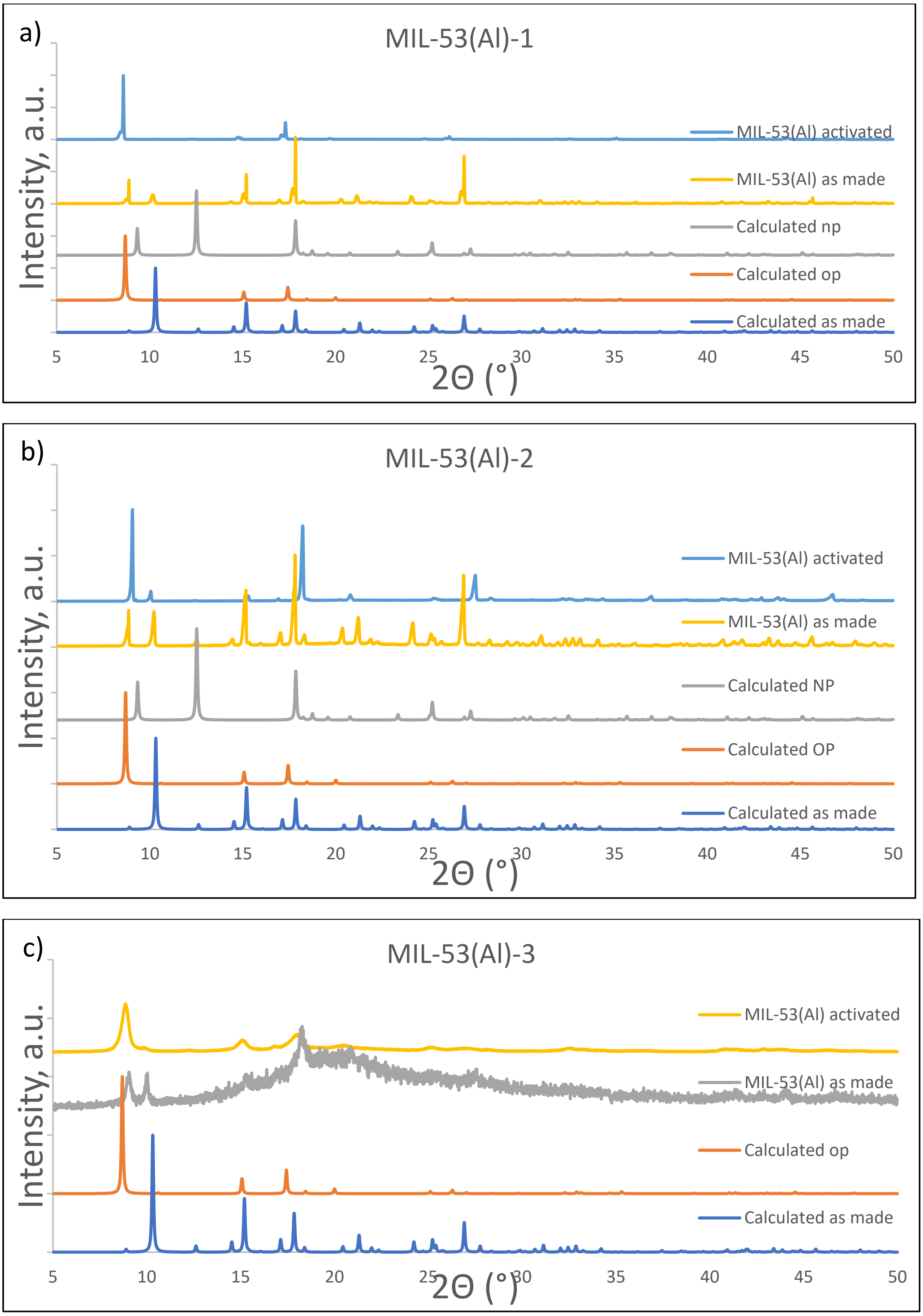


Figure S1. PXRD patterns of MIL-53(Al) samples: a) **MIL-53(Al)-1**; b) **MIL-53(Al)-2**; c) **MIL-53(Al)-3**.

4. SEM images

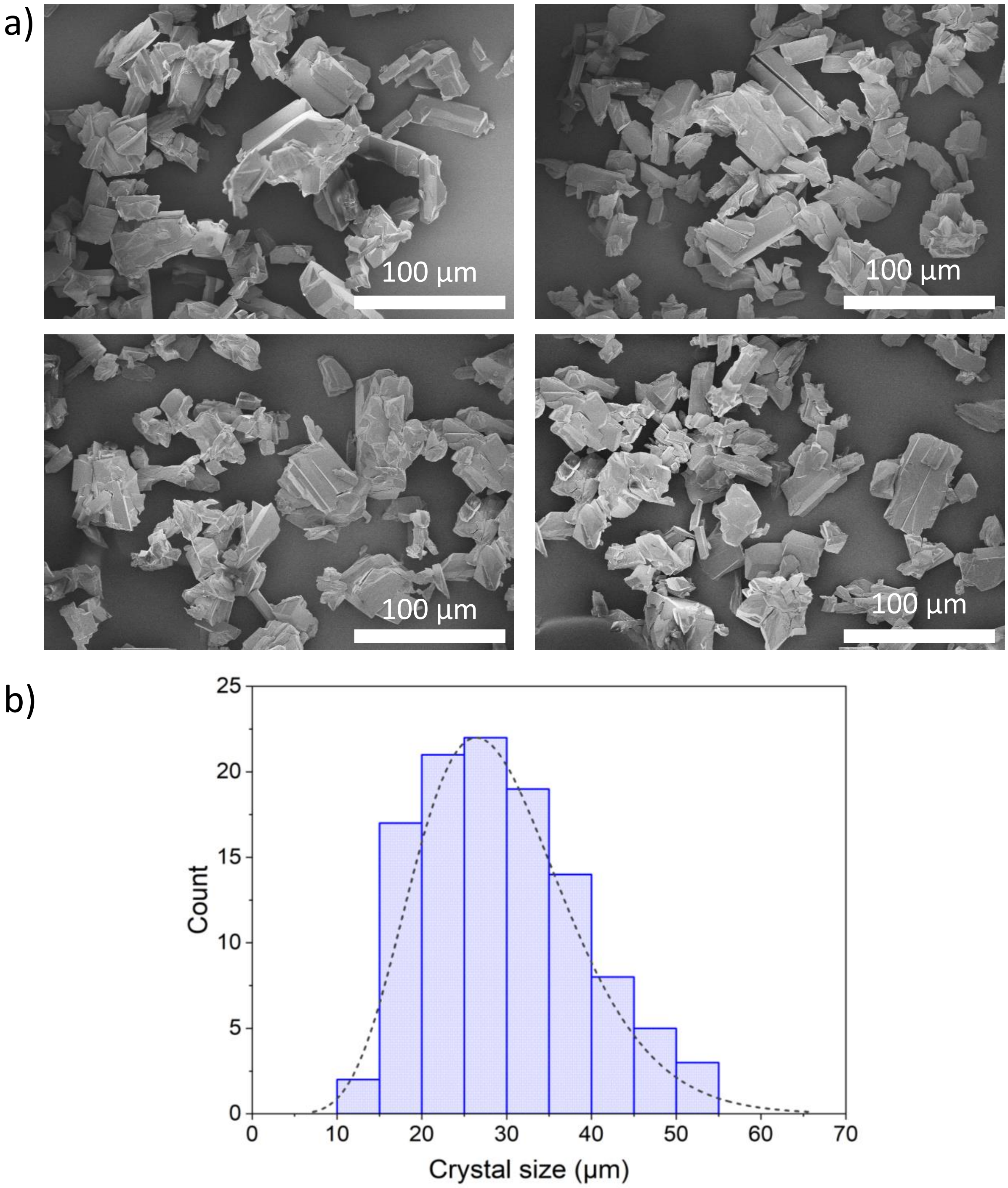


Figure S2. SEM images (a) and crystal size distribution (b), measured for **MIL-53(Al)-1** sample.

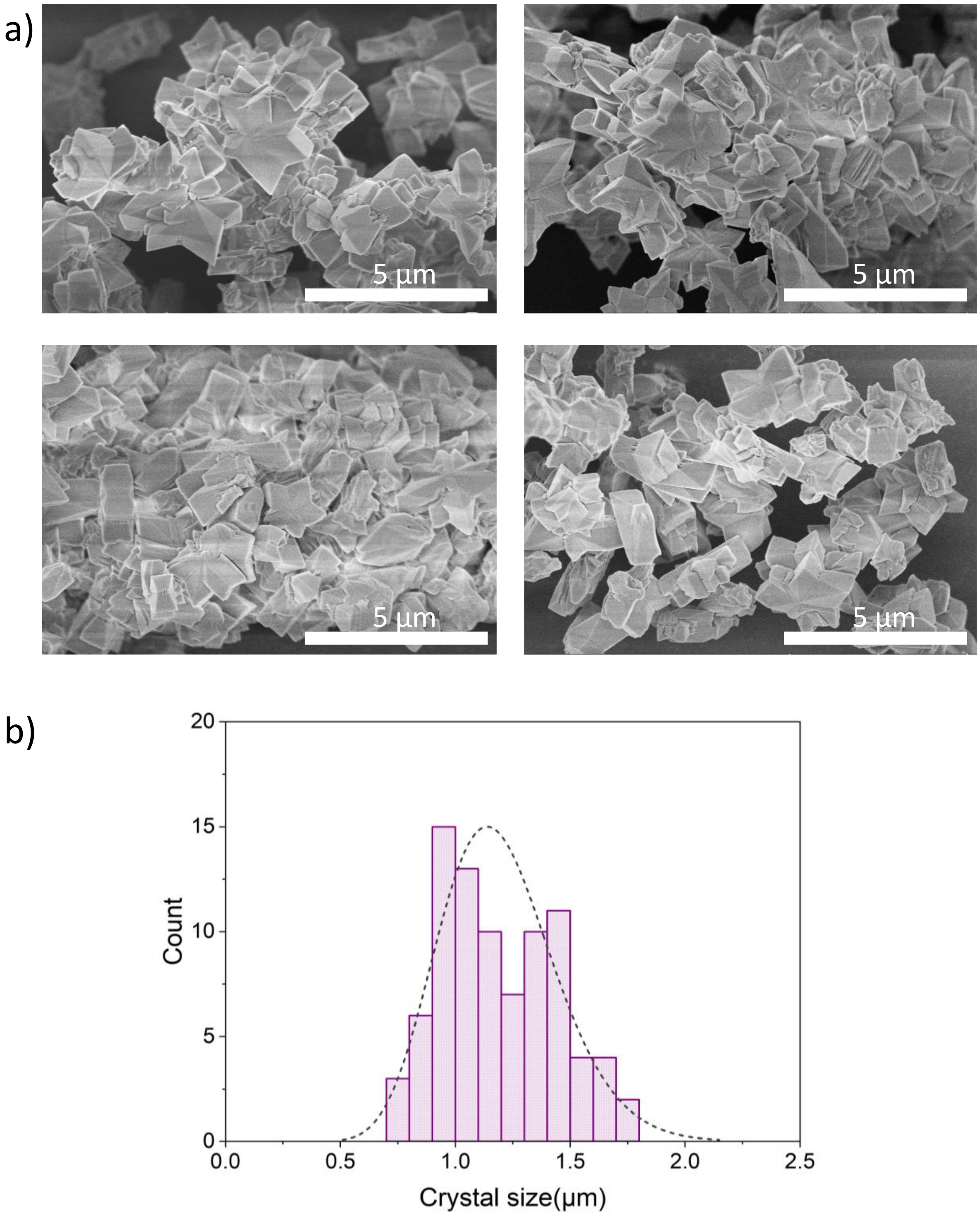


Figure S3. SEM images (a) and crystal size distribution (b), measured for **MIL-53(Al)-2** sample.

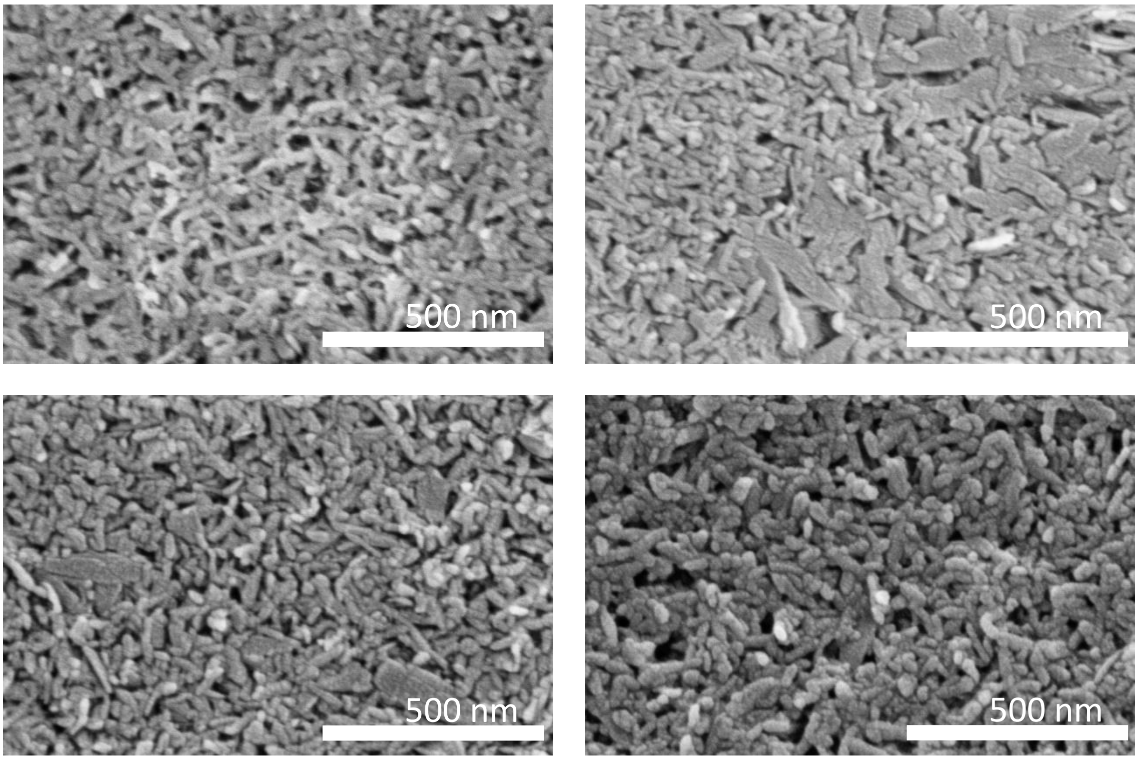
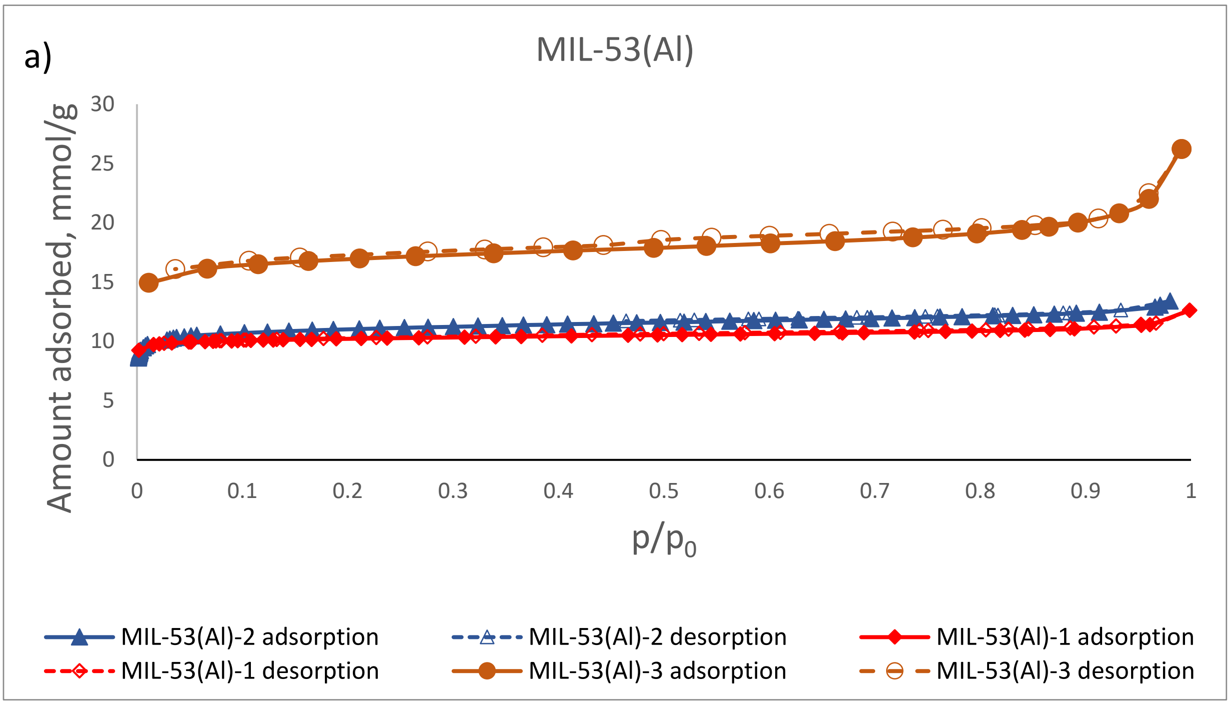


Figure S4. SEM images, measured for **MIL-53(Al)-3** sample.

5. Gas physisorption experiments



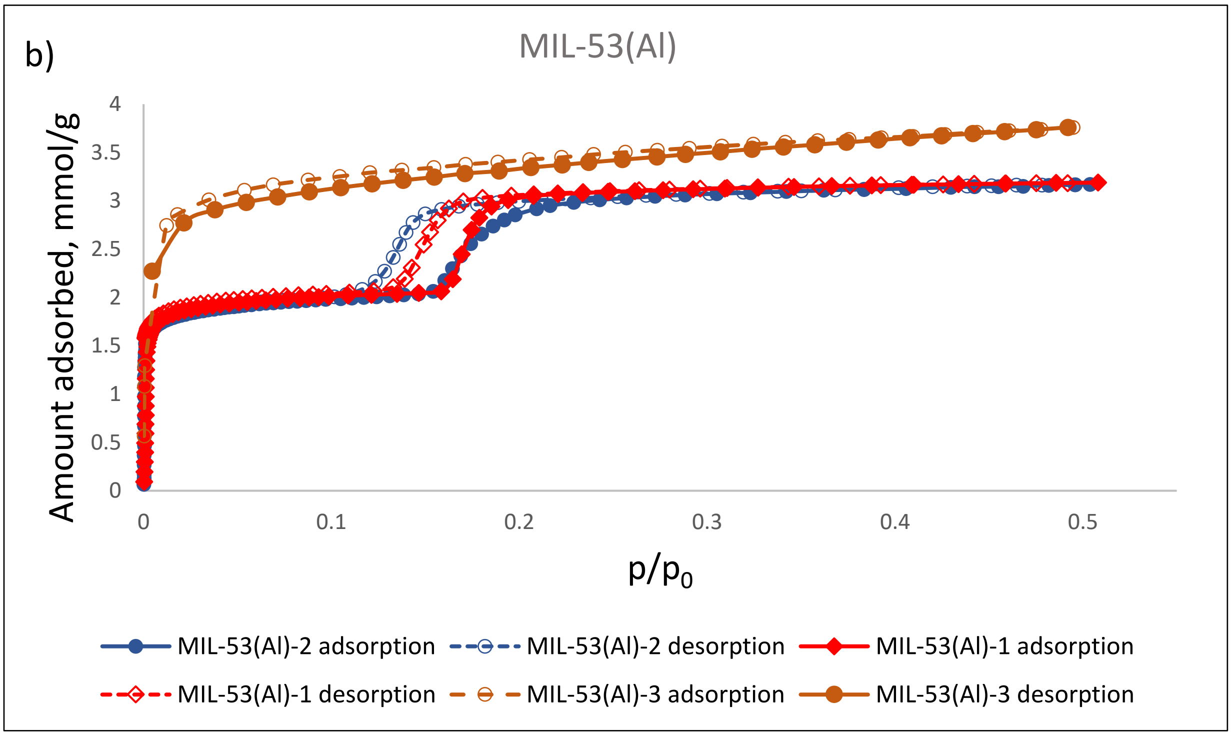


Figure S5. Physisorption isotherms of nitrogen at 77 K (a), *n*-butane at 298 K (b).

6. TG/ DTA curves

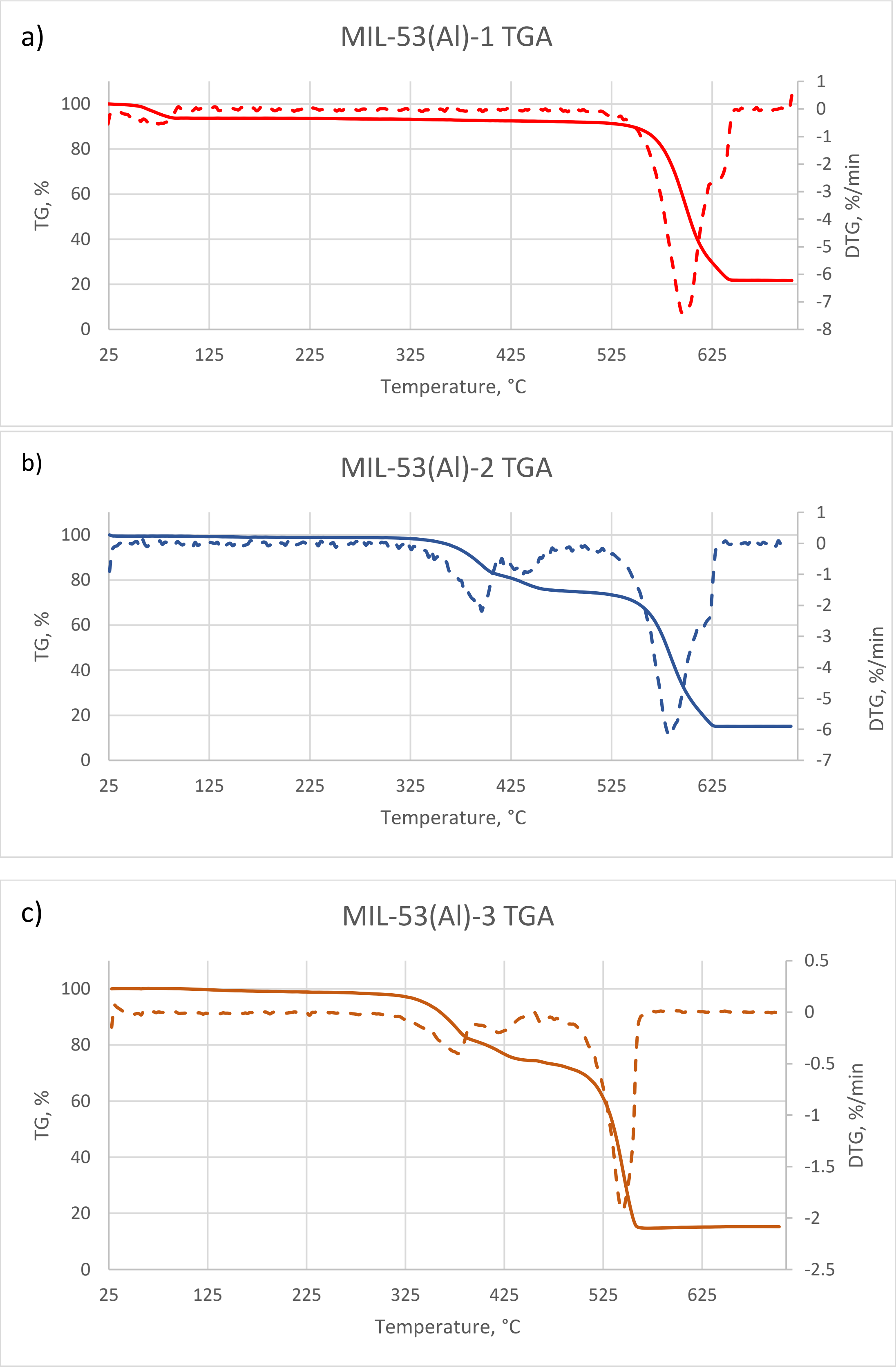


Figure S6. TG / DTA curves for **MIL-53(Al)-1** (a), **MIL-53(Al)-2** (b), **MIL-53(Al)-3** (c). Calculated residual mass is 24%.

7. Diffuse reflectance infrared Fourier-transform spectroscopy analysis (**DRIFT**)

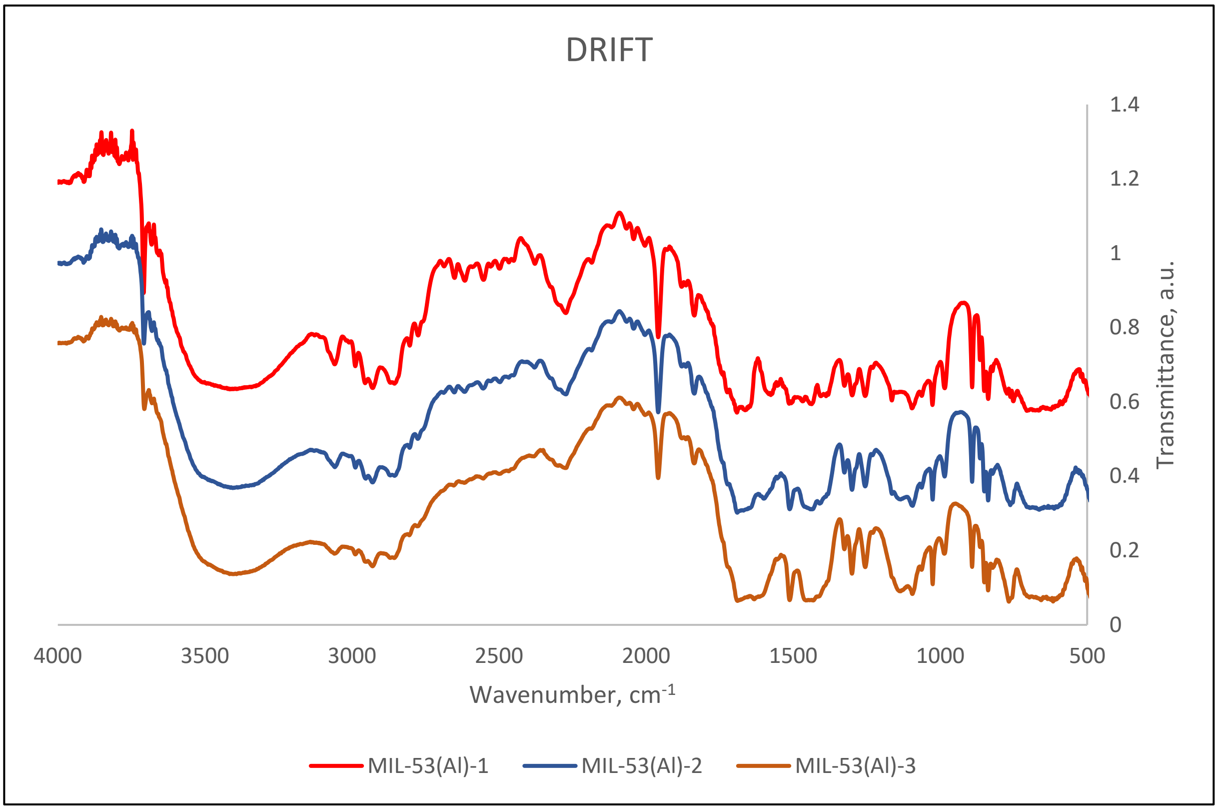


Figure S7. DRIFT spectra for MIL-53(Al) of different crystal sizes.

8. Indexing and Pawley fit for MIL-53(Al)-1

Since experimental PXRD patterns, measured for **MIL-53(Al)-1** do not exactly match with theoretical PXRD patterns, calculated for earlier reported structure of MIL-53(Al) **lp** phase, the experimental PXRD was indexed using X-Cell program, integrated into Materials Studio 5.0 software.[1] The resulted orthorhombic unit cell was subjected to Pawley refinement using Thompson-Cox-Hastings profile function and Berar-Baldinozzi asymmetry correction. The Pawley fit is given in Fig. S8.

Pawley fit data for **MIL-53(Al)-1**: Orthorhombic, *Imma*, a = 6.664(1) Å, b = 17.5487(18) Å, c = 11.6925(7) Å, V = 1367.37(50) Å^3, Thompson-Cox-Hastings profile function coefficients: U = 0.01, V = 0.0346, W = 0.0193, X = 0.0214, Y = 0.0514, Peak asymmetry function coefficients: P_1 = -0.130, P_2 = -0.0088, R_{wp} = 0.1912, R_p = 0.1263.

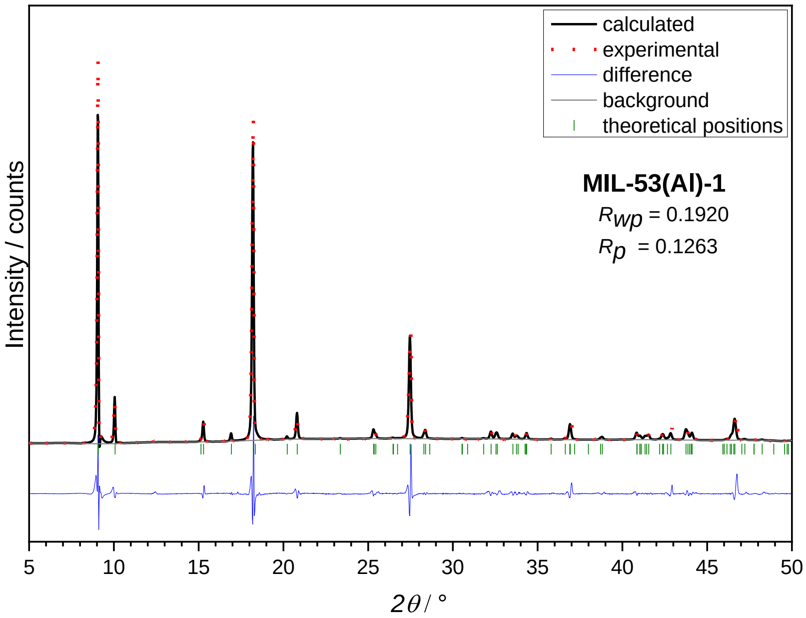


Figure S8. Pawley fit for **MIL-53(Al)-1**.

Table S1. Symmetry and unit cell parameters of MIL-53(Al) phases.

Phase	SG	*a* (Å)	*b* (Å)	*c* (Å)	*α*	*β*	*γ*	*V (Å^3)*
MIL-53(Al)-lp[2]	*Imma*	6.6085	16.675	12.813	90	90	90	1411.9
MIL-53(Al)-np[2]	*Cc*	19.513	7.612	6.576	90	104.24	90	946.7
MIL-53(Al)-1	*Imma*	6.664	17.549	11.693	90	90	90	1367.4

9. Adsorption induced breathing kinetics in MIL-53(Al) upon physisorption of *n*-butane by time-resolved synchrotron PXRD

9.1. Experimental setup

Time-resolved in situ PXRD experiments were conducted at P23 in situ diffraction and imaging beamline of PETRA III synchrotron (DESY). Monochromatic irradiation with E = 20.0 keV (λ=0.619921 Å) was used in all experiments. Reflection intensities were measured using PILATUS 1M (DECTRIS) detector, installed 45 cm back from the sample. In the typical experiment PXRD patterns were collected with 10 Hz rate.

The experimental setup consists of volumetric adsorption instrument BELSORP-max (Microtrac MRB), used as a gas handling system, which was connected to the customized home-built in situ glass capillary adsorption cell. The simplified scheme of the setup is given in Fig. S9. The gas dosing system was connected with in situ cell using 1/8 inch stainless tube. The *n*-butane gas was dosed in the standard volume of the instrument (V_{s1} ~ 25 cm^3) using automatic valve AV2 and further dosed to the measurement cell using automatic valve AV3. The pressure in the standard volume part and in the cell was monitored using electronic manometers P1 and P2. After the experiment, the cell was evacuated by opening the automated valve AV4. In the typical experiment, the pressure of *n*-butane of 120 kPa was built in the standard volume part while the cell was completely evacuated to the vacuum degree of $p \leq 1$ Pa. The valve AV3 was opened after starting the time-resolved PXRD data collection with a delay of 1 second. Typically, the pressure of 60 kPa was registered in the cell after the opening of AV3. Along with the isotherm the resulted pressure exceeds the reopening pressure for MIL-53(Al), derived from *n*-butane isotherm at 298 K as 60 kPa. In the typical experiment, 10 - 100 PXRD patterns per second were measured.

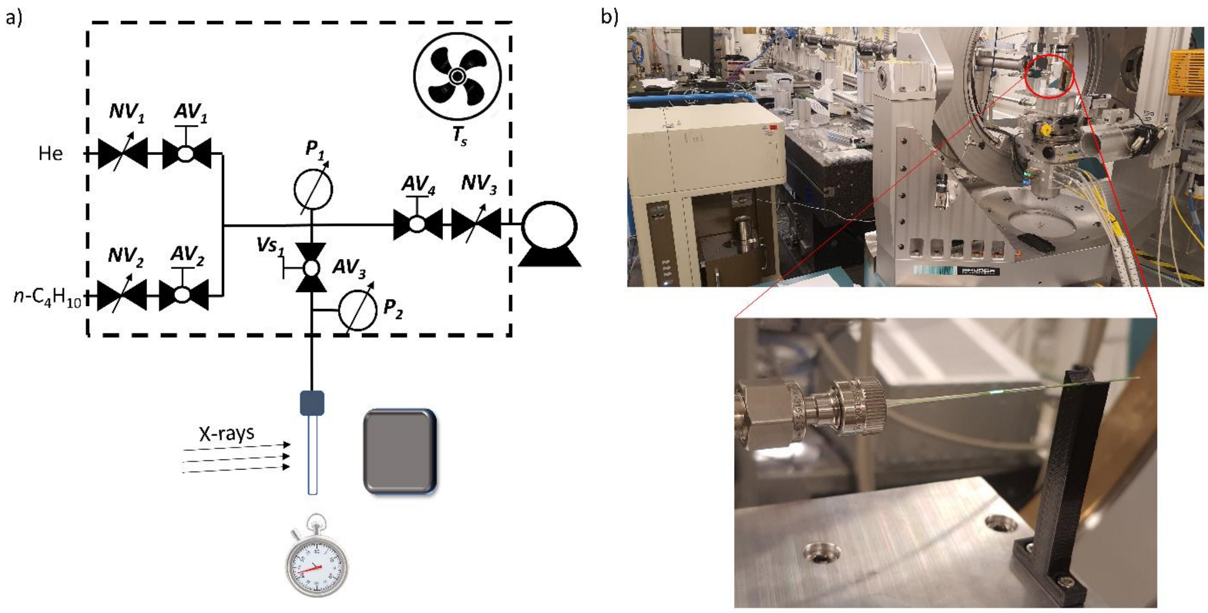


Figure S9. Experimental setup for time-resolved PXRD at P23 beamline at PETRA-III.

9.2. *In situ* time-resolved PXRD

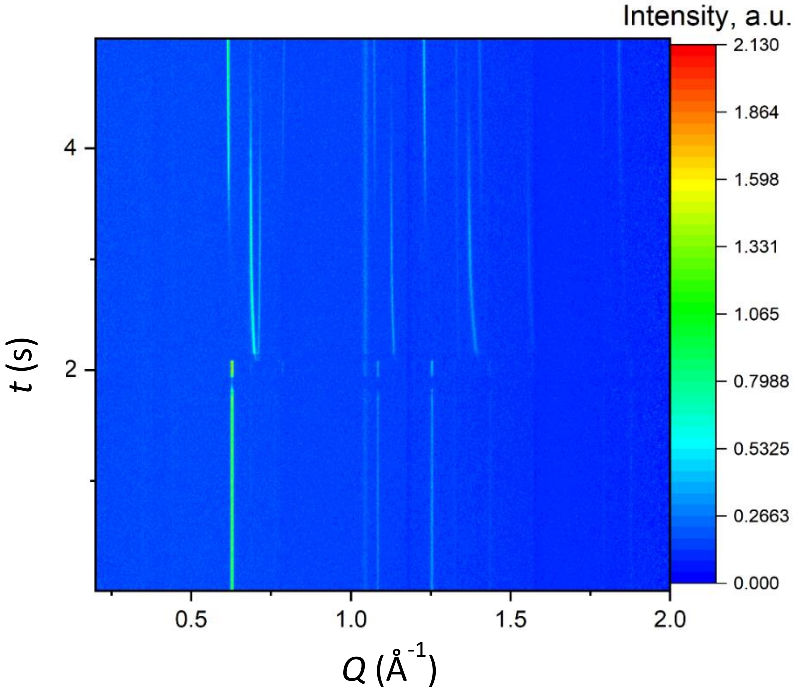


Figure S10. Contour plot of time-resolved PXRD on **MIL-53(Al)-2** measured parallel to *n*-butane adsorption (***lp-np-lp*** transitions).

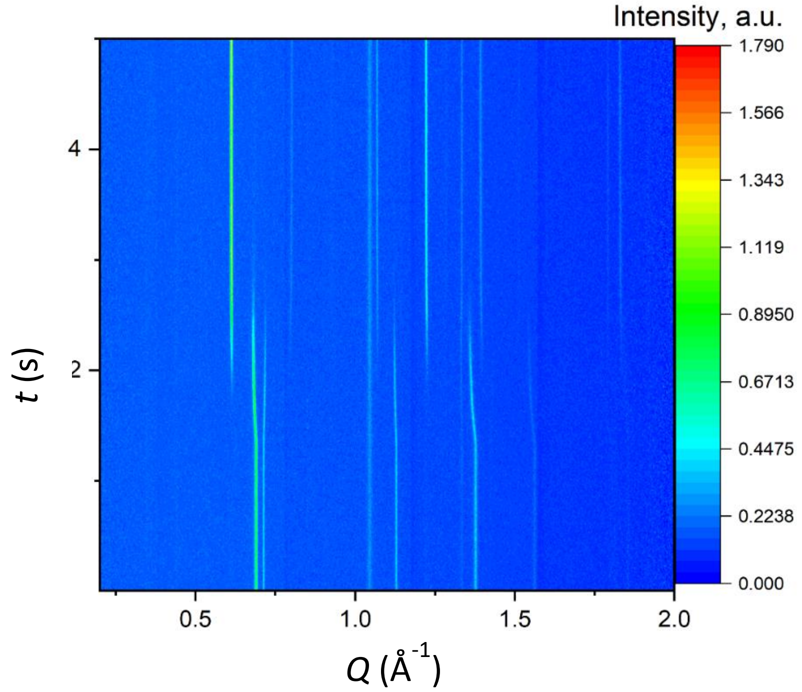


Figure S11. Contour plot of time-resolved PXRD on **MIL-53(Al)-2** measured parallel to *n*-butane adsorption at 298 K (***np-lp*** transition).

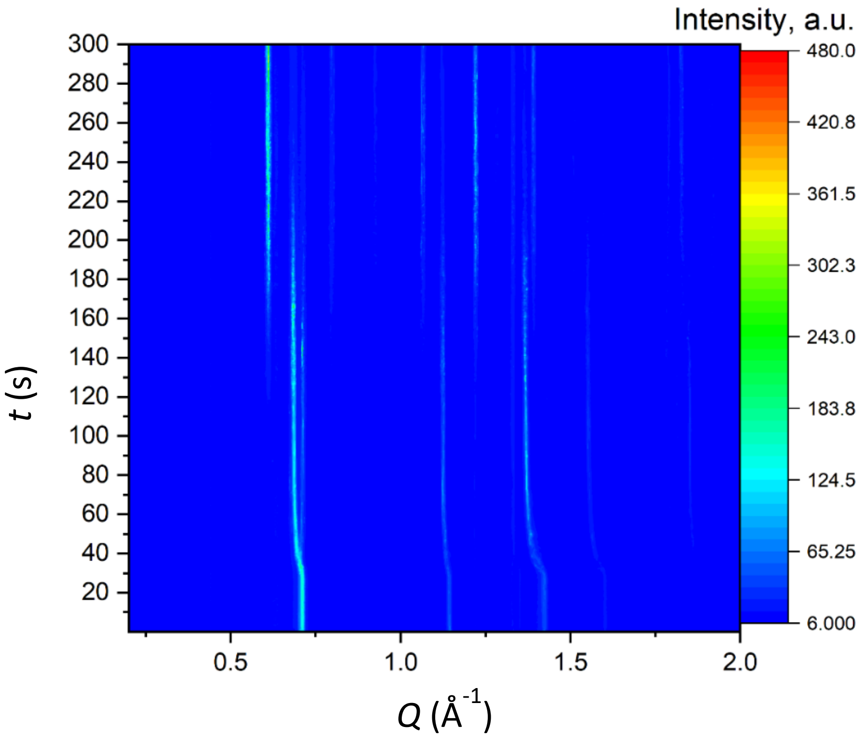


Figure S12. Contour plot of time resolved PXRD on **MIL-53(Al)-1** mesured parallel to *n*-butane adsorption at 298 K (***np-lp*** transition).

9.3. Fitting of intensities using Kolmogorov–Johnson–Mehl–Avrami (KJMA) equation

To fit intensities using KJMA equation, one section of contour plot (the highlighted intensity) was taken. Then maximum intensity of that region was equalized to 0 and minimum intensity equalized to 1. Then the counts of that intensity were plotted and fitted with KJMA equation using the Least Squares method.[3] From that we could calculate equation parameters "**n**" and "**k**"

$$a = e^{(-k*t^n)}$$

Where **a** is the relative inverted intensity of (011) reflection of ***lp*** phase, **k is** reaction/transition rate constant, **t** is time in seconds, **n** is Avrami exponent.

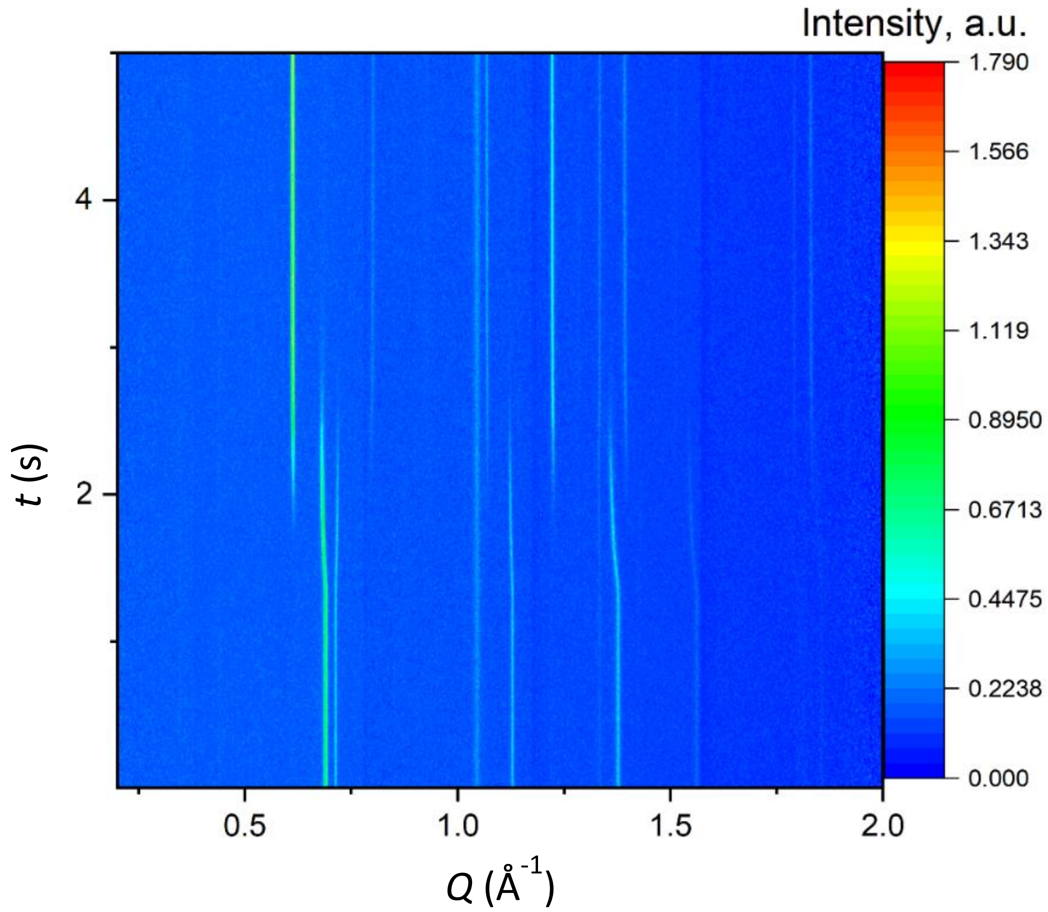


Figure S13. Contour plot of time resolved PXRD on **MIL-53(Al)-2** measured parallel to *n*-butane adsorption (***np-lp*** transition). The intensity of (011) reflection of MIL-53(Al) ***lp*** phase (marked red) was used for the fitting.

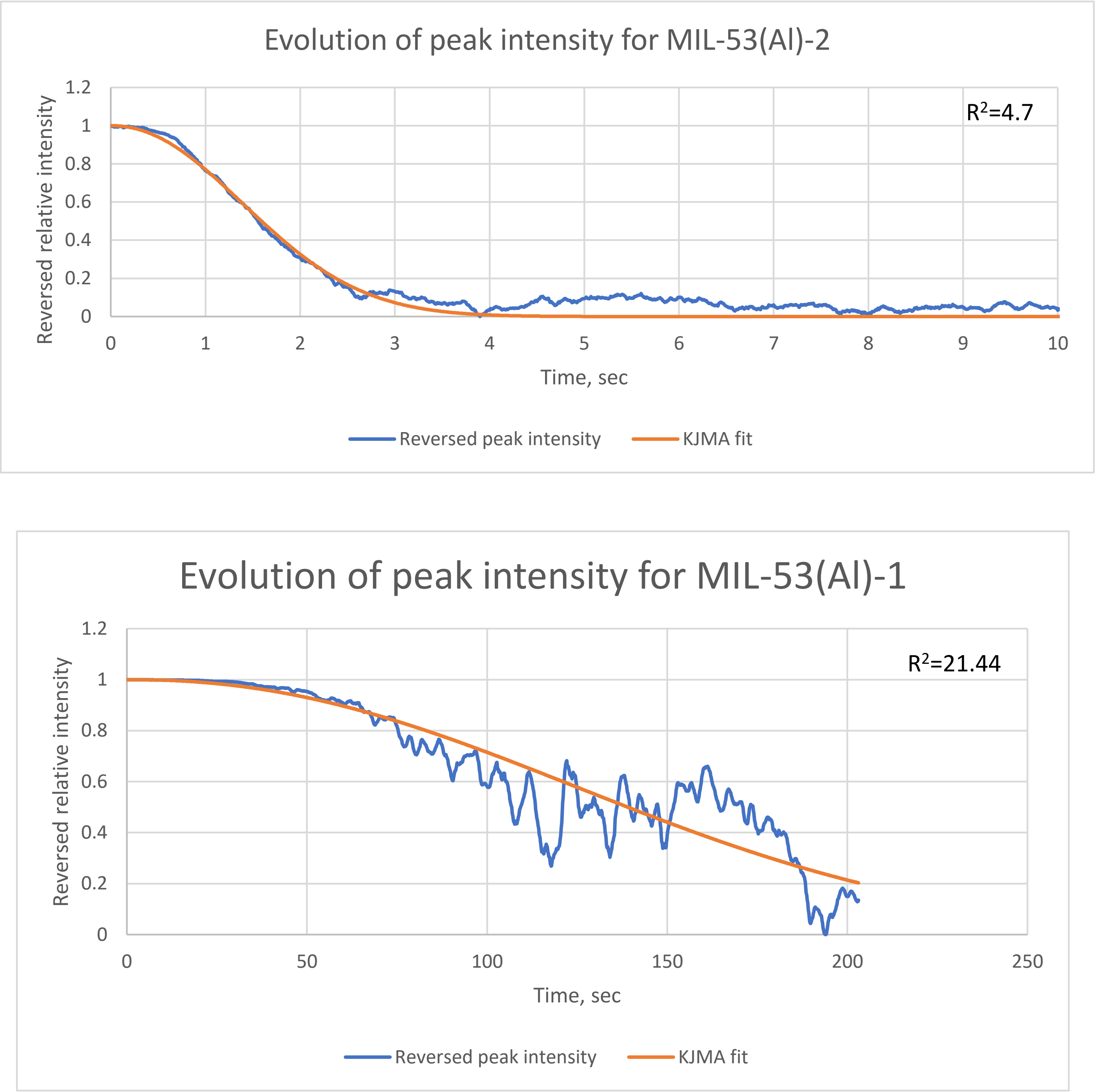


Figure S14. Fitting curves: **MIL-53(Al)-2** (a), **MIL-53(Al)-1** (b).

Table S2. Fitting of *k* value calculations using KJMA equation for **MIL-53(Al)-2** *in situ* PXRD dataset (***np-lp*** transition).

Cycle	***k***	***n***
1	0.27	2.1
4	1.20	
6	1.17	
7	1.34	

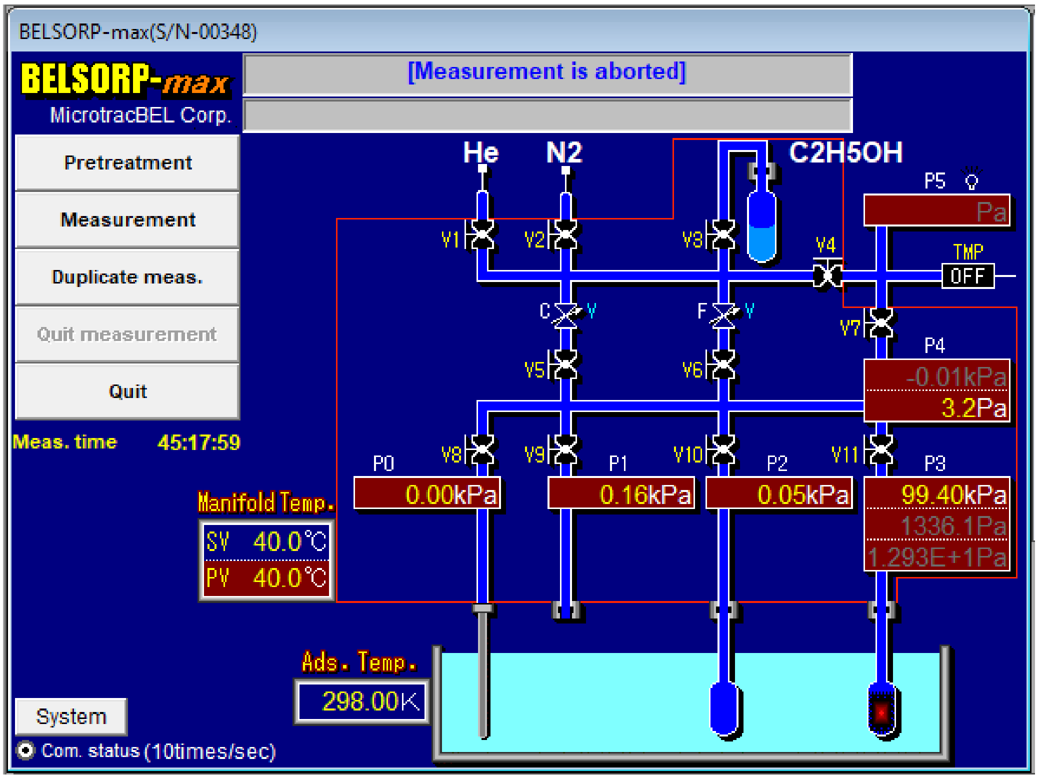
Table S3. Fitting of *k* value calculations using KJMA equation for **MIL-53(Al)-1** *in situ* PXRD dataset (***np-lp*** transition).

Cycle	***k***	***n***
3	$1.34*10^{-5}$	2.2
4	$3.77*10^{-6}$	

10. Accessing the breathing kinetics of *n*-butane adsorption from adsorption pressure drop profiles

10.1. Experimental part

Experiments were conducted using Belsorp-max (Microtrack-MRB) volumetric adsorption device as a gas dosing system in manual mode (Fig. S15). Typically, 20 - 30 mg of the sample was placed in the measurement cell, evacuated upon heating up to 180 °C for 30 minutes and placed in measurement slot. Water bath thermostat was used to control the temperature at 298 K. After the cell was ensured to maintain the measurement temperature, the sample was additionally degassed for 15 minutes in high vacuum and then valve V11 was closed. Further, the *n*-butane gas was dosed into manifold by valves V5 and V6 up to reaching the pressure of 120 kPa on manometer P4. After that the standard volume of the instrument, also denoted as a manifold, was isolated from gas- supply line. After that valve connecting the manifold and measurement cell (V11) was opened to introduce the gas into the cell. Pressure profile in the cell was recorded using internal manometer P3 (Fig. S16). Measurement is stopped after the pressure change does not exceed 0.5% within 300 seconds. For the data analysis using KJMA equation, the pressure profile was normalized in a way, that the maximum pressure of P3 manometer was equalized to 1, and minimum pressure to 0, and curve was fitted to get transition/adsorption parameters.



BELSORP-max(S/N-00348)

[Measurement is aborted]

Meas. time 45:17:59

Manifold Temp. SV 40.0℃ PV 40.0℃

Ads. Temp. 298.00K

P5 Pa

TMP OFF

P4 -0.01kPa 3.2Pa

P0 0.00kPa

P1 0.16kPa

P2 0.05kPa

P3 99.40kPa 1336.1Pa 1.293E+1Pa

Com. status (10times/sec)

Figure S15. Belsorp-max software interface.

10.2. Pressure profile analysis

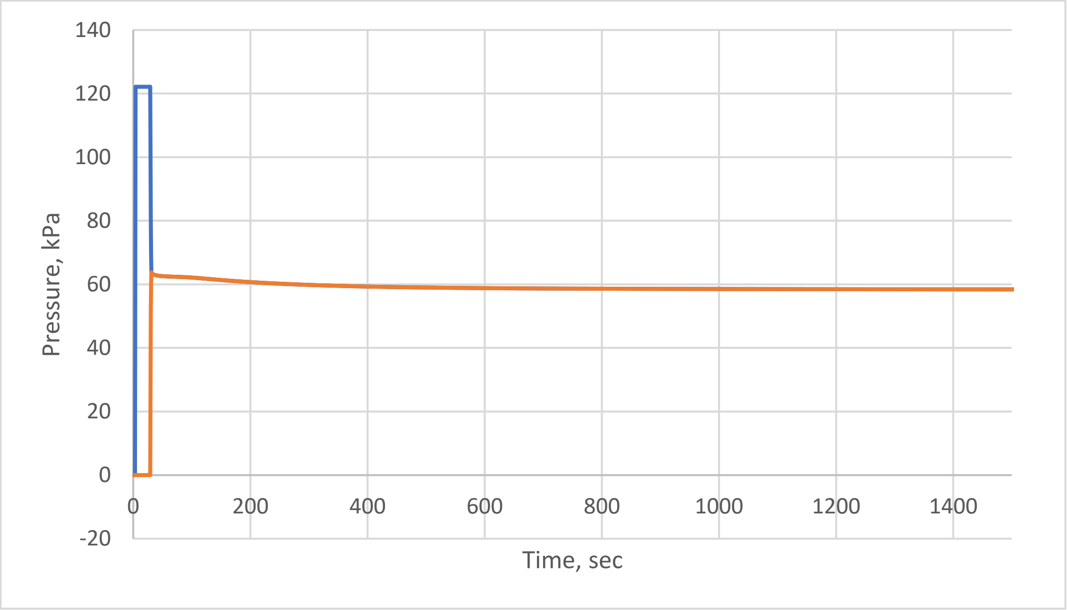


Figure S16. Typical pressure profile in the measurement cell during *n*-butane adsorption at 298 K.

10.3. KJMA fitting

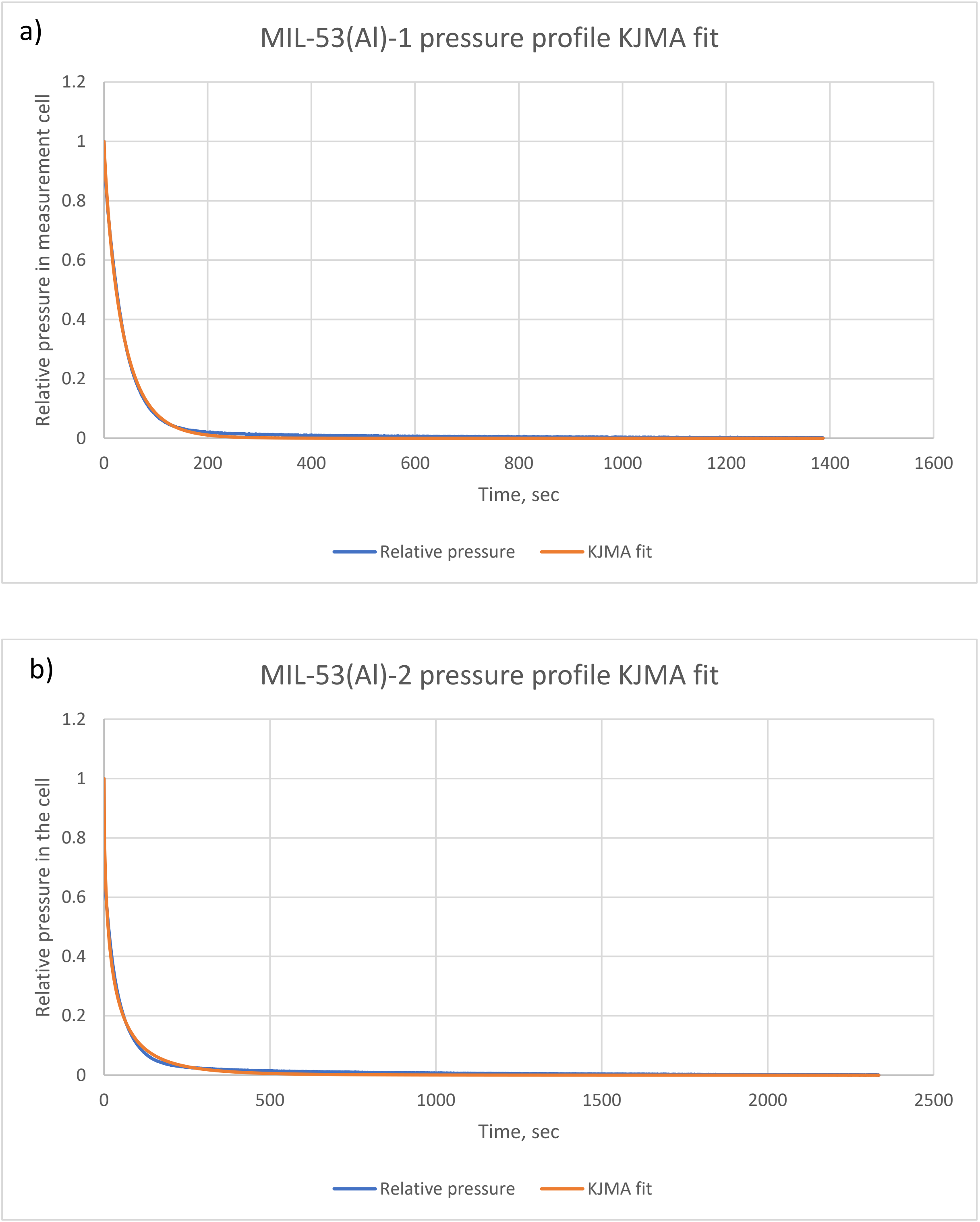


Figure S17. KJMA equation fit of adsorption kinetics pressure profile for **MIL-53(Al)-1** (a), **MIL-53(Al)-2** (b).

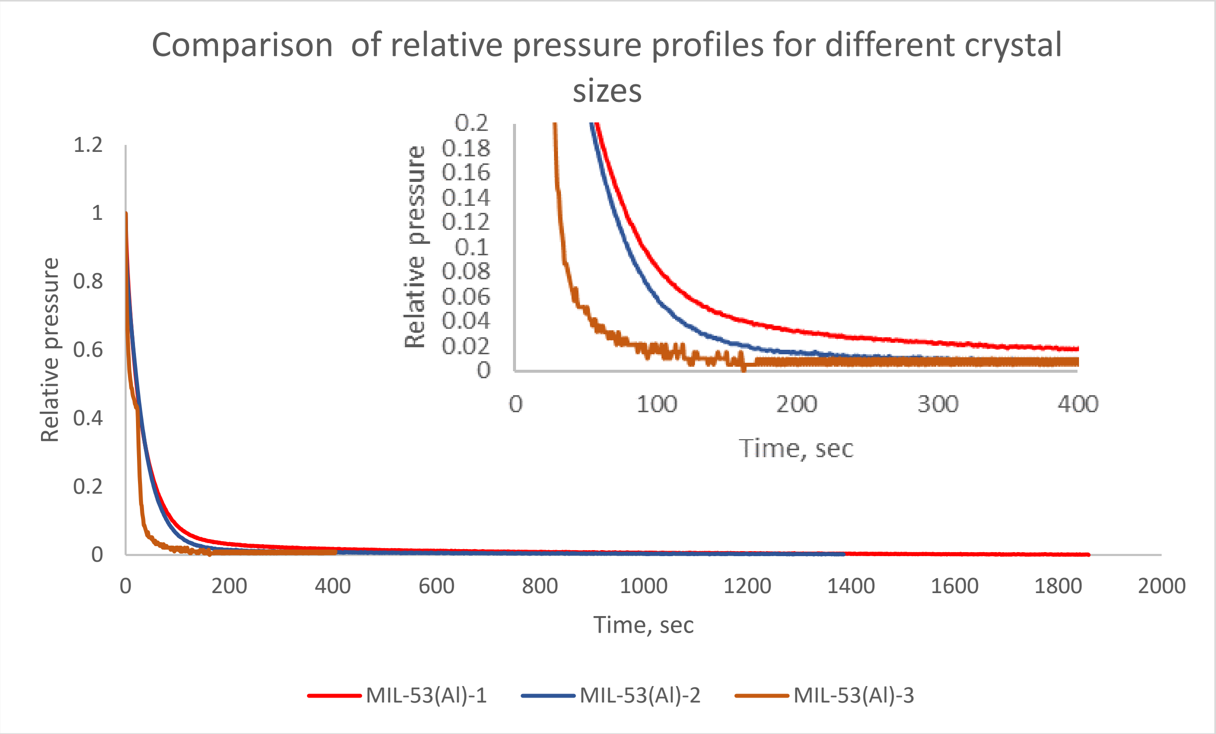


Figure S18. Adsorption kinetics pressure profile of **MIL-53(Al)-1** (red curve), **MIL-53(Al)-2** (blue curve), and **MIL-53(Al)-3** (brown curve).

Table S4. Coefficients k and n obtained from KJMA fit of adsorption pressure profile of **MIL-53(Al)-1** (***lp-np-lp*** transition).

Cycle	**k**	**p** (kPa)	**n**
1	0.012	70	0.820
2	0.018		
3	0.023		
5	0.019		
7	0.022		
9	0.056		

Table S5. Coefficients k and n obtained from KJMA fit of adsorption pressure profile of **MIL-53(Al)-2** (***lp-np-lp*** transition).

Cycle	**k**	**p** (kPa)	**n**
1	0.016	70	0.820
2	0.021		
3	0.025		
4	0.055		
5	0.083		
6	0.059		
7	0.059		
8	0.055		

Table S6. Coefficients **k** and **n** obtained from KJMA fit of adsorption pressure profile of **MIL-53(Al)-3**.

Cycle	**k**	**p** (kPa)	**n**
1	0.096	70	0.820

Table S7. Coefficients **k**, obtained from KJMA fit for ***lp-np*** and ***np-lp*** transitions of **MIL-53(Al)-1**.

Cycle	**k**	**p** (kPa)	**n**
1 ***lp-np***	0.15	10	0.820
1 ***np-lp***	0.058	70	
2 ***lp-np***	0.122	10	
2 ***np-lp***	0.047	70	

Table S8. Coefficients ***k***, obtained from KJMA fit for ***lp-np*** and ***np-lp*** transitions of **MIL-53(Al)-2**.

Cycle	***k***	***p*** (kPa)	***n***
1 ***lp-np***	0.153	10	0.820
1 ***np-lp***	0.096	70	
2 ***lp-np***	0.234	10	
2 ***np-lp***	0.085	70	
3 ***lp-np***	0.272	10	
3 ***np-lp***	0.091	70	

References

1. *Materials Studio 5.0,* Accelrys, San Diego, USA, 2009.
2. T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille and G. Férey, A Rationale for the Large Breathing of the Porous Aluminum Terephthalate (MIL-53) Upon Hydration, *Chem. Eur. J.*, 2004, **10**, 1373–1382.
3. M. Avrami, Granulation, Phase Change, and Microstructure Kinetics of Phase Change. III, *J. Chem. Phys.*, 1941, **9**, 177–184.