

Supporting Information:

Application of DUT-4 MOF structure switching for optical and electrical humidity sensing

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This is the supplementary information for the manuscript entitled: "Application of DUT-4 MOF structure switching for optical and electrical humidity sensing" by Alexander Krylov, Sergei Shipilovskikh, Svetlana Krylova, Nina Slyusarenko, Maria Timofeevaa, Yuliya Ken-

zhebayeva, Semyon Bachinin, Irina Yushina, Aleksandr Cherepakhin, Nikolai Shestakov, Ivan Nemtsev, Alexander Vtyurin, and Valentin Milichko

Synthesis of DUT-4

The DUT-4 crystals were synthesized by modifying the procedure reported by Kaskel and co-workers.^{S2} In a typical synthesis, 2,6-naphthalene dicarboxylic acid (ndc, 0.087 g, 0.4 mmol) was dissolved in 5 ml DMF and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.17 g, 0.45 mmol) was dissolved in 5 ml DMF. Then two solutions were filled in a 20 ml vial and the mixture was hermetically sealed with a lid with a rubber septum to exclude the ingress of the environment and create excess pressure in the vessel. The closed vial was immersed in an ultrasonic bath for 10 min. Then it was heated to 120°C and kept for 24 hours. After 24 h the reaction mixture was cooled to room temperature. After the product was separated from the mother liquor by filtration, after which it was repeatedly washed 3 times with a DMF. The washed powder was dried in the air.

Powder X-ray diffraction

Powder X-ray diffraction (PXRD). Diffraction patterns of the samples were recorded on a Shimadzu 7000-maxima X-ray diffractometer with a 2 kW characteristic Cu $K\alpha$ ($K\alpha_1$ $\lambda=1.54059$ Å, angular range $2\Theta=5^\circ - 50^\circ$) X-ray radiation source and a Bragg-Brentano goniometer geometry. The angular resolution during the analysis was 0.07 degrees at a scanning speed of 1 degree/min (Figure S1).

Raman spectroscopy

DUT-4 ($\text{C}_{48}\text{H}_{28}\text{Al}_4\text{O}_{20}$) belongs to the orthorhombic space group *Pnna* (symmetry international tables number 52). Its point group is D_{2h} (mmm). Structural data for symmetry

analysis were taken from the work of I. Senkovska.^{S1} The Al atoms are located in the 4d Wyckoff position. The oxygen atoms are located in the 4c Wyckoff position. Other atoms are located in the 8e Wyckoff position. The representation of IR active modes at Brillouin zone centre is: $G_{IR} = 35B_{1u} + 36B_{2u} + 35B_{3u}$. The representation of acoustic modes is: $G_{acoustic} = B_{1u} + B_{2u} + B_{3u}$. The representation of Raman modes in the orthorhombic phase at the Brillouin zone centre is: $G_R = 35A_g + 36B_{1g} + 37B_{2g} + 36B_{3g}$.

The transformation of low-wavenumber region Raman spectra DUT-4 over time is presented in Figure S4.

FTIR

Fourier transform infrared absorption (FT-IR) spectra were recorded with the VERTEX 70 (Bruker Optik GMBH) spectrometer in the spectral region of 400-4000 cm^{-1} with spectral resolution 4 cm^{-1} . The FT IR spectrometer was equipped with a Globar as a light source and a wide band KBr beam splitter and RT-DLaTGS a detector (Bruker Optik GMBH), ATR device PIKE MIRacle Diamond.

FT-IR spectra of DUT-4 powder sample initial humidity and after keeping on air (Fig. S11) are quite different.

SEM

The morphological features of the structure have been studied using a high-resolution scanning electron microscope FE-SEM S-5500 (Hitachi, Tokyo, Japan). All of the SEM images were taken using a secondary electron mode at an accelerating voltage of 3 kV, a beam current of 10 μA , and a focal length of 400 to 500 μm . No metal films were deposited on the surface of the samples before capturing the SEM images despite the dielectric samples.

Synchronous thermal analysis

Synchronous thermal analysis (STA) combining thermal gravimetric analysis (TG) with differential scanning calorimetry (DSC) was performed with an STA 449 C Jupiter device (Netzsch). The sample was kept in a platinum crucible with an untight lid at a constant temperature of 35°C in a flow (50 ml/min) of a 1:4 argon – air saturated with water vapour mixture for 24 hours. The gas mixture maintained a constant humidity level of approximately 65%. The initial mass of the sample was precisely 6.4 mg, while the final mass was 7 mg. After 40 minutes, the weight increased and reached 9%. Subsequently, the weight decreased over 18 hours. The weight change was 2.3%.

References

- (S1) I. Senkowska et al. *Microporous and Mesoporous Materials*, **2009**, 122 (1), 93–98.
- (S2) T. Loiseau, C. Mellot-Draznieks, H. Muguerra, G. Férey, M. Haouas and F. Taulelle, *Comptes Rendus Chimie*, **2005**, 8, 765–772..
- (S3) M. Zhao, J. Chen, B. Chen, X. Zhang, Z. Shi, Z. Liu, Q. Ma, Y. Peng, C. Tan, X.-J. Wu and H. Zhang, *JACS*, **2020**, 142, 8953–8961.

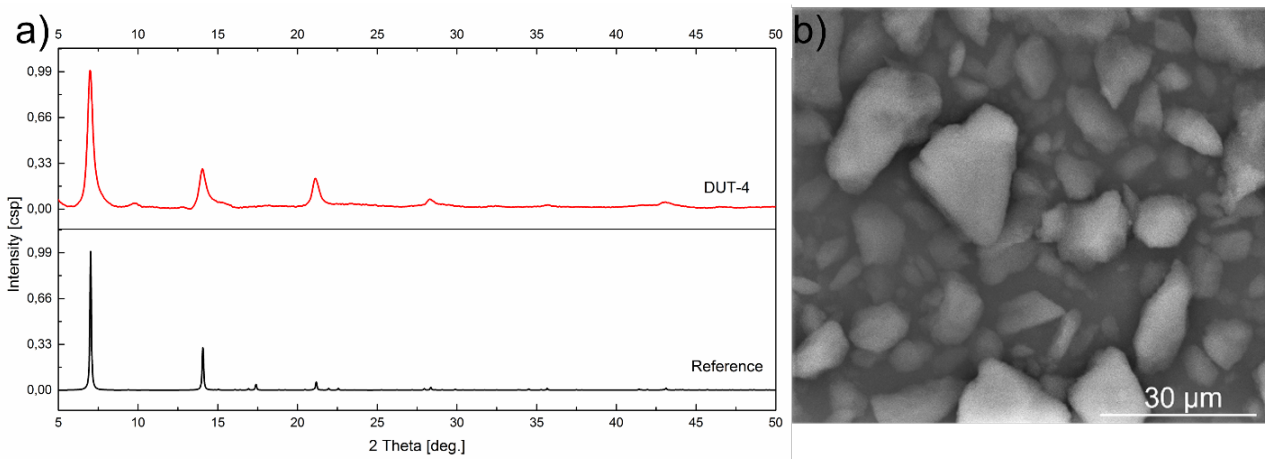


Figure S1: a) Powder X-ray diffractogram of DUT-4 (up) and simulated pattern from cif-File for CCDC 691978 for comparison (down); b) SEM image of DUT-4

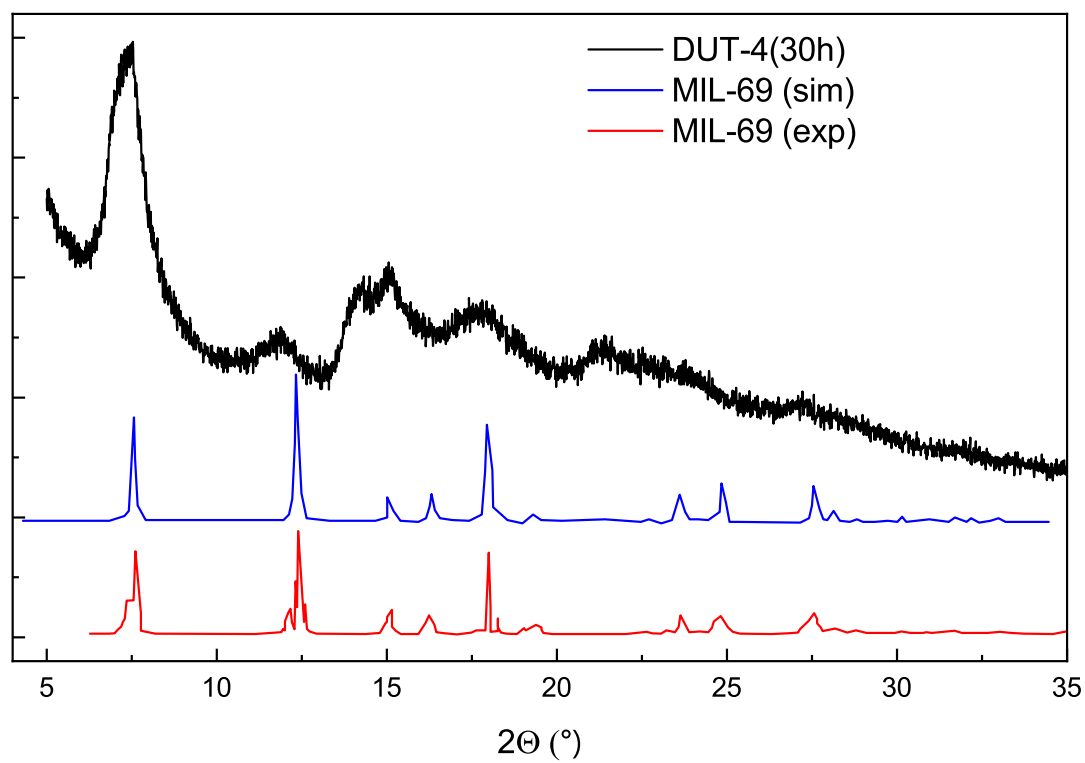


Figure S2: Comparison of modified DUT-4 PXRD data with calculated XRD MIL-69^{S3} and experimental XRD MIL-69.^{S2}

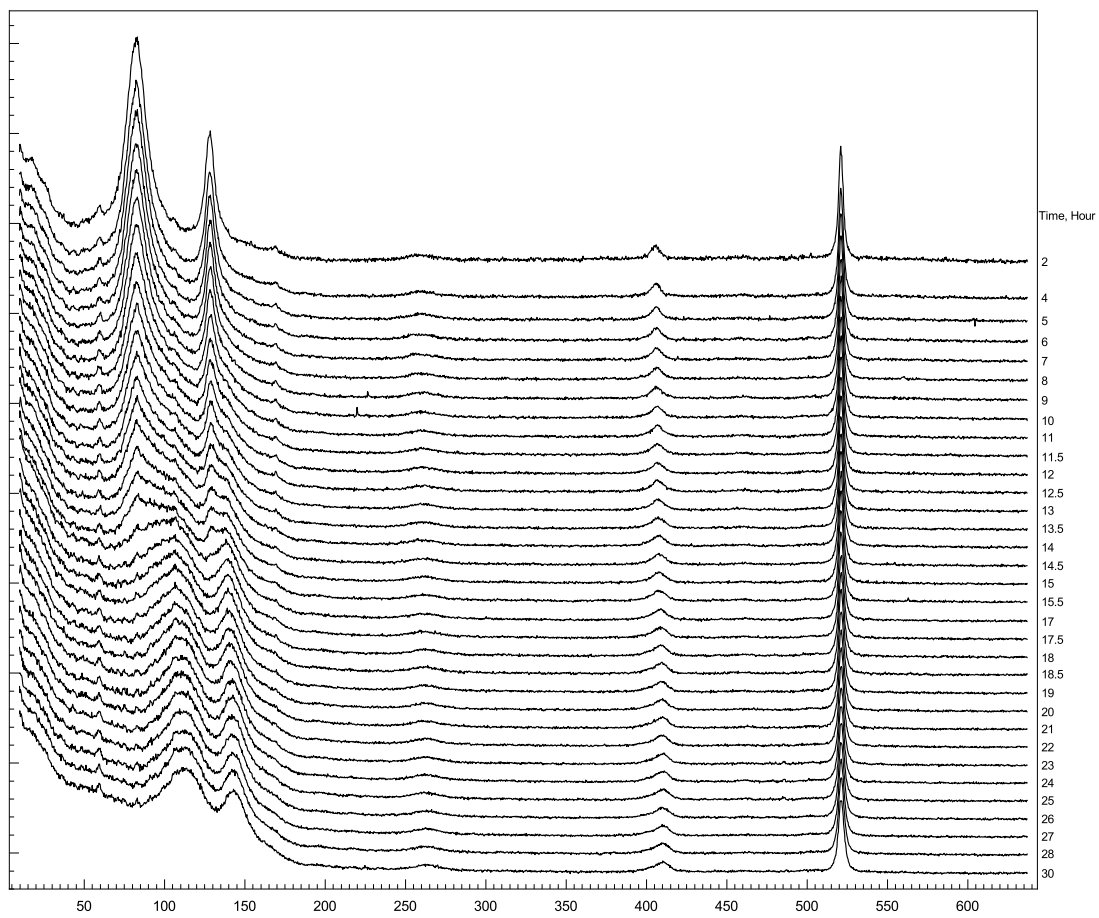


Figure S3: Transformation of low-wavenumber region Raman spectra DUT-4 over time.

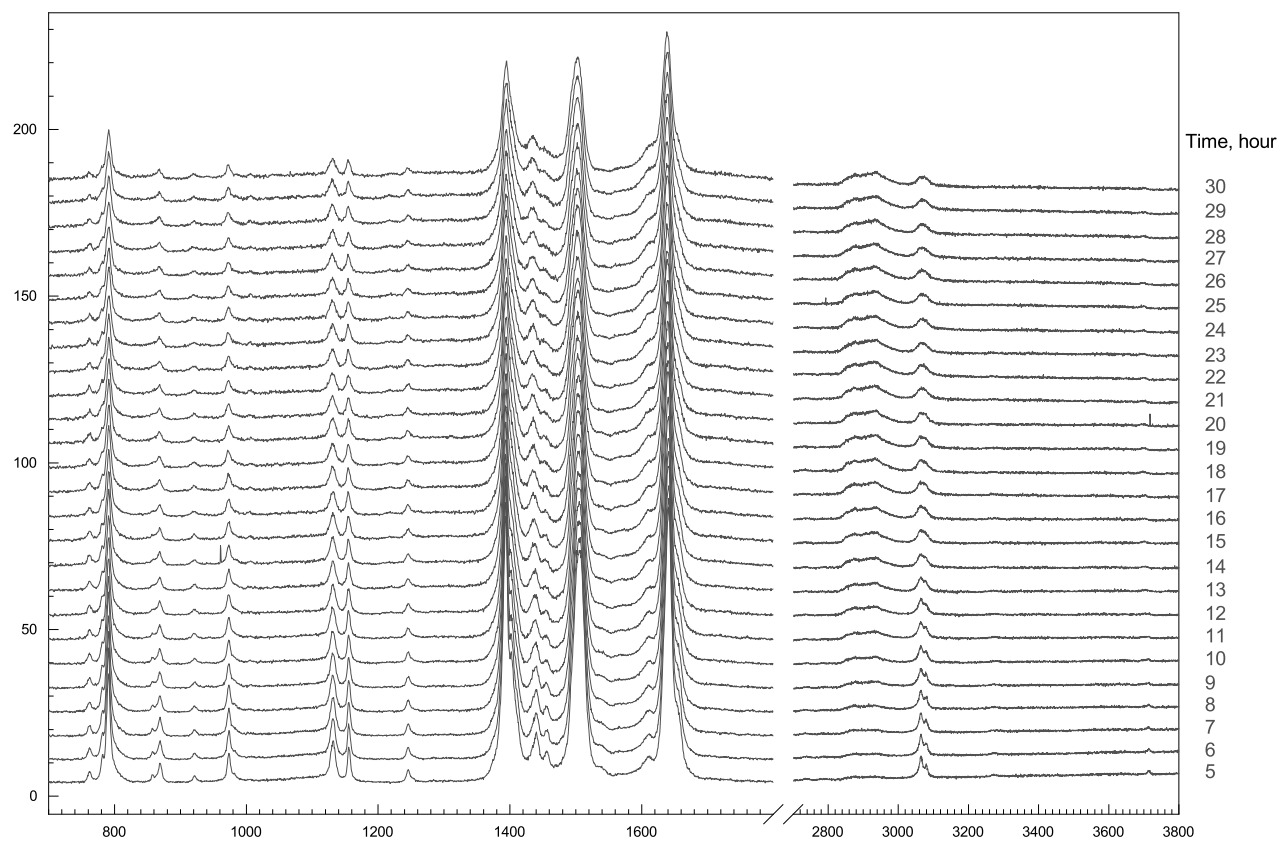


Figure S4: Transformation of fingerprint and high wavenumber region Raman spectra DUT-4 over time.

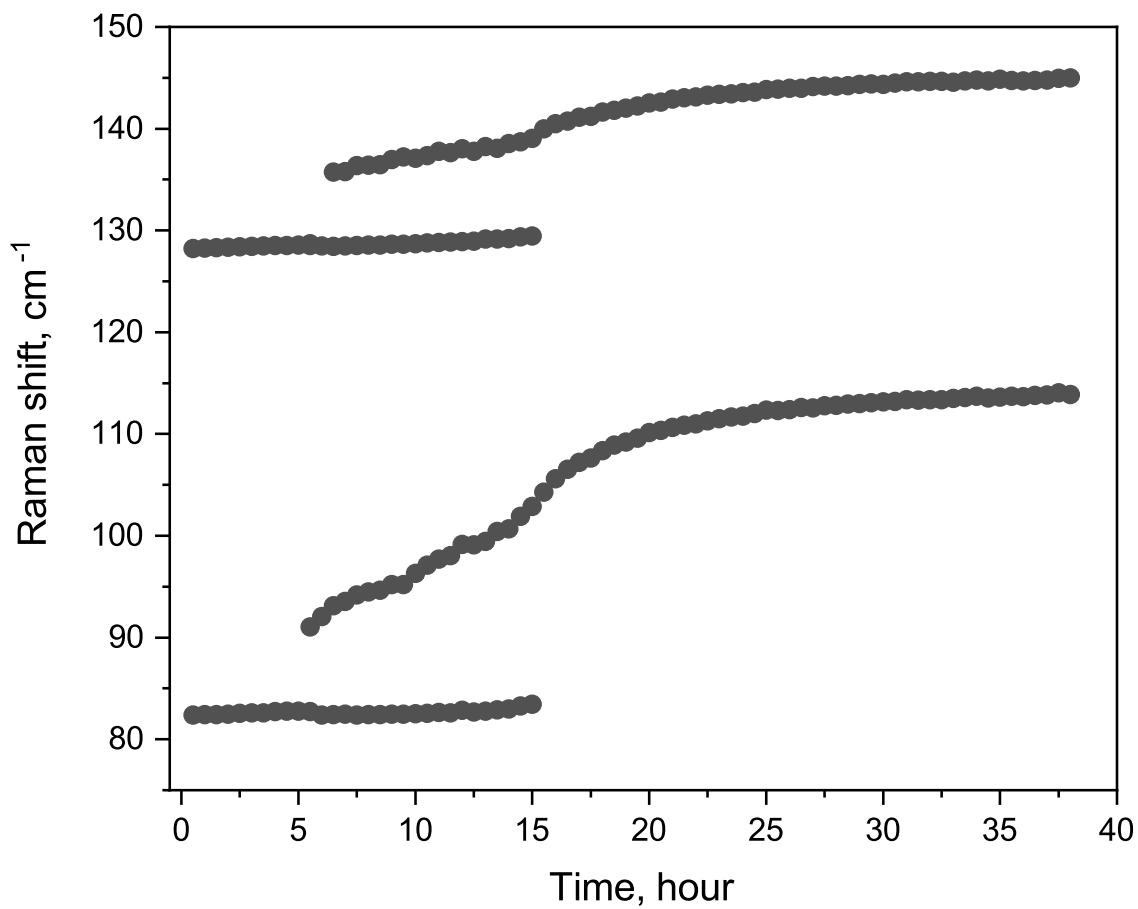


Figure S5: Dependence low-wavenumber line position over time

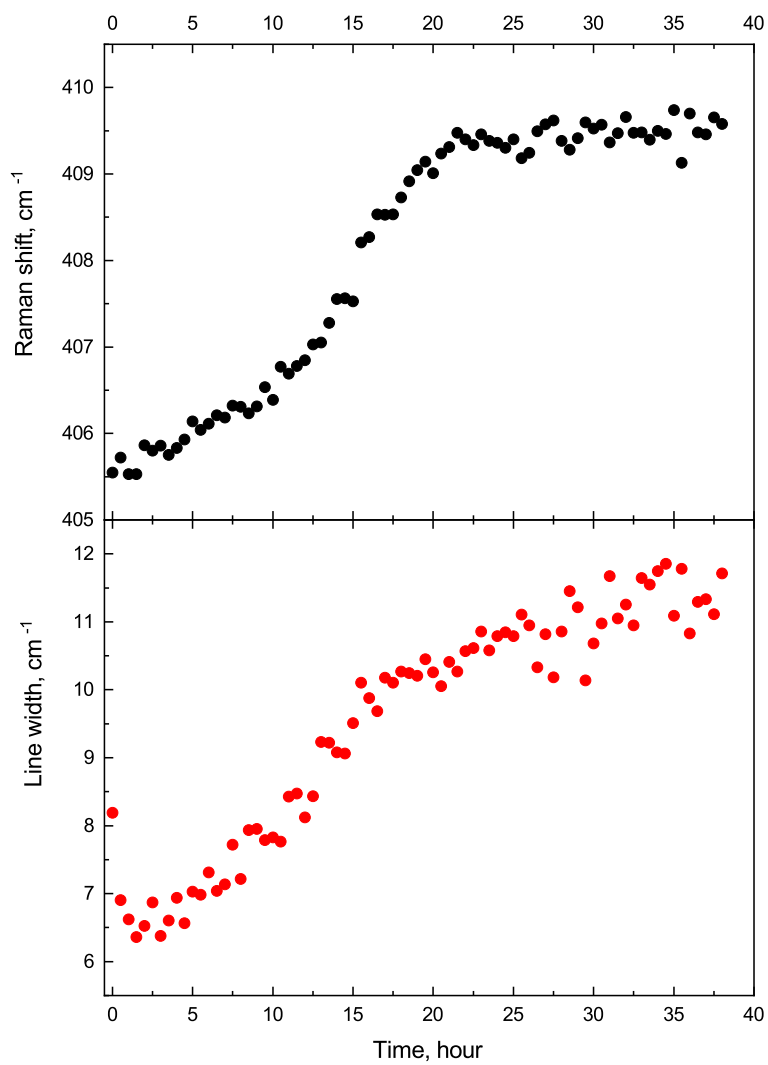


Figure S6: Dependence position and FWHM line at 405 cm⁻¹ over time

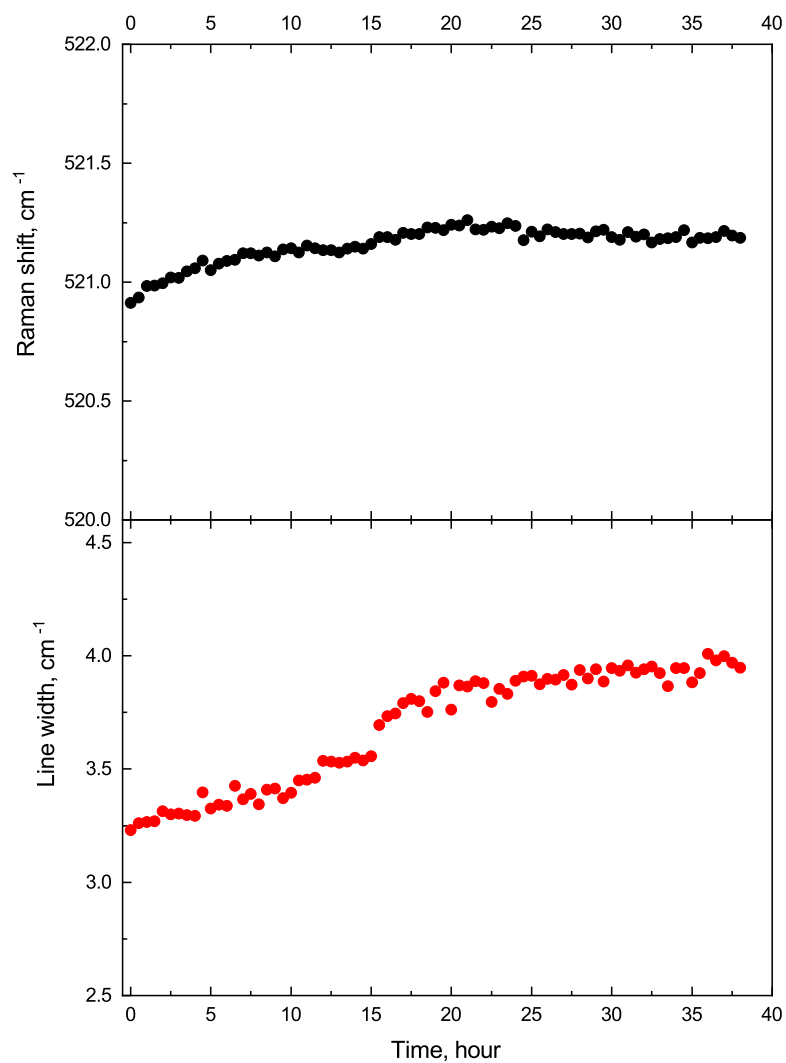


Figure S7: Dependence position and FWHM line at 521 cm⁻¹ over time

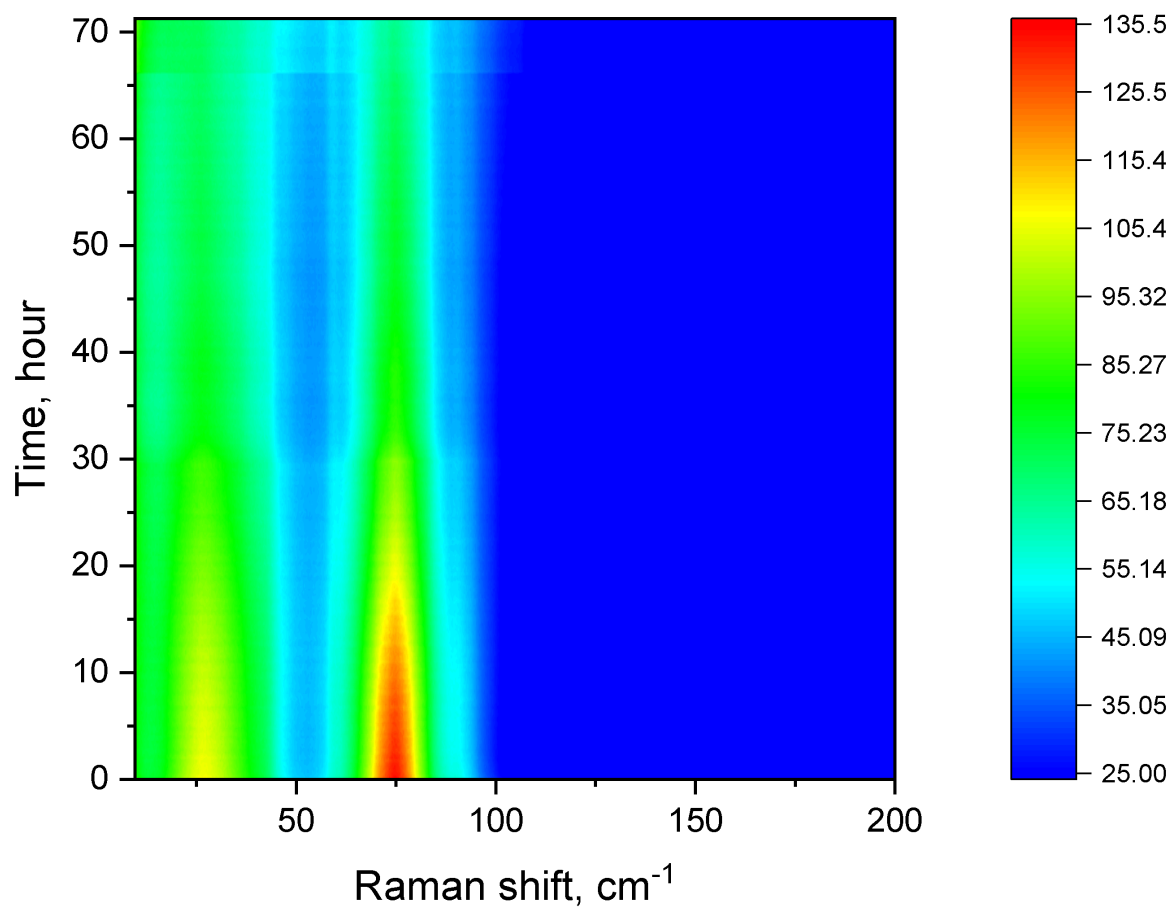


Figure S8: Map of the low-wavenumber region Raman spectra DUT-5 over time.

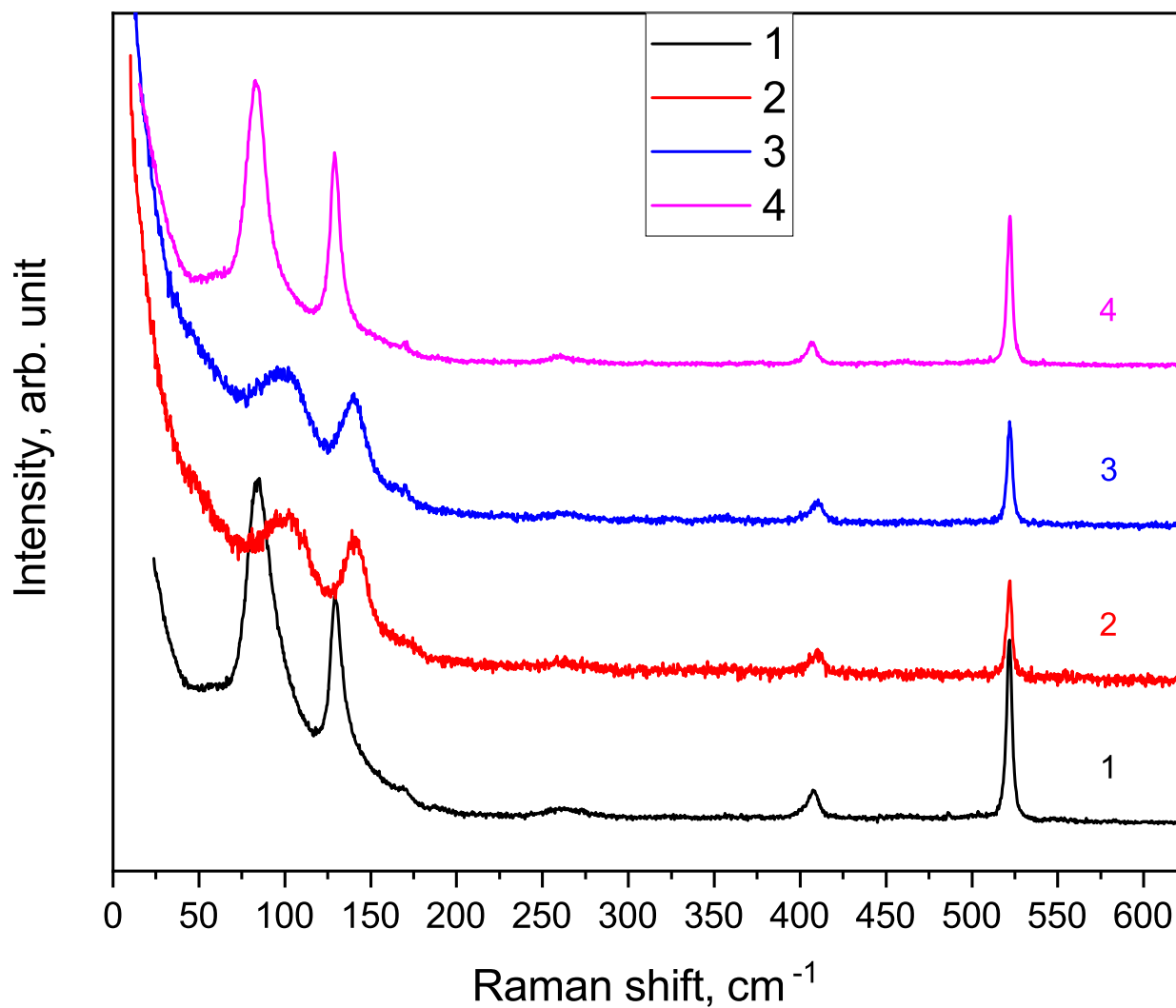


Figure S9: Raman spectra of DUT-4 during wet gas flow experiment. 1 – initial state. 2 – after wet argon gas (humidity 60%) flow 22 hour. 3 – after held at low (1 mBar) vacuum for 3 hour. 4 – after held at low vacuum (1 mBar) for 18 hour.

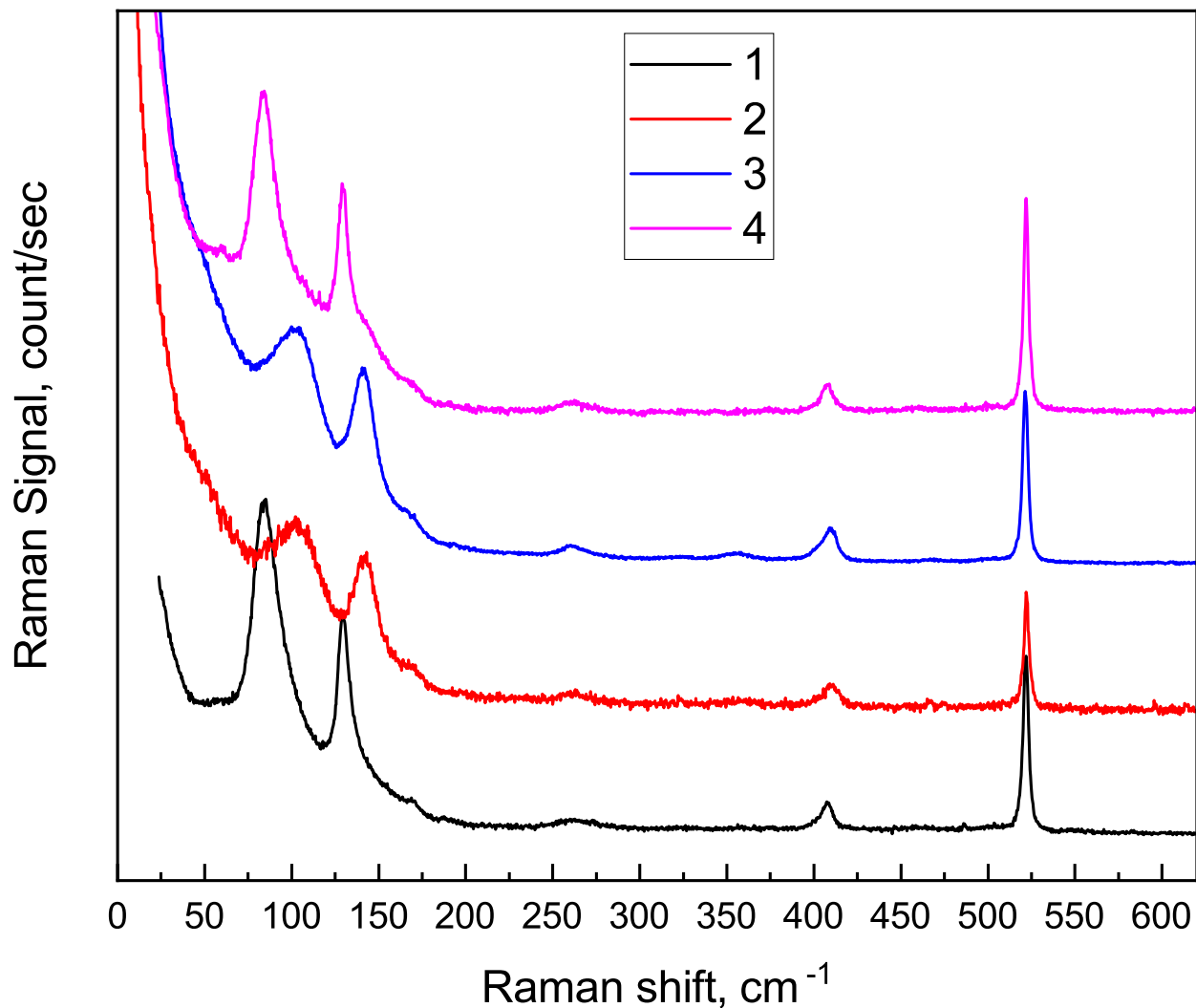


Figure S10: Raman spectra of DUT-4 during high humidity experiment. 1 – initial state. 2 – after storing above water bath (humidity 100%) for 4hour. 3 – after held at dry box (desiccator with P₂O₅ as desiccant) for 3 hour. 4 – after held at vacuum (10⁻³ mBar) for 4 hour.

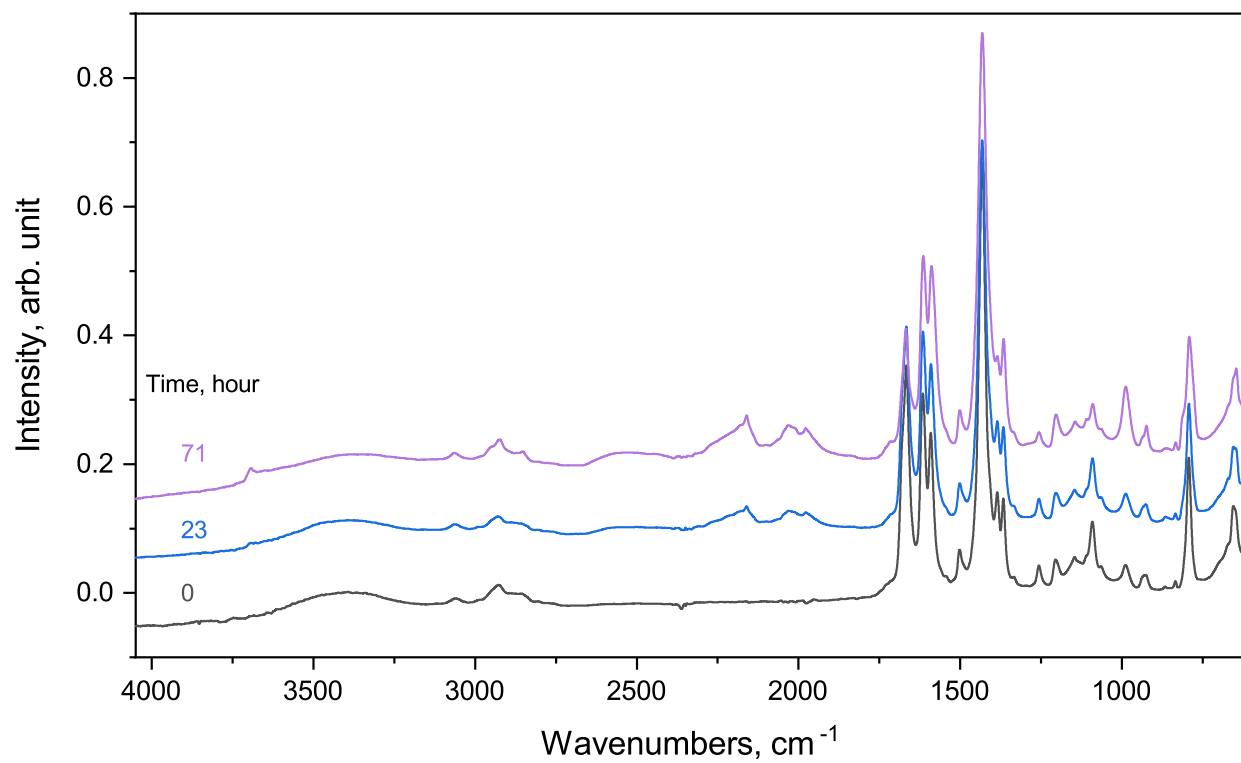


Figure S11: FTIR spectra of DUT-4 with diferent exposition time.

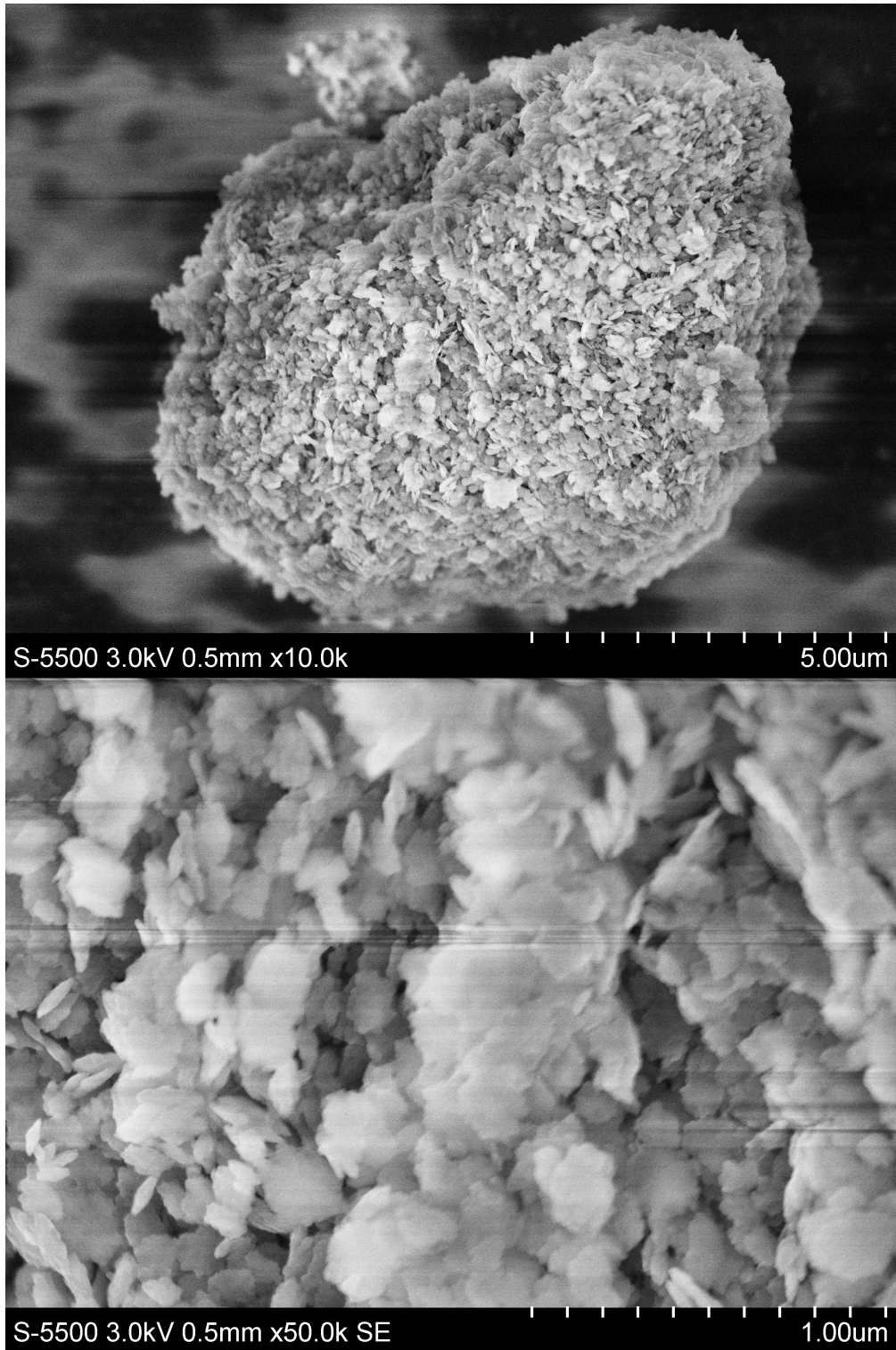


Figure S12: SEM micrographs of DUT-4 before exposure at ambient conditions.

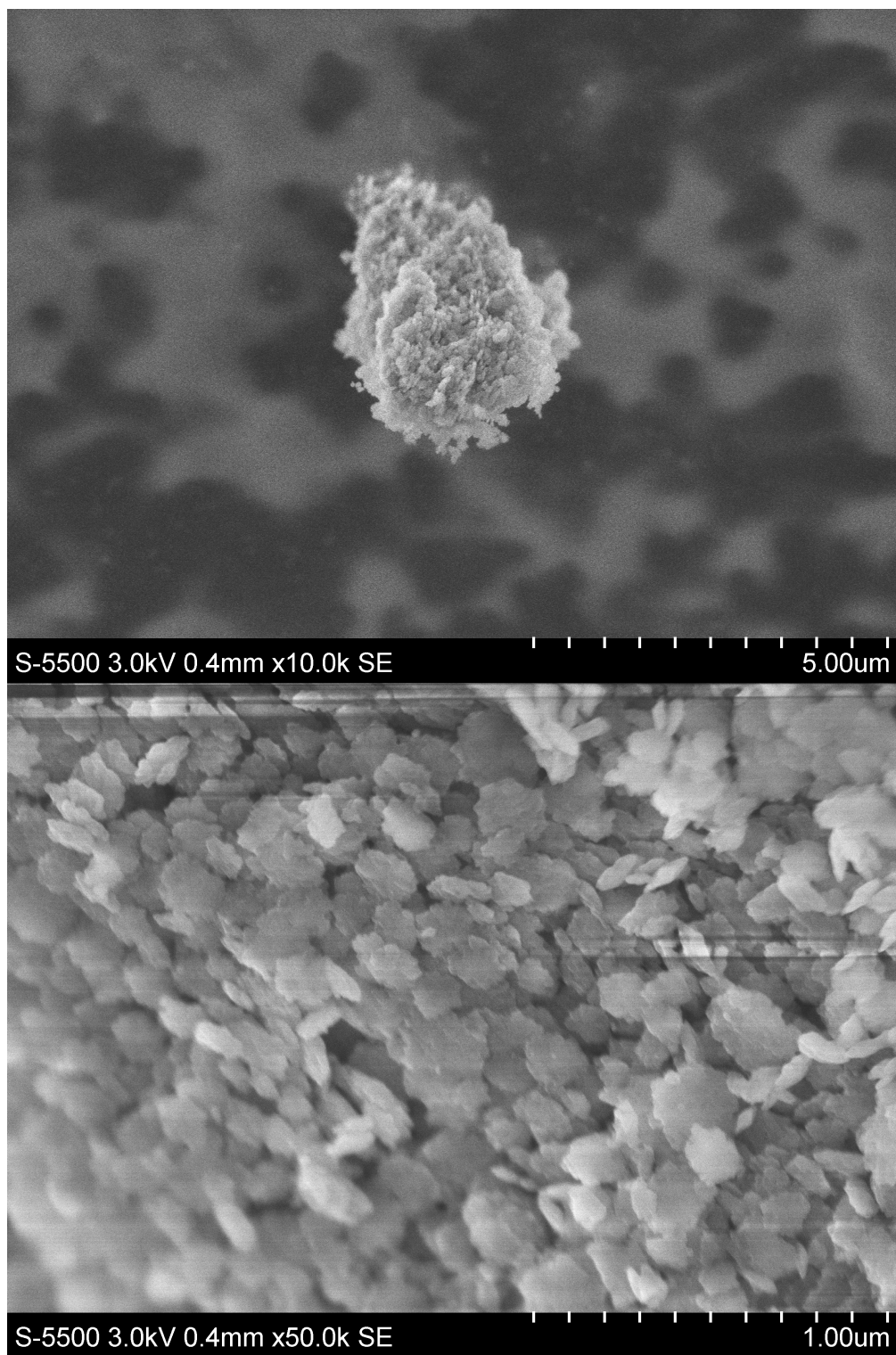


Figure S13: SEM micrographs of DUT-4 after exposure at ambient conditions.

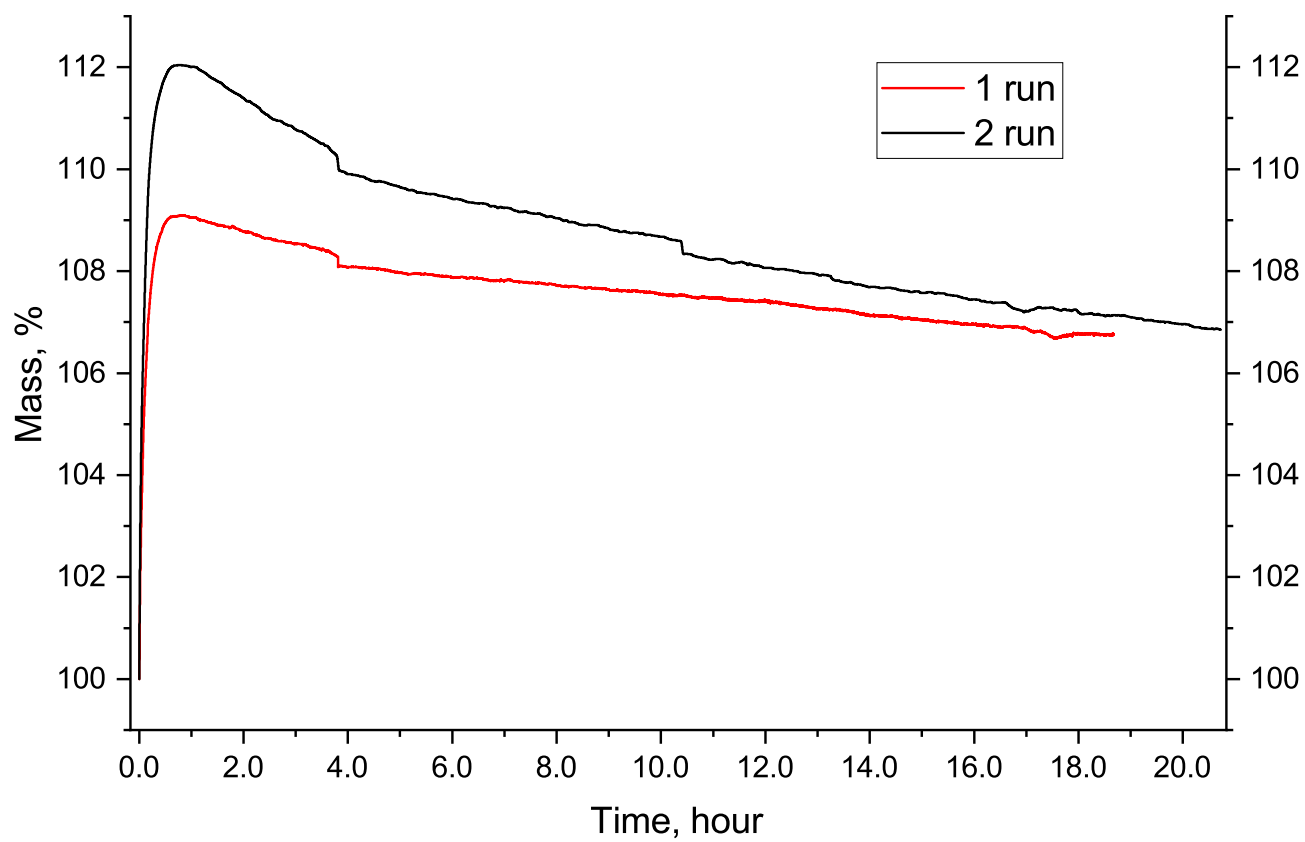


Figure S14: Synchronous thermal analysis. 1 run - sample in wet argon gas flow (humidity 65%); 2 run - the same condition, but before the experiment sample was held in a vacuum.

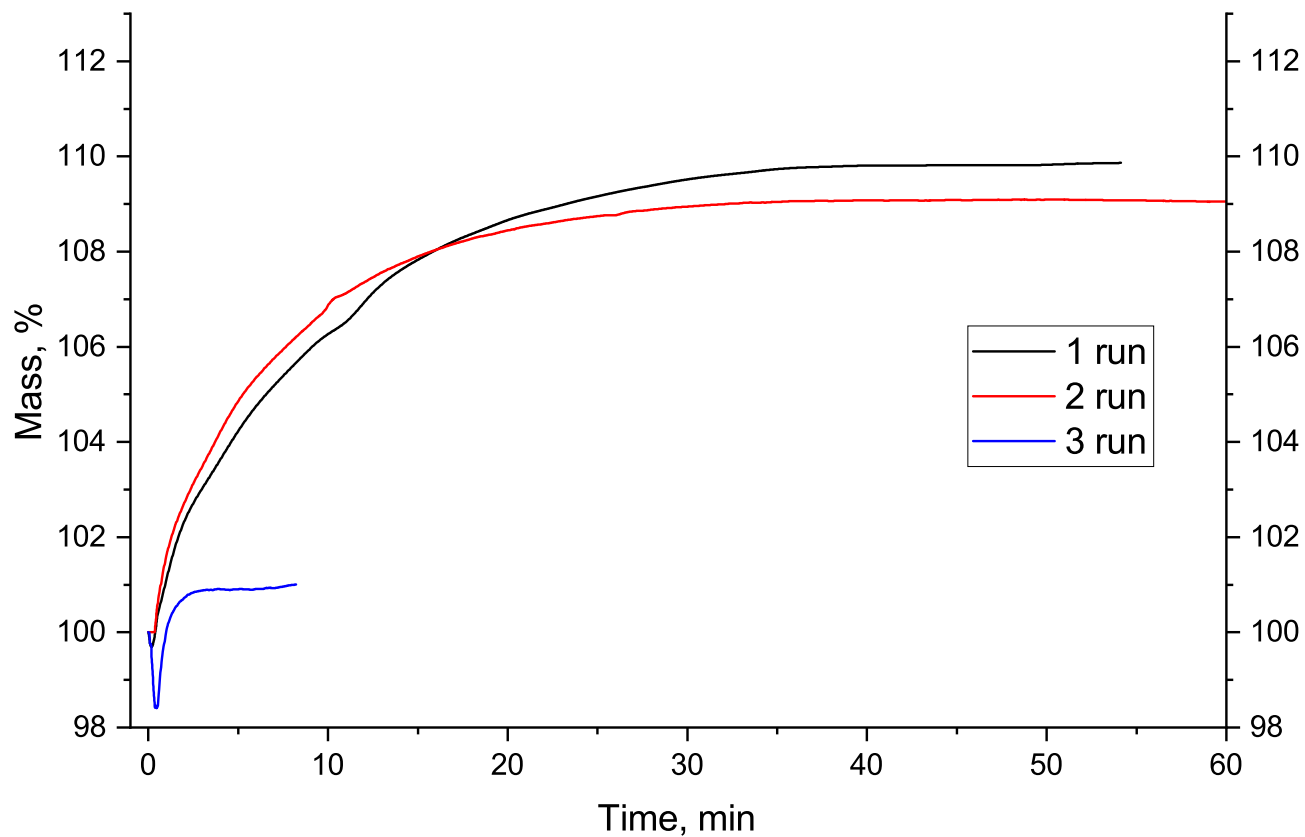


Figure S15: Synchronous thermal analysis. 1 run - sample in wet argon gas flow (humidity 65%); 2 run - the same condition, half of the sample of the 1-run sample before the experiment was held in a vacuum; 3 run - the same condition, the second half of 1-run sample without prior vacuumed.