Electronic Supplementary Information for Paper

Exceptional adsorption-induced cluster and network deformation in the flexible metal-organic framework DUT-8(Ni) observed by *in situ* X-ray diffraction and EXAFS

Volodymyr Bon,^a Nicole Klein,^{a,e} Irena Senkovska,^a Andreas Heerwig,^{a,f} Jürgen Getzschmann,^a Dirk Wallacher,^b Ivo Zizak,^c Maria Brzhezinskaya,^c Uwe Mueller,^d and Stefan Kaskel^a

^a Inorganic Chemistry I, Dresden University of Technology, Bergstrasse 66, 01069 Dresden, Germany. Fax: +49 (351) 463 37287; E-mail: <u>stefan.kaskel@chemie.tu-dresden.de</u>

^b Department Sample Environments, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner Platz 1, Berlin, Germany.

^c Institute of Nanometer Optics and Technology, Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Str. 15, 12489 Berlin, Germany.

^d Macromolecular Crystallography Group, Institute Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Str. 15, 12489 Berlin, Germany.

^ePresent Address: Fraunhofer Institute for Material and Beam Technology, IWS, Winterbergstraße 28, 01277 Dresden, Germany

^fPresent Address:Physical Chemistry, Measurement and Sensor Technology, Technische Universität Dresden, Eisenstuckstr. 5, 01069 Dresden, Germany

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1. Experimental data for single crystal X-ray diffraction of DUT-8(Ni) cp

The microcrystal of activated DUT-8(Ni) was glued to the wall of the capillary in inert atmosphere. Afterwards the capillary was sealed with wax. The data collection was performed at Helmholtz Zentrum Berlin für Materialien and Energie (MX beamline BL14.2).¹ The synchrotron radiation with energy of 14 kEv ($\lambda = 0.88561$ Å) was used for the data collection. The data were collected at room temperature using φ -scan technique ($\Delta \varphi = 1^{\circ}$). Image frames were integrated using the Mosflm 1.0.5 software.² Obtained intensities were scaled with the Scala program. The crystal structure was solved in *P*1 space group by direct methods using SHELXTL program package.³ Because of poor scattered crystal as well as disorder in the crystal structure, only two nickel atoms and their coordination environment could be localized. The unit cell parameters are a = 6.7372(24) Å, b = 8.0420(28) Å, c = 11.9468(43) Å, $\alpha = 90.339(15)^{\circ}$, $\beta = 104.014(17)^{\circ}$, $\gamma = 104.275(15)^{\circ}$. The atomic coordinates, detemined from the single crystal X-ray diffraction measurement are given in Table S1. The organic ligand molecules were simulated using Material Studio 5.0.⁴ Further refinement was performed using X-ray powder diffraction data.

Table	S1.	Atomic	coordinates	for	DUT-8(Ni)	ср	determined	from	single	crystal	X-ray
diffrac	tion.										

Atom	x	у	Z
Ni1	0.08290	0.04634	0.56136
Ni2	0.29973	0.39539	0.56838
01	0.56477	0.37728	0.72026
O2	0.31637	0.05239	0.71480
O3	-0.07933	0.17508	0.47136
O4	0.13056	0.37830	0.71343
O5	0.17022	-0.04104	0.41704
O6	0.10892	0.47795	0.43837
O7	0.39351	0.23466	0.44811
O8	-0.10370	0.07280	0.67040
N1	-0.17750	-0.17678	0.55972
N2	0.59970	0.57850	0.48030
C1	0.30911	0.11455	0.39112
C2	-0.06967	0.31070	0.39334
C3	0.05088	0.23854	0.69411

2. In situ adsorption and X-ray powder diffraction study

The sample of DUT-8(Ni) was prepared as described in ref. 5. In order to get an optimal grain size for X-ray diffraction, the sample was milled in the mortar and sieved using 45 μ m sieves. The activated sample (20-30 mg) was filled into the sample holder for performing *in situ* experiments using nitrogen (77 K), *n*-butane (273 K), carbon dioxide (195 K), ethane (185 K), and ethene (169 K) as probe molecules. Measurements were carried out at the MAGS or KMC-2 beamlines at Helmholtz-Zentrum Berlin für Materialien und Energie (BESSY-II). All experiments were performed using recently constructed sample environment.⁶ The isothermal conditions were created using closed cycle He cryostat. The BELSORP-Max automated dosing system ensured the desired gas pressure as well as

connection with the diffractometer. All X-ray powder diffraction patterns were collected using the monochromatic radiation with E = 8048 keV (λ = 1.5406 Å) in transmission geometry using 2 θ scans. VÅNTEC-2000 2D area detector from Bruker was used for the collection of diffraction images. The image data were integrated using Datasqueeze 2.2 software.⁷ The phase content in all powder XRD patterns was estimated by the Reference Intensity Ratio method using the Match 1.11g software.⁸

3. In situ EXAFS measurements during adsorption of N2 at 77 K

The local environment of the Ni atoms was investigated on basis of the X-ray absorption spectra at the Ni K edge (8333 eV). The spectra in the energy range 8200 eV < E < 9000 eV were recorded at beamline KMC-2 of Helmholtz-Zentrum Berlin for Materialien und Energie. A constant step width of $\Delta k = 0.05$ Å⁻¹ was used. The absorption coefficient $\mu(E) = -\ln(C2/C1)$ of the DUT-8(Ni) sample and the reference (20 μ m Ni foil) μ ref(E)= -ln(C3/C2) was calculated from the intensities C1, C2 and C3 detected by ionisation chambers in front and behind the transmitted sample and reference materials. 25 mg of activated DUT-8(Ni) was loaded to the sample holder with thickness of 1 mm. The latter was put into the adsorption chamber and mounted to the closed cycled He-cryostat. The nitrogen adsorption isotherm was measured at 77 K using BELSORP-max automated dosing gas system, connected to the adsorption chamber by thin copper capillary. The EXAFS spectra were measured at the 5 points of interest.

Data processing, analyses and fits have been performed with the Demeter software package.⁹ The fits were performed in *R*-space in the 1.0 – 3.0 Å range over k^2 -weighted FT of the (*k*) functions performed in the 3.0-15.0 Å⁻¹ interval. A single ΔE_0 and a single S_0^2 have been optimized for all SS (single scattering) paths used in fit. Whereas ΔR (change in half path length) and σ^2 (Debye-Waller factor) were fitted individually for each scattering pair.

The series of electron scattering paths for the first shell of Ni atom were calculated from the crystal structures of both **cp** and **lp** phases using FEFF Version 6 of the Artemis software. In the case of **cp** phase the three Ni—O SS paths with similar Ni-O distance were averaged and fitted with degeneracy parameter of 3 in order to increase the data/parameter ratio. The SS paths with longer Ni—O distance as well as Ni—N and Ni—Ni paths are fitted separately with degeneracy parameter of 1. In the case of N₂@DUT-8(Ni) **lp** phase, Ni—O and Ni—C_{carboxylate} paths were fitted with degeneracy parameter of 4, whereas Ni—N and Ni—Ni paths were treated the same as in **cp** phase. The result of the fit is given in Table S2.

Table S2. Fit parameters for the EXAFS data.

Sample conditions	DUT-8(Ni) cp	DUT-8(Ni) lp
Temperature	77 K	77 K
<i>R</i> -factor	0.0089	0.0094
Independent points	14	16
Number of variables	10	9
S_0^2	1.385 ± 0.065	0.488 ± 0.048
E_{0}	-13.755 ± 1.324	1.378 ± 0.828
$R_{\rm Ni-O1}$ (Å)	$2.0608 \pm 0.004 (N = 3)$	$2.017 \pm 0.007 (N = 4)$
σ^2 (Ni—O1) (Å ²)	-0.0036 ± 0.0047	0.00068 ± 0.00052
$R_{\rm Ni-O}$ (Å)	$1.958 \pm 0.019 (N = 1)$	-
σ^2 (Ni—O2) (Å ²)	-0.0053 ± 0.0031	
$R_{\rm Ni-N}$ (Å)	$1.895 \pm 0.033 (N = 1)$	$1.902 \pm 0.035 (N = 1)$
σ^2 (Ni—N) (Å ²)	-0.0026 ± 0.0011	0.0017 ± 0.0014
$R_{\rm Ni-Ni}$ (Å)	$2.7591 \pm 0.0149 (N = 1)$	$2.660 \pm 0.015 (N = 1)$
σ^2 (Ni—Ni) (Å ²)	0.0073 ± 0.0017	0.0055 ± 0.0016
$R_{\rm Ni-C}$ (Å)	-	$2.926 \pm 0.015 (N = 4)$
σ^2 (Ni—C) (Å ²)		0.0017 ± 0.0014

4. Experimental data and Rietveld plots for DUT-8(Ni) cp phase

The unit cell parameters for the Pawley refinement were taken from the results of single crystal X-ray diffraction measurements on a microcrystal. For the refinement of the profile parameters, the Thompson-Cox-Hasting function was used. The profile asymmetry was corrected using Berrar-Baldinozzi correction. After the refinement of the profile, the starting model was simulated in the Material Studio 5.0 visualization tool using the coordinates for the Ni atoms, obtained from the single crystal X-ray diffraction study. Two structural models in the space groups P1 and $P^{\overline{1}}$ were simulated for the Rietveld refinement. Because of inappropriate ratio of observed reflection's intensity in the XRPD to the structural parameters if every atom is considered as independent, the rigid body constraints for naphtalene rings, carboxylate groups and dabco molecules were used in the refinement. The nickel atoms (as main scattering units in the structure) were refined independently. The combined Rietveld and energy refinement procedure, involving 1 % of energy contribution, was used. Although the centrosymmetric space group would be more appropriate from the symmetry point of view and data/parameters ratio, the refinement in the $P^{\overline{1}}$ does not result in the satisfactory fit. Therefore, the structure was refined in the P1 space group with pretty good fit for all of the reflections. It should be mentioned that non centrosymmetric space groups are often chosen for the refinement of low symmetrical contracted phases. For example, the MIL-53(Cr) It phase was refined in the non centrosymmetric Cc space group although additional crystallographic symmetry is present. The detailed path used for the crystal structure solution and refinement is shown in Fig. S1.



Single crystal X-ray diffraction data

Triclinic P1 a = 6.737(2) Å, b = 8.042(3) Å, c = 11.947(4) Å, $\alpha = 90.339(15)^\circ$, $\beta = 104.014(17)^\circ$, $\gamma = 104.275(15)^\circ$

Structure simulation and geometry optimization

Triclinic P1 a = 6.737 Å, b = 8.042 Å, c = 11.947 Å, $\alpha = 90.339^\circ$, $\beta = 104.014^\circ$, $\gamma = 104.275^\circ$

Rigid body Rietveld refinement

Triclinic P1 a = 6.947(3) Å, b = 8.181(4) Å, c = 12.172(6) Å, $\alpha = 91.14(2)^\circ$, $\theta = 103.87(2)^\circ$, $\gamma = 104.55(2)^\circ$

Figure S1. The path used for the structure solution and refinement of DUT-8(Ni) cp.

Crystal data for DUT-8(Ni) **cp** (Cu*K* $\alpha 1$, $\lambda = 1.5406$ Å): C₃₀H₂₄N₂Ni₂O₈, $M_r = 657.89$, triclinic *P*1, a = 6.947(2) Å, b = 8.181(2) Å, c = 12.172(3) Å, $\alpha = 91.14(3)^{\circ}$, $\beta = 103.87(4)^{\circ}$, $\gamma = 104.55(4)^{\circ}$, V = 647.7(2) Å³, Z = 1, $D_c = 1.687$ g cm⁻³, 3 motion groups, 17 degrees of freedom, 2θ range 5-50°, $R_p = 0.0434$, $R_{wp} = 0.0628$; CCDC-1034317, contains the supplementary crystallographic data for DUT-8(Ni). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif. Final Rietveld refinement plot is shown in Fig. S2.



Figure S2. Rietveld plot for DUT-8(Ni) cp.

5. Experimental data and Rietveld plot for C₂H₆@DUT-8(Ni) IP1 phase

The XRPD measured at $p/p_0 = 0.61$ was used for the pattern indexing procedure, performed using *Xcell* program, implemented into the Material Studio 5.0 package.⁴ From the variety of possible unit cells, the write one was chosen after the analysis of figure of merits, given by the program in combination with the juxtaposition of the unit cell volume with the **cp** phase, as made phase and correlation with the gas uptake in the isotherm. The starting model has been constructed in Material Studio visualizer using *P*1 unit cell setting with unit cell parameters and atom positions adopted from the **cp** phase structure. The structural model was optimized using geometry optimization tool of Material Studio 5.0 using Universal Force Field.⁴ The obtained structural model was "filled" with 9 ethane molecules per unit cell (the amount was calculated from the adsorption isotherm) and optimized again. The created structural model was subjected to the rigid body Rietveld refinement with energy increment of 2 %. Naphtalene unit, carboxylic groupc, dabco molecules, and ethylene molecules were refined as rigid bodies. Both nickel atoms were refined independently. Because of impurity of **lp** phase, the 2θ ranges from 6.30° to 7.00° and from 7.30° to 7.60° were excluded from the refinement.

Crystal data for C₂H₆@DUT-8(Ni) **IP1** (synchrotron, $\lambda = 1.5406$ Å): C₄₈H₇₈N₂Ni₂O₈, M = 928.50, triclinic P1, a = 9.478(1) Å, b = 11.066(1) Å, c = 12.694(1) Å, $a = 101.54(1)^{\circ}$, $\beta = 10.54(1)^{\circ}$, β

92.06(1)°, $\gamma = 100.59(1)°$, V = 1278.5(2) Å³, Z = 1, $D_c = 1.206$ g cm⁻³, 14 motion groups, 75 degrees of freedom, 2θ range 5-50°, $R_p = 0.1144$, $R_{wp} = 0.1596$; CCDC-1034322 contains the supplementary crystallographic data for DUT-8(Ni). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data request/cif. Final Rietveld refinement plot is shown in Fig. S3.



Figure S3. Rietveld plot for C₂H₆@DUT-8(Ni) **IP1**.

6. Experimental data and Pawley plot for C₂H₄@DUT-8(Ni) IP2 phase

In the case of **IP2** phase, the indexing of XRPD, containing predominantly single **IP2** phase was performed using X-Cell utility of Material Studio software. The unit cell was chosen using two criteria: goodness of fit parameters and crystallographic information available about **cp** and **IP1** phases. Unfortunately the quality of XRPD patterns was not sufficient for the Rietveld refinement, therefore only Pawley fit of the unit cell is presented. Pawley fit data for C₂H₄@DUT-8(Ni) **IP2** (synchrotron, $\lambda = 1.5406$ Å): C₄₆H₅₆N₂Ni₂O₈, triclinic *P*1, *a* = 9.612(1) Å, *b* = 11.254(1) Å, *c* = 12.556(1) Å, *a* = 103.50(1)°, $\beta = 94.53(1)°$, $\gamma = 98.33(1)°$, V = 1297.8(2) Å³, U = 2.144 ± 0.168, V = -0.443 ± 0.031, W = 0.0237 ± 0.002, X = 0.471 ± 0.042, Y = 0.0533 ± 0.003, Zero shift - 0.00104, Berar-Baldinozzi asymmetry correction P1 = 3.308, P2 = 0.647, P3 = -6.676, P4 = -1.307, 2θ range 5-50°, $R_p = 10.62$, $R_{wp} = 17.01$. Final Pawley refinement plot is shown in Fig. S4.



Figure S4. Pawley plot for C₂H₄@DUT-8(Ni) **IP2**.

7. Experimental data and Rietveld plot for C₂H₄@DUT-8(Ni) lp phase

Since the XRD pattern of C₂H₄@DUT-8(Ni) phase at $p/p_0 = 0.92$ does not match the theoretical patterns of "as made" DUT-8(Ni), the pattern was indexed using Xcell program in Material Studio 5.0.4 The best match was obtained for the monoclinic unit cell with the unit cell parameters and cell volume very similar to the cell parameters of as made tetragonal phase (monoclinic angle 94°). The analysis of the systematic extinctions suggests $P2_1/m$ space group. The structural model for the Rietveld refinement was created in Material Studio 5.0 visualizer using "as made" structure as a starting model.⁴ After optimization of the geometry, rigid body Rietveld refinement was performed following the same procedure as it was used for DUT-8(Ni) cp phase with only difference that additional 9 ethylene molecules per paddle-wheel unit were placed into the pore. Crystal data for C₂H₄@DUT-8(Ni) lp (synchrotron, $\lambda = 1.5406$ Å): C₄₆H₅₆N₂Ni₂O₈·9C₂H₄, M = 1050.31, monoclinic $P2_1/m$, a = 20.405(1) Å, b = 16.497(1) Å, c = 9.347(1) Å, $\beta =$ 94.12(1)°, V = 3138.2(1) Å³, Z = 2, $D_c = 1.231$ g cm⁻³, 16 motion groups, 78 degrees of freedom, 2θ range 5-50°, $R_p = 0.1101$, $R_{wp} = 0.1471$; CCDC-1034320 contains the supplementary crystallographic data for C_2H_4 (a) DUT-8(Ni) lp. These data can be obtained free charge from the Cambridge Crystallographic of Data Centre via www.ccdc.cam.ac.uk/data request/cif. Final Rietveld refinement plot is shown in Fig. S5.



Figure S5. Rietveld plot for C_2H_4 (a)DUT-8(Ni) lp.

8. Experimental data and Rietveld plot for N₂@DUT-8(Ni) lp phase

The powder XRD pattern, measured at $p/p_0 = 0.95$ in the *in situ* adsorption experiment, does not match exactly the theoretical patterns of DUT-8(Ni) "as made" phase. Therefore, the pattern was indexed using Xcell program of Material Studio 5.0.⁴ As in the previous case, the indeing results in the monoclinic cell with very similar parameters and volume. The starting model for the Rietveld refinement was created in the similar way as described for C₂H₄@DUT-8(Ni) **lp** model, but 15 N₂ molecules were added into the pore. Because of the **cp** impurity presented, the 2θ range from 7.3° to 7.8° was excluded from the refinement. Crystal data for N₂@DUT-8(Ni) **lp** (synchrotron, $\lambda = 1.5406$ Å): C₄₆H₅₆N₂Ni₂O₈·15N₂, M = 1302.31, monoclinic $P2_1/m$, a = 18.657(1) Å, b = 18.736(1) Å, c = 9.433(1) Å, $\beta = 94.42(1)^\circ$, V =3287.6(1) Å³, Z = 2, D_c = 1.514 g cm⁻³, 21 motion groups, 97 degrees of freedom, 2θ range 5-50°, $R_p = 0.1450$, $R_{wp} = 0.1837$; CCDC-1034323 contains the supplementary crystallographic data for N₂@DUT-8(Ni) **lp**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>. Final Rietveld refinement plot is shown in Fig. S6.



Figure S6. Rietveld plot for N₂@DUT-8(Ni) lp.

9. Experimental data and Pawley plot for CO₂@DUT-8(Ni) lp phase

The XRD pattern measured during the *in situ* adsorption experiment at $p/p_0 = 0.96$ was subjected to the Pawley refinement after the successful indexing, performed using Xcell program of Material Studio 5.0 software. Due to the presence of the **cp** phase impurity, the 20 range from 7.3° to 7.7° was excluded from the calculations. Pawley fit data for CO₂@DUT-8(Ni) **lp** (synchrotron, $\lambda = 1.5406$ Å): monoclinic, a = 18.475(1) Å, b = 18.604(1) Å, c =9.431(1) Å, $\beta = 95.45(1)^\circ$, V = 3226.9(2) Å³, U = -0.134 ± 0.036, V = 0.089 ± 0.012, W = -0.002 ± 0.001 , X = 0.286 ± 0.029, Y = 0.041 ± 0.002, Zero shift -0.012, Berar-Baldinozzi asymmetry correction P1 = 5.441, P2 = 0.549, P3 = -10.883, P4 = -1.087, 20 range 5-50°, R_p = 0.0535, R_{wp} = 0.0867. The theoretical pattern was simulated using Material Studio 5.0 software assuming $P2_1/m$ space group and unit cell parameters, obtained from the Pawley refinement. Final Pawley refinement plot is shown in Fig. S7.



Figure S7. Pawley plot for CO₂@DUT-8(Ni) lp

10. Experimental data and Pawley plot for C₄H₁₀@DUT-8(Ni) lp phase

The PXRD pattern, measured at $p/p_0 = 0.95$ during the *in situ* adsorption experiment was used for the data analysis. As for all previous cases, the monoclinic unit cell with cell parameters, similar to all others **lp** phases was chosen. The 20 range $7.3 - 7.7^{\circ}$ was excluded from the Pawley refinement because of **cp** phase impurity. Pawley fit data for C₄H₁₀@DUT-8(Ni) **lp** (synchrotron, $\lambda = 1.5406$ Å): monoclinic, a = 18.520(1) Å, b = 18.191(1) Å, c = 9.409(1) Å, β $= 95.60(1)^{\circ}$, V = 3151.0(8) Å³, U = -0.262 ± 0.024, V = 0.126 ± 0.023, W = -0.0002, X = 0.191 ± 0.013 , Y = 0.014 ± 0.001, Z = -0.001 Zero shift -0.0003, Berar-Baldinozzi asymmetry correction P1 = 3.114, P2 = 0.758, P3 = -6.216, P4 = -1.515, 2 θ range 6-50°, $R_p = 0.1127$, R_{wp} = 0.1597. The theoretical pattern was simulated using Material Studio 5.0 software assuming $P2_1/m$ space group and unit cell parameters obtained from the Pawley refinement. Final Pawley refinement plot is shown in Fig. S8.



Figure S8. Pawley plot for C_4H_{10} @DUT-8(Ni) lp





Figure S9. In situ-powder XRD during adsorption of n-butane on DUT-8(Ni).

Table S2. Results of phase analysis of powder XRDs for *in situ n*-butane experiment at 273K.

Measuring point	DUT-8(Ni) cp, %	DUT-8(Ni) lp, %
1	99	1
2	99	1
3	95	5
4	80	20
5	63	37
6	47	53
7	33	67

12. Phase analysis for *in situ* adsorption of N₂ (77K)



Figure S10. *In situ* powder XRD patterns measured during adsorption of N_2 (77K) on DUT-8(Ni).

Measuring point	DUT-8(Ni) cp, %	DUT-8(Ni) lp, %
Evacuated 77 K	98	2
1	99	1
2	99	1
3	99	1
4	25	75
5	30	70
6	44	56
7	46	54
8	42	58
9	41	59

Table S4. Phase analysis of powder XRD patterns collected *in situ* during N₂ adsorption experiment at 77K.

Phase analysis for in situ adsorption of CO₂ (195 K)



Figure S11. *In situ* powder XRD patterns measured during adsorption of CO_2 (195 K) on DUT-8(Ni).

Table S5. Phase analysis of powder XRD patterns measured during *in situ* CO₂ adsorption experiment at 195K.

	DUT-8(Ni) cp, %	DUT-8(Ni) lp, %
evacuated	98	2
1	98	2
2	100	0

3	100	0
4	98	2
5	92	8
6	83	17
7	69	31
8	59	41
9	49	51
10	43	57
11	41	59
12	36	64

13. Phase analysis for *in situ* adsorption of ethane (185 K)



Figure S12. *In situ* powder XRD patterns measured during adsorption of ethane (185 K) on DUT-8(Ni).

	DUT-8(Ni) cp, %	DUT-8(Ni) IP1, %	DUT-8(Ni) lp, %
evacuated	98	0	2
1	99	0	1
2	97	2	1
3	72	28	0
4	25	75	0
5	19	81	0
6	12	88	0
7	8	92	0
8	8	92	0
9	6	88	6
10	3	87	10
11	0	85	15
12	0	74	26
13	0	64	36

Table S6. Phase analysis of powder XRD patterns measured *in situ* during ethane adsorption experiment at 185 K.



14. Phase analysis for *in situ* adsorption of ethene (169K)

Figure S13. *In situ* powder XRD patterns measured during adsorption of ethane (169 K) on DUT-8(Ni).

Measuring point	DUT-8(Ni) cp, %	DUT-8(Ni) IP2, %	DUT-8(Ni) lp, %
1	98	0	2
2	99	0	1
3	99	0	1
4	99	0	1
5	87	12	1
6	86	13	1
7	46	53	1
8	0	71	29
9	0	71	29
10	0	40	60
11	0	38	62
12	0	33	67
13	0	32	68
14	0	0	100
15	0	96	4
16	0	98	2
17	0	99	1
18	0	99	1

Table S7. Phase analysis of powder XRD patterns measured during *in situ* ethene adsorption experiment at 169K.

15. PXRDs, containing DUT-8(Ni) cp, IP1 and C₂H₆@DUT-8(Ni) lp



Figure S14. Experimental PXRD patterns measured during adsorption of ethane at 185 K: in blue – XRD at $p/p_0 = 0.21$ (DUT-8(Ni) cp), in red XRD at $p/p_0 = 0.61$ (IP1), in light green XRD at $p/p_0 = 0.99$ (mixture of C₂H₆@DUT-8(Ni) lp and IP1).

16. PXRDs containing DUT-8(Ni) cp, IP2 and C₂H₄@DUT-8(Ni) lp



Figure S15. Experimental XRD patterns measured during adsorption of ethane at 169 K: in blue XRD at $p/p_0 = 0.11$ (DUT-8(Ni) **cp**), in red XRD at $p/p_0 = 0.008$ (desorption) (**IP2**), in light green XRD at $p/p_0 = 0.92$ (adsorption) (C₂H₄@DUT-8(Ni) **lp**).

17. PXRDs containing IP1 and IP2 phases



Figure S16. Experimental XRD patterns of **IP1** measured at $p/p_0 = 0.61$ 185 K (ethane adsorption 185 K) in blue, and of **IP2** measured at $p/p_0 = 0.008$ (ethylene desorption 169 K) in red.

18. PXRDs containing DUT-8(Ni) as made (P4/n) and N₂@DUT-8(Ni) ($P2_1/m$).



Figure S17. Theoretical PXRD pattern of "as made" DUT-8(Ni) (green), experimental PXRD pattern of "as made" DUT-8(Ni) (blue), theoretical PXRD pattern of N₂@DUT-8(Ni) **lp** (violet), experimental PXRD pattern of N₂@DUT-8(Ni) **lp** measured at $p/p_0 = 0.95$ and 77K (red). (Reflection marked with asterisk belongs to the DUT-8(Ni) **cp** phase).

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