Electronic Supplementary Information (ESI)

Structural flexibility of a copper-based metal organic framework: sorption of C_4-hydrocarbons and *in situ*-XRD

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Tables

Table SI 1 Pore volumes of $^{3}_{\infty}$[$Cu_4(\mu_4\text{-}O)(\mu_2\text{-}OH)_2(Me_2trzpba)_4$] (**1**) for N_2/ 77 K and CO_2 /298 K sorption.

	After 1st pore filling		Saturation		Ref.
	p/p_0	V_{pore} / cm³ g⁻¹	p/p_0	V_{pore} / cm³ g⁻¹	
N_2 at 77 K	0.001	0.16	0.90	0.58	1
CO_2 at 298 K	0.050	0.13	0.90	0.53	
N_2 at 77 K	0.030	0.16	0.60	0.59	this study
CO_2 at 298 K	0.001	0.14	0.68	0.54	

Table SI 2 Physical properties including critical temperature (T_C), critical pressure (p_C), critical density (ρ_C), boiling point (T_b) and density at boiling point (ρ_b) of carbon dioxide, nitrogen and C_4-hydrocarbons.

	CO_2	**N_2**	***n*-butane**	**isobutane**	**1-butene**	**isobutene**
T_C / K	304.15	126.25	425.15	408.13	419.65	417.85
p_C / MPa	7.38	3.40	3.80	3.65	4.02	4.00
ρ_C / (g cm⁻³)	0.468	0.314	0.228	0.221	0.234	0.234
T_b / K	-	77.15	272.65	261.45	266.95	266.05
ρ_b / (g cm⁻³)	-	0.809	0.601	0.594	0.626	0.626

Table SI 3 Parameters for Langmuir-Fits for different temperatures with fixed N_{max} (283 K).

	283 K	**298 K**	**313 K**	**328 K**	**343 K**
			***n*-butane on 1 with fixed N_{max}**		
N_{max} / mmol g⁻¹			0.980		
b / kPa⁻¹	53.981	16.867	6.307	2.759	1.282
R^2	0.99954	0.99915	0.99927	0.99899	0.99902
			isobutane on 1 with fixed N_{max}		
N_{max} / mmol g⁻¹			0.858		
b / kPa⁻¹	54.111	18.294	6.585	2.887	1.428
R^2	0.99960	0.99985	0.99965	0.99957	0.99982
			1-butene on 1 with fixed N_{max}		
N_{max} / mmol g⁻¹			1.501		
b / kPa⁻¹	20.449	6.380	2.214	0.976	0.562
R^2	0.98974	0.98993	0.99116	0.98607	0.98716
			isobutene on 1 with fixed N_{max}		
N_{max} / mmol g⁻¹			2.124		
b / kPa⁻¹	7.415	3.267	1.377	0.598	0.305
R^2	0.99279	0.99904	0.99319	0.99589	0.98845

Figures

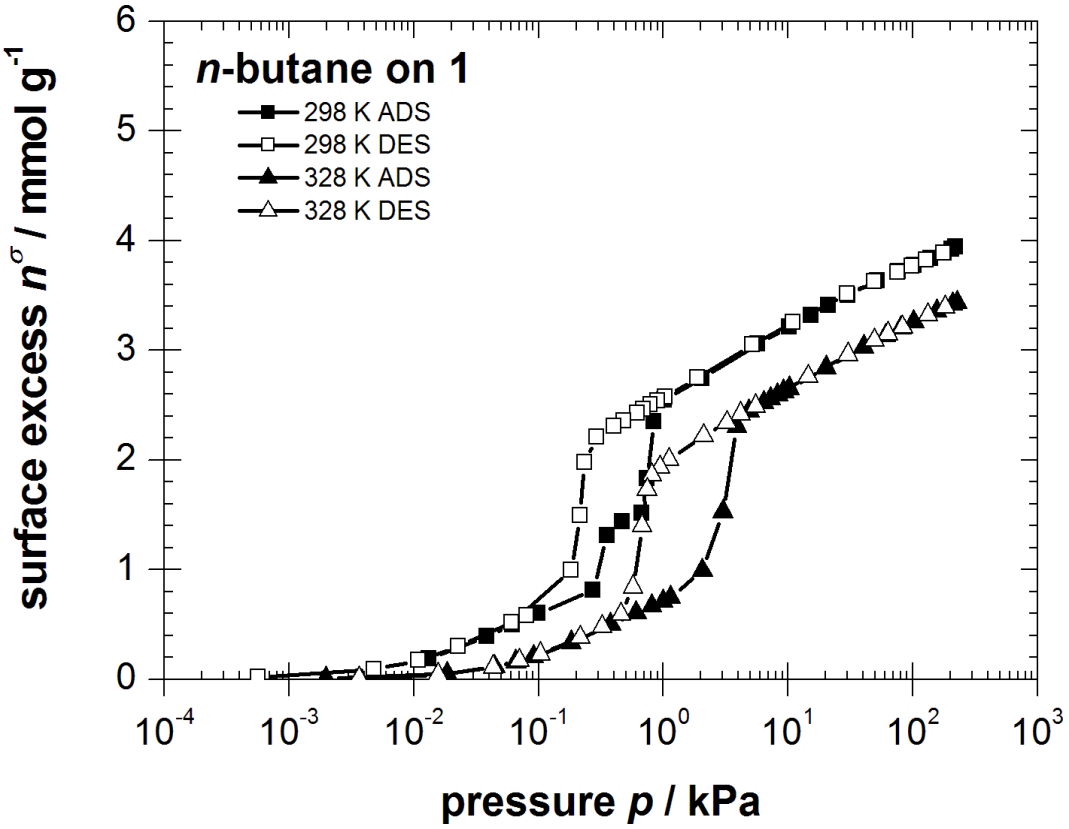

Fig. SI 1 Surface excess as a function of pressure for the sorption of *n*-butane on **1** at 298 K and 328 K (ADS: adsorption, DES: desorption).

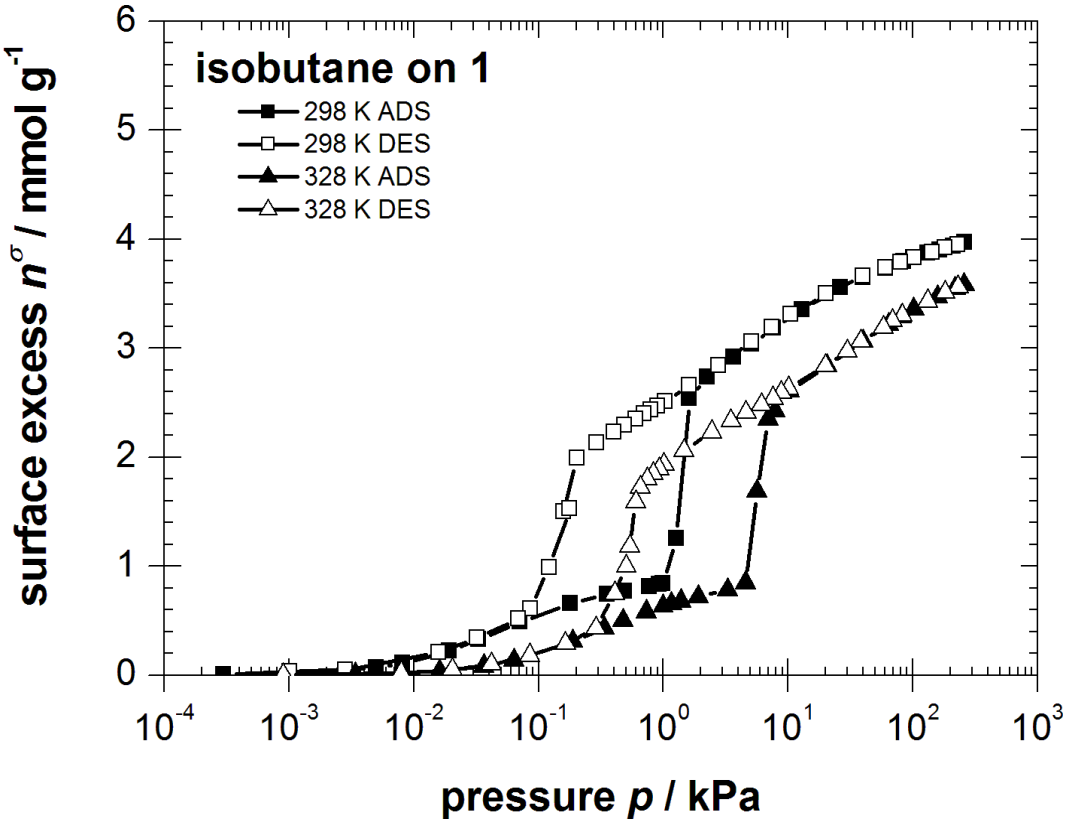

Fig. SI 2 Surface excess as a function of pressure for the sorption of isobutane on **1** at 298 K and 328 K (ADS: adsorption, DES: desorption).

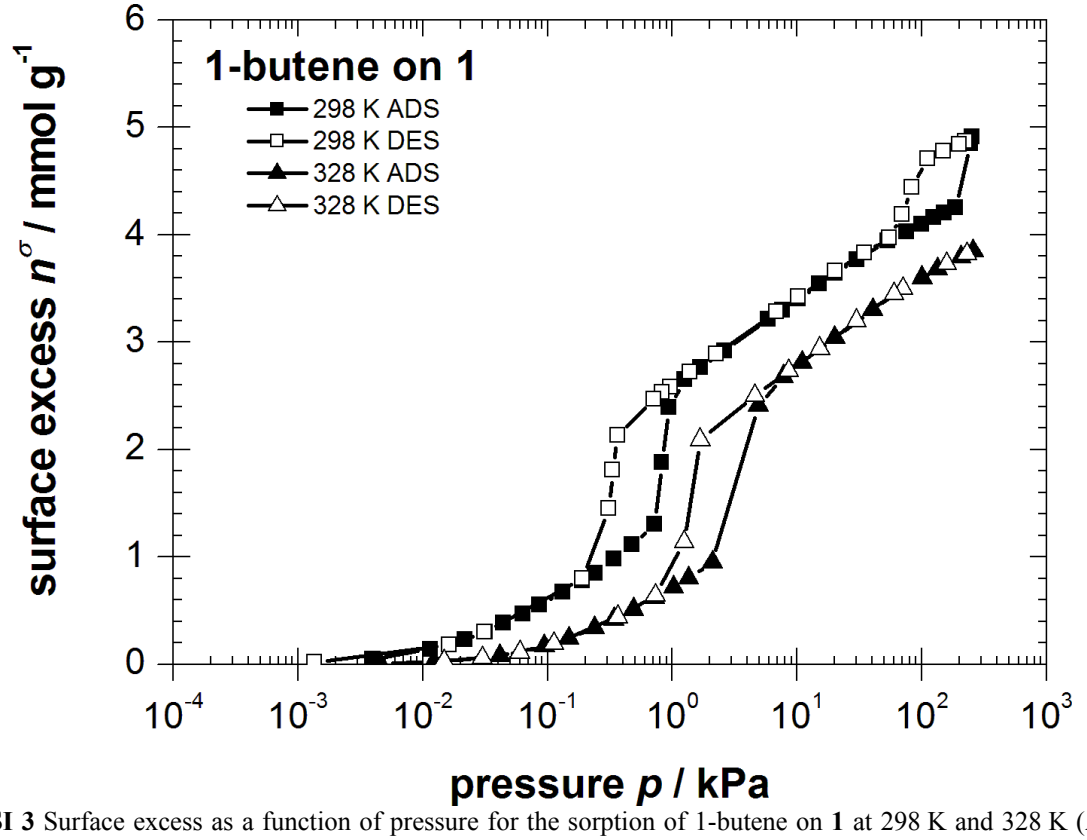

Fig. SI 3 Surface excess as a function of pressure for the sorption of 1-butene on **1** at 298 K and 328 K (ADS: adsorption, DES: desorption).

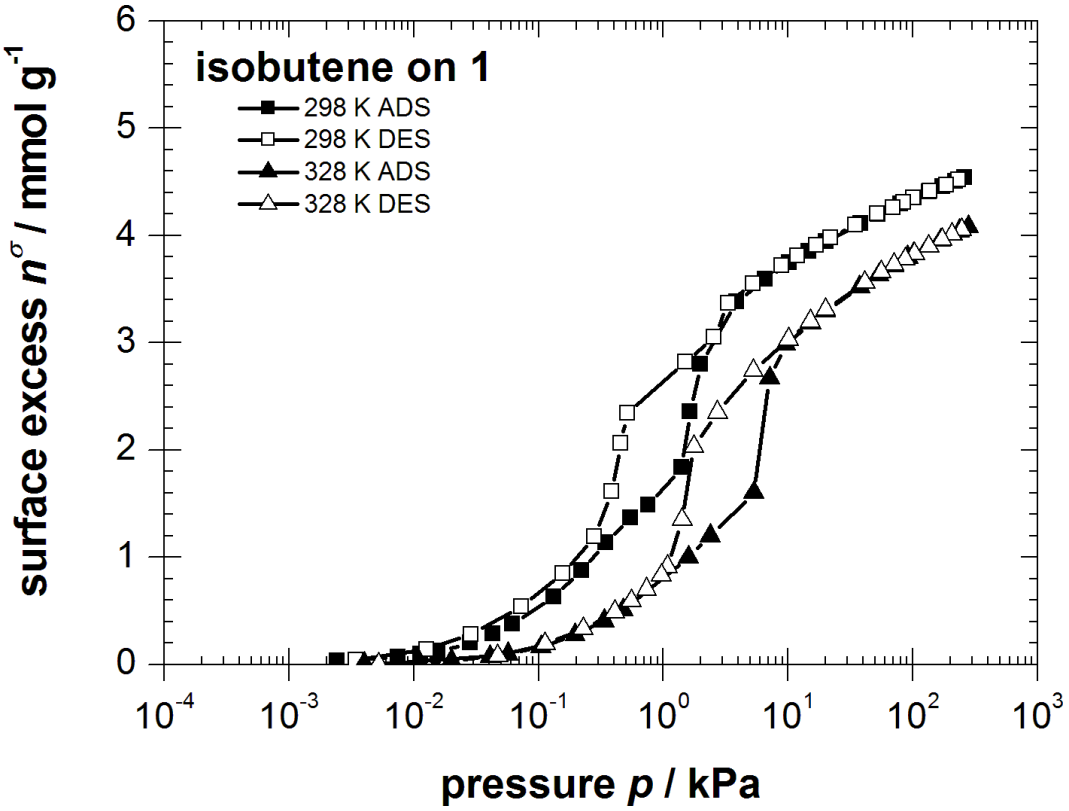

Fig. SI 4 Surface excess as a function of pressure for the sorption of isobutene on **1** at 298 K and 328 K (ADS: adsorption, DES: desorption).

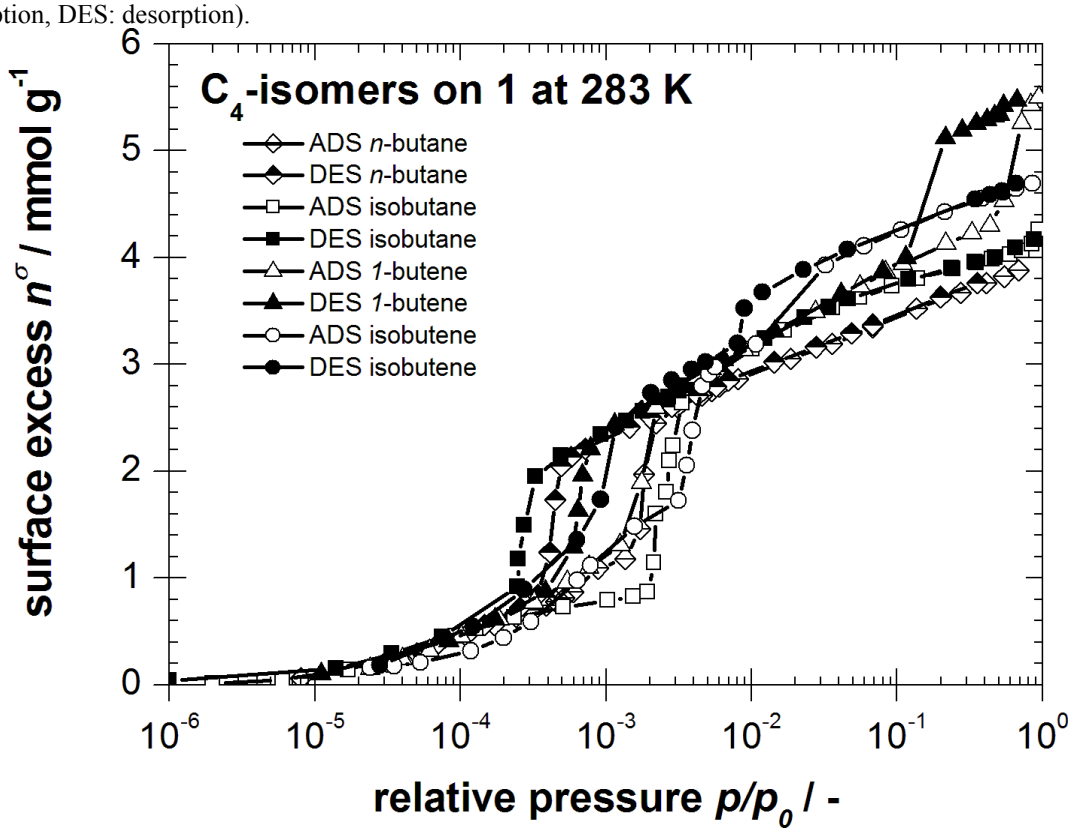

Fig. SI 5 Adsorption (ADS, open symbols) and desorption (DES, closed symbols) isotherms of investigated C_4-hydrocarbons, including *n*-butane (diamonds), isobutane (squares), 1-butene (triangles) and isobutene (circles) on **1** at 283 K up to relative pressures $p/p_0 = 1$.

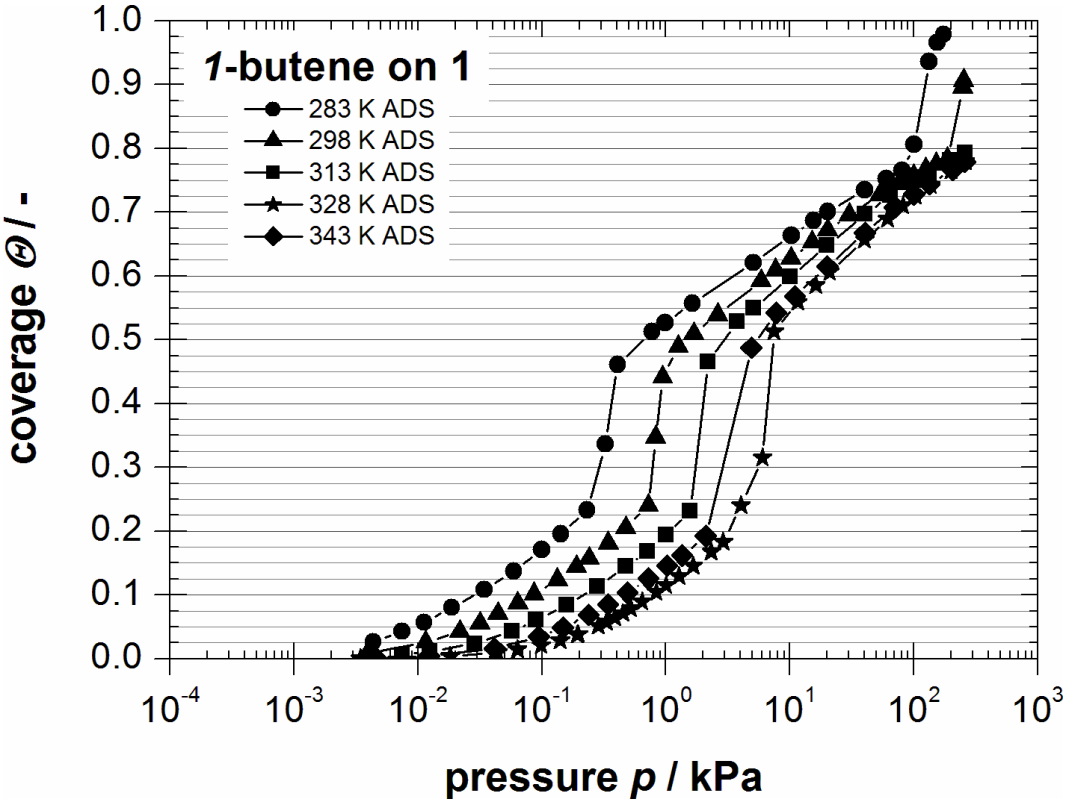

Fig. SI 6 Coverage of 1-butene on **1** as a function of Pressures for different temperatures. Intermediate values were interpolated.

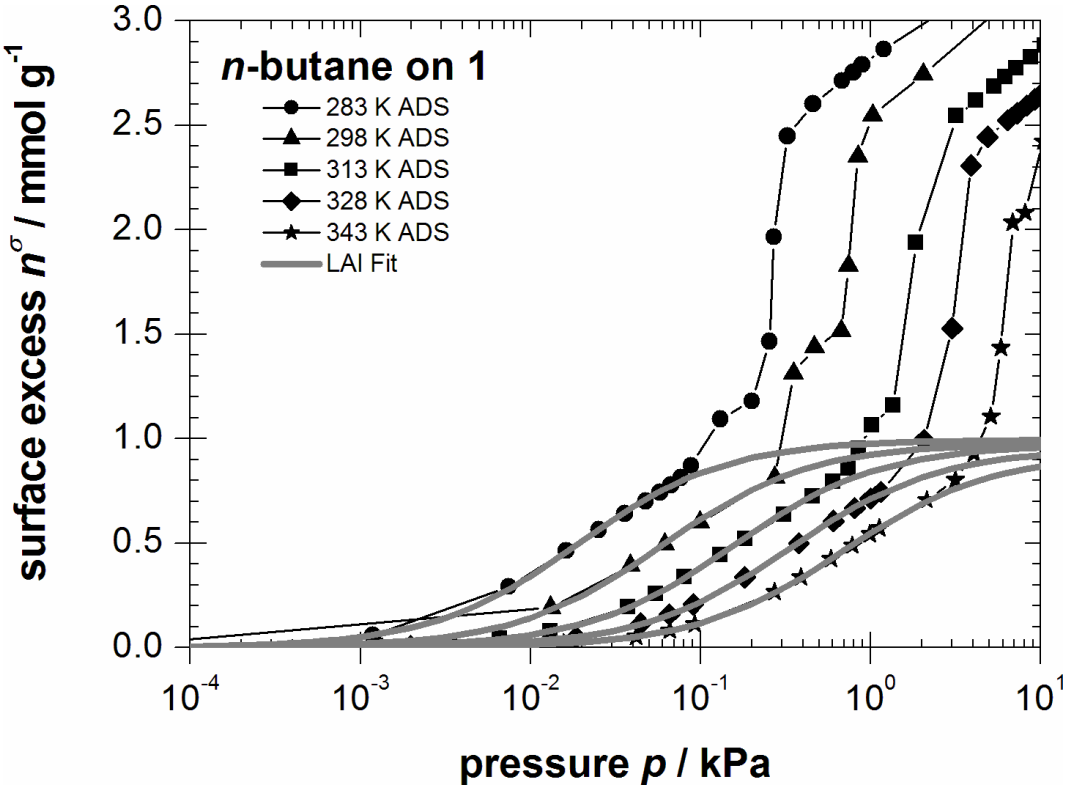

Fig. SI 7 Adsorption isotherms of *n*-butane on **1** at 283 K (circles), 298 K (triangles), 313 K (squares), 328 K (diamonds) and 343 K (stars) with Langmuir-Fits (strong grey lines) for pore filling in low pressure region – black lines are to guide the eyes.

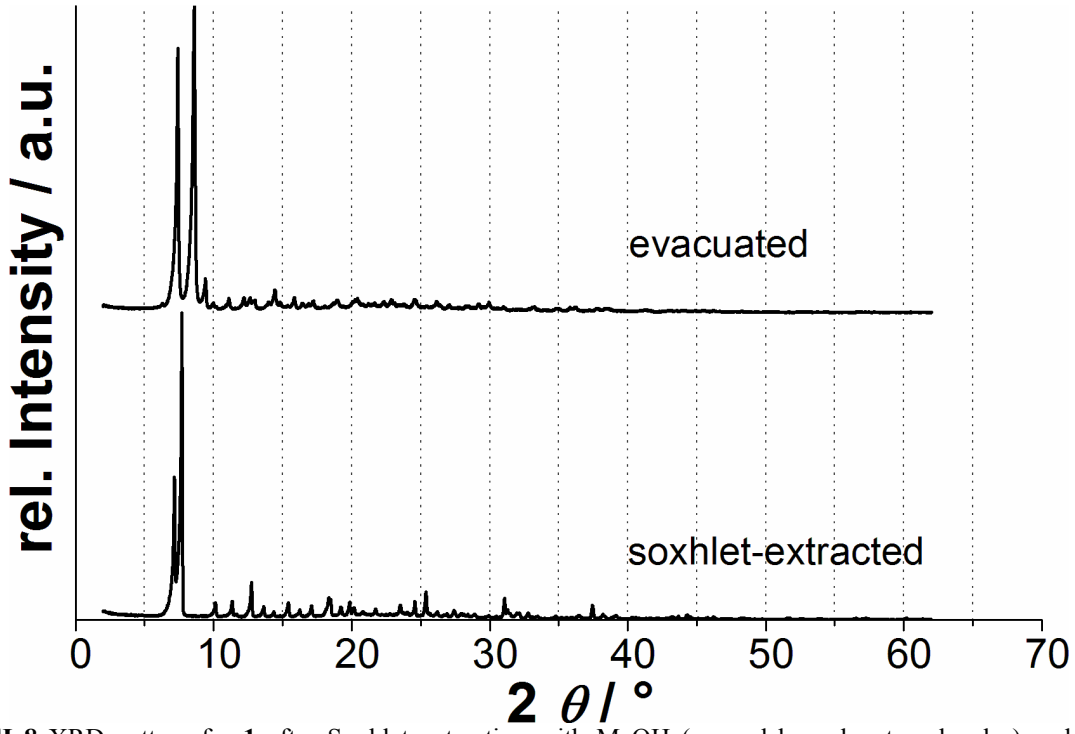

Fig. SI 8 XRD pattern for **1** after Soxhlet extraction with MeOH (opened by solvent molecules) and under vacuum.

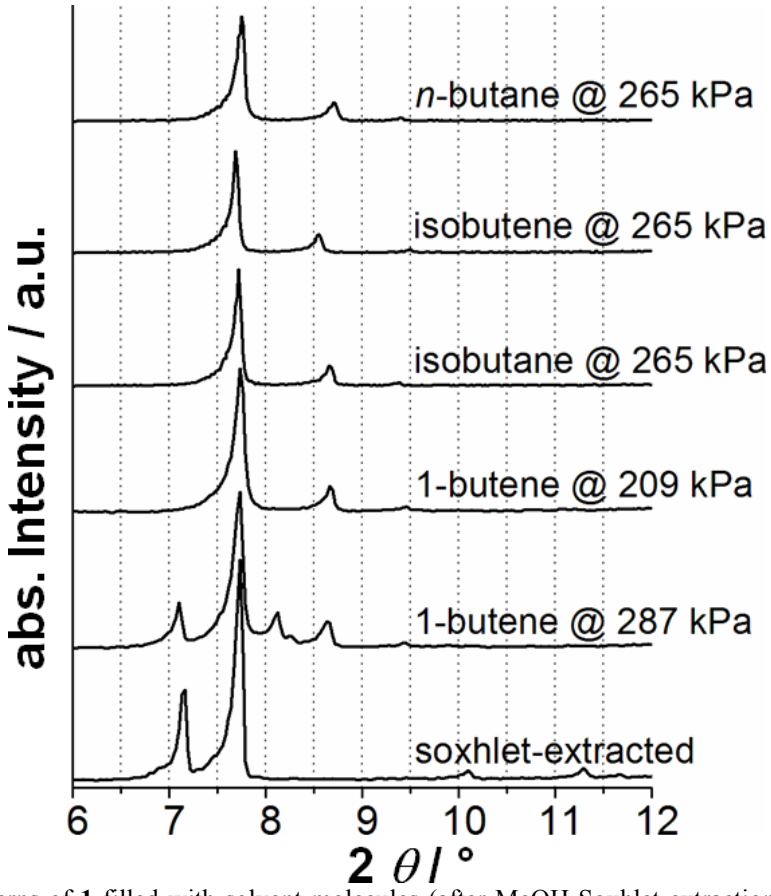

Fig. SI 9 XRD patterns of **1** filled with solvent molecules (after MeOH Soxhlet extraction) and with different sorptives at 298 K and comparable pressures.

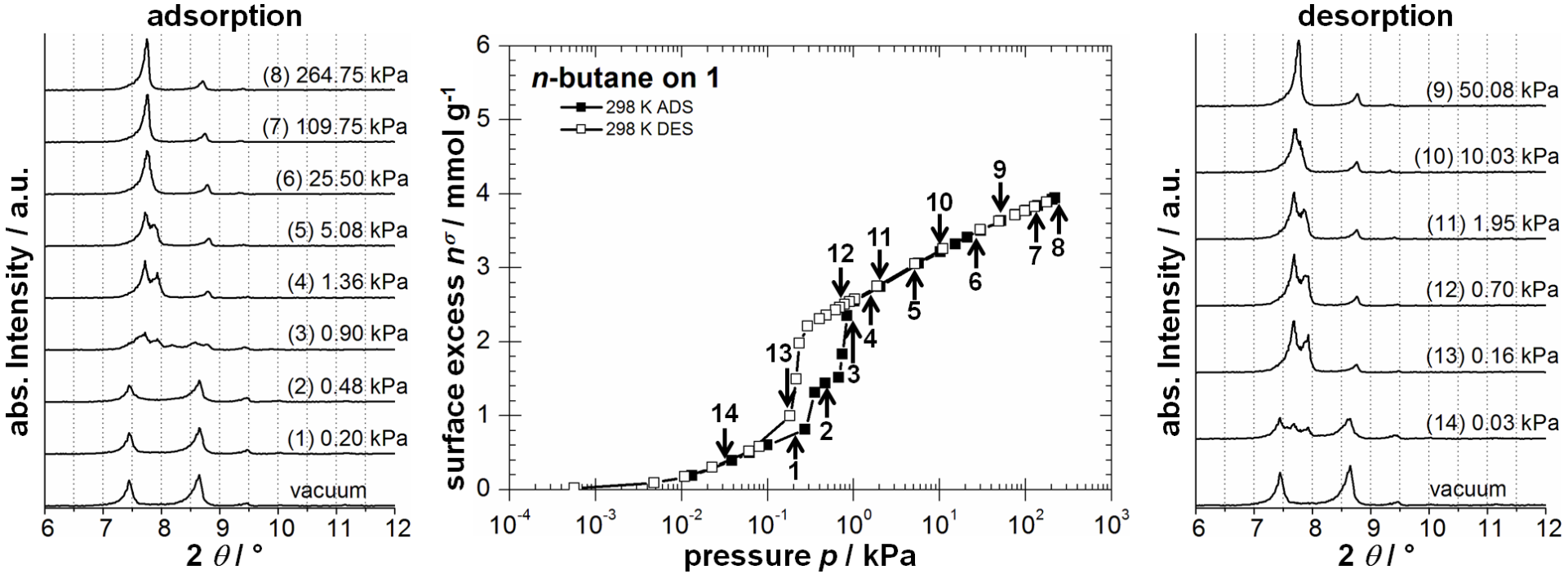

Fig. SI 10 Adsorption (closed symbols) and desorption (open symbols) isotherm of *n*-butane on **1** (center) at 298 K and XRD patterns of **1** at different pressures for adsorption (left) and desorption (right). The respective points on the sorption isotherms at which the XRD patterns were recorded are labelled as 1 – 14. The gate-opening is observed at about 1 kPa (point 3).

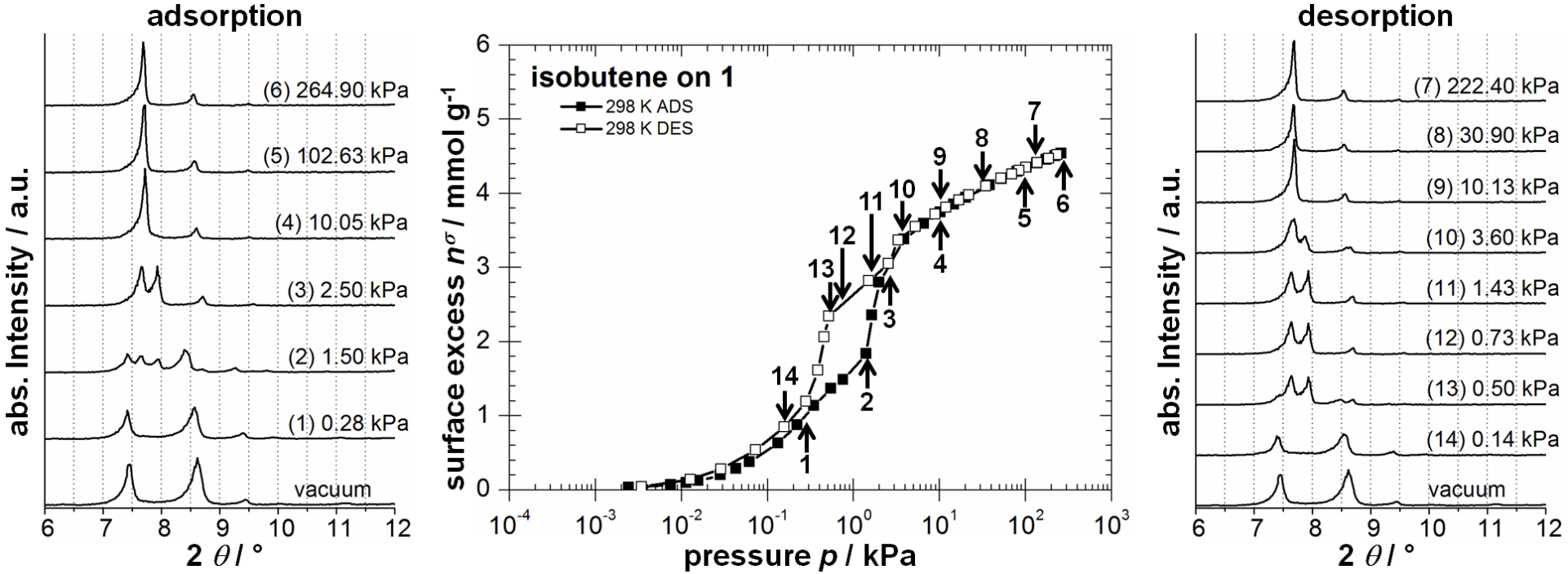

Fig. SI 11 Adsorption (closed symbols) and desorption (open symbols) isotherm of isobutene on **1** (center) at 298 K and XRD patterns of **1** at different pressures for adsorption (left) and desorption (right). The respective points on the sorption isotherms at which the XRD patterns were recorded are labelled as 1 – 14.The gate-opening is observed at about 1.5 kPa (point 2).

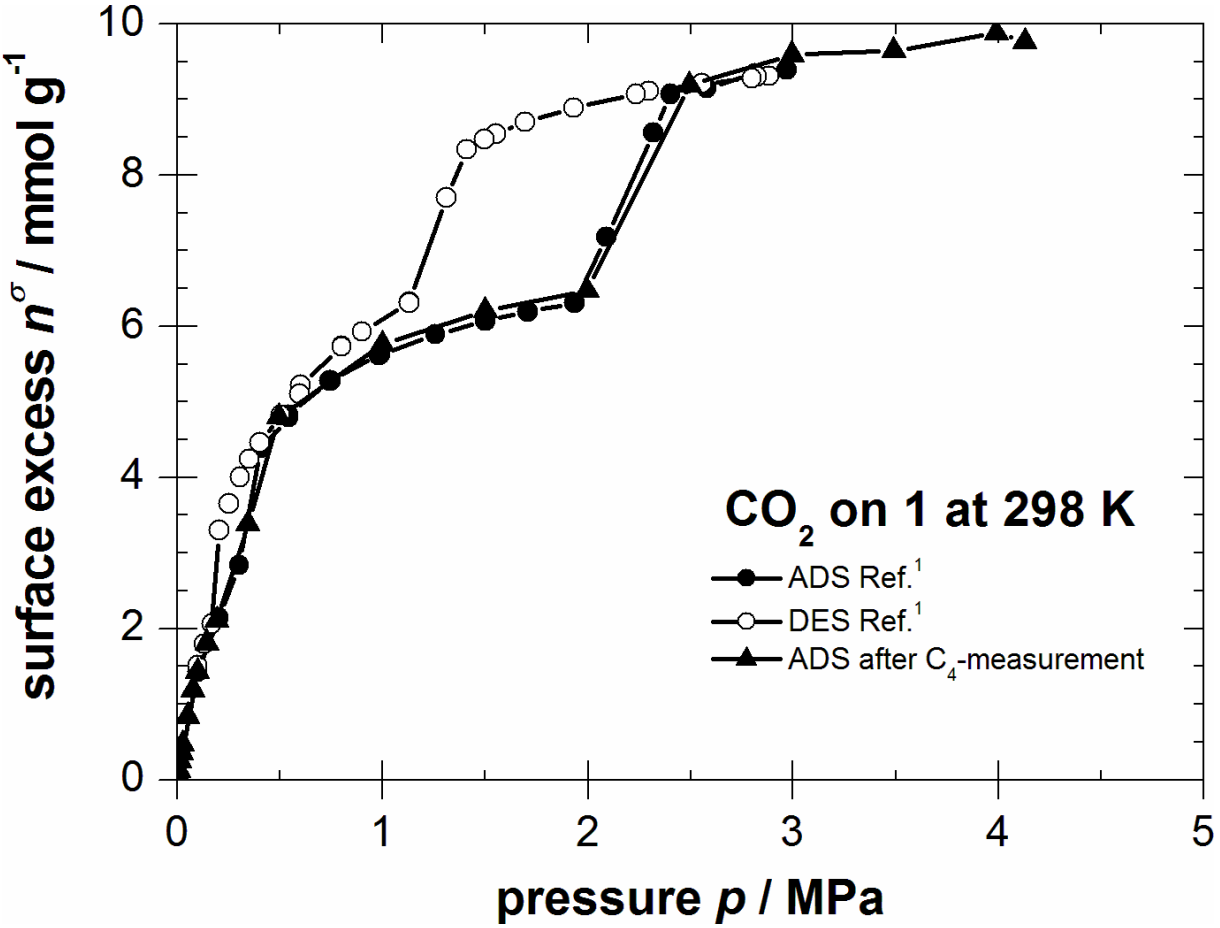

Fig. SI 12 Adsorption and desorption isotherms of carbon dioxide on **1** at 298 K after C_4-hydrocarbon sorption experiments compared to published data byRef.[1]

References

1 J. Lincke, D. Lässig, J. Möllmer, C. Reichenbach, A. Puls, A. Möller, R. Gläser, G. Kalies, R. Staudt, H. Krautscheid, *Micropor. Mesopor. Mater.*, 2011, **142**, 62-69.