Electronic Supplementary Information (ESI) for

A practical guide to calculate the isosteric heat/enthalpy of adsorption via adsorption isotherms in metal-organic frameworks, MOFs

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Content

S1. Clausius-Clapeyron equation

The thermodynamic equation (S1)

$$\frac{dp}{dT} = \frac{\Delta H_{ads}}{\Delta V \cdot T} \tag{S1}$$

with
p = vapor pressure
T = absolute temperature in K(elvin)
ΔH_{ads} = (molar) enthalpy of adsorption in kJ mol^{-1}
$\Delta V = V_{ads} - V_g$, difference of the (molar) volume between the final adsorbed phase and the starting gaseous phase

can be approximated
with $\Delta V \approx -V_g$ since the volume of a gas is much higher than the molar volume of the liquid-like adsorbed phase

$$\frac{dp}{dT} = \frac{\Delta H_{ads}}{-V_g \cdot T} \tag{S2}$$

Further, for the gaseous phase of 1 mol an ideal gas behavior (with the equation of state pV = RT) is assumed, and

$$V_g = \frac{RT}{p} \tag{S3}$$

is substituted to give the Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{p \cdot \Delta H_{ads}}{-RT^2} \quad \text{or} \quad \frac{dp}{p} = \frac{\Delta H_{ads}}{-RT^2}\,dT \tag{S4}$$

(universal gas constant R = 8.314 J K^{-1}·mol^{-1})

If the enthalpy of adsorption is taken as constant over a small temperature interval from T_1 to T_2, the integrated form of the Clausius-Clapeyron equation can be obtained:

$$\ln\frac{p_2}{p_1} = \frac{\Delta H_{ads}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{S5}$$

$$\left(\int_{T_1}^{T_2} \frac{1}{T^2}\,dt = -\frac{1}{T_2} - \left(-\frac{1}{T_1}\right)\right) \tag{S6}$$

The difference of the two quotients can be rewritten:

$$\ln\frac{p_2}{p_1} = \frac{\Delta H_{ads}}{R}\left(\frac{T_1 - T_2}{T_2 \cdot T_1}\right) \tag{S7}$$

or by exchanging T_1 and T_2 in the numerator:

$$\ln\frac{p_2}{p_1} = -\frac{\Delta H_{ads}}{R}\left(\frac{T_2 - T_1}{T_2 \cdot T_1}\right) \tag{S8}$$

From this we obtain Eq. (1) in the manuscript

$$\Delta H_{ads}(n) = -R \cdot \ln\left(\frac{p_2}{p_1}\right)\left(\frac{T_1 \cdot T_2}{T_2 - T_1}\right) \tag{S9}$$

$\Delta H_{ads}(n)$ is typically written as ΔH_{ads} only but as the isosteric heat of adsorption it is a function of the gas uptake (the loading) n. We introduce $\Delta H_{ads}(n)$ here as in the following we will explicitly calculate the isosteric enthalpy of adsorption as a function of loading n.

Note,
(i) when comparing the aforementioned four equations to literature, pay attention to the order of T_1 and T_2 in the difference, which affects the (minus/plus) sign on the right side of the equation.

$$\left(\frac{1}{T_2}-\frac{1}{T_1}\right)=-\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\ and\ \left(\frac{T_1\cdot T_2}{T_2-T_1}\right)=-\left(\frac{T_1\cdot T_2}{T_1-T_2}\right) \tag{S10}$$

(ii) Often the Clausius-Clapeyron equation (1) is written in the literature as

$$Q_{st}=\ -R\cdot\ln\left(\frac{p_2}{p_1}\right)\left(\frac{T_1\cdot T_2}{T_2-T_1}\right) \tag{S11}$$

The use of the symbol Q_{st} which stands for "isosteric heat of adsorption" is misleading (see Section S2 below), especially if at the same time the minus-sign on the right side of the equation is kept.

From the equation

$$\ln\frac{p_2}{p_1}=\frac{\Delta H_{ads}(n)}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \tag{S12}$$

$\Delta H_{ads}(n)$ can be obtained from two experimental adsorption isotherms which were measured at two temperatures T_1 and T_2. Note that T_1 and T_2 are different but should be close. Most often a temperature difference of 10-20 K is used.

Each adsorption isotherm consists of $n_i \mid p_i$ data points. For an equal uptake of n the data triple $n \mid p_1 \mid p_2$ is used.
For a given value of n, the data pairs $\ln p_2 \mid 1/T_2$ and $\ln p_1 \mid 1/T_1$ define a straight line with the negative slope

$$\frac{\Delta H_{ads}(n)}{R}=\frac{\ln p_2-\ln p_1}{\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}<0 \tag{S13}$$

For an adsorption process $T_2 > T_1$ correlates with $p_2 > p_1$, that is, a higher temperature requires a higher pressure to achieve the same loading n.
Hence, $\ln p_2 > \ln p_1$ and $\ln p_2 - \ln p_1 > 0$ and $1/T_2 < 1/T_1$ or $(1/T_2 - 1/T_1) < 0$.

Adsorption is an exothermic process, thus $\Delta H_{ads}(n) < 0$ kJ mol^{-1} is obtained as required.

For any experimentally measured or interpolated loading n a heat of adsorption $\Delta H_{ads}(n)$ is obtained this way. This allows to plot $\Delta H_{ads}(n)$ as a function of loading n (Fig. 5).

By defining

$$\frac{\Delta H_{ads}(n)}{R}=m=\frac{\ln p_2-\ln p_1}{\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}<0 \tag{S14}$$

one obtains

$$\Delta H_{ads}=R\cdot m<0 \tag{S15}$$

Note,
in the literature the equation

$$Q_{st}=-R\cdot m' \tag{S16}$$

is usually given. This is derived from

$$Q_{st}=\ -R\cdot\ln\left(\frac{p_2}{p_1}\right)\left(\frac{T_1\cdot T_2}{T_2-T_1}\right) \tag{S17}$$

with the misleading use of Q_{st} (see below) and

$$m' = \ln\left(\frac{p_2}{p_1}\right)\left(\frac{T_1 \cdot T_2}{T_2 - T_1}\right) \quad \text{(S18)}$$

This expression can be rewritten to

$$m' = \ln\left(\frac{p_2}{p_1}\right)\left(\frac{T_1 \cdot T_2}{T_2 - T_1}\right) = \frac{\ln p_2 - \ln p_1}{\left(\frac{T_2 - T_1}{T_1 \cdot T_2}\right)} = \frac{\ln p_2 - \ln p_1}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{\ln p_2 - \ln p_1}{-\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = -m \quad \text{(S19)}$$

and illustrates that m' > 0, while m < 0.

S2. Virial equation

The virial fit is based on the exponential virial equation:[1,2,3]

$$p = n \cdot \exp\left(\sum_{i=0}^{m} C_i n^i\right) \quad \text{(S20)}$$

with p as the pressure and n the amount adsorbed. C_0 is a constant for the adsorbate-adsorbent interaction, C_1, C_2 etc. are constants for the double, triple etc. interactions in the adsorbent field. The constants C_i depend on temperature, according to[2]

$$\frac{dC_i}{dT} RT^2 = Q_i \quad \text{(S21)}$$

The heat of adsorption Q_{st} (not to be mistaken as the *enthalpy of* adsorption, ΔH_{ads}) is given as[1]

$$Q_{st} = \left(\sum_{i=0}^{m} \frac{dC_i}{dT} RT^2 n^i\right) = \left(\sum_{i=0}^{m} Q_i n^i\right) \quad \text{(S22)}$$

with Q_0 as the heat of adsorption at n = 0, that is Q_{st}^0. The other Q_i ($i \neq 0$) are constants having the units $[Q_i]$ = [(k)J mol$^{-(i+1)}$].[1]

If Q_i is taken as independent from temperature (for small ΔT intervals), the integration of Eq. (S21) gives

$$C_i = -\frac{Q_i}{RT} + const = -\frac{Q_i}{RT} + b_i \quad \text{(S23)}$$

Substituting Eq. (S23) into Eq. (S20) leads to

$$p = n \cdot \exp\left(\sum_{i=0}^{m} \left(-\frac{Q_i}{RT} + b_i\right) n^i\right) = n \cdot \exp\left(-\sum_{i=0}^{m} \frac{Q_i}{RT} n^i\right) \exp\left(\sum_{i=0}^{m} b_i n^i\right) \quad \text{(S24)}$$

or in the logarithmic form

$$\ln p = \ln n - \frac{1}{T}\sum_{i=0}^{m} \frac{Q_i}{R} n^i + \sum_{i=0}^{m} b_i n^i \quad \text{(S25)}$$

The substitution

$$a_i = -\frac{Q_i}{R} \; or \; Q_i = -R \cdot a_i \quad \text{(S26)}$$

then gives the virial equation in a commonly published form:

$$\ln p = \ln n + \frac{1}{T}\sum_{i=0}^{m} a_i n^i + \sum_{i=0}^{m} b_i n^i \quad \text{(S27)}$$

In equation (S27), p is the pressure in kPa, n is the of total amount adsorbed in mmol/g, T is the temperature in K (e.g. 273 K, 293 K), a_i and b_j are the virial coefficients and m represents the number of coefficients required to adequately fit the isotherms.
We note that in order to derive at dimensionless values in the argument of the logarithm (ln) the pressure and amount adsorbed must be divided by their units as in Eq. (S28).

$$\ln\frac{p}{kPa} = \ln\frac{n}{mmol \cdot g^{-1}} + \frac{1}{T}\sum_{i=0}^{m} a_i n^i + \sum_{i=0}^{m} b_i n^i \qquad \text{(S28)}$$

With the units of $[Q_i]$ = [(k)J $mol^{-(i+1)}$] the units of $[a_i]$ are [K·mol^{-i}].

From Eq. (S22) and (S26), the uptake-dependent heat of adsorption Q_{st} (as a function of uptake n) is derived as

$$Q_{st}(n) = -R \cdot \sum_{i=0}^{m} a_i n^i \qquad \text{(S29)}$$

and for the approximation of the heat of adsorption at zero (rather very low) coverage, Q_{st}^0

$$Q_{st}^0(n) = -R \cdot a_0 \qquad \text{(S30)}$$

From the negative sign of the most important virial coefficient a_0 (with the unit K(elvin)) this heat of adsorption $Q_{st}(n)$ and Q_{st}^0 will be positive quantities.
Note that the isosteric heat of adsorption $Q_{st}(n)$ is a differential heat and a positive quantity.[4]

Potential problem with the use of Q_{st}
A problem arises if the positive $Q_{st}(n)$ from the virial fit is taken as the same Q_{st} from the Clausius-Clapeyron equation (see above Eq. (S11, S16, S17) from which Q_{st} will be negative), since both quantities will have the opposite sign (besides a somewhat different value).

Therefore, the Clausius-Clapeyron equation should be used and given with the correct (isosteric) enthalpy of adsorption ΔH_{ads} and not with Q_{st}.
Presumably, the misleading (if not wrong) use of Q_{st} in the Clausius-Clapeyron equation was introduced because the magnitude 'heat of adsorption, Q_{st}' was used for the virial equations.

The quantity *isosteric enthalpy of adsorption* ΔH_{ads} is more meaningful than the simple *heat*, Q. Both magnitudes are equal with opposite sign[4]

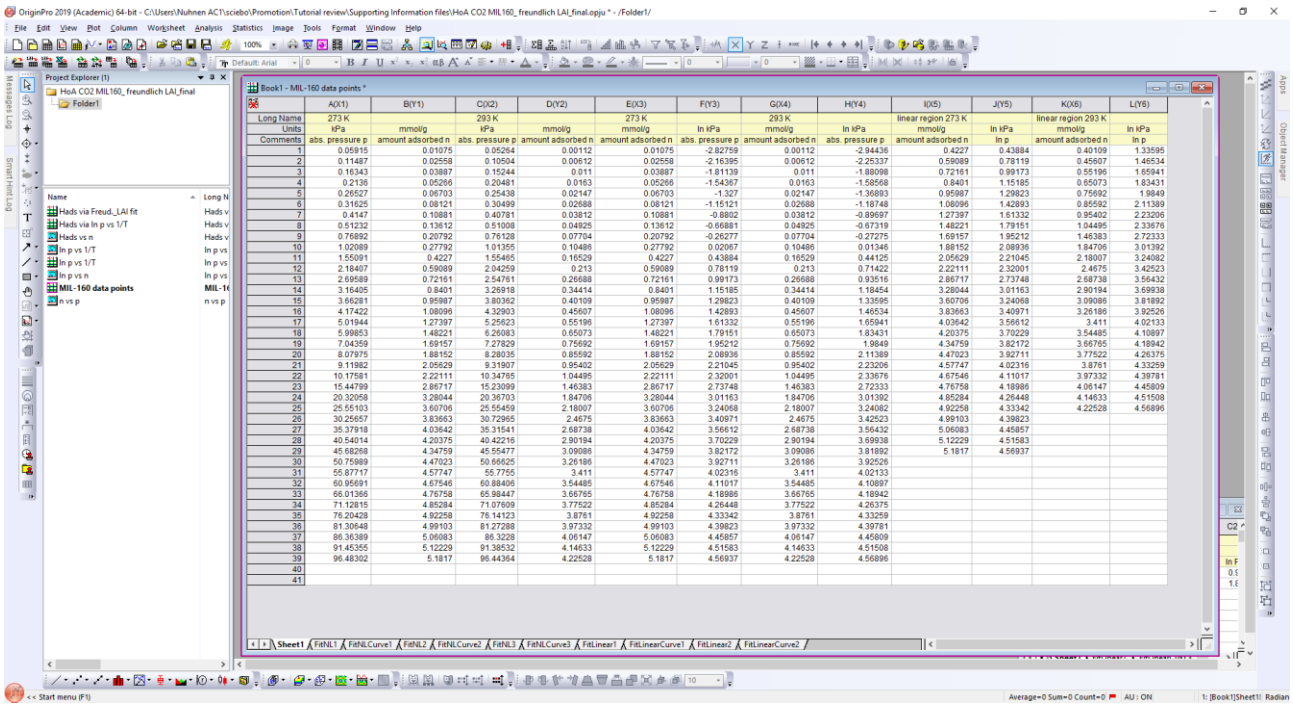
$$\Delta H_{ads} = -Q_{st} \qquad \text{(S31)}$$

which then correctly relates the negative, exothermic (isosteric) enthalpy of adsorption ΔH_{ads} from the Clausius-Clapeyron equation to the positive (isosteric) heat of adsorption Q_{st} from the virial fit.

S3. Freundlich-Langmuir fit of *n* vs. *p* isotherms

A brief illustration how to set up the Freundlich-Langmuir fit with the program Origin is given in the file “HoA detailed description_origin.pdf”.

S3.1 CO_2 adsorption isotherm data on MIL-160 at 273 K and 293 K (see Origin file Or1):



S3.2 Fit information for the isotherm at 273 K (see Origin file Or1):

Nonlinear Curve Fit (NewFunction1 (User)) (26.02.2019 13:16:21)

Notes

Description	Nonlinear Curve Fit
User Name	Nuhnen AC1
Operation Time	26.02.2019 13:16:21
Iteration Algorithm	Levenberg Marquardt
Model	NewFunction1 (User)
Number of Parameters	3
Number of Derived Parameters	0
Number of Datasets	1
Equation	(a*b*p^c)/(1+b*p^c)
Report Status	New Analysis Report
Special Input Handling	

Input Data

		Dep/Indep	Data	Range	Weight Type
B	p	Indep	[Book1]Sheet1!A"2	[1*:39*]	No Weighting
	n	Dep	[Book1]Sheet1!B	[1*:39*]	No Weighting

Parameters

		Value	Standard Error
B	a	5.93098	0.03765
	b	0.05028	8.52726E-4
	c	1.05613	0.01032

Reduced Chi-sqr = 7.31092873215E-4
COD(R^2) = 0.99982145950209
Iterations Performed = 16
Total Iterations in Session = 16
Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.

Statistics

	B
Number of Points	39
Degrees of Freedom	36
Reduced Chi-Sqr	7.31093E-4
Residual Sum of Squares	0.02632
Adj. R-Square	0.99981
Fit Status	Succeeded(100)

Fit Status Code :
100 : Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.

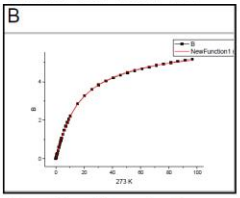
Summary

	a		b		c		Statistics	
	Value	Standard Error	Value	Standard Error	Value	Standard Error	Reduced Chi-Sqr	Adj. R-Square
B	5.93098	0.03765	0.05028	8.52726E-4	1.05613	0.01032	7.31093E-4	0.99981

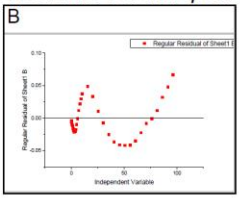
ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
B	Regression	3	359.86417	119.95472	164075.90117	0
	Residual	36	0.02632	7.31093E-4		
	Uncorrected Total	39	359.89049			
	Corrected Total	38	147.41386			

Fitted Curves Plot



Residual vs. Independent Plot



S3.3 Fit information for the isotherm at 293 K (see Origin file Or1):

Nonlinear Curve Fit (NewFunction1 (User)) (26.02.2019 13:16:57)

Notes

Description	Nonlinear Curve Fit
User Name	Nuhnen AC1
Operation Time	26.02.2019 13:16:57
Iteration Algorithm	Levenberg Marquardt
Model	NewFunction1 (User)
Number of Parameters	3
Number of Derived Parameters	0
Number of Datasets	1
Equation	(a*b*p^c)/(1+b*p^c)
Report Status	New Analysis Report
Special Input Handling	

Input Data

		Dep/Indep	Data	Range	Weight Type
D	p	Indep	[Book1]Sheet1!C"2	[1*:39*]	No Weighting
	n	Dep	[Book1]Sheet1!D	[1*:39*]	No Weighting

Parameters

		Value	Standard Error
D	a	5.89269	0.01733
	b	0.01682	8.43552E-5
	c	1.09519	0.00272

Reduced Chi-sqr = 2.58490693727E-5
COD(R^2) = 0.99999008962444
Iterations Performed = 18
Total Iterations in Session = 18
Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.

Statistics

	D
Number of Points	39
Degrees of Freedom	36
Reduced Chi-Sqr	2.58491E-5
Residual Sum of Squares	9.30566E-4
Adj. R-Square	0.99999
Fit Status	Succeeded(100)

Fit Status Code :
100 : Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.

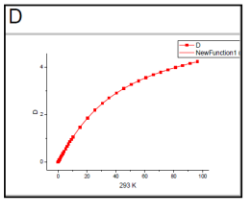
Summary

	a		b		c		Statistics	
	Value	Standard Error	Value	Standard Error	Value	Standard Error	Reduced Chi-Sqr	Adj. R-Square
D	5.89269	0.01733	0.01682	8.43552E-5	1.09519	0.00272	2.58491E-5	0.99999

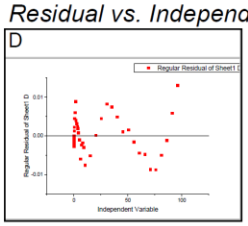
ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
D	Regression	3	191.1773	63.72577	2465302.16	0
	Residual	36	9.30566E-4	2.58491E-5		
	Uncorrected Total	39	191.17823			
	Corrected Total	38	93.89821			

Fitted Curves Plot

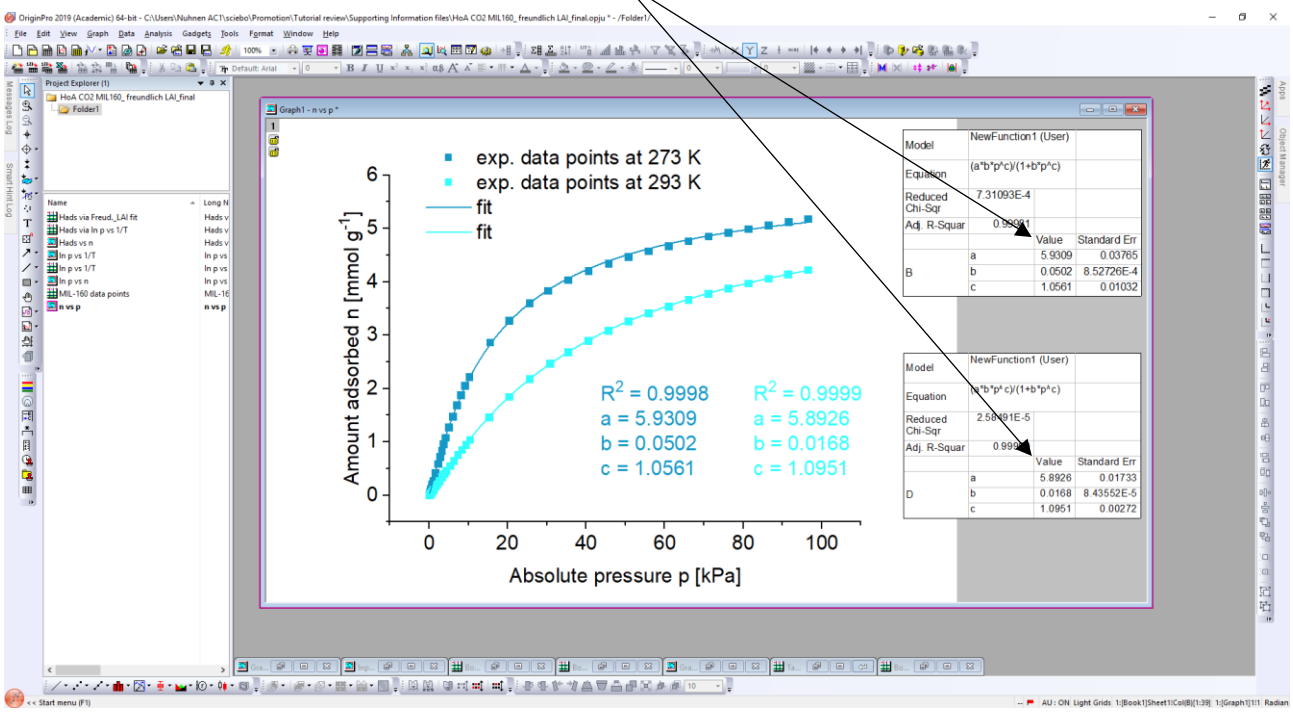


Residual vs. Independent Plot



S3.4 Fitted CO_2 adsorption isotherms on MIL-160 at 273 K and 293 K with fit data (see Origin file Or1):

Use these *a*, *b* and *c* parameters, which were derived here from the fitting procedure as input in the Excel data sheet of the next Section S3.5.



S3.5 Excel data sheet Ex1 for continuum of $n \mid p_1$ and $n \mid p_2$ data pairs ($n \mid p_1 \mid p_2$ data triples):

Paste your isotherm data here or in Origin.

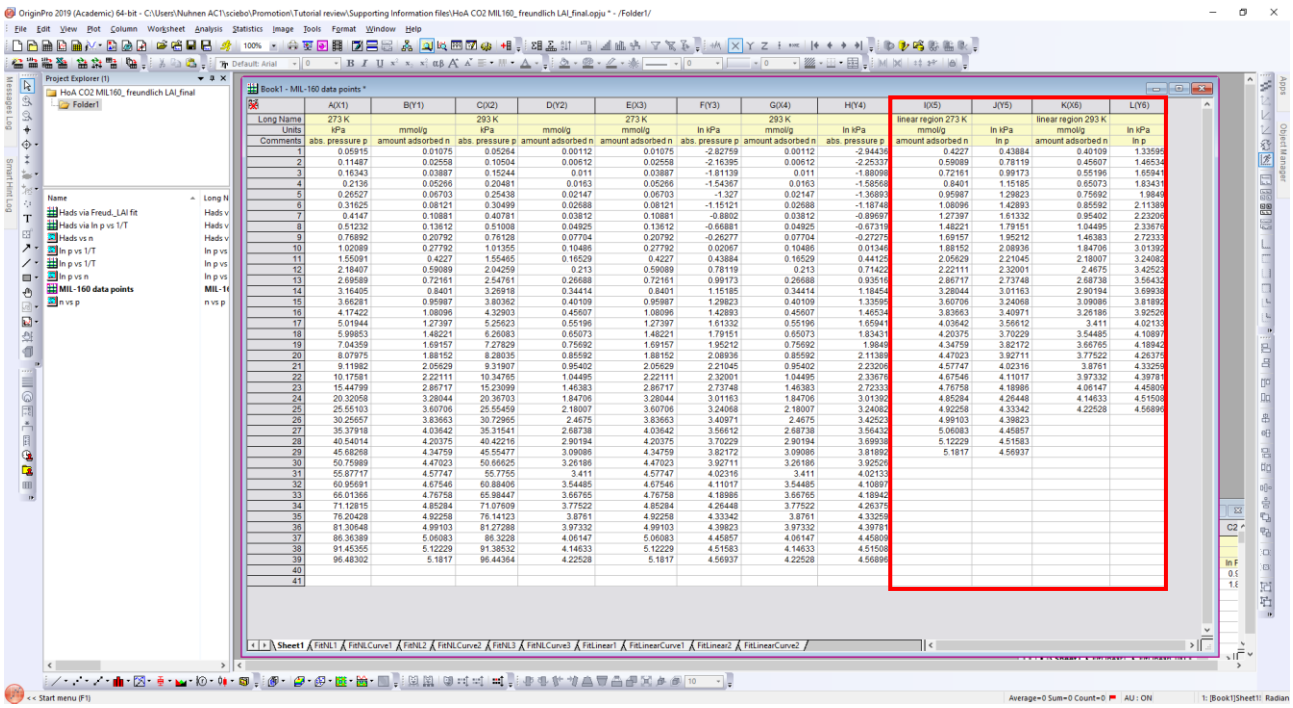
Adjust the temperatures here.

Paste your fitting parameters from Origin here.

Data for the Origin plot of ΔH_{ads} vs n.

					Freundlich Langmuir fit from origin 273K			Freundlich Langmuir fit from origin 293K			
					a	5.9310		a	5.89		
					b	0.0503		b	0.02		
					c	1.0561		c	1.10		
CO2 adsorption		CO2 adsorption				273.1500	293.1500				
273.15 K		293.15 K		R [J/mol/K]	n mmol/g	p kPa	p kPa	Hads [J/mol]	– Hads [KJ/mol]	mmol/g	– Hads [KJ/mol]
kPa	mmol/g	kPa	mmol/g	8.314	0.01	0.0402	0.1233	-37294	37.29	0.01	37.29
0.0006	0.0108	0.0005	0.0011		0.02	0.0777	0.2326	-36513	36.51	0.02	36.51
0.0011	0.0256	0.0011	0.0061		0.03	0.1142	0.3374	-36056	36.06	0.03	36.06
0.0016	0.0389	0.0015	0.0110		0.04	0.1502	0.4394	-35731	35.73	0.04	35.73
0.0021	0.0527	0.0020	0.0163		0.05	0.1858	0.5396	-35478	35.48	0.05	35.48
0.0027	0.0670	0.0025	0.0215		0.06	0.2212	0.6383	-35272	35.27	0.06	35.27
0.0032	0.0812	0.0030	0.0269		0.07	0.2564	0.7359	-35097	35.10	0.07	35.10
0.0041	0.1088	0.0041	0.0381		0.08	0.2914	0.8326	-34945	34.95	0.08	34.95
0.0051	0.1361	0.0051	0.0493		0.09	0.3263	0.9286	-34811	34.81	0.09	34.81
0.0077	0.2079	0.0076	0.0770		0.1	0.3612	1.0240	-34691	34.69	0.1	34.69
0.0102	0.2779	0.0101	0.1049		0.12	0.4306	1.2133	-34483	34.48	0.12	34.48
0.0155	0.4227	0.0155	0.1653		0.14	0.4999	1.4012	-34307	34.31	0.14	34.31
0.0218	0.5909	0.0204	0.2130		0.16	0.5691	1.5879	-34154	34.15	0.16	34.15
0.0270	0.7216	0.0255	0.2669		0.18	0.6384	1.7738	-34018	34.02	0.18	34.02
0.0316	0.8401	0.0327	0.3441		0.2	0.7077	1.9592	-33896	33.90	0.2	33.90
0.0366	0.9599	0.0380	0.4011		0.22	0.7771	2.1442	-33786	33.79	0.22	33.79
0.0417	1.0810	0.0433	0.4561		0.24	0.8466	2.3290	-33685	33.68	0.24	33.68
0.0502	1.2740	0.0526	0.5520		0.26	0.9163	2.5138	-33592	33.59	0.26	33.59
0.0600	1.4822	0.0626	0.6507		0.28	0.9862	2.6985	-33505	33.51	0.28	33.51
0.0704	1.6916	0.0728	0.7569		0.3	1.0563	2.8833	-33424	33.42	0.3	33.42
0.0808	1.8815	0.0828	0.8559		0.32	1.1267	3.0684	-33349	33.35	0.32	33.35
0.0912	2.0563	0.0932	0.9540		0.34	1.1973	3.2537	-33277	33.28	0.34	33.28
0.1018	2.2211	0.1035	1.0449		0.36	1.2682	3.4393	-33210	33.21	0.36	33.21
0.1545	2.8672	0.1523	1.4638		0.38	1.3394	3.6253	-33146	33.15	0.38	33.15
0.2032	3.2804	0.2037	1.8471		0.4	1.4108	3.8118	-33085	33.08	0.4	33.08
0.2555	3.6071	0.2555	2.1801		0.42	1.4826	3.9988	-33027	33.03	0.42	33.03
0.3026	3.8366	0.3073	2.4675		0.44	1.5547	4.1862	-32971	32.97	0.44	32.97
0.3538	4.0364	0.3532	2.6874		0.46	1.6272	4.3743	-32918	32.92	0.46	32.92
0.4054	4.2038	0.4042	2.9019		0.48	1.7000	4.5630	-32866	32.87	0.48	32.87
0.4568	4.3476	0.4555	3.0909		0.5	1.7731	4.7523	-32817	32.82	0.5	32.82
0.5076	4.4702	0.5067	3.2619		0.52	1.8466	4.9423	-32770	32.77	0.52	32.77
0.5588	4.5775	0.5578	3.4110		0.54	1.9205	5.1330	-32724	32.72	0.54	32.72
0.6096	4.6755	0.6088	3.5449		0.56	1.9948	5.3245	-32680	32.68	0.56	32.68
0.6601	4.7676	0.6598	3.6677		0.58	2.0695	5.5168	-32637	32.64	0.58	32.64
0.7113	4.8528	0.7108	3.7752		0.6	2.1446	5.7099	-32595	32.60	0.6	32.60
0.7620	4.9226	0.7614	3.8761		0.62	2.2201	5.9038	-32555	32.56	0.62	32.56
0.8131	4.9910	0.8127	3.9733		0.64	2.2961	6.0985	-32516	32.52	0.64	32.52
0.8636	5.0608	0.8632	4.0615		0.66	2.3725	6.2942	-32478	32.48	0.66	32.48
0.9145	5.1223	0.9139	4.1463		0.68	2.4493	6.4908	-32441	32.44	0.68	32.44
0.9648	5.1817	0.9644	4.2253		0.7	2.5265	6.6883	-32405	32.41	0.7	32.41
					0.72	2.6043	6.8868	-32370	32.37	0.72	32.37
					0.74	2.6825	7.0863	-32336	32.34	0.74	32.34
					0.76	2.7611	7.2868	-32302	32.30	0.76	32.30
					0.78	2.8403	7.4884	-32270	32.27	0.78	32.27
					0.8	2.9199	7.6910	-32238	32.24	0.8	32.24
					0.82	3.0001	7.8946	-32206	32.21	0.82	32.21
					0.84	3.0807	8.0994	-32176	32.18	0.84	32.18
					0.86	3.1619	8.3054	-32146	32.15	0.86	32.15
					0.88	3.2436	8.5124	-32116	32.12	0.88	32.12
					3.78	28.9354	70.9031	-29833	29.83	3.78	29.83
					3.8	29.3387	71.8670	-29822	29.82	3.8	29.82
					3.82	29.7494	72.8483	-29811	29.81	3.82	29.81
					3.84	30.1675	73.8474	-29799	29.80	3.84	29.80
					3.86	30.5934	74.8648	-29788	29.79	3.86	29.79
					3.88	31.0273	75.9011	-29777	29.78	3.88	29.78
					3.9	31.4693	76.9568	-29766	29.77	3.9	29.77
					3.92	31.9198	78.0325	-29755	29.75	3.92	29.75
					3.94	32.3790	79.1288	-29744	29.74	3.94	29.74
					3.96	32.8471	80.2463	-29733	29.73	3.96	29.73
					3.98	33.3244	81.3856	-29722	29.72	3.98	29.72
					4	33.8112	82.5474	-29711	29.71	4	29.71
					4.02	34.3078	83.7325	-29700	29.70	4.02	29.70
					4.04	34.8145	84.9415	-29689	29.69	4.04	29.69
					4.06	35.3316	86.1751	-29679	29.68	4.06	29.68
					4.08	35.8594	87.4343	-29668	29.67	4.08	29.67
					4.1	36.3983	88.7198	-29657	29.66	4.1	29.66
					4.12	36.9487	90.0325	-29647	29.65	4.12	29.65
					4.14	37.5109	91.3732	-29636	29.64	4.14	29.64
					4.16	38.0852	92.7430	-29625	29.63	4.16	29.63
					4.18	38.6722	94.1427	-29615	29.61	4.18	29.61
					4.2	39.2723	95.5735	-29604	29.60	4.2	29.60

S3.6 Chosen “linear region” of $n \mid \ln p$ data pairs of CO_2 adsorption isotherm data on MIL-160 at 273 K and 293 K (see Origin file Or1):



S3.7 Linear fit information for the isotherm at 273 K (see Origin file Or1):

Linear Fit (10.03.2020 12:22:47)

Notes

Description	Perform Linear Fitting
User Name	Nuhnen AC1
Operation Time	10.03.2020 12:22:47
Equation	y = a + b*x
Report Status	Report generated from Data Changed
Weight	No Weighting
Special Input Handling	
Data Filter	No

Input Data

	Input X Data Source	Input Y Data Source	Range
	[Book1]Sheet1!I"273 K"	[Book1]Sheet1!J	[1*:29*]

Parameters

		Value	Standard Error	t-Value	Prob>|t|
J	Intercept	0.49083	0.04285	11.45425	7.14453E-12
	Slope	0.77883	0.01217	64.01305	4.99276E-31

Slope is significantly different from zero (See ANOVA Table).
Standard Error was scaled with square root of reduced Chi-Sqr.
Some input data points are missing.

Statistics

	J
Number of Points	29
Degrees of Freedom	27
Residual Sum of Squares	0.3208
Pearson's r	0.99672
R-Square (COD)	0.99345
Adj. R-Square	0.99321

Summary

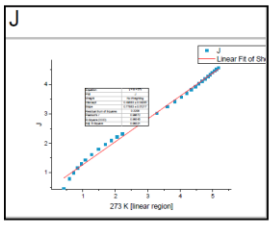
	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
J	0.49083	0.04285	0.77883	0.01217	0.99321

ANOVA

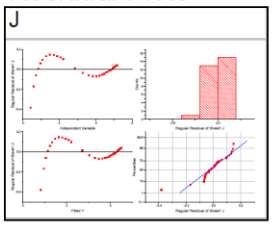
		DF	Sum of Squares	Mean Square	F Value	Prob>F
J	Model	1	48.68715	48.68715	4097.67067	5.00289E-31
	Error	27	0.3208	0.01188		
	Total	28	49.00796			

At the 0.05 level, the slope is significantly different from zero.

Fitted Curves Plot



Residual Plots



S3.8 Linear fit information for the isotherm at 293 K (see Origin file Or1):

Linear Fit (10.03.2020 12:22:46)

Notes

Description	Perform Linear Fitting
User Name	Nuhnen AC1
Operation Time	10.03.2020 12:22:46
Equation	y = a + b*x
Report Status	Report generated from Data Changed
Weight	No Weighting
Special Input Handling	
Data Filter	No

Input Data

	Input X Data Source	Input Y Data Source	Range
	[Book1]Sheet1!K"293 K"	[Book1]Sheet1!L	[1*:25*]

Parameters

		Value	Standard Error	t-Value	Prob>|t|
L	Intercept	1.37289	0.05644	24.32267	6.53187E-18
	Slope	0.7785	0.02043	38.11202	2.73037E-22

Slope is significantly different from zero (See ANOVA Table).
Standard Error was scaled with square root of reduced Chi-Sqr.
Some input data points are missing.

Statistics

	L
Number of Points	25
Degrees of Freedom	23
Residual Sum of Squares	0.43833
Pearson's r	0.99218
R-Square (COD)	0.98441
Adj. R-Square	0.98373

Summary

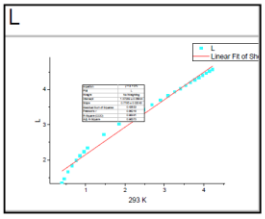
	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
L	1.37289	0.05644	0.7785	0.02043	0.98373

ANOVA

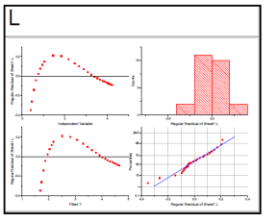
		DF	Sum of Squares	Mean Square	F Value	Prob>F
L	Model	1	27.68213	27.68213	1452.52645	2.73195E-22
	Error	23	0.43833	0.01906		
	Total	24	28.12046			

At the 0.05 level, the slope is significantly different from zero.

Fitted Curves Plot

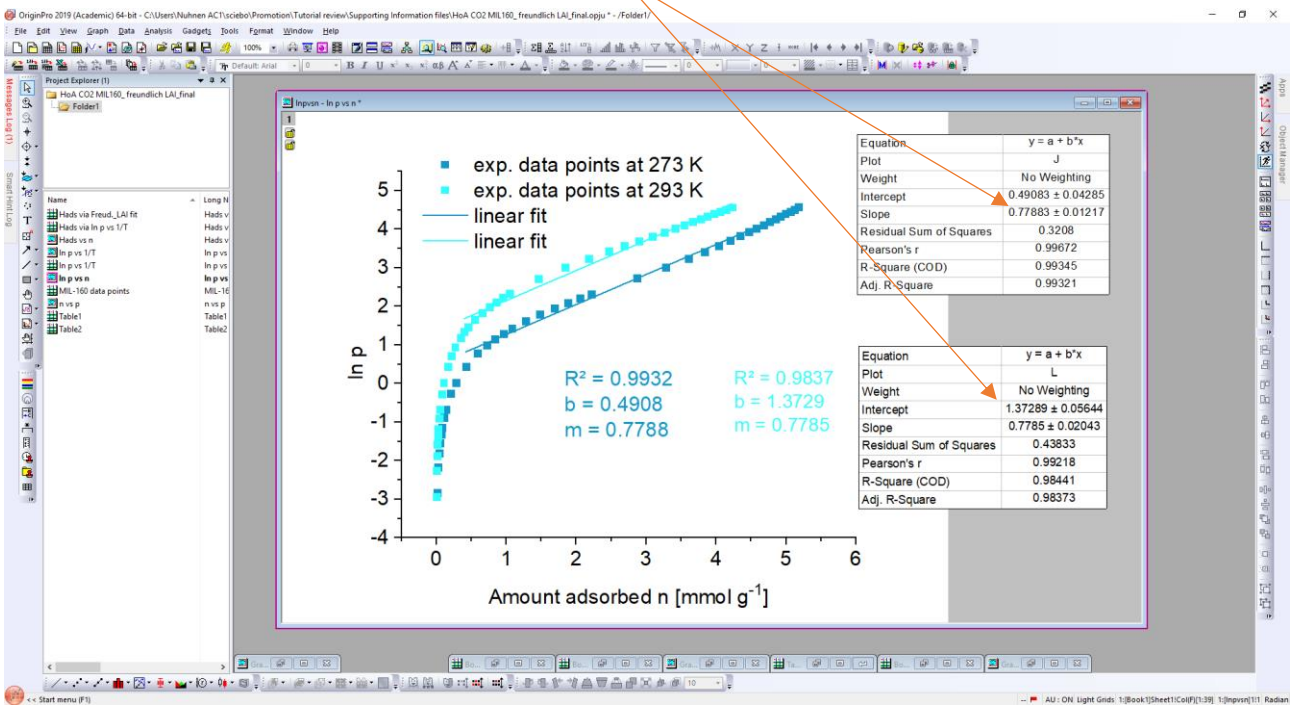


Residual Plots



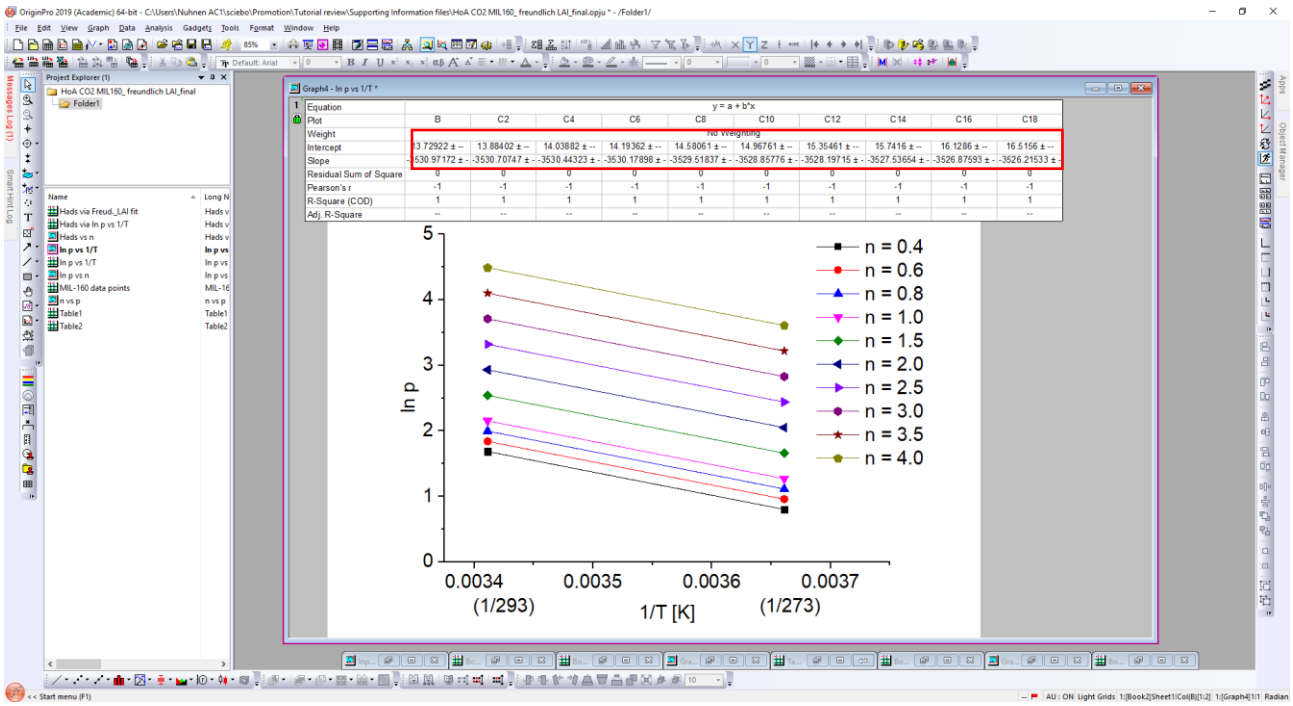
S3.9 Linear fitted CO_2 adsorption isotherms on MIL-160 at 273 K and 293 K with fit data (see Origin file Or1):

Use the slope and intercept derived here from the fitting procedure as input in the Excel data sheet of the next Section S3.10.



S3.10 Fit of ln$p$ vs1/T_1 and 1/T_2 at equal loading n (see Origin file Or1):

Use the slope derived here from the fitting of the ln$p$ vs 1/T plot for a given n as input in the Excel data sheet of the next Section S3.11.



S3.11 $\Delta H_{ads}(n)$ from $\ln p_1 \mid 1/T_1$ and $\ln p_2 \mid 1/T_2$ at equal loading n (see Excel sheet Ex2):

Paste your isotherm data here or in Origin.

Paste your fitting parameters from the ln*p* vs *n* plot isotherms here.

Here is the data for the ln*p* vs 1/*T* plot for a given *n*.

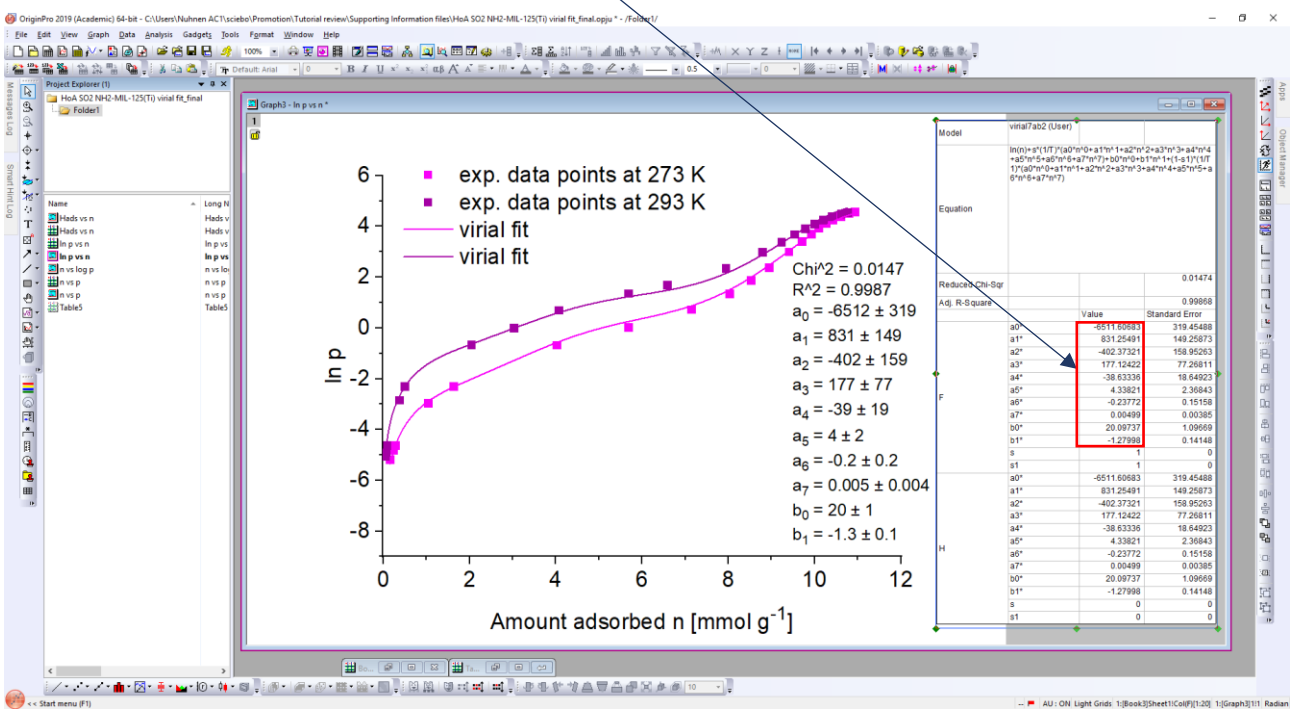
Data for the ΔH_{ads} vs *n* plot.

					linear fit 273K			linear fit 293K															
					b	0.49083		b	1.37289														
					m	0.77883		m	0.7785														
CO2			CO2			273.15	293.15																
273.15			293.15		n mmol/g	lnP kPa	lnP kPa																
kPa	mmol/g		kPa	mmol/g	0.4	0.802362	1.68429																
0.00059155	0.010754464		0.00052636	0.00111607	0.6	0.958128	1.83999																
0.0011487	0.025580357		0.00105044	0.00612054	0.8	1.113894	1.99569																
0.00163426	0.038866071		0.0015244	0.01099554	1	1.26966	2.15139																
0.00213595	0.052660714		0.00204809	0.01630357	1.5	1.659075	2.54064																
0.00265271	0.067026786		0.00254378	0.02147321	2	2.04849	2.92989																
0.00316253	0.081209821		0.00304987	0.026875	2.5	2.437905	3.31914																
0.00414698	0.108808036		0.00407805	0.03811607	3	2.82732	3.70839																
0.00512316	0.136120536		0.00510077	0.04925446	3.5	3.216735	4.09764																
0.00768921	0.207915179		0.00761282	0.07704018	4	3.60615	4.48689																
0.01020887	0.277915179		0.01013554	0.10485714																			
0.01550908	0.422696429		0.01554655	0.16529018																			
0.02184068	0.590888393		0.02042586	0.213	n = 0.4			n = 0.6			n = 0.8			n = 1			n = 1.5						
0.02695891	0.721607143		0.0254761	0.26687946	1/T [K]	ln p kPa		1/T [K]	ln p kPa		1/T [K]	ln p kPa		1/T [K]	ln p kPa		1/T [K]	ln p kPa					
0.03164051	0.840098214		0.03269175	0.34413839	0.003660992	0.802362		0.003660992	0.958128		0.003660992	1.113894		0.00366099	1.26966		0.00366099	1.659075					
0.03662809	0.959866071		0.03803623	0.40108929	0.003411223	1.68429		0.003411223	1.83999		0.003411223	1.99569		0.00341122	2.15139		0.00341122	2.54064					
0.04174218	1.080955357		0.04329032	0.45606696																			
0.0501944	1.27396875		0.05256233	0.55195536																			
0.0599853	1.482205357		0.06260828	0.65072768	n = 2			n = 2.5			n = 3			n = 3.5			n = 4						
0.07043588	1.691571429		0.07278288	0.75691518	1/T [K]	ln p kPa		1/T [K]	ln p kPa		1/T [K]	ln p kPa		1/T [K]	ln p kPa		1/T [K]	ln p kPa					
0.08079753	1.881522321		0.08280349	0.85592411	0.003660992	2.04849		0.003660992	2.437905		0.003660992	2.82732		0.00366099	3.216735		0.00366099	3.60615					
0.09119825	2.056294643		0.09319074	0.95401786	0.003411223	2.92989		0.003411223	3.31914		0.003411223	3.70839		0.00341122	4.09764		0.00341122	4.48689					
0.10175815	2.221111607		0.10347654	1.04494643																			
0.15447993	2.867165179		0.15230985	1.46382589																			
0.20320579	3.280441964		0.20367029	1.84705804	Hads via ln p vs 1/T plot																		
0.25551028	3.607058036		0.25554588	2.18006696																			
0.30256575	3.836625		0.30729654	2.46749554	R [J/mol*K]	8.314	Hads = m * R																
0.35379179	4.036419643		0.35315411	2.68737946																			
0.4054014	4.20375		0.40422164	2.9019375	n mmol/g	Slope m of ln p vs 1/T	– Hads [J/mol]	– Hads [kJ/mol]															
0.45682677	4.347589286		0.45554768	3.09086161	0.4	-3530.97172	29356.49888	29.35649888															
0.50759885	4.470232143		0.50666253	3.26186161	0.6	-3530.70747	29354.30191	29.35430191															
0.5587717	4.57746875		0.55775499	3.41099554	0.8	-3530.44323	29352.10501	29.35210501															
0.60956912	4.675455357		0.60884064	3.54485268	1	-3530.17898	29349.90804	29.34990804															
0.66013655	4.767584821		0.65984471	3.66765179	1.5	-3529.51837	29344.41573	29.34441573															
0.71128154	4.852839286		0.71076091	3.77522321	2	-3528.85776	29338.92342	29.33892342															
0.76204282	4.922580357		0.76141234	3.87610268	2.5	-3528.19715	29333.43111	29.33343111															
0.81306475	4.99103125		0.81272878	3.97332143	3	-3527.53654	29327.93879	29.32793879															
0.86363885	5.060830357		0.86322795	4.06146875	3.5	-3526.87593	29322.44648	29.32244648															
0.91453546	5.122290179		0.91385325	4.14632589	4	-3526.21533	29316.95425	29.31695425															
0.96483025	5.181696429		0.96443642	4.22528125																			

S3.12 Virial fit for SO_2 adsorption isotherms on NH_2-MIL-125(Ti) at 273 K and 293 K in an ln*p* vs *n* plot (see Origin file Or2):

A brief illustration how to set up the virial fit with the program Origin is given in the file “HoA detailed description_origin.pdf”.

Use these a_i and b_i parameters which are derived here from the virial fitting procedure as input in the Excel data sheet of the next Section S3.13.



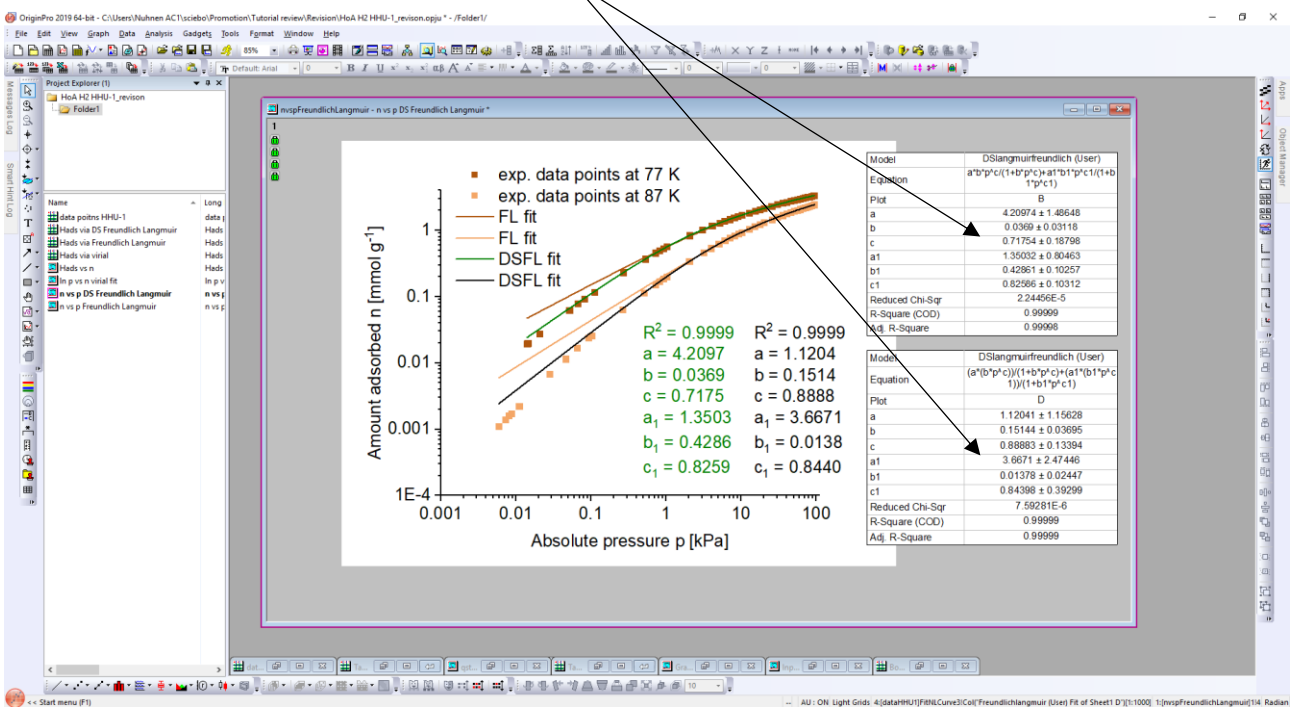
S3.13 $\Delta H_{ads}(n)$ from virial fit for SO_2 adsorption isotherms on NH_2-MIL-125(Ti) at 273 K and 293 K (Excel sheet Ex3):

R [J/mol/K]	parameter from virial fit in origin		
8.314	a0	-6511.60683	
	a1	831.25491	
	a2	-402.37321	
	a3	177.12422	
	a4	-38.63336	
	a5	4.33821	
	a6	-0.23772	
	a7	0.00499	
	n		
	mmol/g	– Hads[J/mol]	– Hads[kJ/mol]
	0.16	53111.54606	53.11154606
	0.18	52993.64047	52.99364047
	0.2	52877.82337	52.87782337
	0.22	52764.03517	52.76403517
	0.24	52652.21739	52.65221739
	0.26	52542.31263	52.54231263
	0.28	52434.26458	52.43426458
	0.3	52328.01796	52.32801796
	0.32	52223.51858	52.22351858
	0.34	52120.71325	52.12071325
	0.36	52019.54981	52.01954981
	0.38	51919.97713	51.91997713
	0.4	51821.94506	51.82194506
	0.42	51725.40444	51.72540444
	0.44	51630.3071	51.6303071
	0.46	51536.60579	51.53660579
	0.48	51444.25427	51.44425427
	0.5	51353.20719	51.35320719
	0.52	51263.42015	51.26342015
	0.54	51174.84965	51.17484965

	9.98	13773.86189	13.77386189
	10	13674.52408	13.67452408
	10.02	13575.62236	13.57562236
	10.04	13477.17189	13.47717189
	10.06	13379.18799	13.37918799
	10.08	13281.68606	13.28168606
	10.1	13184.68162	13.18468162
	10.12	13088.1903	13.0881903
	10.14	12992.22784	12.99222784
	10.16	12896.81009	12.89681009

S3.14 Dual-site Freundlich-Langmuir fitted H_2 adsorption isotherms on HHU-1 at 77 K and 87 K with fit data (see Origin file Or4):

Use these *a*,*b* and *c* parameters, which were derived here from the fitting procedure as input in the Excel data sheet of the next Section S3.15.



S3.15 Excel data sheet Ex4 for continuum of $n \mid p_1$ and $n \mid p_2$ data pairs ($n \mid p_1 \mid p_2$ data triples):

Adjust the temperatures here.

Paste your fitting parameters from Origin here.

Data for the Origin plot of ΔH_{ads} vs n.

G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W
Freundlich Langmuir fit from origin 77 K			a	4.20974	Freundlich Langmuir fit from origin 87 K		a	1.12041								
			b	0.0369			b	0.15144								
			c	0.71754			c	0.88883								
			a1	1.35032			a1	3.6671								
			b1	0.42861			b1	0.01378								
			c1	0.82586			c1	0.8439								
		77.15	87.15								77.15		p for all n's from column H at 77 K	87.15		p for all n's column H at 87 K
R [J/mol/K]	mmol/g	P kPa	P kPa		Hads [J/mol]	– Hads [KJ/mol]		mmol/g	– Hads [KJ/mol]		mmol/g	P kPa	P kPa	mmol/g	P kPa	P kPa
	0.01	0.00458	0.0297		-10450.2515	10.4502515		0.01	10.4502515		0.00306456	0.00102	0.00458	0.00052304	0.00102	0.0297
	0.02	0.011	0.0658		-9999.005642	9.999005642		0.02	9.999005642		0.00311168	0.00104	0.011	0.00053201	0.00104	0.0658
	0.03	0.0185	0.105		-9705.334249	9.705334249		0.03	9.705334249		0.00315862	0.00106	0.0185	0.00054095	0.00106	0.105
	0.04	0.0267	0.146		-9497.125233	9.497125233		0.04	9.497125233		0.00320536	0.00108	0.0267	0.00054988	0.00108	0.146
8.314	0.05	0.0356	0.19		-9361.485517	9.361485517		0.05	9.361485517		0.00325192	0.0011	0.0356	0.00055879	0.0011	0.19
	0.06	0.045	0.235		-9239.872345	9.239872345		0.06	9.239872345		0.00329831	0.00112	0.045	0.00056767	0.00112	0.235
	0.07	0.0549	0.283		-9167.260922	9.167260922		0.07	9.167260922		0.00334452	0.00114	0.0549	0.00057654	0.00114	0.283
	0.08	0.0653	0.331		-9073.308286	9.073308286		0.08	9.073308286		0.00339056	0.00116	0.0653	0.00058539	0.00116	0.331
	0.09	0.0761	0.381		-9004.130513	9.004130513		0.09	9.004130513		0.00343643	0.00118	0.0761	0.00059422	0.00118	0.381
	0.1	0.0874	0.433		-8945.386868	8.945386868		0.1	8.945386868		0.00348213	0.0012	0.0874	0.00060303	0.0012	0.433
	0.12	0.111	0.539		-8833.267419	8.833267419		0.12	8.833267419		0.00352768	0.00122	0.111	0.00061182	0.00122	0.539
	0.14	0.136	0.651		-8753.159009	8.753159009		0.14	8.753159009		0.00357307	0.00124	0.136	0.0006206	0.00124	0.651
	0.16	0.163	0.768		-8664.751593	8.664751593		0.16	8.664751593		0.0036183	0.00126	0.163	0.00062935	0.00126	0.768
	0.18	0.191	0.891		-8609.027298	8.609027298		0.18	8.609027298		0.00366338	0.00128	0.191	0.00063809	0.00128	0.891
	0.2	0.22	1.01		-8519.62647	8.51962647		0.2	8.51962647		0.00370831	0.0013	0.22	0.00064681	0.0013	1.01
	0.22	0.251	1.15		-8508.369397	8.508369397		0.22	8.508369397		0.0037531	0.00132	0.25	0.00065552	0.00132	1.15
	0.24	0.284	1.28		-8416.563592	8.416563592		0.24	8.416563592		0.00379774	0.00134	0.28	0.00066421	0.00134	1.28
	0.26	0.318	1.42		-8364.686249	8.364686249		0.26	8.364686249		0.00384225	0.00136	0.32	0.00067288	0.00136	1.42
	0.28	0.353	1.57		-8342.337764	8.342337764		0.28	8.342337764		0.00388661	0.00138	0.35	0.00068154	0.00138	1.57
	0.3	0.39	1.72		-8295.213839	8.295213839		0.3	8.295213839		0.00393084	0.0014	0.39	0.00069018	0.0014	1.72
	0.34	0.468	2.05		-8257.167863	8.257167863		0.34	8.257167863		0.00397494	0.00142	0.47	0.00069881	0.00142	2.05
	0.38	0.552	2.39		-8192.177303	8.192177303		0.38	8.192177303		0.0040189	0.00144	0.55	0.00070742	0.00144	2.39
	0.42	0.643	2.76		-8143.771288	8.143771288		0.42	8.143771288		0.00406274	0.00146	0.64	0.00071602	0.00146	2.76
	0.46	0.74	3.15		-8097.185804	8.097185804		0.46	8.097185804		0.00410645	0.00148	0.74	0.0007246	0.00148	3.15
	0.5	0.844	3.56		-8046.069456	8.046069456		0.5	8.046069456		0.00415003	0.0015	0.84	0.00073317	0.0015	3.56
	0.55	0.985	4.12		-7999.132699	7.999132699		0.55	7.999132699		0.00419349	0.00152	0.98	0.00074172	0.00152	4.12
	0.6	1.13	4.73		-8003.273607	8.003273607		0.6	8.003273607		0.00423684	0.00154	1.13	0.00075026	0.00154	4.73
	0.65	1.30	5.38		-7939.639838	7.939639838		0.65	7.939639838		0.00428006	0.00156	1.30	0.00075879	0.00156	5.38
	0.7	1.48	6.08		-7898.488897	7.898488897		0.7	7.898488897		0.00432316	0.00158	1.48	0.0007673	0.00158	6.08
	0.75	1.68	6.84		-7848.353853	7.848353853		0.75	7.848353853		0.00436615	0.0016	1.68	0.0007758	0.0016	6.84
	0.8	1.89	7.65		-7815.567718	7.815567718		0.8	7.815567718		0.00440903	0.00162	1.89	0.00078429	0.00162	7.65
	0.85	2.12	8.53		-7782.276097	7.782276097		0.85	7.782276097		0.0044518	0.00164	2.12	0.00079276	0.00164	8.53
	0.9	2.37	9.47		-7743.513106	7.743513106		0.9	7.743513106		0.00449445	0.00166	2.37	0.00080122	0.00166	9.47
	0.95	2.63	10.48		-7728.117523	7.728117523		0.95	7.728117523		0.004537	0.00168	2.63	0.00080967	0.00168	10.48
	1	2.93	11.56		-7672.572892	7.672572892		1	7.672572892		0.00457944	0.0017	2.93	0.0008181	0.0017	11.56

The formula for the DSFL fit cannot easily be transformed into a p = f(n) form. Hence, about 12000 $n \mid p_1$ and $n \mid p_2$ data pairs were manually generated with the given n = f(p) formula (see Eq. 10 in the paper) using a variable increment of Δp as low as 0.00002. These $n \mid p_1$ and $n \mid p_2$ data pairs are listed in columns R | S and U | V in the Excel file Ex4. Then about 60 $n \mid p_1 \mid p_2$ data triples were manually generated by choosing an uptake, e.g., 0.01, for which the respective p_1 and p_2 pressures are then found through the Excel inherent function SLOOKUP(0.01;R11:S12160;2;TRUE) and SLOOKUP(0.01;U11:V12160;2;TRUE). This function operates such that it searches for the nearest uptake values to 0.01 and then gives the correlated pressure to this nearest uptake value. The found (correlated) pressure values are listed in column T and W, from which they are copied to column I and J in order to calculate the isosteric enthalpy of adsorption ΔH_{ads} vs n in columns O and P.

S4. MOF structures

S4.1 MIL-160:

MIL-160 (*Matériaux Institut Lavoisier*) is an Al-MOF, which was described by Cadiau *et al.* in 2015.[5] They obtained the MOF by applying reflux conditions for aqueous solutions of 2,5-furandicarboxylic acid, sodium hydroxide and aluminum chloride. MIL-160 is constructed by cis-μ-OH-connected, vertex-sharing {AlO_6} octahedra, that form helical chains, which are then joined by the linker 2,5-furandicarboxylate (Fig. S1).

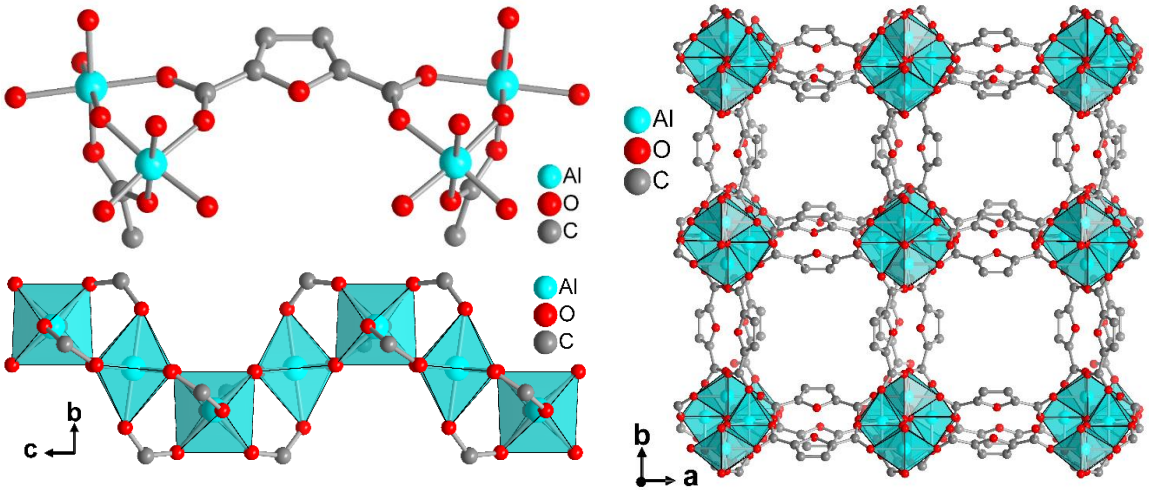


Fig. S1 Structural elements in MIL-160 with extended asymmetric unit, the fourfold helical chain of cis vertex-bridged {AlO_6}-polyhedra as the inorganic building unit, and the 3D framework structure of square-shaped one-dimensional channels. Graphics produced from cif-file for MIL-160 (CSD-Refcode PIBZOS).[6]

MIL-160 consists of chains of {AlO_6}-polyhedra that are surrounded by linker molecules.[5] This results in a chemical formula of $[Al(OH)(O_2C\text{-}C_4H_2O\text{-}CO_2)\ n\ H_2O]_m$ and microporous square-shaped channels of 5 Å edge length.[5,7] The material exhibits a surface area of 1070 $m^2\ g^{-1}$ and a pore volume of 0.40 $cm^3\ g^{-1}$ from $AlCl_3$ and NaOH (theoretically: 1250 $m^2\ g^{-1}$, 0.48 $cm^3\ g^{-1}$),[5] respectively 1150 $m^2\ g^{-1}$ and 0.46 $cm^3\ g^{-1}$, from $Al(OH)(CH_3COO)_2$,7 although very recent theoretical calculations suggested a surface area of 776 $m^2\ g^{-1}$ and a pore volume of 0.45 $cm^3\ g^{-1}$.[8]

The hydrophilic character of the MOF is also due to the heteroatom in the furan moiety of the linker. This resulted in a highly hydrothermally stable material with promising water sorption characteristics. Cadiau *et al.* denoted MIL-160 as the most promising Al-MOF for heat pump applications.[5]

S4.2 NH_2-MIL-125(Ti):

NH_2-MIL-125(Ti) is based on $Ti_8O_8(OH)_4^{12+}$ SBUs and aminoterephthalic acid (H_2N-BDC), and is isostructural to unmodified MIL-125(Ti) (Fig. S2).[9]

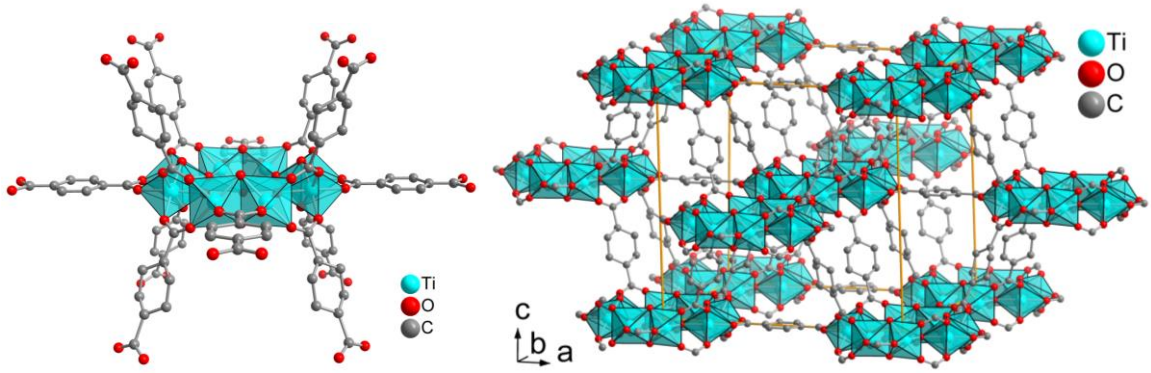


Fig. S2 Structure of titanium terephthalate MIL-125 (isostructural to NH_2-MIL-125(Ti)).[9] The SBU is an eight-membered ring of edge- and vertex-sharing TiO_6 octahedra, which is connected to 12 neighboring SBUs in a body-centered cubic (bcc) packing arrangement. Structure drawn from the deposited cif-file under CCDC 751157 (MIL-125).[9]

Titanium aminoterephthalate, NH_2-MIL-125(Ti) is a hydrophilic MOF, showing a steep rise of the isotherm, and complete water loading at a relative pressure as low as p/p_0 = 0.2. Most notably, it is also much more hydrophilic than NH_2-UiO-66, although pore sizes are similar and the linker molecule is the same. The main reason for the increased hydrophilicity of NH_2-MIL-125(Ti) can be explained by the structure of the SBU: Compared to $Zr_6O_4(OH)_4^{12+}$ (679 g/mol), the $Ti_8O_8(OH)_4^{12+}$ cluster (579 g/mol) has a lower formula weight and contains more hydrophilic M^{4+} and O^{2-} ions. From these results, NH_2-MIL-125(Ti) is of strong interest for further examination concerning water sorption for heat transformation.[10]

S4.3 HHU-1 (Zr-ADC):

The reaction of acetylenedicarboxylic acid (H_2ADC) with $ZrOCl_2 \cdot 8H_2O$ in DMF yielded the MOF **HHU-1** of ideal formula $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(ADC)_6]$.[11]·The structure of **HHU-1** was determined from powder diffraction data with *a* = 17.925(3) Å in space group $Fm\bar{3}m$ using the crystal structure of the terephthalate UiO-66 as a starting point. The UiO-type hexanuclear $[Zr_6O_4(OH)_4]^{12+}$ SBU with the attached ADC linkers and the face-centered cubic (fcc) packing diagram of the **fcu** network are shown in Figure S3. The contact diameters for the surrounding van der Waals radii of the octahedral and tetrahedral cages are about 9.6 Å and 5.8 Å diameter respectively, with a triangular window diameter 4.4 Å.[11]

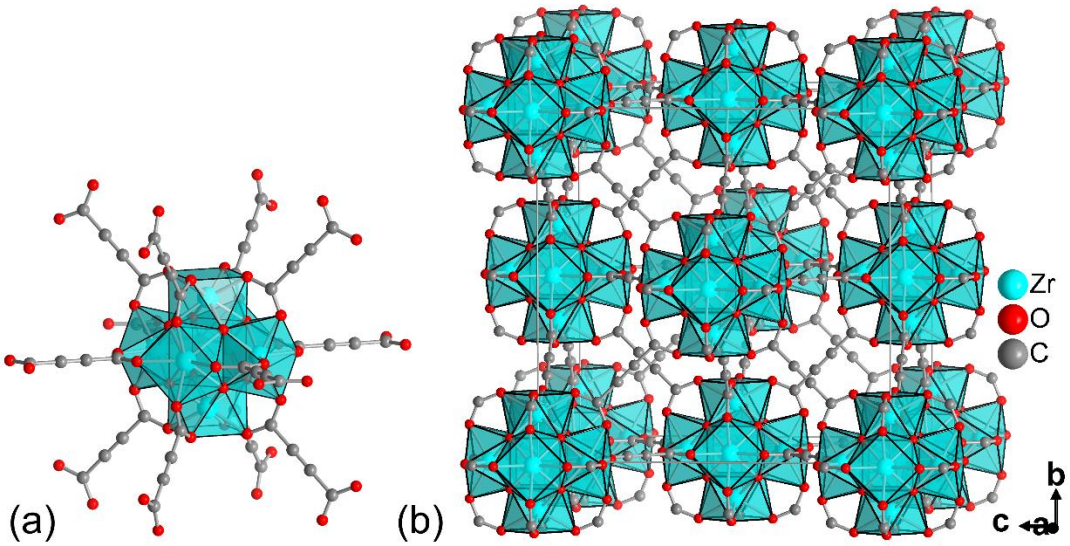


Fig. S3 (a) Secondary building unit of $\{Zr_6(O)_4(OH)_4\}$ with the 12 surrounding and connecting acetylenedicarboxylate linkers and the edge-sharing square-antiprismatic ZrO_8 coordination as polyhedra. (b) fcc packing diagram of the **fcu** framework in **HHU-1**. The refined guest atoms are not shown for clarity.[11]

Water vapor adsorption for **HHU-1** displays a Type Ib isotherm with an early water uptake at P/P_0 = 0.05, which indicates a high hydrophilicity, probably due to the small micropores with the synergistic effects of the triple bond C≡C of the ADC linker, and the μ_3-OH and μ_3-O groups on the $[Zr_6O_4(OH)_4]^{12+}$ SBU.[11]

S5. CO_2 adsorption isotherms with Freundlich-Langmuir fit of MIL-160 at 273 K, 283 K and 293 K

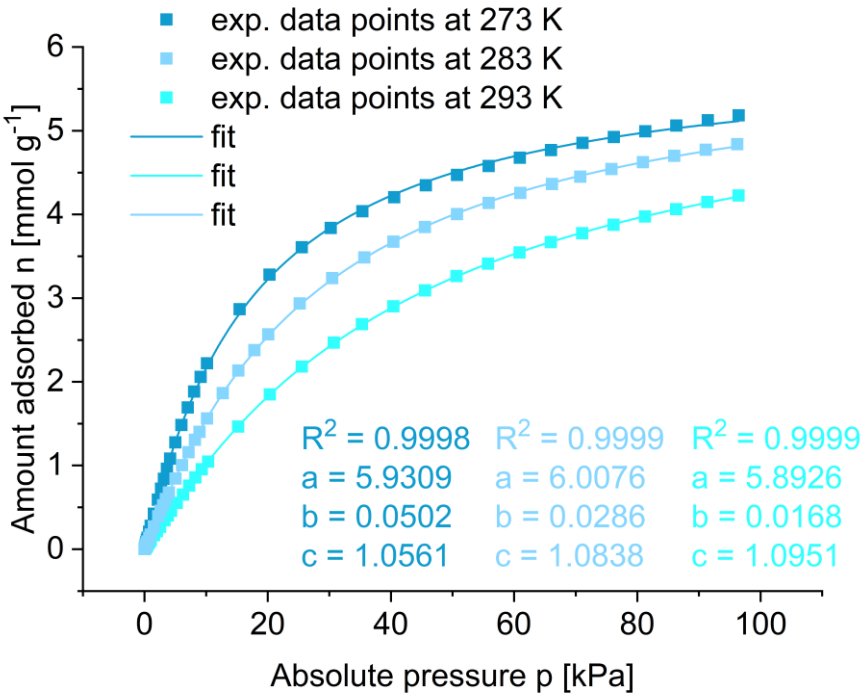


Fig. S4 Freundlich-Langmuir fit for CO_2 isotherms of MIL-160 at 273 K, 283 K and 293.

S6. SO_2 adsorption isotherms of NH_2-MIL-125(Ti) at 273 K and 293 K

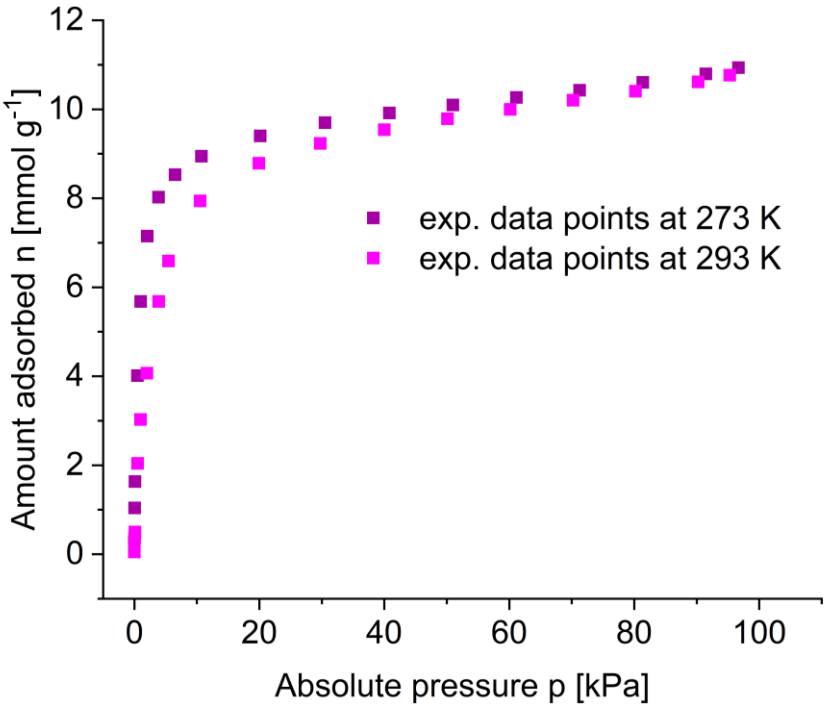


Fig. S5 SO_2 adsorption isotherms of NH_2-MIL-125(Ti) at 273 K and 293 K in a linear-scale *n* vs *p* plot. The amount adsorbed *n* starts at 0.05 mmol g^{-1}.

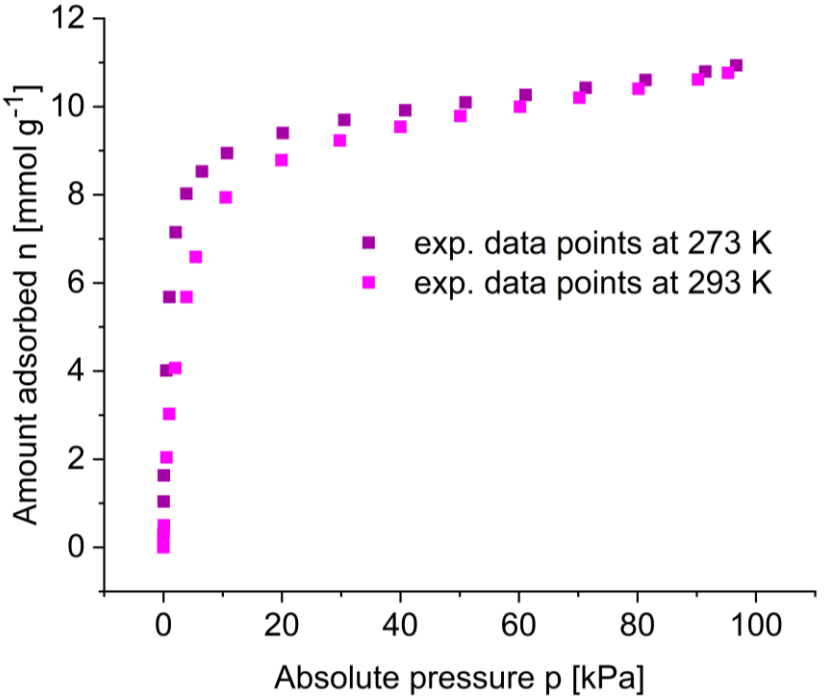


Fig. S6 SO_2 adsorption isotherms of NH_2-MIL-125(Ti) at 273 K and 293 K in a linear-scale *n* vs *p* plot. The amount adsorbed *n* starts at 0.0002 mmol g^{-1}.

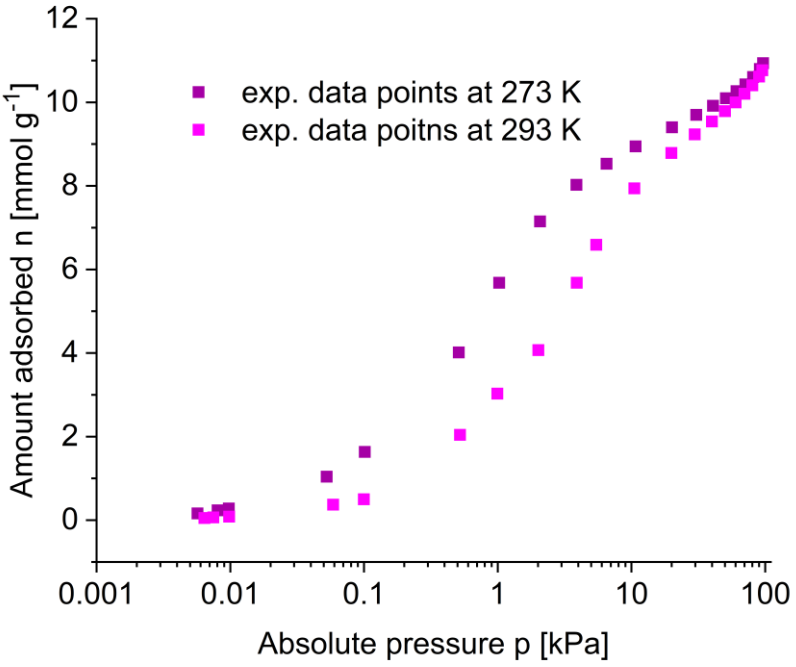


Fig. S7 SO_2 adsorption isotherms of NH_2-MIL-125(Ti) at 273 K and 293 K in a linear *n*- vs logarithmic *p*-scale plot. The amount adsorbed *n* starts at 0.05 mmol g^{-1}.

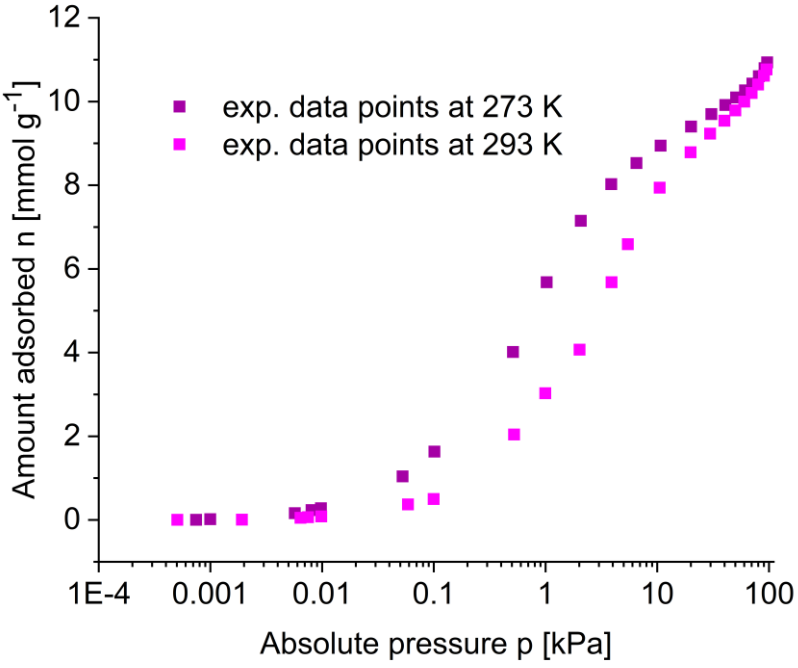


Fig. S8 SO_2 adsorption isotherms of NH_2-MIL-125(Ti) at 273 K and 293 K in a linear *n*- vs logarithmic *p*-scale plot. The amount adsorbed *n* starts at 0.0002 mmol g^{-1}.

S7. Virial analysis for SO_2 isotherms of NH_2-MIL-125(Ti) at 273 K and 293 K with a larger number of a_i and b_i fit parameters

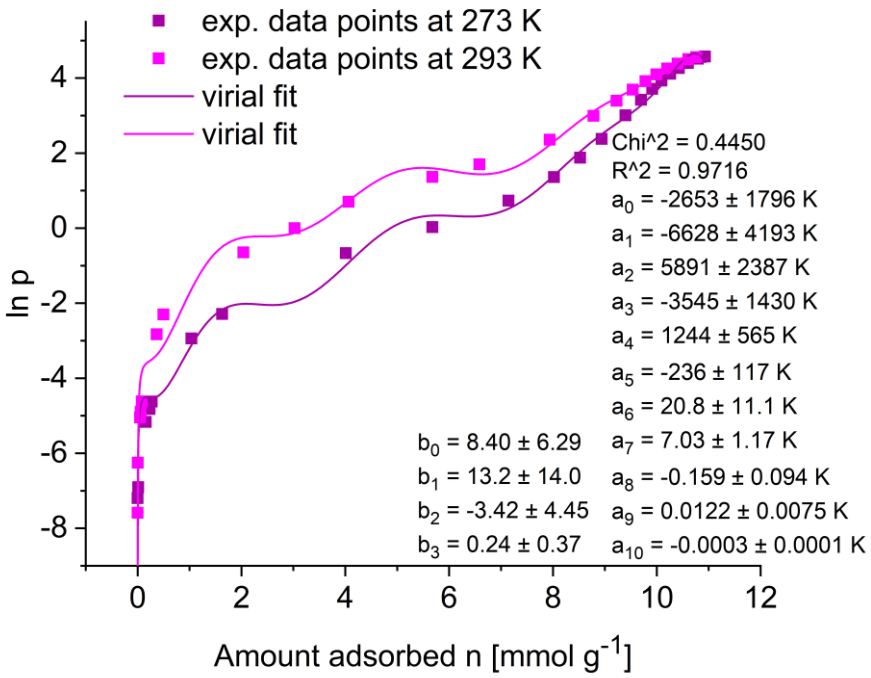


Fig. S9 Virial analysis for SO_2 isotherms of NH_2-MIL-125(Ti) at 273 K and 293 K with additional low uptake points, starting at n = 0.0002 mmol g^{-1} and a larger number of a_i and b_i fit parameters.

S8. Enthalpy of adsorption for CO_2 on MIL-100(Cr)

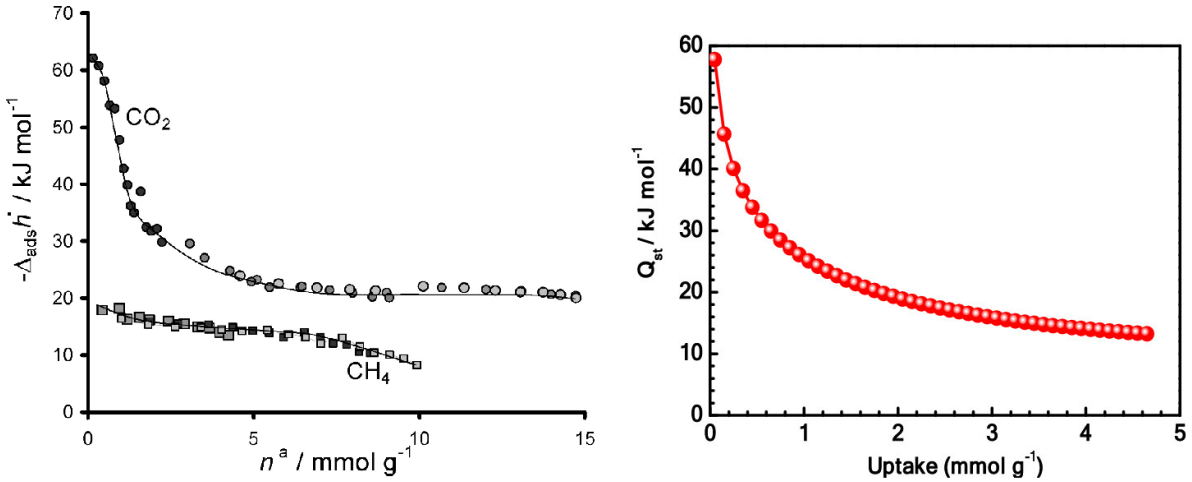


Fig. S10 Enthalpy of adsorption for CO_2 on MIL-100(Cr) determined (left) by microcalorimetry[12] and (right) calculated from adsorption isotherms at 273, 298 and 323 K with a Freundlich-Langmuir fit and Clausius-Clapeyron approach.[13] Left: Reproduced from ref. 12 with permission from the American Chemical Society, copyright 2008. Right: Reproduced from ref. 13 with permission from the American Chemical Society, copyright 2019.

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