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Methane Preconcentration by Adsorption
A methodology for materials and conditions selection

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Adsorption

In the supplementary material, selection and optimization of fitting procedures (adsorption model and parameterization) for experimentally measured adsorption isotherms (Figure 1 – 6) are discussed. Methane and nitrogen adsorption isotherms were collected in two temperature regions: at "high" temperatures (T= 196, 273, and 296 K) to calculate the isosteric enthalpy of adsorption and evaluate the selectivity for CH_4 over N_2, and at "low" temperature (T = 77 K) to determine the adsorbent surface area. Details on the applied fitting procedures and the derived parameters are given in the following sections.

High temperature adsorption isotherms (196, 273, 296 K)

Adsorption isotherms of CH_4 and N_2 were collected in the pressure range from 0 to 100 kPa at three temperatures (196, 273 and 296 K). Based on this data, the selectivity of CH_4 over N_2 and the isosteric enthalpy of adsorption were calculated for all six candidate adsorbents, as presented in the "Results and discussion" section of the manuscript. Isotherms were fitted by both a second order virial equation (Eq. 1) and a Langmuir equation, and the goodness of fit was compared (as shown in Figure O1).

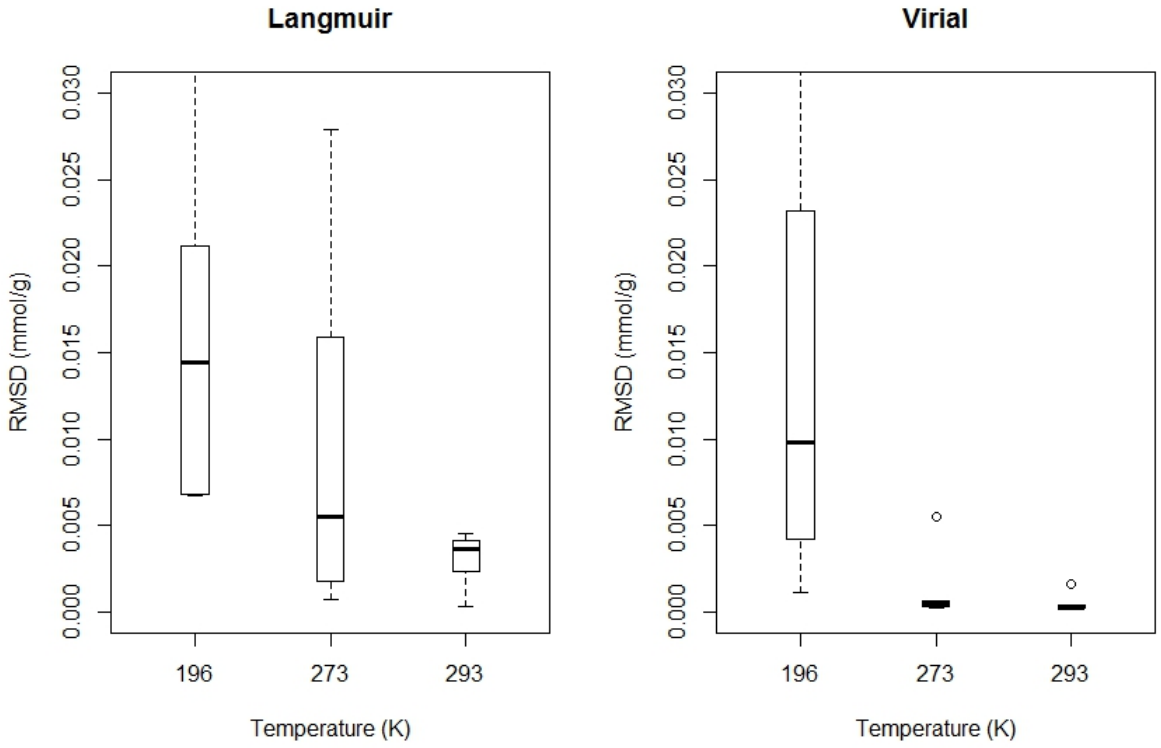

Figure O1: Root-mean square deviation (RMSD) of CH_4 isotherms from Langmuir and virial equation fits for all candidate materials at different adsorption temperatures.

$$RMSD = \sqrt{\sum_{k=0}^{n}(y_i - f_i)^2}/n \qquad \text{(Eq. O1)}$$

The goodness of fit was determined by summing the least square residuals for each point, according to Eq. O1. Figure O1 reveals that the agreement of the virial equation with the experimental data is superior to the Langmuir model especially at higher temperatures. In Table O1 the respective error

values are given and in Table O2 the optimized fit parameters for a second order virial equation for each candidate material are given.

CH_4	T	HayeSep D	MWCNT	HKUST-1	ZIF-8	Z5A	Z13X
Langmuir	*196 K*	0.0067022	0.0067880	0.0374812	0.0176922	0.0112182	0.0211841
	273 K	0.0007018	0.0017387	0.0278759	0.0048329	0.0061464	0.0158652
	296 K	0.0003203	0.0023366	0.0044858	0.0041373	0.0041196	0.0031918
Virial	*196 K*	0.0011105	0.0047162	0.0320524	0.0042345	0.0148083	0.0232007
	273 K	0.0003261	0.0006095	0.0054833	0.0002609	0.0004430	0.0004663
	296 K	0.0001979	0.0004289	0.0016017	0.0002049	0.0001780	0.0002803

Table O1: Root-mean square deviation (RMSD) (mmol/g) of CH_4 isotherms from Langmuir and virial equation fits for all candidate materials at different adsorption temperatures.

	Material	a_0	a_1	a_2	b_0	b_1	b_2	ΔH_0 (kJ mol^{-1})
CH_4	HayeSep D	-2397.720	1052.420	-1906.380	14.515	-3.916	9.454	19.935
	MWCNT	-1899.880	-1238.260	4554.410	12.556	7.724	-23.561	15.796
	HKUST-1	-1882.530	-130.870	-8.977	10.958	0.633	0.056	15.651
	ZIF-8	-1676.200	-51.416	52.072	11.650	0.263	-0.258	13.936
	Zeolite 5A	-2547.020	-292.460	7.361	13.711	1.138	0.292	21.176
	Zeolite 13X	-2206.770	-488.529	419.245	13.248	2.020	-1.842	18.347
N_2	HayeSep D	-1519.140	-105.573	-10420.700	12.865	0.226	54.753	12.630
	MWCNT	-1696.560	-1579.990	-10000.000	13.049	10.115	50.408	14.105
	HKUST-1	-1698.160	21.277	-476.111	11.463	0.033	2.425	14.119
	ZIF-8	-1365.400	1675.840	-13963.400	11.738	-8.398	71.200	11.352
	Zeolite 5A	-3140.820	443.578	-16.857	16.041	-0.828	0.067	26.113
	Zeolite 13X	-2201.770	781.992	-3238.400	13.811	-3.541	16.597	18.306

Table O2: Fit parameters for second order virial-type equation and the derived isosteric enthalpy of adsorption for the studied candidate adsorbents.

Low temperature adsorption isotherms (77 K)

Adsorption isotherms of CH_4 and N_2 at liquid nitrogen temperature (77 K) were determined for all candidate adsorbents and fitted with both the BET and Langmuir model to determine the surface area of each material. The quality of each fit was assessed based on the R^2 value. In Table O3, the specific surface areas (SSA) calculated using the BET and the Langmuir model, as well as the number of data points included in the fit and the R^2 values are given. Numbers in bold correspond to a better model fit (R^2 values). The model selection agrees well with the qualitative evaluation as discussed in the section “surface area” of the main manuscript. For the metal-organic frameworks (HKUST-1 and ZIF-8), the calculated surface area was highly dependent on the selected model For methane adsorption on HayeSep D both models agreed similarly well, but resulted in very different surface areas. Based on its slightly higher R^2 value and better consistency with the macroporous structure of HayeSep D the BET model was selected.

	N_2						CH_4					
	BET			Langmuir			BET			Langmuir		
	No. Points	R^2	SSA (m^2/g)	No. Points	R^2	SSA (m^2/g)	No. Points	R^2	SSA (m^2/g)	No. Points	R^2	SSA (m^2/g)
HSD	**11**	**0.995**	**609**	11	0.996	640	**9**	**0.999**	**856**	9	0.996	1300
	18	**0.999**	**692**				**7**	**0.999**	**887**	7	0.998	1181
CNT	**11**	**0.999**	**390**	6	0.999	385	**7**	**1.000**	**481**	7	0.998	547
	5	**1.000**	**361**				**16**	**1.000**	**501**			
HKUST-1	16	0.997	1532	**40**	**1.000**	**1690**	**54**	**0.816**	**2183**	54	0.552	5178
	7	1.000	1462				**57**	**0.770**	**1505**	57	0.931	2526
ZIF-8	28	0.986	1473	**34**	**1.000**	**1702**	**48**	**0.784**	**1240**	22	0.977	1988
	24	0.953	1619				**32**	**0.936**	**1753**			
Z5A	14	1.000	462	**40**	**1.000**	**537**	10	0.965	552	**57**	**0.999**	**622**
Z13X	6	1.000	540	**29**	**0.999**	**628**	17	0.812	510	**18**	**0.973**	**794**

Table O3: Fitting parameters of the BET and the Langmuir model for N_2 and CH_4 adsorption isotherms of different candidate adsorbents, including the number of fitted points, R^2values and the specific surface area (SSA). The numbers in bold indicate a better model fit (R^2 value).