

Supplementary data

S1. Frontal analysis and equilibrium constants

Experimental Procedure:

The column was first equilibrated with pure CO₂ at desired temperature and pressure for 15 minutes. After a stable baseline was established, methanol was pumped into the column continuously at 11 increasing concentrations: 0.5, 1, 2, 3, 5, 8, 10, 12, 15, 17.5 and 20 vol.%. The total volumetric flow rate was kept constant at 2.00 mL min⁻¹. A 5-min interval was set for the column to achieve adsorption equilibrium under each concentration. The signal of the photodiode array detector (PDA) was recorded at 200 nm. Figure S1 shows the breakthrough curve on the silica gel SIL-300 column by staircase frontal analysis.

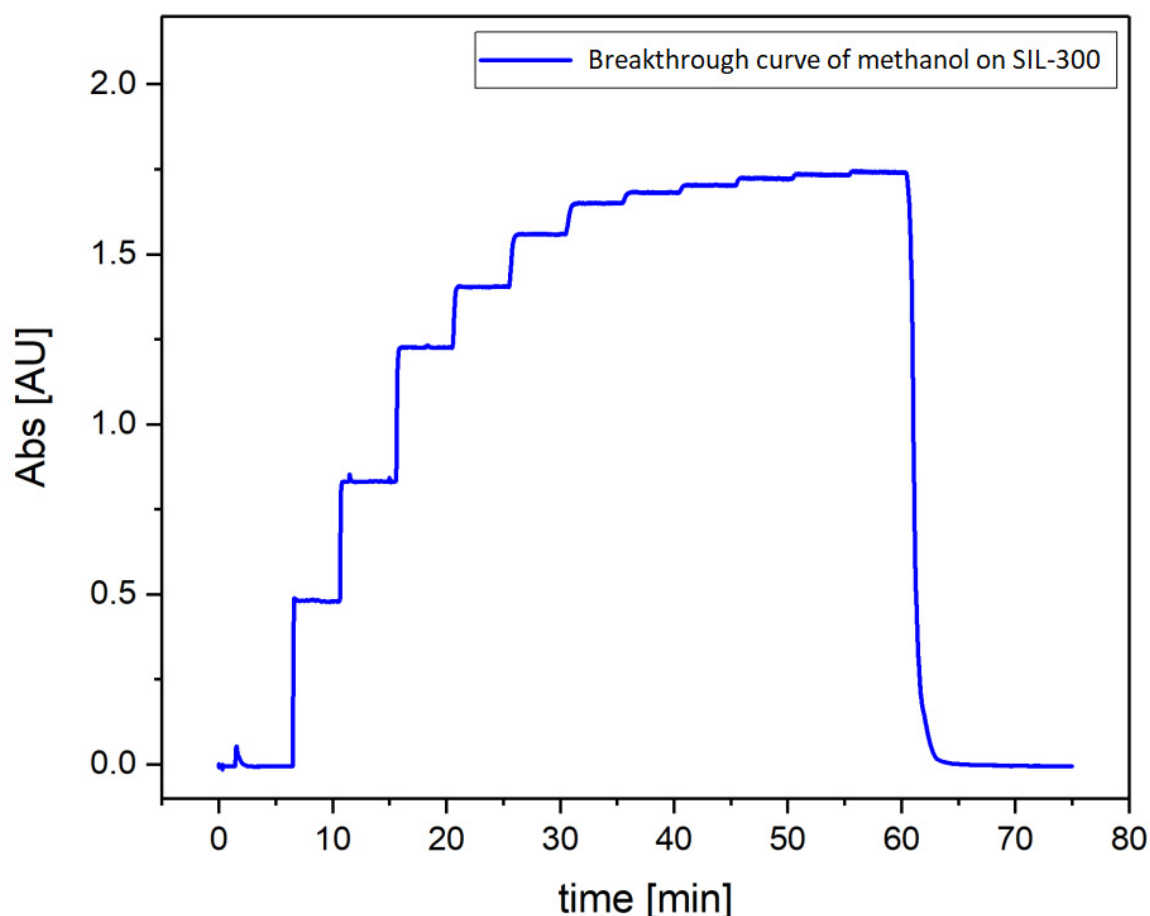


Figure S1: The breakthrough curve of staircase frontal analysis on SIL-300 column. SFC conditions: 200 bar, 40 °C, flow rate 2 mL min⁻¹, detection at 200 nm.

Data processing:

The values of methanol loading, q , were determined by the following mass balance:

$$V_{0,p} \cdot (c_2 - c_1) + V_c \cdot [\varepsilon_t \cdot (c_2 - c_1) + (1 - \varepsilon_t) \cdot (q_2 - q_1)] = \dot{V}_{avg} \cdot (c_2 - c_1) \cdot (t_2 - t_{injection,2})$$

where $V_{0,p}$ is the plant hold-up volume, *i.e.*, the volume of the plant from the point of injection to the detector, not including the column. V_c is the geometrical volume of the column. ε_t is the total porosity of the column, which is the volume of mobile phase in the column. It is the sum of the internal porosity (ε_i) and the external porosity (ε_e). c_1 and c_2 are the concentrations of the modifier in the initial and newly established equilibrium states, respectively. q_1 and q_2 are the corresponding loadings of the modifier at the initial and the latter equilibrium states. $t_{injection,2}$ is the moment at which methanol concentration changed to c_2 at the pumps, while t_2 is the time when the outlet concentration profile reaches a plateau value at concentration c_2 . $\dot{V}_{avg}$ is the volumetric flow rate of the mobile phase.

Langmuir parameters determined:

Table S1: Fitted Langmuir parameters to the adsorption isotherm data.

Adsorbent	T (°C)	q_{max} (g mL ⁻¹)	$K_{eq,Langmuir}$ (mL g ⁻¹)	R ²
SIL-60	40	1.7±0.1	17±3	0.9815
SIL-100	40	1.4±0.1	11±2	0.9898
SIL-300	40	1.6±0.1	5.3±0.7	0.9960
SIL-Aerogel	40	2.5±0.2	7.1±0.8	0.9961
SIL-Aerogel	45	2.6±0.2	6.6±0.7	0.9966
SIL-Aerogel	50	2.6±0.2	7.0±0.7	0.9968
SIL-Aerogel	55	2.7±0.2	6.8±0.7	0.9971
SIL-Aerogel	60	2.8±0.2	6.9±0.7	0.9973

S2 Paired t-test for correction factor

Table S2: Calculation of corrected adsorption constant $K_{eq,L}^{corr}$ by selected correction factor.

	(SIL-60)		(SIL-100)	(SIL-300)	(SIL-Aerogel)
Measured $K_{eq,L}$	16.5		11.2	5.3	7.1
$K'_{eq,L}$	61.6	58.3	24.2	62.5	
$K_{eq,L}^{corr}$ (correction factor =0.19)	11.704	11.077	4.598	11.875	

Table S3: Data of paired t-test for correction factor selection.

Correction factor	Speculated K_{eq} (SIL-60)	Speculated K_{eq} (SIL-100)	Speculated K_{eq} (SIL-300)	Speculated K_{eq} (SIL-Aerogel)	d_1 (SIL-60)	d_2 (SIL-100)	d_3 (SIL-300)	d_4 (SIL-Aerogel)	$\bar{d}$	$s_{\bar{d}}$	t
0.10	6.16	5.83	2.42	6.25	-10.34	-5.37	-2.88	-0.85	- 4.8 6	3.5 5	- 1.3 7
0.11	6.78	6.41	2.66	6.88	-9.72	-4.79	-2.64	-0.23	- 4.3 4	3.5 0	- 1.2 4
0.12	7.39	7.00	2.90	7.50	-9.11	-4.20	-2.40	0.40	- 3.8 3	3.4 6	- 1.1 1
0.13	8.01	7.58	3.15	8.13	-8.49	-3.62	-2.15	1.03	- 3.3 1	3.4 3	- 0.9 6
0.14	8.62	8.16	3.39	8.75	-7.88	-3.04	-1.91	1.65	- 2.7 9	3.4 1	- 0.8 2
0.15	9.24	8.75	3.63	9.38	-7.26	-2.46	-1.67	2.28	- 2.2 8	3.3 9	- 0.6 7

0.16	9.86	9.33	3.87	10.00	-6.64	-1.87	-1.43	2.90	- 1.7 6	3.3 8	- 0.5 2
0.17	10.47	9.91	4.11	10.63	-6.03	-1.29	-1.19	3.53	- 1.2 4	3.3 8	- 0.3 7
0.18	11.09	10.49	4.36	11.25	-5.41	-0.71	-0.94	4.15	- 0.7 3	3.3 8	- 0.2 2
0.19	11.70	11.08	4.60	11.88	-4.80	-0.12	-0.70	4.78	- 0.2 1	3.4 0	- 0.0 6
0.20	12.32	11.66	4.84	12.50	-4.18	0.46	-0.46	5.40	0.3 1	3.4 2	0.0 9
0.21	12.94	12.24	5.08	13.13	-3.56	1.04	-0.22	6.03	0.8 2	3.4 4	0.2 4
0.22	13.55	12.83	5.32	13.75	-2.95	1.63	0.02	6.65	1.3 4	3.4 8	0.3 8
0.23	14.17	13.41	5.57	14.38	-2.33	2.21	0.27	7.28	1.8 5	3.5 2	0.5 3
0.24	14.78	13.99	5.81	15.00	-1.72	2.79	0.51	7.90	2.3 7	3.5 7	0.6 6
0.25	15.40	14.58	6.05	15.63	-1.10	3.38	0.75	8.53	2.8 9	3.6 2	0.8 0
0.26	16.02	15.16	6.29	16.25	-0.48	3.96	0.99	9.15	3.4 0	3.6 8	0.9 2
0.27	16.63	15.74	6.53	16.88	0.13	4.54	1.23	9.78	3.9 2	3.7 5	1.0 5
0.28	17.25	16.32	6.78	17.50	0.75	5.12	1.48	10.40	4.4 4	3.8 2	1.1 6
0.29	17.86	16.91	7.02	18.13	1.36	5.71	1.72	11.03	4.9 5	3.9 0	1.2 7
0.30	18.48	17.49	7.26	18.75	1.98	6.29	1.96	11.65	5.4 7	3.9 8	1.3 7

Difference of paired observation: $d = \text{speculated } K_{eq} - \text{measured } K_{eq}$

Sample mean difference: $\bar{d} = \frac{\sum_{i=1}^n d_i}{n}$

Sample variance: $s_d^2 = \frac{\sum_{i=1}^n (d_i - \bar{d})^2}{n-1}$

Standard error of the mean difference: $s_{\bar{d}} = \frac{s_d}{\sqrt{n}}$

T-statistic: $t = \frac{\bar{d} - \mu_{d0}}{s_{\bar{d}}}$

Null hypothesis: $\mu_d = 0$

Alternate hypothesis: $\mu_d \neq 0$

Speculated $K_{eq} = correction\ factor \cdot K_{eq, regression}$