Understanding CO_2 adsorption in a flexible zeolite through a combination of structural, kinetic and modelling techniques

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Supporting information

Experimental
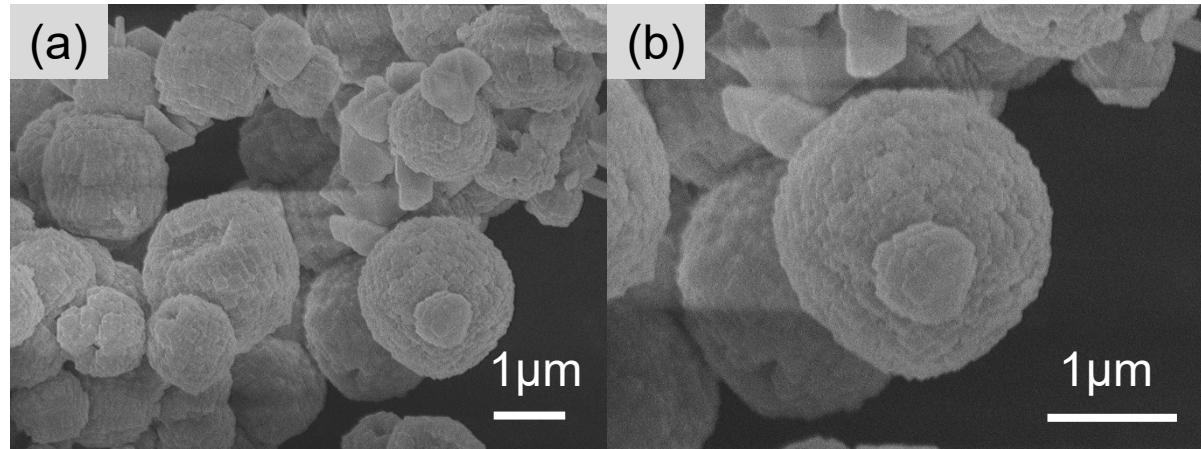
Figure S1: SEM micrographs of (Na,TEA)-ZSM-25 crystals, showing uniform particle size of 1 − 2 μm
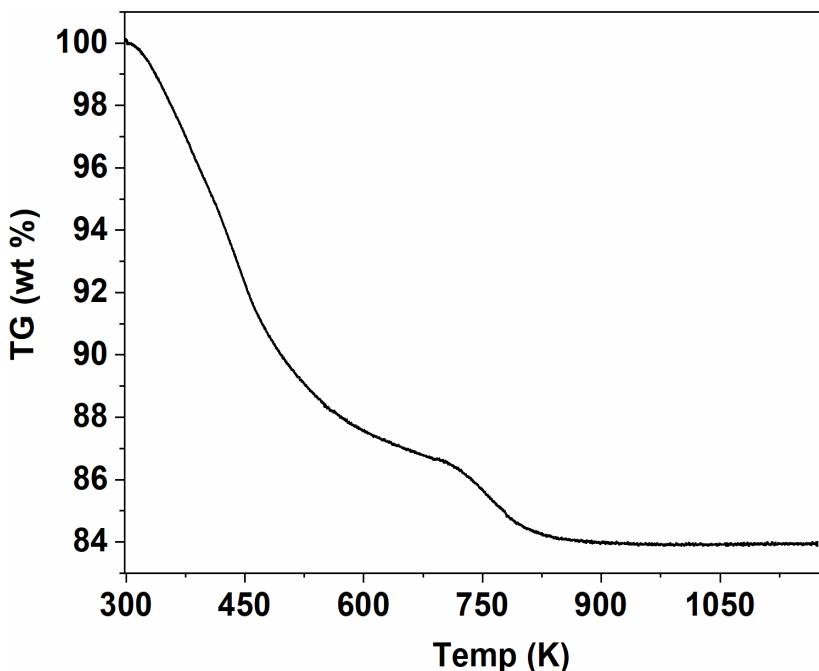
Figure S2: Thermogravimetry on (Na,TEA)-ZSM-25

The Rigid Adsorbent Lattice Fluid

The Rigid Adsorbent Lattice Fluid (RALF) model has been described in great detail in refs. [1,2]. It was shown that the model can accurately describe and predict equilibrium adsorption behaviour in both *'frozen'* as well as flexible adsorbents, with a minimum of modelling parameters. The equilibrium behaviour of the system is derived through the residual Gibbs energy, which for a single adsorbate is given by equation 1. Here we opt for the chemical engineering nomenclature as used in various textbooks, where the term residual refers to the departure of a thermodynamic property from that of an ideal gas at the same temperature and pressure[3,4] .

$$\frac{G^R(T,P,N)}{RT} = rN\left[-\frac{\tilde{\rho}}{\tilde{T}} + \frac{(1-\tilde{\rho})\ln(1-\tilde{\rho})}{\tilde{\rho}} + 1\right] + N(z - 1 - \ln z) \qquad \text{S1}$$

Equation 1 is the expression for the residual Gibbs energy of the adsorbed phase given in ref.[1] written for a single adsorbate, given that the combinatorial term for a single adsorbate becomes zero due to the rigid nature of the solid.   The reduced quantities are defined by:

$$\tilde{T} = \frac{T}{T^*} \qquad\qquad \tilde{P} = \frac{P}{P^*} \qquad\qquad \tilde{\rho} = \frac{\rho}{\rho^*}$$

Where T^*, P^* and ρ^* are the characteristic temperature, pressure and density of the lattice fluid. N is the total number of moles in the system and r is the overall number of lattice sites per molecule. The compressibility factor is as usual, i.e. $z = \frac{PV}{NRT} = r\frac{\tilde{P}}{\tilde{\rho}\tilde{T}}$. For an adsorbent, the density of the mixture does not correspond to the equilibrium value as given by an Equation of State. For the compressibility factor of a single component in equilibrium, z^{EoS}, the following holds:

$$z^{EoS} - 1 = r\left[-\frac{\tilde{\rho}}{\tilde{T}} - \frac{\ln(1-\tilde{\rho})}{\tilde{\rho}} - 1 \right]$$

S2

As is evident from equation 1, knowledge of the density of the system is essential to obtain the Gibbs energy. The volume of the adsorbent including the micropores, V_s, is taken as the system volume and therefore the density is given by:

$$\rho = \frac{\sum_j m_j}{V_s} = \frac{m_s}{w_s V_s} = \frac{\rho_s}{w_s}$$

S3

Since in this work we are dealing with a framework which can undergo volumetric changes upon adsorption, this expansion or contraction needs to be taken into account. In its simplest form, neglecting any compressibility effects (which is reasonable under normal adsorption conditions), the solid volume is given by:

$$V_s = V_s^0 + \Delta V_s$$

S4

Where V_s^0 is the solid volume under vacuum and ΔV_s can either be determined experimentally or a model function.

Through the residual Gibbs energy we can determine the adsorbed and fluid phase chemical potentials by carrying out the derivations with respect to number of moles of component k, i.e.

$$\frac{\mu_k^{R}}{RT} = \frac{1}{RT}\left(\frac{\partial G^R}{\partial N_k} \right)_{T,P,N_{j\neq k}} = \ln\varphi_k$$

For the adsorbed phase of a flexible adsorbent this yields (using subscript 1 to denote the single adsorbate):

$$\frac{\boldsymbol{\mu_{1,A}^{R}}}{\boldsymbol{RT}} = -\frac{\widetilde{\rho}}{\widetilde{T}}\left(\frac{2\sum_j \phi_j P_{j1}^*}{P^*} - 1 \right) r_1 + \left[\frac{(1-\widetilde{\rho})\ln(1-\widetilde{\rho})}{\widetilde{\rho}} + 1 \right] r_1^0$$
$$+ \left(1 + \frac{rN}{r_1\rho_s}\frac{\partial\rho_s}{\partial N_1} \right)(z^{EoS} - 1)\frac{r_1}{r} - \ln z - \frac{z-1}{r}\frac{rN}{\rho_s}\frac{\partial\rho_s}{\partial N_1}$$

S5

Whilst for the fluid phase it is given by:

$$\frac{\boldsymbol{\mu_{1,F}^{R}}}{\boldsymbol{RT}} = \left[-\frac{\widetilde{\rho}_1}{\widetilde{T}_1} + \frac{(1-\widetilde{\rho}_1)\ln(1-\widetilde{\rho}_1)}{\widetilde{\rho}_1} + 1 \right] r_1^0 + z - 1 - \ln z$$

S6

For the calculation of adsorption isotherms, we can now use the usual equilibrium condition, which is for the chemical potentials of component k to be equal in the adsorbed and fluid phase. Isotherms can be constructed by solving equation 7 for the number of moles adsorbed, N_k, at any given combination of pressure and temperature.

$$\mu_{k,F}(P,T) = \mu_{k,A}(N_k, P, T)$$

S7

Zero Length Column

The mass balance for CO_2 in the ZLC is:

$$V_s \frac{d\bar{q}}{dt} + V_f \frac{dc}{dt} = -F_{out} c \qquad \text{S8}$$

Where V_s and V_f are the solid and fluid volumes, respectively, $\bar{q}$ the average adsorbed phase concentration, c the fluid phase concentration of CO_2, F_{in} is the inlet flowrate and F_{out} is the outlet flowrate.

An overall mass balance (including the carrier gas) on the cell gives the outlet flowrate:

$$F_{out} = F_{in} - \frac{V_S}{c_{tot}} \frac{d\bar{q}}{dt} \qquad \text{S9}$$

Where c_{tot} is the total concentration in the ZLC, which is constant and derived from pressure and temperature with the ideal gas law, which is an appropriate equation of state under the measurement conditions.

The average adsorbed phase concentration can be computed from an overall mass balance on the adsorbent as given in the main text:

$$\frac{d\bar{q}}{dt} = -\frac{3}{R} J|_{r=R} \qquad \text{S10}$$

Structural characterisation
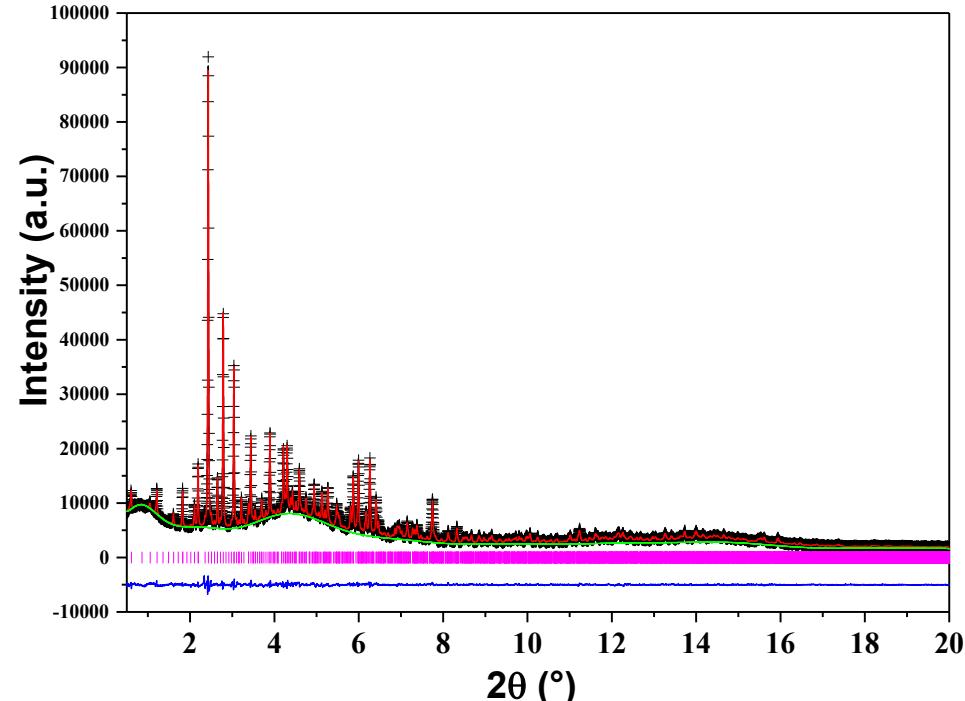
Figure S3: Rietveld refinement of calcined dehydrated (Na,H)-ZSM-25. Synchrotron data in black, calculated pattern in red, background model in green, peak positions in pink, difference between observed and calculated in blue.
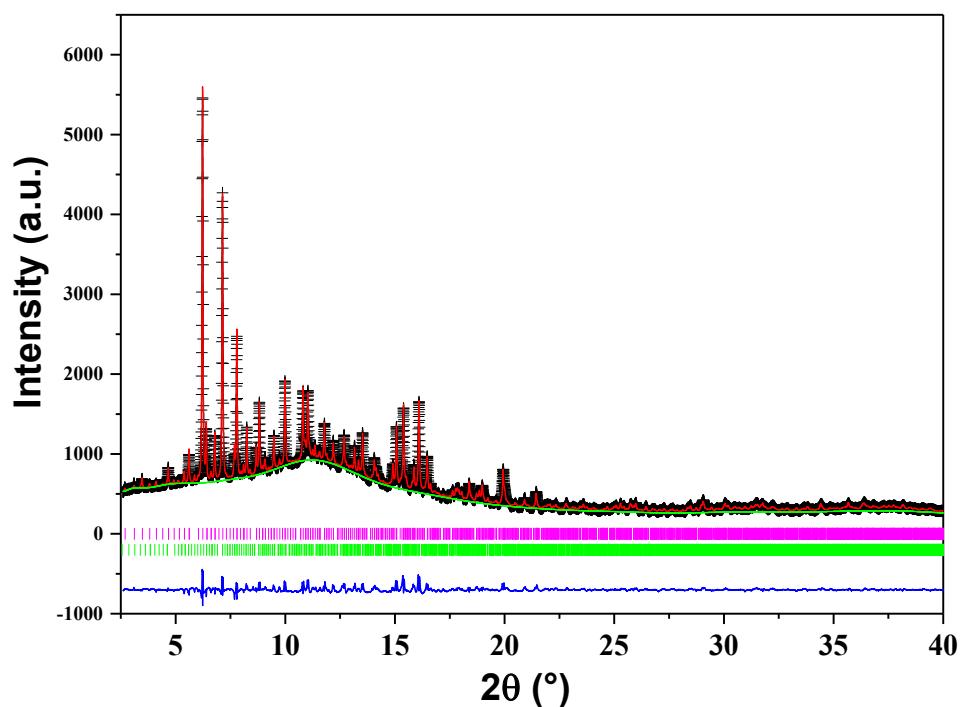
Figure S4: Rietveld refinement of calcined dehydrated (Na,TEA)-ZSM-25. Synchrotron data in black, calculated pattern in red, background model in green, peak positions in pink, difference between observed and calculated in blue.
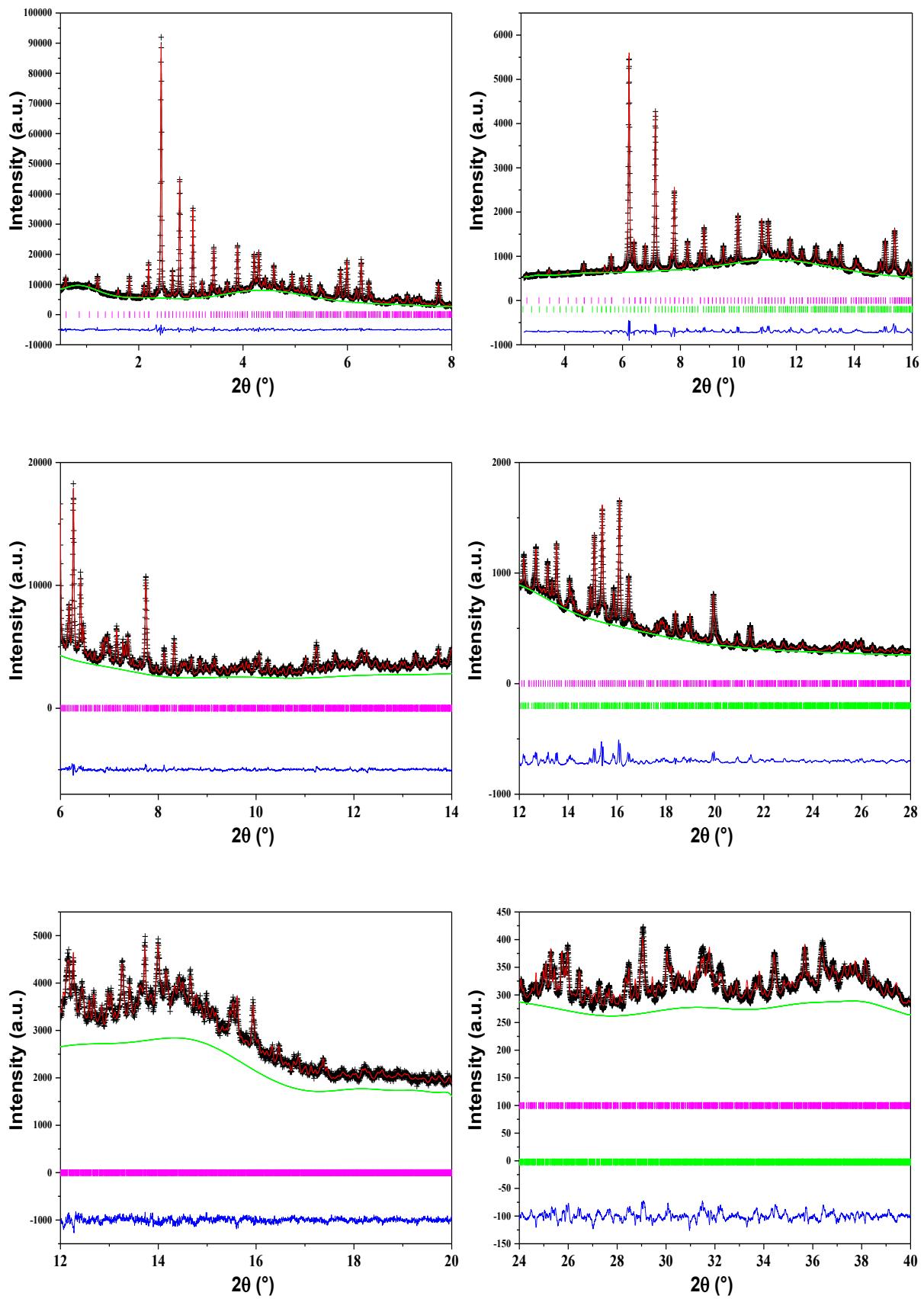
Figure S5: Rietveld plots, zoomed in on different 2θ ranges for (Na,H)-ZSM-25 (left) and (Na,TEA)-ZSM-25 (right)

Table S1: Refinement summary for dehydrated calcined (Na,H)-ZSM-25 and templated (Na,TEA)-ZSM-25. Also listed for reference is information on hydrated templated (Na,TEA)-ZSM-25 as reported in ref. [5]

Sample	(Na,H)-ZSM-25 (dehydrated)	(Na,TEA)-ZSM-25 (dehydrated)	(Na,TEA)-ZSM-25 (hydrated), ref. [5]
Measured Chemical Formula	$Na_{285}H_{40}[Si_{1106}Al_{325}O_{2880}]$	$Na_{285}N_{40}C_{320}[Si_{1115}Al_{325}O_{2880}]$	$Na_{285}N_{40}C_{320}[Si_{1115}Al_{325}O_{2880}].O_{600}$
Refined Chemical Formula	$Na_{282}[Si_{1106}Al_{325}O_{2880}]$	$Na_{273}N_{38}C_{304}[Si_{1106}Al_{325}2880}]$	$Na_{296}N_{38}C_{305}[Si_{1106}Al_{334}O_{2880}].O_{812}$
T (K)	298	298	298
Space Group	$I\bar{4}3m$	$I\bar{4}3m$	$Im\bar{3}m$
X-ray Source	Synchrotron X-ray, ID-31, ESRF, Grenoble	Synchrotron X-ray, I-11, DLS, Oxfordshire	Synchrotron X-ray, ID-31, ESRF, Grenoble
λ (Å)	0.320012	0.826956	0.632480
a (Å)	42.631(1)	42.980(1)	45.0711(3)
V (Å³)	77480(5)	79396(6)	91558(2)
R_p	1.9%	2.3%	4.1%
R_{wp}	2.4%	3.1%	5.4%
GOF	1.7	0.7	2.9

Table S2: Cation positions as determined from Rietveld refinements for dehydrated, calcined (Na,H)-ZSM-25

Site	Type	x	y	z	Occ	Mult	Biso
Si1	Si	0.847(2)	0.574(2)	0.525(2)	0.77	48	0.71
Si1	Al	0.847(2)	0.574(2)	0.525(2)	0.23	48	0.71
Si2	Si	0.860(2)	0.593(2)	0.457(2)	0.77	48	0.71
Si2	Al	0.860(2)	0.593(2)	0.457(2)	0.23	48	0.71
Si3	Si	0.807(2)	0.628(2)	0.542(2)	0.77	48	0.71
Si3	Al	0.807(2)	0.628(2)	0.542(2)	0.23	48	0.71
Si4	Si	0.819(2)	0.648(2)	0.470(2)	0.77	48	0.71
Si4	Al	0.819(2)	0.648(2)	0.470(2)	0.23	48	0.71
Si5	Si	0.737(2)	0.644(2)	0.529(2)	0.77	48	0.71
Si5	Al	0.737(2)	0.644(2)	0.529(2)	0.23	48	0.71
Si6	Si	0.749(2)	0.629(2)	0.456(2)	0.77	48	0.71
Si6	Al	0.749(2)	0.629(2)	0.456(2)	0.23	48	0.71
Si7	Si	0.695(2)	0.591(2)	0.541(2)	0.77	48	0.71
Si7	Al	0.695(2)	0.591(2)	0.541(2)	0.23	48	0.71
Si8	Si	0.711(2)	0.576(2)	0.473(2)	0.77	48	0.71
Si8	Al	0.711(2)	0.576(2)	0.473(2)	0.23	48	0.71
Si9	Si	0.627(2)	0.575(2)	0.525(2)	0.77	48	0.71
Si9	Al	0.627(2)	0.575(2)	0.525(2)	0.23	48	0.71
Si10	Si	0.644(2)	0.593(2)	0.458(2)	0.77	48	0.71
Si10	Al	0.644(2)	0.593(2)	0.458(2)	0.23	48	0.71
Si11	Si	0.569(2)	0.076(2)	0.025(2)	0.77	48	0.71
Si11	Al	0.569(2)	0.076(2)	0.025(2)	0.23	48	0.71
Si12	Si	0.583(2)	0.092(2)	0.959(2)	0.77	48	0.71
Si12	Al	0.583(2)	0.092(2)	0.959(2)	0.23	48	0.71
Si13	Si	0.529(2)	0.132(2)	0.040(2)	0.77	48	0.71
Si13	Al	0.529(2)	0.132(2)	0.040(2)	0.23	48	0.71
Si14	Si	0.543(2)	0.149(2)	0.973(2)	0.77	48	0.71
Si14	Al	0.543(2)	0.149(2)	0.973(2)	0.23	48	0.71
Si15	Si	0.704(2)	0.652(2)	0.808(2)	0.77	48	0.71
Si15	Al	0.704(2)	0.652(2)	0.808(2)	0.23	48	0.71
Si16	Si	0.686(2)	0.638(2)	0.180(2)	0.77	48	0.71
Si16	Al	0.686(2)	0.638(2)	0.180(2)	0.23	48	0.71
Si17	Si	0.751(2)	0.566(2)	0.703(2)	0.77	48	0.71
Si17	Al	0.751(2)	0.566(2)	0.703(2)	0.23	48	0.71
Si18	Si	0.737(2)	0.582(2)	0.316(2)	0.77	48	0.71
Si18	Al	0.737(2)	0.582(2)	0.316(2)	0.23	48	0.71
Si19	Si	0.689(2)	0.639(2)	0.737(2)	0.77	48	0.71
Si19	Al	0.689(2)	0.639(2)	0.737(2)	0.23	48	0.71
Si20	Si	0.701(2)	0.652(2)	0.249(2)	0.77	48	0.71
Si20	Al	0.701(2)	0.652(2)	0.249(2)	0.23	48	0.71
Si21	Si	0.685(2)	0.820(2)	0.581(2)	0.77	48	0.71
Si21	Al	0.685(2)	0.820(2)	0.581(2)	0.23	48	0.71

Si22	Si	0.702(2)	0.807(2)	0.431(2)	0.77	48	0.71
Si22	Al	0.702(2)	0.807(2)	0.431(2)	0.23	48	0.71
Si23	Si	0.960(2)	0.688(2)	0.639(2)	0.77	48	0.71
Si23	Al	0.960(2)	0.688(2)	0.639(2)	0.23	48	0.71
Si24	Si	0.972(2)	0.706(2)	0.345(2)	0.77	48	0.71
Si24	Al	0.972(2)	0.706(2)	0.345(2)	0.23	48	0.71
Si25	Si	0.916(2)	0.814(2)	0.541(2)	0.77	48	0.71
Si25	Al	0.916(2)	0.814(2)	0.541(2)	0.23	48	0.71
Si26	Si	0.930(2)	0.796(2)	0.469(2)	0.77	48	0.71
Si26	Al	0.930(2)	0.796(2)	0.469(2)	0.23	48	0.71
Si27	Si	0.929(2)	0.360(2)	0.759(2)	0.77	48	0.71
Si27	Al	0.929(2)	0.360(2)	0.759(2)	0.23	48	0.71
Si28	Si	0.918(2)	0.348(2)	0.258(2)	0.77	48	0.71
Si28	Al	0.918(2)	0.348(2)	0.258(2)	0.23	48	0.71
Si29	Si	0.759(2)	0.359(2)	0.153(2)	0.77	48	0.71
Si29	Al	0.759(2)	0.359(2)	0.153(2)	0.23	48	0.71
Si30	Si	0.260(2)	0.918(2)	0.570(2)	0.77	48	0.71
Si30	Al	0.260(2)	0.918(2)	0.570(2)	0.23	48	0.71
O1	O	0.818(3)	0.592(3)	0.541(3)	1	48	0.29
O2	O	0.850(3)	0.629(3)	0.457(3)	1	48	0.29
O3	O	0.768(3)	0.628(3)	0.543(3)	1	48	0.29
O4	O	0.788(3)	0.632(3)	0.455(3)	1	48	0.29
O5	O	0.707(3)	0.627(3)	0.542(3)	1	48	0.29
O6	O	0.741(3)	0.592(3)	0.457(3)	1	48	0.29
O7	O	0.657(3)	0.592(3)	0.539(3)	1	48	0.29
O8	O	0.681(3)	0.596(3)	0.462(3)	1	48	0.29
O9	O	0.101(3)	0.591(3)	0.537(3)	1	48	0.29
O10	O	0.121(3)	0.591(3)	0.464(3)	1	48	0.29
O11	O	0.539(3)	0.096(3)	0.038(3)	1	48	0.29
O12	O	0.571(3)	0.128(3)	0.959(3)	1	48	0.29
O13	O	0.688(3)	0.620(3)	0.818(3)	1	48	0.29
O14	O	0.685(3)	0.599(3)	0.179(3)	1	48	0.29
O15	O	0.705(3)	0.768(3)	0.652(3)	1	48	0.29
O16	O	0.704(3)	0.789(3)	0.351(3)	1	48	0.29
O17	O	0.740(3)	0.688(3)	0.601(3)	1	48	0.29
O18	O	0.739(3)	0.682(3)	0.379(3)	1	48	0.29
O19	O	0.631(3)	0.572(3)	0.487(3)	1	48	0.29
O20	O	0.789(3)	0.565(3)	0.701(3)	1	48	0.29
O21	O	0.768(3)	0.5692)	0.299(3)	1	48	0.29
O24	O	0.351(3)	0.570(3)	0.179(3)	1	48	0.29
O25	O	0.316(3)	0.538(3)	0.820(3)	1	48	0.29
O26	O	0.318(3)	0.539(3)	0.264(3)	1	48	0.29
O27	O	0.351(3)	0.570(3)	0.733(3)	1	48	0.29
O28	O	0.817(3)	0.356(3)	0.492(3)	1	48	0.29

O29	O	0.931(3)	0.761(3)	0.682(3)	1	48	0.29
O30	O	0.931(3)	0.797(3)	0.351(3)	1	48	0.29
O31	O	0.959(3)	0.815(3)	0.456(3)	1	48	0.29
O32	O	0.928(3)	0.851(3)	0.540(3)	1	48	0.29
O33	O	0.931(3)	0.798(3)	0.509(3)	1	48	0.29
O34	O	0.759(3)	0.932(3)	0.460(3)	1	48	0.29
O35	O	0.796(3)	0.930(3)	0.571(4)	1	48	0.29
O36	O	0.796(3)	0.650(3)	0.848(3)	1	48	0.29
O37	O	0.760(3)	0.681(3)	0.157(3)	1	48	0.29
O38	O	0.744(3)	0.120(3)	0.348(3)	1	48	0.29
O39	O	0.744(3)	0.103(3)	0.654(3)	1	48	0.29
O40	O	0.620(3)	0.069(3)	0.241(3)	1	48	0.29
O41	O	0.602(3)	0.070(3)	0.757(3)	1	48	0.29
O42	O	0.898(3)	0.542(3)	0.189(3)	1	48	0.29
O43	O	0.878(3)	0.540(3)	0.812(3)	1	48	0.29
O44	O	0.848(3)	0.511(3)	0.208(3)	1	48	0.29
O47	O	0.344(3)	0.259(3)	0.042(3)	1	48	0.29
O48	O	0.346(3)	0.295(3)	0.929(3)	1	48	0.29
O65	O	0.568(3)	0.073(3)	-0.013(3)	1	48	0.29
O66	O	0.546(3)	0.150(3)	0.011(3)	1	48	0.29
O67	O	0.491(3)	0.134(3)	0.037(3)	1	48	0.29
O68	O	0.844(3)	0.575(3)	0.487(3)	1	48	0.29
O69	O	0.739(3)	0.642(3)	0.491(3)	1	48	0.29
O70	O	0.711(3)	0.574(3)	0.511(3)	1	48	0.29
O45	O	0.315(3)	0.315(3)	0.036(4)	1	24	0.29
O46	O	0.348(3)	0.348(3)	0.963(4)	1	24	0.29
O49	O	0.682(3)	0.682(3)	0.818(5)	1	24	0.29
O50	O	0.650(3)	0.650(3)	0.182(4)	1	24	0.29
O51	O	0.738(3)	0.738(3)	0.564(3)	1	24	0.29
O52	O	0.705(3)	0.705(3)	0.426(4)	1	24	0.29
O53	O	0.595(3)	0.595(3)	0.531(4)	1	24	0.29
O54	O	0.627(3)	0.627(2)	0.460(4)	1	24	0.29
O55	O	0.707(3)	0.651(4)	0.707(3)	1	24	0.29
O56	O	0.736(3)	0.652(4)	0.264(3)	1	24	0.29
O22	O	0.735(5)	0.653(3)	0.653(3)	1	24	0.29
O23	O	0.741(4)	0.683(3)	0.317(3)	1	24	0.29
O57	O	0.565(3)	0.040(3)	0.040(3)	1	24	0.29
O58	O	0.575(4)	0.074(3)	0.926(3)	1	24	0.29
O59	O	0.847(4)	0.537(3)	0.537(3)	1	24	0.29
O60	O	0.852(4)	0.575(3)	0.425(3)	1	24	0.29
O61	O	0.705(4)	0.573(3)	0.573(3)	1	24	0.29
O62	O	0.707(3)	0.540(3)	0.460(3)	1	24	0.29
O63	O	0.622(4)	0.541(3)	0.541(3)	1	24	0.29
O64	O	0.636(3)	0.575(2)	0.425(2)	1	24	0.29

Na1	Na	0.067(4)	0.067(4)	0.067(4)	0.5(2)	8	1.36
Na2	Na	0.364(3)	0	0	1.0(2)	12	1.36
Na3	Na	0.157(4)	0	0	0.9(2)	12	1.36
Na4	Na	0.074(2)	0.257(2)	0.074(2)	1.0(1)	24	1.36
Na5	Na	0.107(3)	0.401(4)	0.107(3)	0.5(1)	24	1.36
Na6	Na	0.502(3)	0.064(3)	0.064(3)	0.7(1)	24	1.36
Na7	Na	0.423(3)	0.232(2)	0.232(2)	0.7(2)	24	1.36
Na8	Na	0.068(5)	0.402(4)	0.402(4)	0.4(1)	24	1.36
Na9	Na	0.167(4)	0.393(3)	0.393(3)	0.6(1)	24	1.36
Na10	Na	0.363(7)	0.168(5)	0.168(5)	0.3(2)	24	1.36
Na11	Na	0.048(3)	0.172(2)	0.172(2)	0.9(1)	24	1.36
Na12	Na	0.143(3)	0.265(2)	0.265(2)	0.9(2)	24	1.36
Na13	Na	0.169(2)	0.169(2)	-0.035(2)	1.0(2)	24	1.36
Na14	Na	0.212(4)	0.212(4)	0.356(5)	0.5(1)	24	1.36
Na15	Na	0.211(2)	0.561(2)	0.016(2)	0.8(1)	48	1.36
Na16	Na	0.236(2)	0.339(2)	-0.010(3)	0.8(1)	48	1.36

Table S3: Cation positions as determined from Rietveld refinements for dehydrated, templated (Na,TEA)-ZSM-25

Site	Type	x	y	z	Occ	Mult	Biso
Si1	Si	0.850(3)	0.578(3)	0.526(3)	0.77	48	0.71
Si1	Al	0.850(3)	0.578(3)	0.526(3)	0.23	48	0.71
Si2	Si	0.859(3)	0.591(3)	0.460(4)	0.77	48	0.71
Si2	Al	0.859(3)	0.591(3)	0.460(4)	0.23	48	0.71
Si3	Si	0.809(3)	0.633(3)	0.538(3)	0.77	48	0.71
Si3	Al	0.809(3)	0.633(3)	0.538(3)	0.23	48	0.71
Si4	Si	0.820(3)	0.647(3)	0.469(3)	0.77	48	0.71
Si4	Al	0.820(3)	0.647(3)	0.469(3)	0.23	48	0.71
Si5	Si	0.737(3)	0.643(3)	0.534(3)	0.77	48	0.71
Si5	Al	0.737(3)	0.643(3)	0.534(3)	0.23	48	0.71
Si6	Si	0.745(3)	0.634(3)	0.463(3)	0.77	48	0.71
Si6	Al	0.745(3)	0.634(3)	0.463(3)	0.23	48	0.71
Si7	Si	0.697(3)	0.587(3)	0.542(3)	0.77	48	0.71
Si7	Al	0.697(3)	0.587(3)	0.542(3)	0.23	48	0.71
Si8	Si	0.709(3)	0.577(3)	0.469(3)	0.77	48	0.71
Si8	Al	0.709(3)	0.577(3)	0.469(3)	0.23	48	0.71
Si9	Si	0.626(3)	0.575(3)	0.527(3)	0.77	48	0.71
Si9	Al	0.626(3)	0.575(3)	0.527(3)	0.23	48	0.71
Si10	Si	0.642(3)	0.592(3)	0.461(3)	0.77	48	0.71
Si10	Al	0.642(3)	0.592(3)	0.461(3)	0.23	48	0.71
Si11	Si	0.570(3)	0.077(3)	0.028(3)	0.77	48	0.71
Si11	Al	0.570(3)	0.077(3)	0.028(3)	0.23	48	0.71
Si12	Si	0.581(3)	0.091(3)	0.960(4)	0.77	48	0.71
Si12	Al	0.581(3)	0.091(3)	0.960(4)	0.23	48	0.71
Si13	Si	0.533(3)	0.136(3)	0.040(3)	0.77	48	0.71
Si13	Al	0.533(3)	0.136(3)	0.040(3)	0.23	48	0.71
Si14	Si	0.543(3)	0.149(3)	0.972(3)	0.77	48	0.71
Si14	Al	0.543(3)	0.149(3)	0.972(3)	0.23	48	0.71
Si15	Si	0.700(3)	0.652(3)	0.810(3)	0.77	48	0.71
Si15	Al	0.700(3)	0.652(3)	0.810(3)	0.23	48	0.71
Si16	Si	0.689(3)	0.640(3)	0.182(3)	0.77	48	0.71
Si16	Al	0.689(3)	0.640(3)	0.182(3)	0.23	48	0.71
Si17	Si	0.751(3)	0.572(4)	0.703(4)	0.77	48	0.71
Si17	Al	0.751(3)	0.572(4)	0.703(4)	0.23	48	0.71
Si18	Si	0.736(3)	0.579(3)	0.314(3)	0.77	48	0.71
Si18	Al	0.736(3)	0.579(3)	0.314(3)	0.23	48	0.71
Si19	Si	0.690(3)	0.639(3)	0.743(3)	0.77	48	0.71
Si19	Al	0.690(3)	0.639(3)	0.743(3)	0.23	48	0.71
Si20	Si	0.700(3)	0.645(3)	0.248(3)	0.77	48	0.71
Si20	Al	0.700(3)	0.645(3)	0.248(3)	0.23	48	0.71
Si21	Si	0.690(3)	0.822(3)	0.581(3)	0.77	48	0.71
Si21	Al	0.690(3)	0.822(3)	0.581(3)	0.23	48	0.71

Si22	Si	0.701(3)	0.810(3)	0.432(4)	0.77	48	0.71
Si22	Al	0.701(3)	0.810(3)	0.432(4)	0.23	48	0.71
Si23	Si	0.963(3)	0.685(3)	0.635(3)	0.77	48	0.71
Si23	Al	0.963(3)	0.685(3)	0.635(3)	0.23	48	0.71
Si24	Si	0.968(3)	0.703(3)	0.349(3)	0.77	48	0.71
Si24	Al	0.968(3)	0.703(3)	0.349(3)	0.23	48	0.71
Si25	Si	0.917(3)	0.815(3)	0.542(3)	0.77	48	0.71
Si25	Al	0.917(3)	0.815(3)	0.542(3)	0.23	48	0.71
Si26	Si	0.927(3)	0.798(3)	0.469(3)	0.77	48	0.71
Si26	Al	0.927(3)	0.798(3)	0.469(3)	0.23	48	0.71
Si27	Si	0.932(3)	0.360(3)	0.758(3)	0.77	48	0.71
Si27	Al	0.932(3)	0.360(3)	0.758(3)	0.23	48	0.71
Si28	Si	0.919(3)	0.351(3)	0.259(3)	0.77	48	0.71
Si28	Al	0.919(3)	0.351(3)	0.259(3)	0.23	48	0.71
Si29	Si	0.757(3)	0.360(3)	0.153(3)	0.77	48	0.71
Si29	Al	0.757(3)	0.360(3)	0.153(3)	0.23	48	0.71
Si30	Si	0.259(4)	0.918(3)	0.572(3)	0.77	48	0.71
Si30	Al	0.259(4)	0.918(3)	0.572(3)	0.23	48	0.71
O1	O	0.822(6)	0.598(6)	0.540(7)	1	48	0.29
O2	O	0.847(6)	0.626(6)	0.540(7)	1	48	0.29
O3	O	0.771(6)	0.630(5)	0.541(5)	1	48	0.29
O4	O	0.786(6)	0.637(5)	0.461(5)	1	48	0.29
O5	O	0.707(5)	0.625(6)	0.545(6)	1	48	0.29
O6	O	0.736(5)	0.598(6)	0.459(6)	1	48	0.29
O7	O	0.659(5)	0.588(5)	0.537(6)	1	48	0.29
O8	O	0.678(5)	0.590(5)	0.462(5)	1	48	0.29
O9	O	0.102(6)	0.592(6)	0.537(5)	1	48	0.29
O10	O	0.118(5)	0.592(7)	0.464(6)	1	48	0.29
O11	O	0.544(5)	0.100(5)	0.038(6)	1	48	0.29
O12	O	0.569(5)	0.128(7)	0.960(7)	1	48	0.29
O13	O	0.688(6)	0.620(5)	0.823(6)	1	48	0.29
O14	O	0.687(6)	0.601(6)	0.179(7)	1	48	0.29
O15	O	0.702(6)	0.774(5)	0.649(6)	1	48	0.29
O16	O	0.707(6)	0.790(5)	0.354(6)	1	48	0.29
O17	O	0.743(6)	0.683(6)	0.601(6)	1	48	0.29
O18	O	0.742(6)	0.682(6)	0.382(5)	1	48	0.29
O19	O	0.631(5)	0.570(5)	0.489(7)	1	48	0.29
O20	O	0.790(7)	0.569(6)	0.705(5)	1	48	0.29
O21	O	0.771(6)	0.571(6)	0.297(6)	1	48	0.29
O24	O	0.346(6)	0.567(6)	0.179(5)	1	48	0.29
O25	O	0.318(6)	0.542(6)	0.822(6)	1	48	0.29
O26	O	0.320(5)	0.545(5)	0.264(7)	1	48	0.29
O27	O	0.346(5)	0.566(6)	0.737(5)	1	48	0.29
O28	O	0.818(6)	0.351(6)	0.492(6)	1	48	0.29

O29	O	0.933(6)	0.762(5)	0.676(5)	1	48	0.29
O30	O	0.933(7)	0.792(6)	0.350(6)	1	48	0.29
O31	O	0.957(7)	0.816(5)	0.456(6)	1	48	0.29
O32	O	0.930(7)	0.847(6)	0.542(6)	1	48	0.29
O33	O	0.928(6)	0.799(6)	0.509(7)	1	48	0.29
O34	O	0.762(6)	0.927(5)	0.457(7)	1	48	0.29
O35	O	0.794(6)	0.929(6)	0.571(6)	1	48	0.29
O36	O	0.792(5)	0.652(7)	0.847(6)	1	48	0.29
O37	O	0.761(6)	0.681(6)	0.154(6)	1	48	0.29
O38	O	0.742(6)	0.119(7)	0.349(6)	1	48	0.29
O39	O	0.745(5)	0.101(6)	0.650(6)	1	48	0.29
O40	O	0.619(6)	0.072(6)	0.242(6)	1	48	0.29
O41	O	0.602(5)	0.070(6)	0.756(6)	1	48	0.29
O42	O	0.900(6)	0.542(6)	0.185(6)	1	48	0.29
O43	O	0.878(5)	0.542(6)	0.814(6)	1	48	0.29
O44	O	0.851(6)	0.508(6)	0.203(6)	1	48	0.29
O47	O	0.349(6)	0.262(6)	0.041(6)	1	48	0.29
O48	O	0.350(6)	0.293(6)	0.932(5)	1	48	0.29
O65	O	0.567(5)	0.075(6)	-0.011(6)	1	48	0.29
O66	O	0.546(5)	0.150(6)	0.010(5)	1	48	0.29
O67	O	0.492(6)	0.137(5)	0.039(6)	1	48	0.29
O68	O	0.846(6)	0.576(6)	0.489(7)	1	48	0.29
O69	O	0.735(5)	0.647(6)	0.494(6)	1	48	0.29
O70	O	0.714(5)	0.575(5)	0.511(5)	1	48	0.29
O45	O	0.318(6)	0.318(6)	0.042(10)	1	24	0.29
O46	O	0.348(6)	0.348(6)	0.960(9)	1	24	0.29
O49	O	0.683(6)	0.683(6)	0.820(9)	1	24	0.29
O50	O	0.657(6)	0.657(6)	0.182(9)	1	24	0.29
O51	O	0.736(6)	0.736(6)	0.572(8)	1	24	0.29
O52	O	0.707(5)	0.707(5)	0.427(9)	1	24	0.29
O53	O	0.596(5)	0.596(5)	0.532(8)	1	24	0.29
O54	O	0.625(5)	0.625(5)	0.46110)	1	24	0.29
O55	O	0.711(6)	0.648(10)	0.711(6)	1	24	0.29
O56	O	0.732(6)	0.652(8)	0.268(6)	1	24	0.29
O22	O	0.741(8)	0.654(7)	0.654(7)	1	24	0.29
O23	O	0.748(8)	0.678(5)	0.322(5)	1	24	0.29
O57	O	0.567(7)	0.043(6)	0.043(6)	1	24	0.29
O58	O	0.570(8)	0.070(5)	0.930(5)	1	24	0.29
O59	O	0.852(7)	0.544(7)	0.544(7)	1	24	0.29
O60	O	0.850(8)	0.570(6)	0.430(6)	1	24	0.29
O61	O	0.705(8)	0.572(6)	0.572(6)	1	24	0.29
O62	O	0.711(7)	0.542(5)	0.458(5)	1	24	0.29
O63	O	0.623(8)	0.544(6)	0.544(6)	1	24	0.29
O64	O	0.627(7)	0.570(5)	0.430(5)	1	24	0.29

Na1	Na	0.040(4)	0.040(4)	0.040(4)	1	8	1.36
Na2	Na	0.234(4)	0.234(4)	0.234(4)	0.99998	8	1.36
Na3	Na	0.282(5)	0.282(5)	0.282(5)	0.99998	8	1.36
Na4	Na	0.438(5)	0.438(5)	0.438(5)	1	8	1.36
Na5	Na	0.14(13)	0	0	0.49861	12	1.36
Na6	Na	0.051(3)	0.519(5)	0.051(3)	0.9378	24	1.36
Na7	Na	0.426(5)	0.231(3)	0.231(3)	1	24	1.36
Na8	Na	0.074(5)	0.212(3)	0.212(3)	1	24	1.36
Na9	Na	0.191(5)	0.409(3)	0.409(3)	0.8475	24	1.36
Na10	Na	0.033(6)	0.159(4)	0.159(4)	1	24	1.36
Na11	Na	0.144(6)	0.262(3)	0.262(3)	0.99859	24	1.36
Na12	Na	0.102(3)	0.102(3)	0.470(4)	1	24	1.36
Na13	Na	0.224(3)	0.224(3)	0.372(5)	1	24	1.36
Na14	Na	0.224(3)	0.587(3)	0.013(3)	1	48	1.36
N1	N	0.5	0	0	0.4(2)	6	2.00
C1a	C	0.478	0	0.030	0.2(1)	48	2.00
C1b	C	0.5	0	0.061	0.4(2)	24	2.00
N2	N	0.340	0	0	0.9(2)	12	2.00
C2a	C	0.318	0	0.030	0.4(1)	48	2.00
C2b	C	0.340	0	0.061	0.9(1)	48	2.00
C2c	C	0.362	0	0.030	0.4(1)	48	2.00
N3x	N	0.136	0.136	0.136	0.5(1)	8	2.00
C31ax	C	0.114	0.114	0.114	0.5(1)	8	2.00
C31bx	C	0.136	0.093	0.093	0.2(1)	24	2.00
C32ax	C	0.157	0.157	0.114	0.5(1)	24	2.00
C32bx	C	0.150	0.150	0.079	0.5(1)	24	2.00
N3y	N	0.119	0.119	0.119	0.5(1)	8	2.00
C31ay	C	0.140	0.140	0.140	0.5(1)	8	2.00
C31by	C	0.162	0.162	0.119	0.2(1)	24	2.00
C32ay	C	0.141	0.098	0.098	0.5(1)	24	2.00
C32by	C	0.176	0.105	0.105	0.5(1)	24	2.00
N4x	N	0.266	0.266	0.266	0.5(1)	8	2.00
C41ax	C	0.244	0.244	0.244	0.5(1)	8	2.00
C41bx	C	0.266	0.223	0.223	0.2(1)	24	2.00
C42ax	C	0.287	0.287	0.244	0.5(1)	24	2.00
C42bx	C	0.280	0.280	0.209	0.5(1)	24	2.00
N4y	N	0.200	0.200	0.200	0.5(1)	8	2.00
C41ay	C	0.222	0.222	0.222	0.5(1)	8	2.00
C41by	C	0.243	0.243	0.200	0.2(1)	24	2.00
C42ay	C	0.222	0.179	0.179	0.5(1)	24	2.00
C42by	C	0.257	0.186	0.186	0.5(1)	24	2.00
N5x	N	0.377	0.377	0.377	0.5(1)	8	2.00
C51ax	C	0.355	0.355	0.355	0.5(1)	8	2.00
C51bx	C	0.377	0.334	0.334	0.2(1)	24	2.00

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C52ax	C	0.398	0.398	0.355	0.5(1)	24	2.00
C52bx	C	0.390	0.390	0.319	0.5(1)	24	2.00
N5y	N	0.343	0.343	0.343	0.5(1)	8	2.00
C51ay	C	0.364	0.364	0.364	0.5(1)	8	2.00
C51by	C	0.385	0.385	0.342	0.2(1)	24	2.00
C52ay	C	0.364	0.321	0.321	0.5(1)	24	2.00
C52by	C	0.400	0.329	0.329	0.5(1)	24	2.00
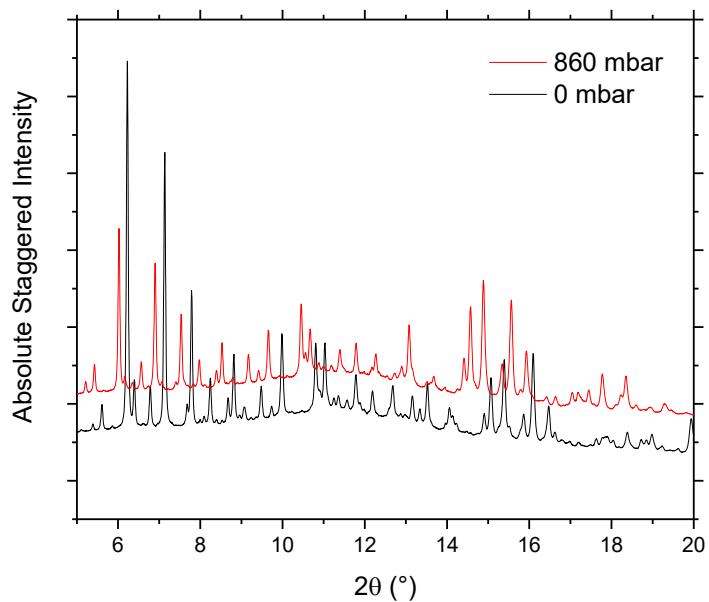
Figure S6: Effect of CO_2 on X-ray diffraction patterns. Patterns in vacuum and at pCO_2 = 860 mbar, all at 298 K. The shift in peak positions is due to lattice expansion upon CO_2 exposure.
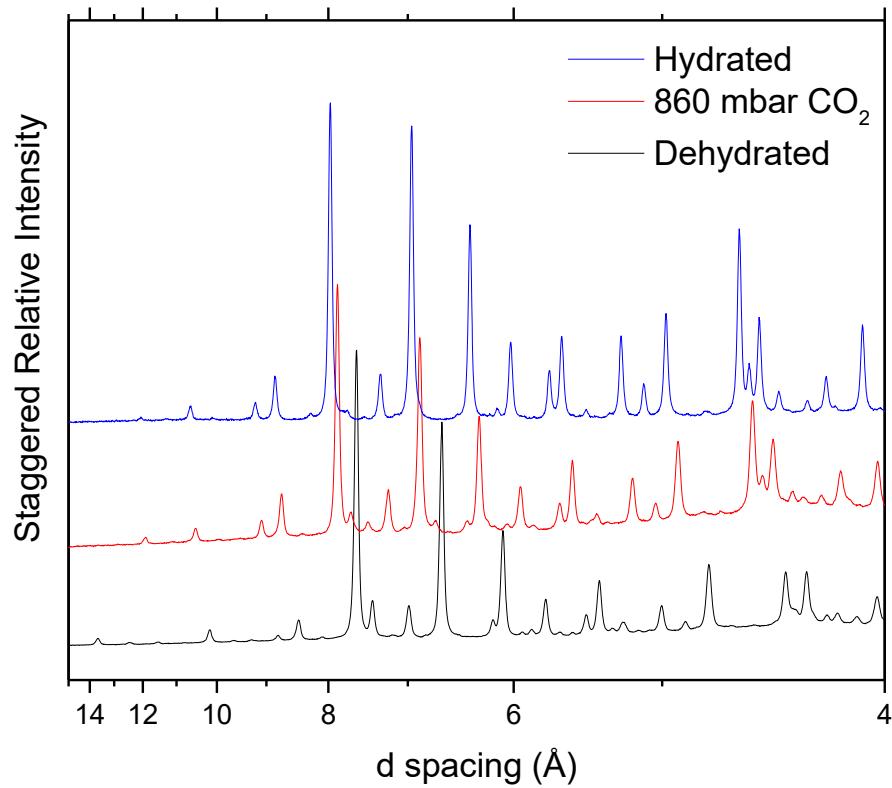
Figure S7: Comparison of synchrotron XRD patterns of as-prepared samples: dehydrated, exposed to 860 mbar of CO_2 and hydrated (all at 298 K), clearly showing that the d-spacings for the sample exposed to CO_2 is intermediate between dehydrated and hydrated structures.


*Figure S8: Variable pressure PXRD patterns of (Na,TEA)-ZSM-25 at 298 K.*

Experimental CO_2 isotherms

Table S4: Autosorb isotherm raw data. Sample mass is m = 0.1041 g

T = 268 K		T = 268 K		T = 288 K		T = 308 K		T = 328 K	
P (Torr)	V (cm³ STP)	P (Torr)	V (cm³ STP)	P (Torr)	V (cm³ STP)	P (Torr)	V (cm³ STP)	P (Torr)	V (cm³ STP)
0.222353	1.10856	0.0389078	0.406072	0.0891234	0.27378	0.439473	0.348694	0.867298	0.23189
0.395849	1.41881	0.0835534	0.661989	0.153284	0.403515	0.791547	0.503764	1.60526	0.360364
0.589525	1.67494	0.153355	0.889739	0.305663	0.597038	1.54394	0.727719	3.20222	0.555978
0.780135	1.90085	0.310718	1.20219	0.655585	0.870241	2.35377	0.8988	4.58079	0.681387
0.955528	2.10714	0.483543	1.44181	0.768112	0.936897	3.91732	1.14234	6.1953	0.801751
1.15578	2.36688	0.635535	1.61725	1.57231	1.28507	5.79705	1.3664	7.69102	0.894981
1.33875	2.63619	0.769571	1.75843	2.29218	1.51628	7.62931	1.553	16.265	1.2907
1.52833	2.96076	0.971659	1.96416	3.06002	1.73162	11.5954	1.89751	30.4937	1.74822
1.90236	3.60787	1.1632	2.16639	3.81301	1.93618	15.5615	2.25307	46.2651	2.21234
2.29116	4.11699	1.35043	2.38005	4.57413	2.15242	19.1278	2.61904	60.8885	2.70868
2.66686	4.47304	1.53713	2.62032	6.11558	2.66117	22.4589	3.02296	76.8724	3.34286
3.06184	4.75812	1.90184	3.15773	7.62379	3.21303	26.2057	3.46904	116.426	4.47912
3.82054	5.16058	2.2983	3.70963	9.55675	3.78387	30.1489	3.88338	152.432	5.0715
4.59163	5.46334	2.68588	4.12001	11.4384	4.22609	34.0371	4.20163	189.396	5.47806
6.08988	5.8852	3.05684	4.42305	13.314	4.57522	37.6503	4.4435	228.334	5.79948
7.61435	6.19028	3.81612	4.8843	15.4835	4.8724	45.671	4.85373	265.771	6.04904
11.6195	6.75818	4.57633	5.22058	19.0093	5.27461	53.463	5.15945	304.282	6.26749
15.7747	7.09558	6.0976	5.698	22.7042	5.59091	60.789	5.38968	380.153	6.60861
19.5099	7.29549	7.61252	6.02989	30.218	6.05741	75.8518	5.75582	455.708	6.85572
22.7453	7.43565	3.75417	4.91768	45.0288	6.63835	154.239	6.80298	532.459	7.04917
30.233	7.67634	1.87916	3.39538	60.3804	7.00167	228.498	7.26964	608.471	7.24299
45.6163	7.9924	0.755997	1.83884	113.672	7.64383	304.493	7.57806	756.227	7.45919
61.3715	8.20545	0.380467	1.35748	190.285	8.08314	456.359	7.96459	683.065	7.38314
75.9164	8.35276			379.901	8.61573	607.872	8.22408	607.92	7.27465
151.319	8.79319			755.513	9.15324	755.993	8.43013	527.115	7.14052
304.23	9.23619			375.166	8.67364	603.03	8.26664	454.708	6.98191
608.285	9.71129			145.568	7.96365	448.843	8.03978	379.942	6.76569
756.795	9.91882			75.0457	7.36918	299.423	7.6765	302.714	6.4338
599.74	9.76707			37.802	6.56335	226.371	7.39632	227.601	6.00952
298.037	9.3071			7.60381	3.5167	148.617	6.91822	189.463	5.70488
148.416	8.88047			3.67197	1.92831	73.4038	5.88808	152.683	5.32433
73.6961	8.43647			1.81132	1.36361	61.1189	5.57827	113.744	4.73012
60.8591	8.29985			0.740831	0.899209	46.1175	5.06936	74.5537	3.65253
45.3814	8.08811					30.2035	4.14041	60.7109	3.05955
30.4995	7.7866					14.9806	2.3834	44.1777	2.41033
14.5334	7.13616					7.52392	1.6417	30.796	1.9553
7.51041	6.32378							13.6929	1.34217
3.77545	5.22019							7.53397	1.00334
1.8946	3.9109								
0.755125	1.95679								
0.379474	1.39418								

Figure S9: CO$_2$ isotherm including desorption branch at 288 K and 308 K, showing minimal hysteresis effects.

Model functions used to describe the volumetric behaviour of ZSM-25

The quadratic volume function used in Figure 4a has the following form:

$$V_s(\bar{q}) = \alpha \cdot (\bar{q} + \beta)^2 + \frac{1}{\rho_0} \qquad 11$$

Table S5: Model parameters for quadratic volumetric function in RALF

Quadratic volume function parameter	Value	
α	2.77×10^{-6}	m^3 mol^{-1}
β	0.3	mol kg^{-1}
ρ_0	2020	kg m^{-3}

The switch function used in Figure 4b has the following form:

$$V_s = \left(1 - f(\bar{q})\right) \cdot V_{s,1}(\bar{q}) + f(\bar{q}) \cdot V_{s,2}(\bar{q}) \qquad 12$$

Here $V_{s,i}(\bar{q})$ are two linear functions of the form:

$$V_{s,i}(\bar{q}) = \alpha_i \bar{q} + \frac{1}{\rho_{i,0}} \qquad 13$$

where α_i and $\frac{1}{\rho_{i,0}}$ are the slope and intercept, respectively, and c is a constant. f is a switch function of the form:

$$f(\bar{q}) = \frac{1}{2}(\tanh\{w(\bar{q} - \bar{q}_{trans})\} + 1) \qquad 14$$

where $\bar{q}_{trans}$ loosely corresponds to the critical amount adsorbed upon which the structural transition occurs and w describes the steepness of the switch function. The parameters describing this volumetric function are listed in Table S6.

Table S6: Model parameters for switch volumetric function in RALF

Switch volume function parameter	Value	
α_1	5.01×10^{-6}	$m^3\ mol^{-1}$
α_2	4.07×10^{-6}	$m^3\ mol^{-1}$
$\rho_{1,0}$	2020	$kg\ m^{-3}$
$\rho_{2,0}$	1879	$kg\ m^{-3}$
n_{trans}	3.1	$mol\ kg^{-1}$
w	1.0	

Single site RALF model

Table S7: Characteristic parameters for CO_2 (ref. [28]) and (Na,TEA)-ZSM-25 as used in the RALF single site model

Pure component parameters	CO_2	(Na,TEA)-ZSM-25
P^* (MPa)	630	1250
T^* (K)	300	2050
ρ^* (kg/m^3)	1515	2640
M (kg/mol)	0.044	∞
Binary parameters	CO_2 – (Na,TEA)-ZSM-25	
$\kappa_{CO2,s}$ (quadratic)	−0.22	
ξ_{CO2} (quadratic)	0.16	
$\kappa_{CO2,s}$ (switch)	−0.20	
ξ_{CO2} (switch)	0.25	
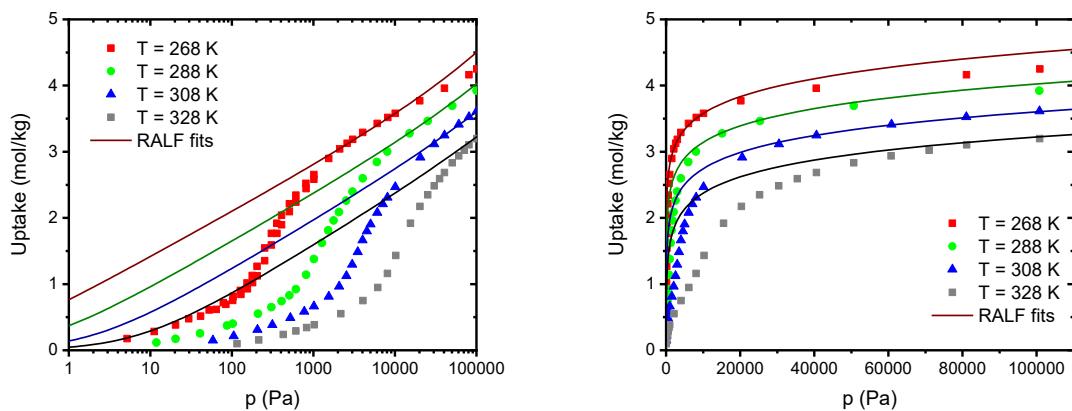
Figure S10: RALF model predictions and experimental data, using a single set of solid characteristic parameters and quadratic volume function.
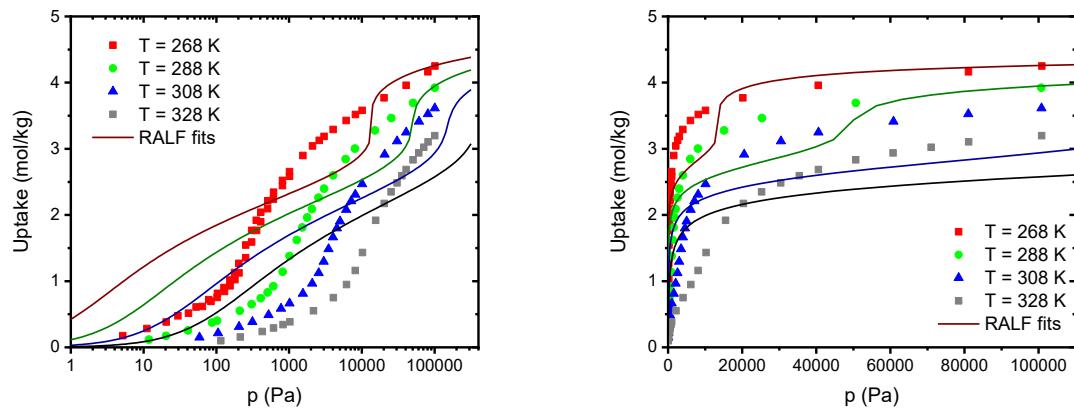
Figure S11: RALF model predictions and experimental data, using a single set of solid characteristic parameters and switch volume function.

Zero Length Column experiments
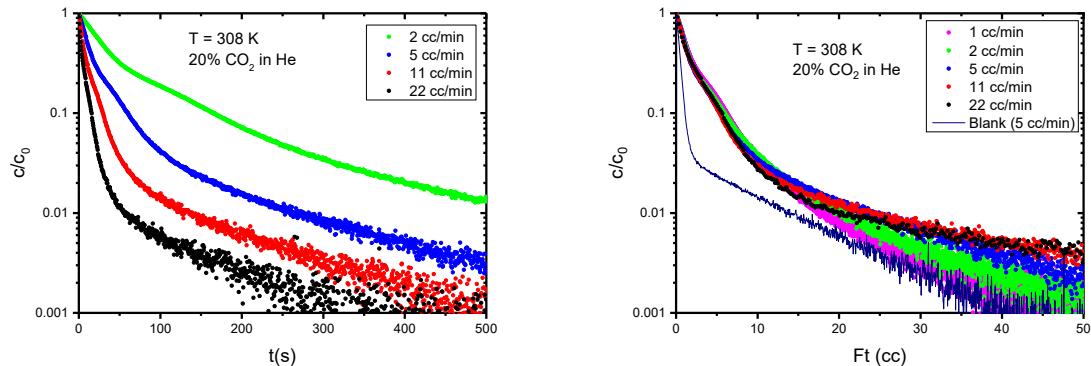
Figure S12: Normalised gas phase concentration as measured by the mass spectrometer, prior to deconvolution. Left) c/c0 vs. time. Right) c/c0 vs. flowrate times time (Ft plot).
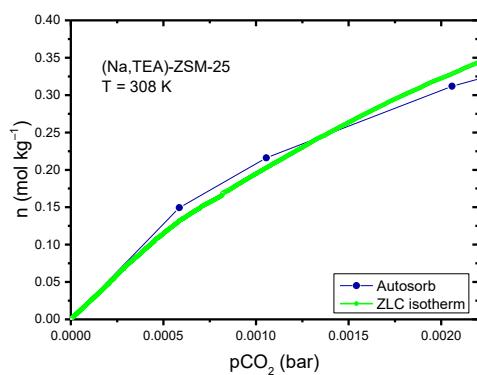
Figure S13: Comparison of Autosorb isotherm and isotherm derived from ZLC data at low flow rates and 308 K. Good agreement of the data at low CO_2 partial pressure is seen for both techniques, suggesting the data collected by volumetric method has reached equilibrium.
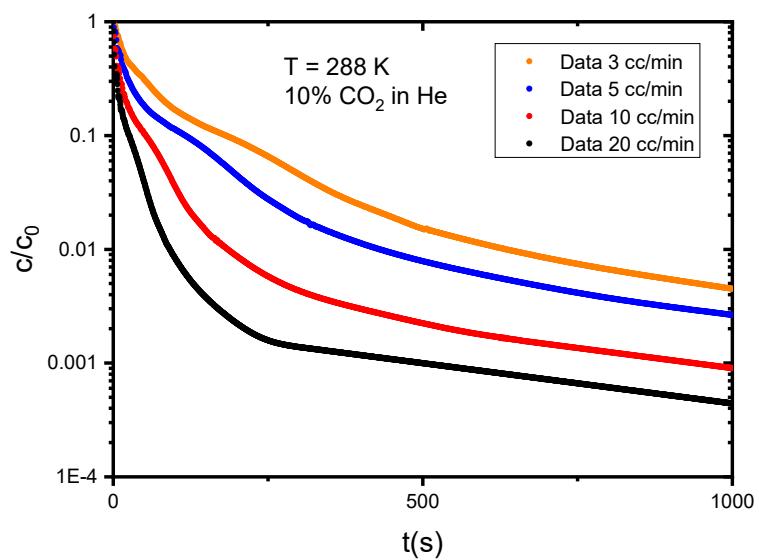
Figure S14: c/c0 vs time for ZSM-25 at 288 K in pCO₂ = 0.1 bar
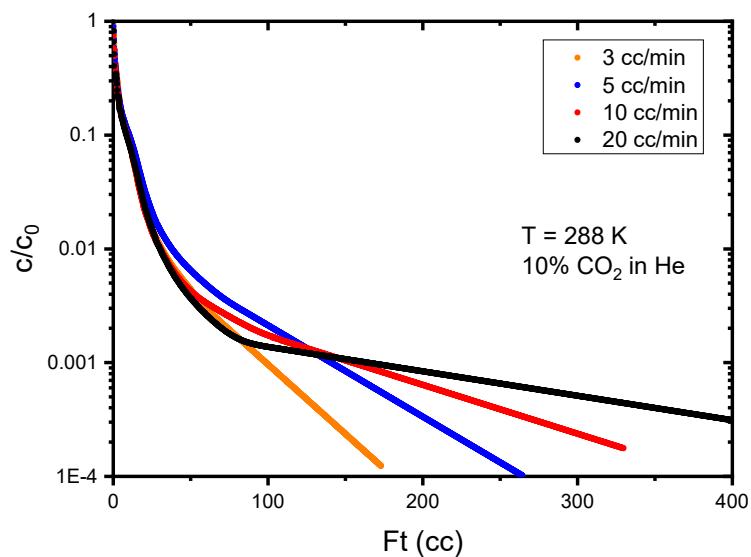
Figure S15: c/c0 vs. Ft for ZSM-25 at 288 K in pCO₂ = 0.1 bar
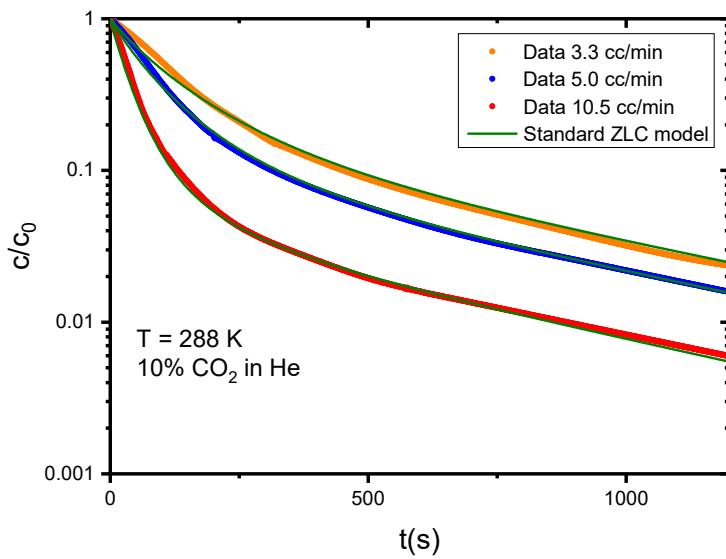
*Figure S16: Analysis of 'cut' data using the standard ZLC model assuming linear isotherm (equation **Error! Reference source not found.**) obtaining an identical value for the diffusivity in the narrow pore structure, i.e. $D/R^2 = 1.8 \times 10^{-4}$ s⁻¹.*

Table S8: Model parameters for the standard ZLC model fits to 'cut' and renormalized ZSM-25 data at 288 K

Flow rate (cm³/min)	L_{app}	γ_{app}	D/R^2 (s⁻¹)
3.2	17	0.3	1.8×10^{-4}
5.0	26	0.3	1.8×10^{-4}
10.5	54	0.3	1.8×10^{-4}
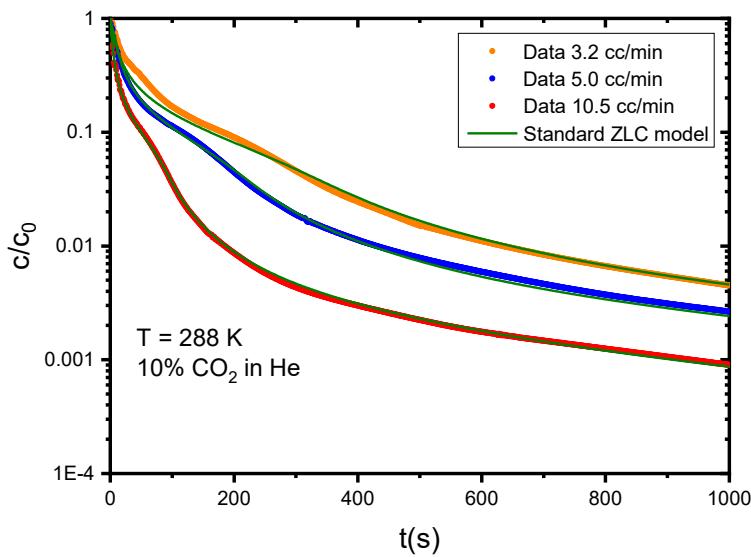
Figure 17: Deconvoluted experimental and simulated ZLC data using RALF model at T = 288 K, showing good agreement using the kinetic model in equation 30, with the parameters in Table S9

Discussion

Table S9: Kinetic model parameters used to fit full ZLC curves at 288 K

| Kinetic model parameter	Value	
D_0/R^2	1.8×10^{-4}	s^{-1}
$\bar{q}_{\tau,trans}$	0.6	$mol\ kg^{-1}$
A	3.6×10^{-4}	s^{-1}
B	8.3	-
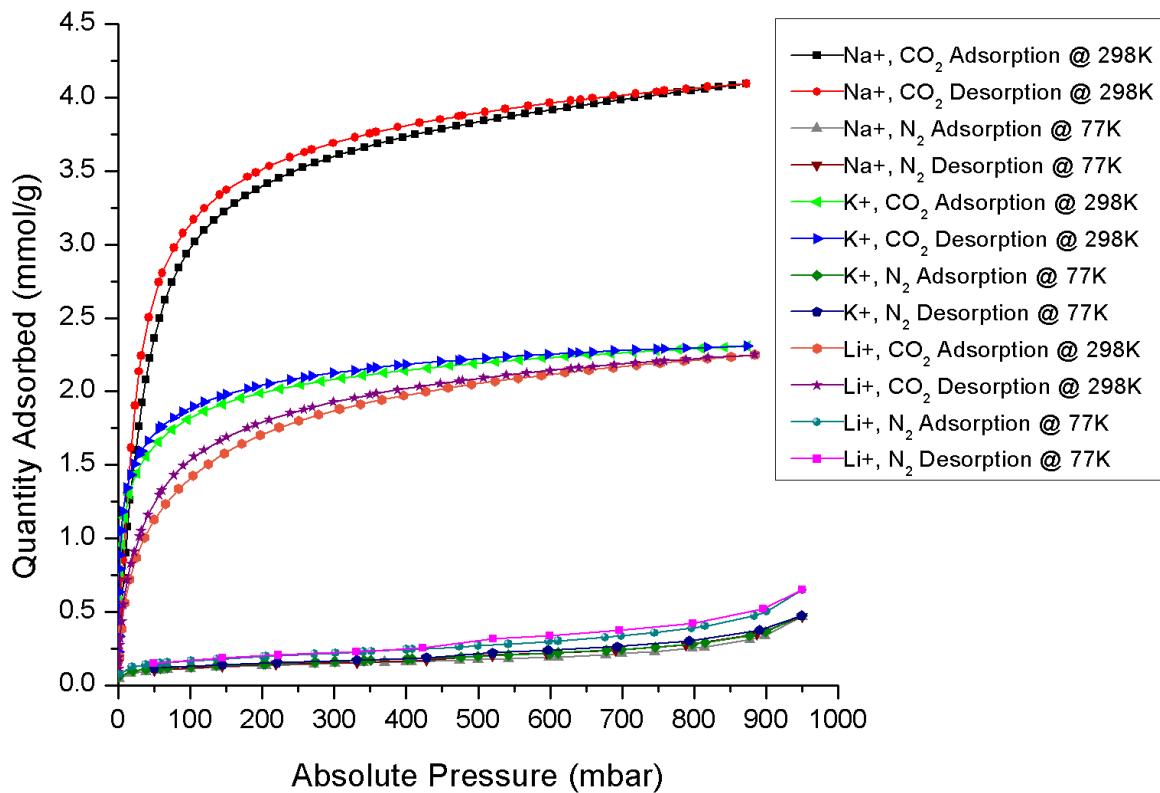
Figure S18: Isotherms for different cation forms of (M,TEA)-ZSM-25showing that Li and K show a standard type I isotherm, with no step up to 1 bar.

Table S10: Window sizes in dehydrated and hydrated structures of (Na,TEA)-ZSM-25

Cages connected by window	Dehydrated window size (Å)	Hydrated window size (Å)
lta – d8r	2.6	3.8
d8r – pau	2.4	3.9
pau – d8r	2.6	4.1
d8r – pau	2.5	3.8
pau – oto	2.7	3.0
pau – oto	3.3	3.1
pau – oto	3.3	3.0

oto – phi	2.6	3.5
oto – phi	2.4	3.8
oto – phi	2.3	3.8
oto – phi	2.8	3.5
phi – gsm	2.3	3.4
phi – gsm	2.4	3.4
gsm - gsm	2.4	3.4
phi - oto	2.8	2.8
phi - oto	3.0	2.8
gsm - phi	2.6	3.2
oto – plg	2.5	3.8
oto – plg	2.6	3.8
plg – oto	2.3	3.6
plg – oto	2.5	3.6
phi – oto	2.6	2.5
oto – plg	2.6	3.2
oto – plg	2.2	3.2

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