Supporting Information

Hiding Extra-Framework Cations in Zeolites L and Y by Internal Ion Exchange and its Effect on CO_2 Adsorption

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S1. Synthesis and ion exchange of Potassium Zeolite L.

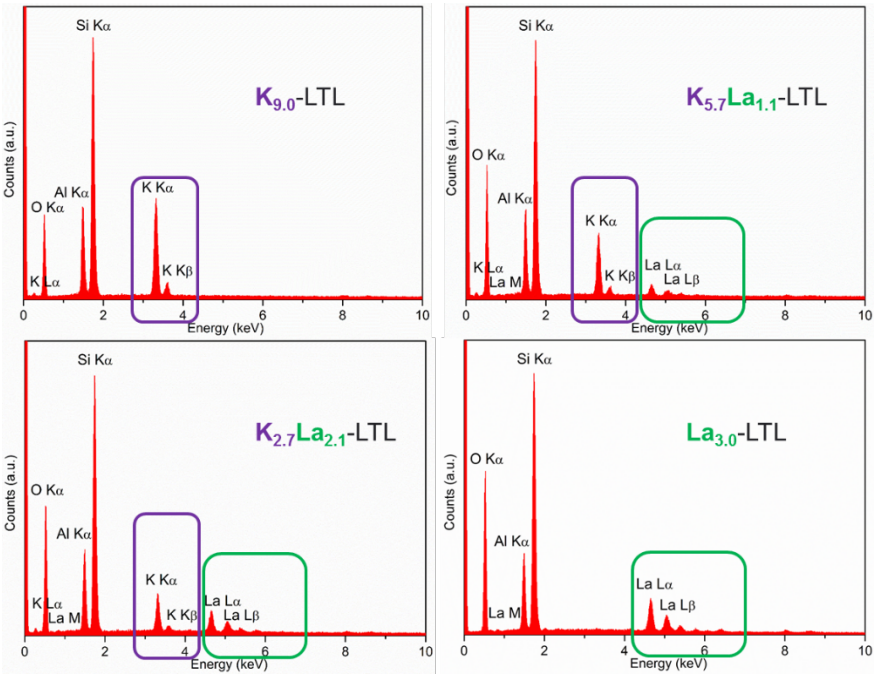
Solution A was prepared by dissolving aluminium isopropoxide (1.54 g, Sigma-Aldrich) in potassium hydroxide (1.28 g, Alfa Aesar) and water (2.51 g) at 373 K, until clear. After solution A was cooled to room temperature the water loss due to evaporation was corrected. Solution B was prepared by mixing Ludox HS-40 (5.52 g, Sigma-Aldrich) with water (4.82 g) until homogeneous, which took around 3 min. Solution A was then added to solution B and the mixture was stirred until thickening of the gel started. The gel was loaded into a 40 mL PTFE (Teflon) liner inside a stainless-steel autoclave and heated at 453 K for 48 h. After crystallisation the autoclave was cooled to room temperature and the product was filtered and washed five times with distilled water (650 mL), ensuring the pH of the final wash water was 7. The product was then dried at 333 K overnight.

1.0 g of zeolite $K_{9.0}$-L ($K_{9.0}Al_{9.0}Si_{27.0}O_{72}$) was repeatedly ion exchanged with 0.5 M lanthanum nitrate solution or 0.5 M calcium nitrate solution at 333 K for 2-4 h. Sample was then filtered and washed with deionised water, dried in a 343 K oven overnight and a cation content was measured using SEM-EDX. When the $La^{3+}(Ca^{2+})/Al^{3+}$ ratio remained constant, the sample was calcined at 1073 K in flowing oxygen gas for 10 h. Then the process of ion exchange and calcination was repeated to reach required unit cell compositions, for example for the fully-exchanged La-L, $K_{9.0}$-L was exchanged 100x and calcined 10x. Each time 0.05-0.1 g of sample

with required content of cations, before and after calcination, was kept for further analysis. The studied compositions were: $K_{5.7}La_{1.1}Al_{9.0}Si_{27.0}O_{72}$ ($K_{5.7}La_{1.1}$-L), $K_{2.7}La_{2.1}Al_{9.0}Si_{27.0}O_{72}$ ($K_{2.7}La_{2.1}$-L), $La_{3.0}Al_{9.0}Si_{27.0}O_{72}$ ($La_{3.0}$-L), $K_{6.2}Ca_{1.4}Al_{9.0}Si_{27.0}O_{72}$ ($K_{6.2}Ca_{1.4}$-L) and $Ca_{3.8}K_{1.4}Al_{9.0}Si_{27.0}O_{72}$ ($Ca_{3.8}K_{1.4}$-L).

For comparison, commercially-obtained $Na_{56.0}$-Y ($Na_{56.0}Al_{56.0}Si_{136.0}O_{384}$), was also ion exchanged 10× with 0.5 M lanthanum nitrate solution at 333 K for 6 h and heated twice at 673 K to obtain $La_{18.7}$-Y ($La_{18.7}Al_{56.0}Si_{136.0}O_{384}$).

S2. EDX Spectra of K-L, K,La-L and La-L samples.



S3. Crystallographic details of dehydrated samples.

	$K_{9.0}$-L	**$K_{5.7}La_{1.1}$-L (before calcination)**	**$K_{5.7}La_{1.1}$-L (after calcination)**	**$K_{2.7}La_{2.1}$-L (before calcination)**
Unit cell	$K_{9.0}Al_{9.0}Si_{27.0}O_{72}$	$K_{5.7}La_{1.1}Al_{9.0}Si_{27.0}O_{72}$	$K_{5.7}La_{1.1}Al_{9.0}Si_{27.0}O_{72}$	$K_{2.7}La_{2.1}Al_{9.0}Si_{27.0}O_{72}$
Temperature/K	298	298	298	298
Space group	*P6/mmm*	*P6/mmm*	*P6/mmm*	*P6/mmm*
X-ray source	Cu	Cu	Cu	Cu
Diffractometer	Stoe	Stoe	Stoe	Stoe
Wavelength (Å)	1.54056	1.54056	1.54056	1.54056
a/ Å **c/ Å**	18.43881(16) 7.48766(7)	18.28369(21) 7.50227(10)	18.39583(24) 7.42565(12)	18.30167(23) 7.43186(13)
Volume/Å^3	2204.66(4)	2171.96(5)	2176.23(6)	2155.81(6)
R_p	0.0324	0.0374	0.0402	0.0388
R_{wp}	0.0441	0.0501	0.0530	0.0519
χ^2	2.275	1.959	2.276	2.027
	$K_{2.7}La_{2.1}$-L (after calcination)	**$La_{3.0}$-L**	**$Na_{56.0}$-Y**	**$La_{18.7}$-Y**
Unit cell	$K_{2.7}La_{2.1}Al_{9.0}Si_{27.0}O_{72}$	$La_{3.0}Al_{9.0}Si_{27.0}O_{72}$	$Na_{56.0}Al_{56.0}Si_{136.0}O_{384}$	$La_{18.7}Al_{56.0}Si_{136.0}O_{384}$
Temperature/K	298	298	298	298
Space group	*P6/mmm*	*P6/mmm*	$Fd\bar{3}m$	$Fd\bar{3}m$

X-ray source	Cu	Cu	Cu	Cu
Diffractometer	Stoe	Stoe	Stoe	Stoe
Wavelength (Å)	1.54056	1.54056	1.54056	1.54056
a/ Å **c/ Å**	18.38886(29) 7.37587(14)	18.1425(6) 7.36463(21)	24.78528(26)	24.7938(4)
Volume/Å^3	2160.00(7)	2099.32(12)	15225.9(5)	15241.5(8)
R_p	0.0366	0.0328	0.0285	0.0407
R_{wp}	0.0485	0.0423	0.0395	0.0544
χ^2	1.907	1.564	1.682	2.140

S4. Fractional atomic coordinates, occupancies and isotropic displacement parameters (in Å^2) for dehydrated samples.

Zeolite L (LTL)

$K_{9.0}$-L	**x**	**y**	**z**	**Occup.**	**Multipl.**	**Uiso**
Si1	0.09332(15)	0.35680(16)	0.5	0.75	12	0.0008(4)
Al1	0.09332(15)	0.35680(16)	0.5	0.25	12	0.0008(4)
Si2	0.16557(16)	0.49789(14)	0.21146(17)	0.75	24	0.0008(4)
Al2	0.16557(16)	0.49789(14)	0.21146(17)	0.25	24	0.0008(4)
O1	0.0	0.2735(4)	0.5	1.0	6	0.0008(4)
O2	0.16534(20)	0.3307(4)	0.5	1.0	6	0.0008(4)
O3	0.26384(15)	0.52767(29)	0.2543(6)	1.0	12	0.0008(4)
O4	0.10256(22)	0.3243(4)	1.0	1.0	24	0.0008(4)
O5	0.42487(15)	0.84973(31)	0.2713(6)	1.0	12	0.0008(4)
O6	0.14649(28)	0.47819(28)	0.0	1.0	12	0.0008(4)
K1 (site I)	0.3333	0.6667	0.5	1.023(5)	2	0.025
K2 (site II)	0.0	0.5	0.5	1.005(4)	3	0.025
K3 (site III)	0.0	0.31904(25)	0.0	0.6410(29)	6	0.025
$K_{5.7}La_{1.1}$-L (before calcination)	**x**	**y**	**z**	**Occup.**	**Multipl.**	**Uiso**
Si1	0.09313(21)	0.35716(22)	0.5	0.75	12	0.0067(5)
Al1	0.09313(21)	0.35716(22)	0.5	0.25	12	0.0067(5)
Si2	0.16412(22)	0.49741(19)	0.20972(26)	0.75	24	0.0067(5)
Al2	0.16412(22)	0.49741(19)	0.20972(26)	0.25	24	0.0067(5)
O1	0.0	0.2730(6)	0.5	1.0	6	0.0067(5)
O2	0.16697(29)	0.3339(6)	0.5	1.0	6	0.0067(5)
O3	0.26372(21)	0.5274(4)	0.2556(9)	1.0	12	0.0067(5)
O4	0.10009(28)	0.41576(31)	0.3245(5)	1.0	24	0.0067(5)
O5	0.42676(21)	0.8535(4)	0.2696(9)	1.0	12	0.0067(5)
O6	0.1434(4)	0.4766(4)	0.0	1.0	12	0.0067(5)
K1 (site I)	0.3333	0.6667	0.5	1.026(7)	2	0.025
K2 (site II)	0.0	0.5	0.5	0.734(7)	3	0.025
K3 (site III)	0.0	0.321(7)	0.0	0.245(4)	6	0.05
La2 (site II)	0.0	0.5	0.5	0.26445	3	0.025
La3 (site III)	0.0	0.323(11)	0.0	0.04623	6	0.025
$K_{5.7}La_{1.1}$-L (after calcination)	**x**	**y**	**z**	**Occup.**	**Multipl.**	**Uiso**
Si1	0.09171(22)	0.35388(25)	0.5	0.75	12	0.0075(5)
Al1	0.09171(22)	0.35388(25)	0.5	0.25	12	0.0075(5)
Si2	0.16574(23)	0.49792(20)	0.21439(28)	0.75	24	0.0075(5)
Al2	0.16574(23)	0.49792(20)	0.21439(28)	0.25	24	0.0075(5)
O1	0.0	0.2710(6)	0.5	1.0	6	0.0075(5)
O2	0.16609(30)	0.3321(6)	0.5	1.0	6	0.0075(5)
O3	0.26514(20)	0.5301(4)	0.2576(9)	1.0	12	0.0075(5)

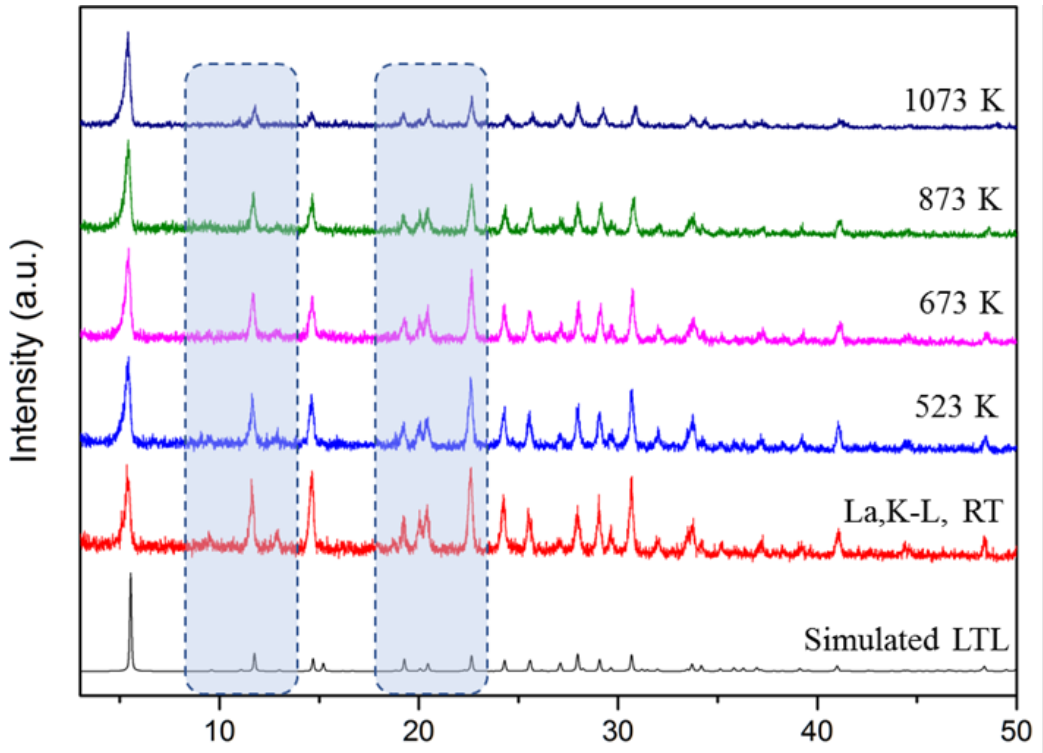
O4	0.10200(34)	0.41314(33)	0.3274(6)	1.0	24	0.0075(5)
O5	0.42546(22)	0.8509(4)	0.2728(9)	1.0	12	0.0075(5)
O6	0.1503(5)	0.4804(4)	0.0	1.0	12	0.0075(5)
K1 (site I)	0.3333	0.6667	0.5	0.676(4)	2	0.025
K2 (site II)	0.0	0.5	0.5	0.537(6)	3	0.025
K3 (site III)	0.0	0.3180(5)	0.0	0.465(4)	6	0.025
La1 (site I)	0.3333	0.6667	0.5	0.324(4)	2	0.025
La2 (site II)	0.0	0.5	0.5	0.16017	3	0.025
$K_{2.7}La_{2.1}$-L (before calcination)	**x**	**y**	**z**	**Occup.**	**Multipl.**	**Uiso**
Si1	0.09174(25)	0.35465(27)	0.5	0.75	12	0.0084(6)
Al1	0.09174(25)	0.35465(27)	0.5	0.25	12	0.0084(6)
Si2	0.16507(27)	0.49769(22)	0.21394(30)	0.75	24	0.0084(6)
Al2	0.16507(27)	0.49769(22)	0.21394(30)	0.25	24	0.0084(6)
O1	0.0	0.2711(7)	0.5	1.0	6	0.0084(6)
O2	0.16707(32)	0.3340(6	0.5	1.0	6	0.0084(6)
O3	0.26373(23)	0.5274(5)	0.2571(10)	1.0	12	0.0084(6)
O4	0.1025(4)	0.4148(4)	0.3274(7)	1.0	24	0.0084(6)
O5	0.42594(25)	0.8519(5)	0.2733(10)	1.0	12	0.0084(6)
O6	0.1486(5)	0.4809(5)	0.0	1.0	12	0.0084(6)
K1 (site I)	0.3333	0.6667	0.5	0.584(5)	2	0.025
K3 (site III)	0.0	0.3244(10)	0.0	0.253(4)	6	0.025
La1 (site I)	0.3333	0.6667	0.5	0.372(5)	2	0.055
La2 (site II)	0.0	0.5	0.5	0.4514(23)	3	0.055
$K_{2.7}La_{2.1}$-L (after calcination)	**x**	**y**	**z**	**Occup.**	**Multipl.**	**Uiso**
Si1	0.09174(26)	0.35219(30)	0.5	0.75	12	0.0077(7)
Al1	0.09174(26)	0.35219(30)	0.5	0.25	12	0.0077(7)
Si2	0.16494(27)	0.49770(23)	0.21643(34)	0.75	24	0.0077(7)
Al2	0.16494(27)	0.49770(23)	0.21643(34)	0.25	24	0.0077(7)
O1	0.0	0.2742(7)	0.5	1.0	6	0.0077(7)
O2	0.1652(4)	0.3303(7)	0.5	1.0	6	0.0077(7)
O3	0.26584(23)	0.5316(5)	0.2613(11)	1.0	12	0.0077(7)
O4	0.1045(4)	0.4134(4)	0.3293(8)	1.0	24	0.0077(7)
O5	0.42489(27)	0.8497(5)	0.2781(12)	1.0	12	0.0077(7)
O6	0.1520(5)	0.4831(5)	0.0	1.0	12	0.0077(7)
K1 (site I)	0.3333	0.6667	0.5	0.365(5)	2	0.025
K3 (site II)	0.0	0.3186(9)	0.0	0.321(5)	6	0.034
La1 (site I)	0.3333	0.6667	0.5	0.635(5)	2	0.055
La2 (site II)	0.0	0.5	0.5	0.2686(22)	3	0.055
$La_{3.0}$-L	**x**	**y**	**z**	**Occup.**	**Multipl.**	**Uiso**
Si1	0.0887(4)	0.3512(4)	0.5	0.75	12	0.0030(8)
Al1	0.0887(4)	0.3512(4)	0.5	0.25	12	0.0030(8)
Si2	0.1671(4)	0.4989(4)	0.2156(5)	0.75	24	0.0030(8)
Al2	0.1671(4)	0.4989(4)	0.2156(5)	0.25	24	0.0030(8)
O1	0.0	0.2631(12)	0.5	1.0	6	0.0030(8)
O2	0.1637(5)	0.3275(10)	0.5	1.0	6	0.0030(8)
O3	0.2634(4)	0.5267(8)	0.2709(16	1.0	12	0.0030(8)
O4	0.1008(5)	0.4095(5)	0.3330(10)	1.0	24	0.0030(8)
O5	0.4334(5)	0.8667(9)	0.2706(16)	1.0	12	0.0030(8)
O6	0.1500(8)	0.4853(8)	0.0	1.0	12	0.0030(8)
La1 (site I)	0.3333	0.6667	0.5	0.851(5)	2	0.025

La2 (site II)	0.0	0.5	0.5	0.3323(31)	3	0.025
La3 (site III)	0.0	0.3471(26)	0.0	0.0432(20)	6	0.025

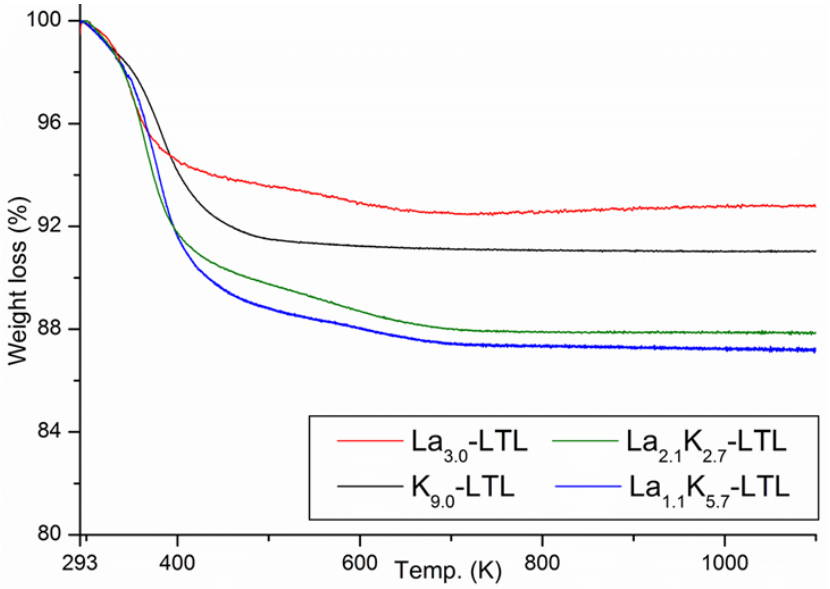
Zeolite Y (FAU)

$Na_{56.0}$-Y	**x**	**y**	**z**	**Occup.**	**Multipl.**	**Uiso**
Si1	0.12496(12)	0.94508(11)	0.03571(12)	0.71	192	0.0060(4)
Al1	0.12496(12)	0.94508(11)	0.03571(12)	0.29	192	0.0060(4)
O1	0.17637(20)	0.17637(20)	0.96588(35)	1.0	96	0.0060(4)
O2	0.17846(22)	0.17846(22)	0.31876(28)	1.0	96	0.0060(4)
O3	0.25289(22)	0.25289(22)	0.14493(28)	1.0	96	0.0060(4)
O4	0.10637(19)	0.89363(19)	0.0	1.0	96	0.0060(4)
Na2	0.05539(32)	0.05539(32)	0.05539(32)	0.555(11)	32	0.045
Na3	0.23386(20)	0.23386(20)	0.23386(20)	0.950(11)	32	0.045
Na4	0.0	0.0	0.0	0.472(13)	16	0.045
$La_{18.7}$-Y	**x**	**y**	**z**	**Occup.**	**Multipl.**	**Uiso**
Si1	0.12647(19)	0.94602(17)	0.03748(21)	0.71	192	0.0277(13)
Al1	0.12647(19)	0.94602(17)	0.03748(21)	0.29	192	0.0277(13)
O1	0.17765(31)	0.17765(31)	0.9724(4)	1.0	96	0.0277(13)
O2	0.17886(35)	0.17886(35)	0.3210(5)	1.0	96	0.0277(13)
O3	0.24893(30)	0.24893(30)	0.1393(4)	1.0	96	0.0277(13)
O4	0.11011(34)	0.88990(34)	0.0	1.0	96	0.0277(13)
La2	0.06831(10)	0.06831(10)	0.06831(10)	0.6044(27)	32	0.005

S5. XRD patterns of K,La-L samples heated at different temperatures.

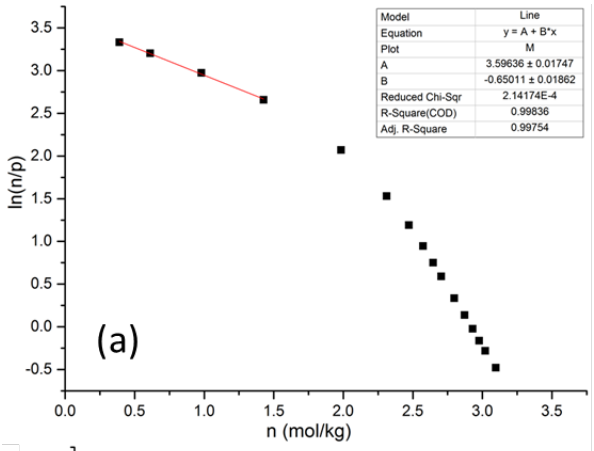


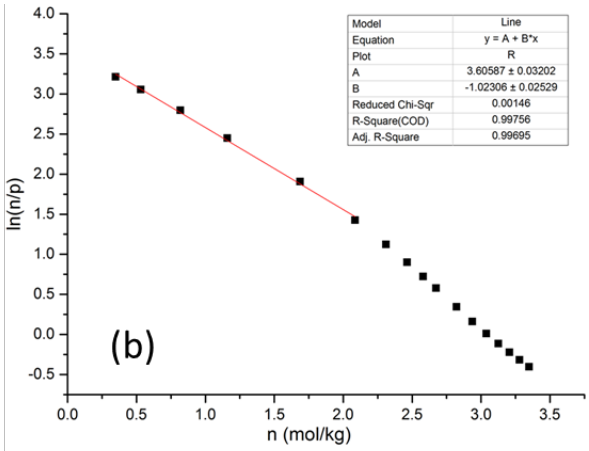
S6. TGA graphs of K-, K,La- and La-L samples.

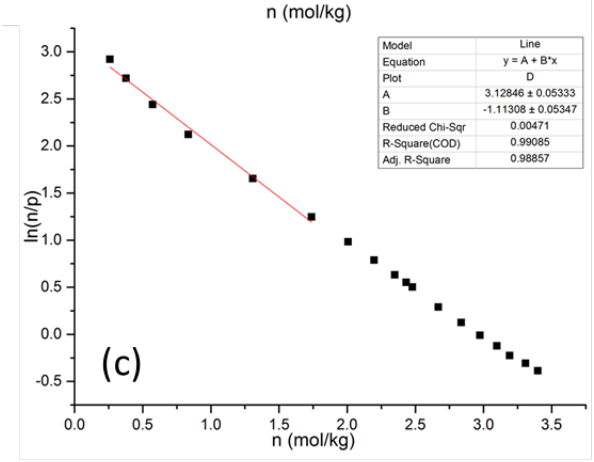


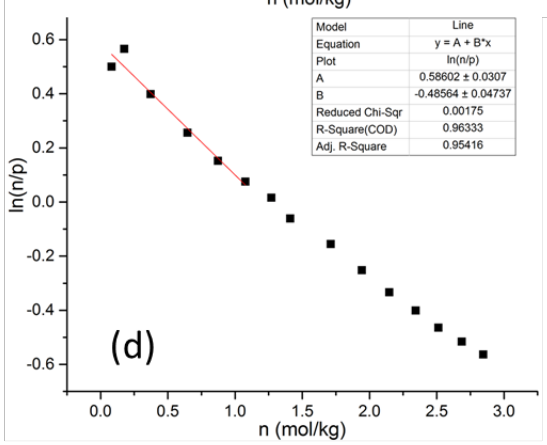
S7. Colour change from white (K-L) to light pink for $La_{3.0}$-L.

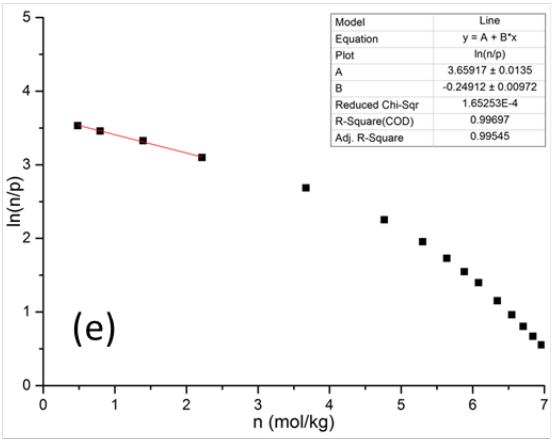
S8. Plots to derive Henry law constants at 298 K for (a) $K_{9.0}$-L, (b) $K_{5.7}La_{1.1}$-L, (c) $K_{2.7}La_{2.1}$-L, (d) $La_{3.0}$-L, (e) $Na_{56.0}$-Y and (f) $La_{18.7}$-Y.

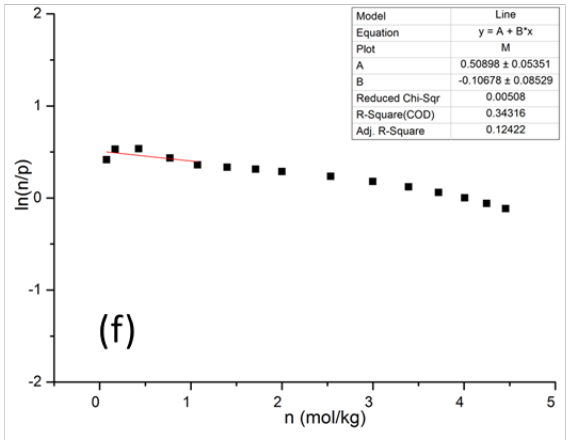




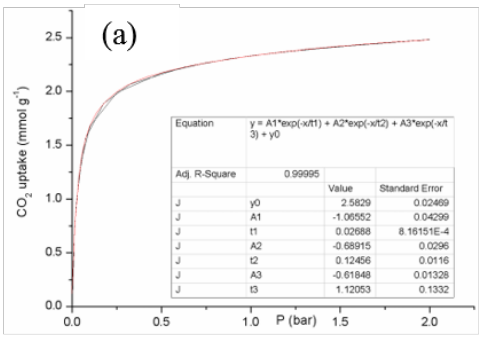


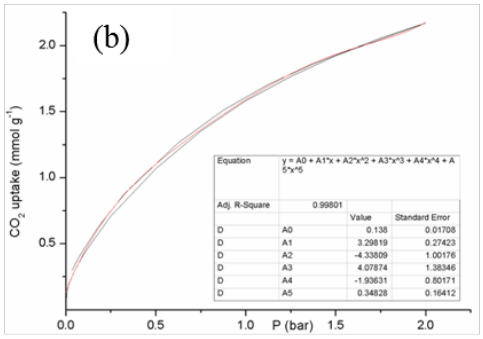


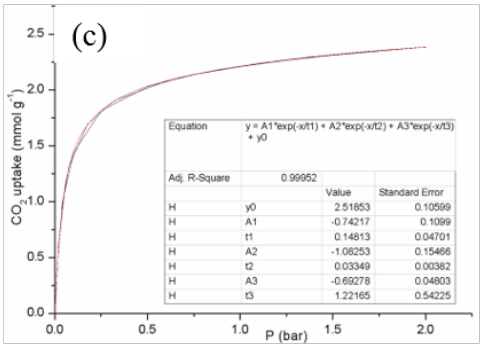


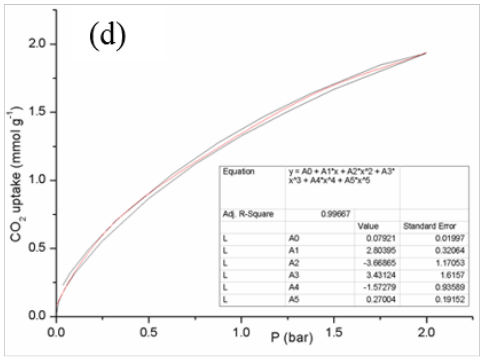


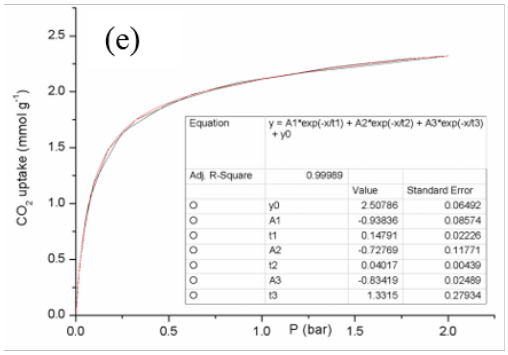
S9. Fitted CO_2 adsorption isotherms for K-L (a,c and e) and La-L (b,d and f) at different temperatures: (a) and (b) 278 K, (c) and (d) 288 K, and (e) and (f) 298 K. The isotherms were fitted by virial equations using Desmos software. Clausius-Clapeyron equations for K-L (g) and La-L (h) at uptakes 0.75 (■), 1.0 (●), 1.25 (▲) and 1.5 mmol g^{-1} (▼) used for the calculation of the isosteric heats of adsorption.

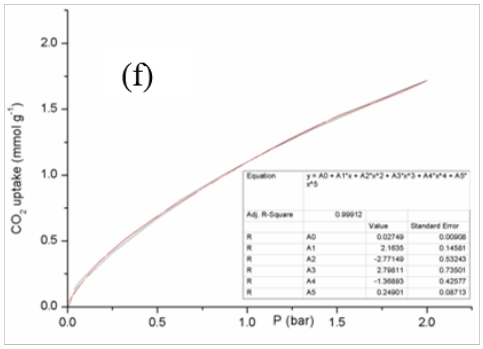


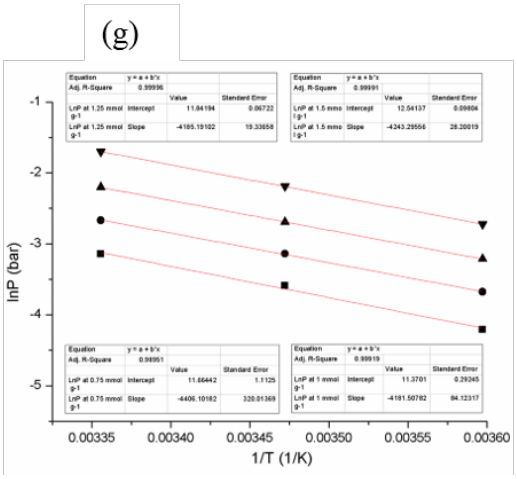


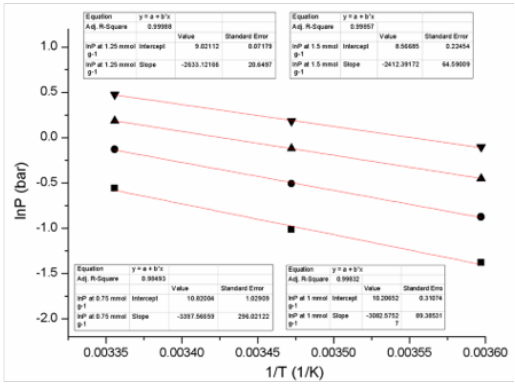




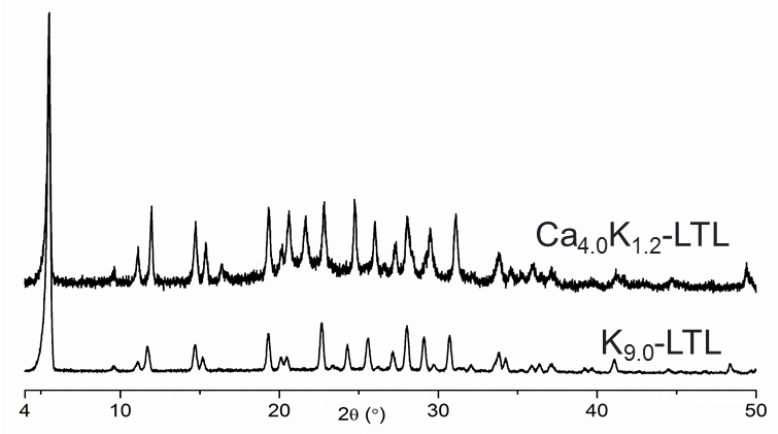




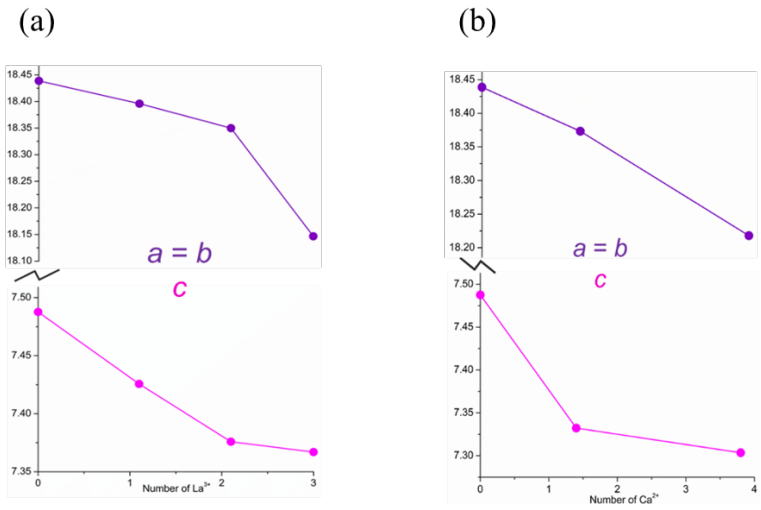




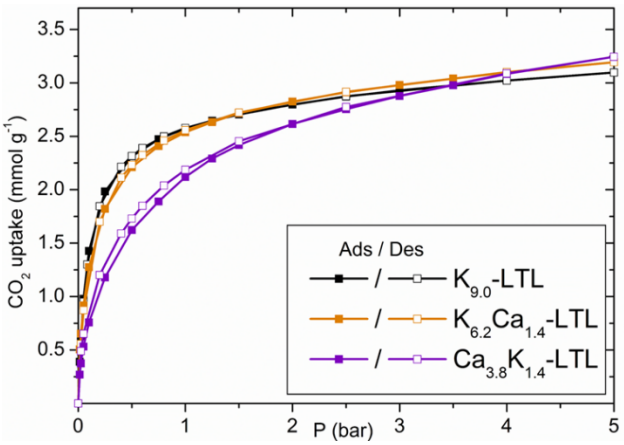
S10. XRD pattern of $Ca_{4.0}K_{1.2}$-L sample.



S11. Unit cell parameters vs. number of exchanging cations in (a) K,La-L and (b) K,Ca-L samples.



S12. CO_2 isotherms at 298 K on Ca,K-L samples.



S13. Rietveld plots of PXRD profiles (λ = 1.54056 Å, T = 298 K) of dehydrated (a) $Na_{56.0}$-Y and (b) $La_{18.7}$-Y (Observed – black, calculated – red, difference – blue, phase – pink and background – green).