# Modulation of CO<sub>2</sub> Adsorption Thermodynamics and Selectivity in Alkali-Carbonate Activated N-Rich Porous Carbons

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Summary: The supplementary information contains complete EGA spectra for all samples and a detaield discussion of the signal assignments, Ellingham diagrams determined by DFT, XRD spectra of washed and unwashed samples, deconvoluted XPS specra of all samples, figures of merit for BET analysis, N<sub>2</sub> isotherms at 77K, CO<sub>2</sub> isotherms at variale temperatures, thermodynamic data, structure-function correlation plots, and temperature swing adsorption data.

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Sample	Yield (wt%)	C (at%)	N (at%)	O (at%)	N/C	
SM20-Carb	26	67	26	7	0.4	
SM40-Carb	32	63	32	5	0.6	
SM60-Carb	38	56	40	4	0.8	
SM80-Carb	57	51	45	3	1.2	

Table S1. Yield, Surface composition by XPS, and N/C ratios by CHN Analysis



**Figure S1.** All relevant signals for evolved gas analysis for samples pyrolyzed without an activator. Precursor nitrogen content increases from left to right, panel a) shows K20, b) K40, c) K60, and d) K80.



**Figure S2.** All relevant signals for evolved gas analysis for potassium activated samples. Precursor nitrogen content increases from left to right, panel a) shows K20, b) K40, c) K60, and d) K80.



Figure S3. All relevant signals for evolved gas analysis for sodium activated samples. Precursor nitrogen content increases from left to right, panel a) shows Na20, b) Na40, c) Na60, and d) Na80.





Figure S5. Evolved gas analysis spectra of mass 28 for a) potassium samples, b) sodium samples, and c) Li samples



**Figure S6.** Evolved gas analysis spectra of the ratio of m/z values of 17/18 of a) potassium samples, b) sodium samples, and c) Li samples.

Discussion S1: Figures S1-S4 show the entire temperature dependent evolved gas analysis spectra, while S5-S6 highlight regions of interest. The m/z values of interest where 2, 12, 14, 15, 16, 17, 18, 27, 28, 44, and 52. Species were assigned to these values based on the fragmentation data, however because the signal to noise for key fragments is often high these assignments are not always absolute. For some samples m/z value of two was observed which corresponds to H<sub>2</sub> gas. The source of this could be varied as it is observed in all samples with low N-content but its temperature is varied depending if the sample was pyrolyzed with an activator or not. As such we assume this may form during pyrolysis for samples with an activator as a product of the redox type reactions which form the metallic species, and for samples activated without an activator (SMX-pyro) it may form as a result of forming carbon-carbon or carbon-nitrogen double bonds. An m/z value of 17 was also observed for activated samples. This could represent a variety of species most prominently ammonia or hydroxyl fragments from water cracking under ionization. Critical fragments 15, 16 were not informative as the intensities were low. However, if mass 17 was a fragment of 18 then the ratio should be constant if water was evolved and a peak would be resolved if ammonia was evolved. Figure S6 then clearly shows ammonia evolution. Its intensity increases with precursor N-content furthering this conclusion. Some water (18) desorbs from the samples around 100°C for all samples. For the nitrogen rich samples or the pyrolyzed samples, mass 27 evolves independent of other features, suggesting it's a primary peak and not a fragment, which may indicate the formation of hydrogen cyanide. This may account for N-content loss in samples like SM20-Pyro which likely did not evolve another nitrogen containing gas. Mass 28 indicates the loss of CO or N<sub>2</sub> gas the SMX-pyro samples, unfortunately the mass 14 fragment was too weak to be used. If oxygen content was high (SM20) this is likely CO evolution, when N-content is high it is likely  $N_2$ . When its moderate it is likely both. A more detailed study is presented in our previous work with the samples. During activation it is almost certainly CO as XRD shows the decomposition of cyanate species to cyanide. Mass 44 is also observed which is associated with CO<sub>2</sub>, it is evolved in SMX-Pyro samples only when they have large Ocontent. Lastly, mass 52 is evolved and may be cyanogen (NCCN) which forms only with samples with large Ncontents SM60-80-Pyro and the M80 samples. M60 samples do not evolve the gas as N-content is sequestered as a salt.

Samples with a relatively large amount of precursor oxygen content (*viz.*, SM20-Carb) exhibited a broad CO<sub>2</sub> evolution feature occurring from ~300 - 750°C and preceding CO evolution near 730 °C. The broad evolution of CO<sub>2</sub> (independent of CO) implicates the volatilization of oxygen motifs present on the native SMX-Carb precursors as well as decomposition of the carbonate salt via Eq. 27. These motifs may also have shifted the product distribution of Eqs. 28 and 29 from CO toward CO<sub>2</sub>, further contributing to the feature's broadness. XRD analysis of the samples near 600 °C revealed residual unreacted carbonate salts in addition to the formation of cyanate and cyanide species. By 800 °C, these crystalline intermediates were all converted to the cyanamide salt, a known product of reactions from molten lithium and N-containing lithium salts (Fig. S10).<sup>1</sup> The surface-bound/intercalation products of Eqs. 26-29 were not directly observed in the XRD, perhaps due to amorphous surface complexes and/or nanoscale metal-intercalated compound that are difficult to resolve with powder XRD. These results are in agreement with our previous work, suggesting that the conclusions are not limited to potassium oxalate activation and could be in a more general way to the activation of N-rich carbons.



**Figure S7.** XRD spectra of unwashed potassium activated samples after measured *ex-situ* at different temperatures during activation. Reference patterns for KCN - #01-074-2141, KOCN - #01-075-2920, KHCO<sub>3</sub> - #00-012-0292, and  $K_2CO_3$  - #01-073-0470.



**Figure S8.** XRD spectra of unwashed sodium activated samples after measured *ex-situ* at different temperatures during activation. Reference patterns for NaCN - #00-037-1490, NaOCN - #00-014-0093, and Na<sub>2</sub>CO<sub>3</sub> - #01-075-6816.



**Figure S9.** XRD spectra of unwashed lithium activated samples after measured *ex-situ* at different temperatures during activation. Measurements at elevated temperatures were done using Kapton tape to prevent degradation of the sample in air. The tape signal was subtracted out resulting in weak singal to noise for samples taken near 600 °C. The reference patterns for LiCN was - #01-071-6144, LiCNO - #01-080-9303, Li<sub>2</sub>CO<sub>3</sub> - #01-087-0729, and LiCN<sub>2</sub> #00-031-0718.



**Figure S10.** XRD patterns taken after activation at 800°C prior to acid washing for a) K<sup>+</sup>-activated, b) Na<sup>+</sup>-activated, and c) Li-activated.



**Figure S11.** Shows the absolute Gibbs energy of formation for the reaction  $M_2CO_3(s) + X$ (s)  $\rightarrow MCN(s) + MOCN(s) + CO_2(g)$ , where M is either Li, Na, or K and X represents the carbon species in this case  $C_3N_4$ .



**Figure S12.** Shows the absolute Gibbs energy of formation for the reaction  $M_2CO_3(s) + X(s) \rightarrow MCN(s) + MOCN(s) + CO_2(g)$ , where M is either Li, Na, or K and X represents the carbon species in this case  $C_{16}N_{16}$ .



**Figure S13.** Shows the absolute Gibbs energy of formation for the reaction  $M_2CO_3(s) + X(s) \rightarrow MCN(s) + MOCN(s) + CO_2(g)$ , where M is either Li, Na, or K and X represents the carbon species in this case a combination of  $N_2$  gas and graphite.



**Figure S14.** Shows the absolute Gibbs energy of formation for the reaction  $M_2CO_3(s) + C_3H_9N(s) \rightarrow MC_3H_9N(s) + CO_2(g) + O_2(g)$ , where M is either Li, Na, or K.



**Figure S15.** Shows the absolute Gibbs energy of formation for the reaction  $M_2CO_3(s) + C_4H_5N(s) \rightarrow MC_4H_5N(s) + CO_2(g) + O_2(g)$ , where M is either Li, Na, or K.



**Figure S16.** Shows the absolute Gibbs energy of formation for the reaction  $M_2CO_3(s) + C_5H_5N(s) \rightarrow MC_5H_5N(s) + CO_2(g) + O_2(g)$ , where M is either Li, Na, or K.



Figure S17. Shows a reorganization of the absolute Gibbs energy of potassium reactions with solvents from S13-S16.



Figure S18. Shows a reorganization of the absolute Gibbs energy of sodium reactions with solvents from S13-S16.



Figure S19. Shows a reorganization of the absolute Gibbs energy of lithium reactions with solvents from S13-S16.



Figure S20. Plot shows the CO<sub>2</sub> evolution spectra for SM80-Carb, activated with same molar equivalents either  $K_2C_2O_4$  (black) or  $K_2CO_3$  (red).



**Figure S21.** Comparison between the N/C determined by XPS and elemental analysis. At high N/C ratios were surface area is lower there is deviation between the bulk and the surface.



**Figure S22.** XPS survey scans for each sample. Panel a shows lithium activated b sodium activated, and c potassium activated



Figure S23. Deconvolution of the C1s spectra of all samples: a) SM20, b) SM40, c) SM60, d) SM80, e) K20, f) K40, g) K60, h) K80, i) Na20, j) Na40, k) Na60, l) Na80, m) Li20, n) Li40, o) Li60, and p) Li80.



Figure S24. Deconvolution of the N1s spectra of all samples: a) SM20, b) SM40, c) SM60, d) SM80, e) K20, f) K40, g) K60, h) K80, i) Na20, j) Na40, k) Na60, l) Na80, m) Li20, n) Li40, o) Li60, and p) Li80. The insets on e and i serve to more clearly show the region of interest. The y-axis of the precursor samples (a-d) is different than those of the activated samples (e-p).

аа



Figure S25. Deconvolution of the O1s spectra of all samples: a) SM20, b) SM40, c) SM60, d) SM80, e) K20, f) K40, g) K60, h) K80, i) Na20, j) Na40, k) Na60, l) Na80, m) Li20, n) Li40, o) Li60, and p) Li80.



**Figure S26.** Nitrogen isotherms taken at 77K for the potassium activated samples. Adsorption branches are shown as dark lines while the lighter branches are the desorption branches.



Figure S27. Nitrogen isotherms taken at 77K for the sodium activated samples. Adsorption branches are shown as dark lines while the lighter branches are the desorption branches.



**Figure S28.** Nitrogen isotherms taken at 77K for the lithium activated samples. Adsorption branches are shown as dark lines while the lighter branches are the desorption branches.



Figure S29. Multipoint BET analysis from N<sub>2</sub> isotherms at 77K.



**Figure 30.** Cumulative pore volume plots grouped by samples activated from the same precursor composition. Panel a) shows samples activated from SM20-Carb, b) SM40-Carb, c) SM60-Carb, and d) SM80-Carb



**Figure S31.** Differential pore volume plots grouped by precursor compositions. Panel a) shows samples activated from SM80-Carb, b) SM60-Carb, c) SM40-Carb, and d) SM20-Carb.

Equation S1. Scherrer Equation;

$$\tau = \frac{\kappa\lambda}{\beta\cos\left(\theta\right)}$$

Equation S2. Bragg's law;

 $n\lambda = 2d \sin(\theta)$ 

Here  $\tau$  is the crystalline domain size in Å, K = 0.89 (constant) the incident wavelength  $\lambda$  = 1.5418 Å,  $\beta$  is the full width at half max of the peak around 27 (2 $\theta$ ) corresponding to the 002 reflection at an angle of 2 $\theta$  in radians, d is the inter-sheet distance, and n is the diffraction order (1).



Figure S32. XRD spectra for a) K-activated samples, b) Na-activated samples, and c) Li-activated samples.

Table S2.

Sample	X <sub>c</sub> (°)	FWHM (°)	d-spacing	τ (Å)
K20	20.02	13.97	4.44	5.71
K40	23.41	13.53	3.80	5.93
K60	26.25	5.80	3.39	13.93
K80	26.86	2.67	3.32	30.27
Na20	20.51	14.50	4.33	5.51
Na40	25.05	9.51	3.55	8.47
Na60	26.19	5.481	3.40	14.73
Na80	26.84	2.75	3.32	29.4
Li20	24.30	9.97	3.66	8.07
Li40	25.36	8.65	3.51	9.32
Li60	25.87	6.54	3.44	12.33
Li80	26.24	5.24	3.40	15.41

Sample	Qa (mmol/g)	Qb (mmol/g)	Ha (kJ/mol)	Hb (kJ/mol)	Sa (J/molK)	Sb (J/molK)	R <sup>2</sup>	Reduced Chi-	K <sub>H</sub> N₂ (mmol/	R <sup>2</sup>
								square	g*torr)	
K20	-	7.91	-	-17.27	-	-38.15	0.995	1.972	0.00045	>0.999
K40	0.24	5.55	-50.11	-22.76	-111.03	-51.33	>0.999	0.066	0.00026	0.999
K60	0.75	4.10	-31.06	-23.97	-52.5	-57.39	>0.999	0.057	0.00014	0.997
K80	0.48	2.37	-43.36	-23.41	-87.63	-49.22	>0.999	0.083	0.00012	0.997
Na20	0.60	13.80	-24.02	-18.04	-40.88	-46.91	>0.999	0.004	0.00046	>0.999
Na40	0.74	6.80	-27.06	-21.32	-41.76	-51.11	>0.999	0.039	0.00031	0.999
Na60	1.02	4.56	-29.03	-24.11	-43.70	-56.21	>0.999	0.136	0.00017	0.990
Na80	0.99	3.60	-33.74	-29.99	-59.50	-76.09	>0.999	0.132	0.000097	0.997
Li20	0.70	7.53	-30.12	-22.63	-53.68	-57.03	>0.999	0.028	0.00035	0.998
Li40	0.64	6.21	-32.73	-24.38	-60.48	-62.63	>0.999	0.040	0.00023	0.995
Li60	0.84	4.15	-33.51	-25.24	-58.20	-60.95	>0.999	0.109	0.00018	0.996
Li80	0.87	3.95	-27.23	-26.96	-36.37	-66.77	>0.999	0.160	0.00021	0.998

Table S3. Contains isotherm fitting parameters



**Figure S33.** Relationship between inter-sheet distance and N-content of the activated material measure from XPS.



Figure S34. Variable temperature  $CO_2$  isotherms for the potassium activated samples a) K20, b) K40, c) K60, and d) K80.



**Figure S35.** Variable temperature CO<sub>2</sub> isotherms for the sodium activated samples a) Na20, b) Na40, c) Na60, and d) Na80.



**Figure S36.** Variable temperature  $CO_2$  isotherms for the lithium activated samples a) Li20, b) Li40, c) Li60, and d) Li80.



Figure S37. Correlation between micropore volume quantified by  $N_2$  porosimetry at 77K and CO<sub>2</sub> uptake at 114 Torr and 30 °C.



**Figure S38.** Enthalpy (black) and entropy (blue) of adsorption plotted as a function of loading (bottom) and coverage (top) for the K20 sample.



**Figure S39.** Enthalpy (black) and entropy (blue) of adsorption plotted as a function of loading (bottom) and coverage (top) for the K40 sample.



**Figure S40.** Enthalpy (black) and entropy (blue) of adsorption plotted as a function of loading (bottom) and coverage (top) for the K60 sample.



**Figure S41.** Enthalpy (black) and entropy (blue) of adsorption plotted as a function of loading (bottom) and coverage (top) for the K80 sample.



**Figure S42.** Enthalpy (black) and entropy (blue) of adsorption plotted as a function of loading (bottom) and coverage (top) for the Na20 sample.



**Figure S43.** Enthalpy (black) and entropy (blue) of adsorption plotted as a function of loading (bottom) and coverage (top) for the Na40 sample.



**Figure S44.** Enthalpy (black) and entropy (blue) of adsorption plotted as a function of loading (bottom) and coverage (top) for the Na60 sample.



Figure S45. Enthalpy (black) and entropy (blue) of adsorption plotted as a function of loading (bottom) and coverage (top) for the Na80 sample.



**Figure S46.** Enthalpy (black) and entropy (blue) of adsorption plotted as a function of loading (bottom) and coverage (top) for the Li20 sample.



**Figure S47.** Enthalpy (black) and entropy (blue) of adsorption plotted as a function of loading (bottom) and coverage (top) for the Li40 sample.



**Figure S48.** Enthalpy (black) and entropy (blue) of adsorption plotted as a function of loading (bottom) and coverage (top) for the Li60 sample.



**Figure S49.** Enthalpy (black) and entropy (blue) of adsorption plotted as a function of loading (bottom) and coverage (top) for the Li80 sample.



**Figure S50.** Gibbs energy of adsorption plotted as a function of loading (bottom) and coverage (top) for the K20 sample.



**Figure S51.** Gibbs energy of adsorption plotted as a function of loading (bottom) and coverage (top) for the K40 sample.



## CO<sub>2</sub> Loading (mmol/g)

**Figure S52.** Gibbs energy of adsorption plotted as a function of loading (bottom) and coverage (top) for the K60 sample.



**Figure S53.** Gibbs energy of adsorption plotted as a function of loading (bottom) and coverage (top) for the K80 sample.



**Figure S54.** Gibbs energy of adsorption plotted as a function of loading (bottom) and coverage (top) for Na20 sample at 30 °C.



**Figure S55.** Gibbs energy of adsorption plotted as a function of loading (bottom) and coverage (top) for the Na40 sample at 30 °C.







**Figure S57.** Gibbs energy of adsorption plotted as a function of loading (bottom) and coverage (top) for the Na80 sample at 30 °C.



**Figure S59.** Gibbs energy of adsorption plotted as a function of loading (bottom) and coverage (top) for the Li40 sample at 30 °C.



Figure S60. Gibbs energy of adsorption plotted as a function of loading (bottom) and coverage (top) for the Li60 sample at 30 °C.

## $CO_2$ Fractional Coverage ( $\theta$ )



Figure S61. Gibbs energy of adsorption plotted as a function of loading (bottom) and coverage (top) for the Li80 sample at 30 °C.



**Figure S62.** Shows the correlation between the Gibbs free energy of adsorption calculated at 0.1% coverage  $CO_2$  and 30°C for a) pyridinic, b) pyrrolic, c) graphitic, and d oxidic content measured by XPS.



**Figure S63.** Correlation plots between Henry's constant for N<sub>2</sub>, CO<sub>2</sub> uptake at 15% CO<sub>2</sub>, and selectivity (IAST) all at 30 °C against sample chemical properties. Ellipses were calculated from 95% confidence intervals.

#### Table S4. Correlation coefficients for figure S63.

	К <sub>Н</sub> № (mmol*g <sup>-1</sup> *Torr <sup>-1</sup> ) 30°С	CO2 Uptake (mmol/g) 30°C	Selectivity (IAST) 15% CO2 30°C	XPS N- Content (at%)	Pyridinic N-Content (at%)	Pyrrolic N-Content (at%)	Pyridinic+ Pyrrolic N- Content (at%)	Graphitic N-Content (at%)	Oxidic N- Content (at%)	N/C XPS	N/C EA
KH N2 (mmol/(g*Torr)		-0.75	-0.84	-0.95	-0.93	-0.97	-0.95	-0.60	-0.79	-0.94	-0.95
30°C		-0.75	-0.64	-0.95	-0.95	-0.87	-0.95	-0.00	-0.79	-0.94	-0.95
CO2 Uptake (mmol/g) 30°C	-0.75		0.75	0.81	0.76	0.91	0.86	0.29	0.49	0.80	0.75
Selectivity											
15% CO2 30°C	-0.84	0.75		0.87	0.90	0.78	0.89	0.46	0.60	0.89	0.90
XPS N-Content											
(at%)	-0.95	0.81	0.87		0.99	0.87	0.99	0.70	0.84	1.00	0.98
Pyridinic N- Content (at%)	-0.93	0.76	0.90	0.99		0.82	0.97	0.72	0.85	1.00	0.99
(0(70)			0.00	0.00		0.01					0.00
Pyrrolic N- Content (at%)	-0.87	0.91	0.78	0.87	0.82		0.93	0.31	0.52	0.86	0.81
Pyridinic+ Pyrrolic N-											
(at%)	-0.95	0.86	0.89	0.99	0.97	0.93		0.59	0.76	0.99	0.97
Graphitic N- Content	0.00	0.00	0.46	0.70	0.70	0.24	0.50		0.00	0.70	0.70
(at%)	-0.60	0.29	0.46	0.70	0.72	0.31	0.59		0.92	0.70	0.70
Oxidic N- Content (at%)	-0.79	0.49	0.60	0.84	0.85	0.52	0.76	0.92		0.84	0.85
(at/0)	0.73	0.13	0.00	0.01		0.02		0.02		0.01	0.00
N/C XPS	-0.94	0.80	0.89	1.00	1.00	0.86	0.99	0.70	0.84		0.99
N/C EA	-0.95	0.75	0.90	0.98	0.99	0.81	0.97	0.70	0.85	0.99	



Figure S64. Correlation plots between Henry's constant for N<sub>2</sub>, CO<sub>2</sub> uptake at 15% CO<sub>2</sub>, and selectivity (IAST) all at 30 °C against sample various physical properties. Ellipses were calculated from 95% confidence intervals.

	К <sub>н</sub> N <sub>2</sub> (mmol*g <sup>-1</sup> *Torr <sup>-1</sup> ) 30°С	CO2 Uptake (mmol/g) 30°C	Selectivity (IAST) 15% CO2 30°C	pore volume <1nm (cc/g)	pore volume 1- 2nm (cc/g)	pore volume 2- 50nm (cc/g)	BET Surface Area (m²/g)	d-spacing (Å)	Tau (Å)	Number of Sheets	La (Å)
К <sub>Н</sub> N <sub>2</sub> (mmol*g <sup>-1</sup> *Torr <sup>-1</sup> ) 30°С		-0.75	-0.83	0.89	0.58	0.50	0.75	0.91	-0.74	-0.76	0.80
CO2 Uptake (mmol/g) 30°C	-0.75		0.76	-0.77	-0.70	-0.70	-0.77	-0.78	0.48	0.49	-0.44
Selectivity (IAST) 15% CO2 30°C	-0.83	0.76		-0.76	-0.53	-0.53	-0.68	-0.73	0.86	0.87	-0.85
pore volume <1nm (cc/g)	0.89	-0.77	-0.77		0.86	0.79	0.95	0.93	-0.72	-0.74	0.66
pore volume 1- 2nm (cc/g)	0.58	-0.70	-0.53	0.86		0.96	0.97	0.76	-0.52	-0.53	0.30
pore volume 2- 50nm (cc/g)	0.50	-0.70	-0.53	0.79	0.96		0.93	0.71	-0.52	-0.53	0.30
BET Surface Area (m <sup>2</sup> /g)	0.75	-0.77	-0.68	0.95	0.97	0.93		0.88	-0.64	-0.66	0.50
d-spacing (Å)	0.91	-0.78	-0.73	0.93	0.76	0.71	0.88		-0.64	-0.66	0.65
Tau (Å)	-0.74	0.48	0.86	-0.72	-0.52	-0.52	-0.64	-0.64		1.00	-0.88
Number of Sheets	-0.76	0.49	0.87	-0.74	-0.53	-0.53	-0.66	-0.66	1.00		-0.88
La (Å)	0.80	-0.44	-0.85	0.66	0.30	0.30	0.50	0.65	-0.88	-0.88	

### Table S5. Correlation coefficients for figure S64



**Figure S65.** Correlation plots between the dual site Langmuir fit parameters against sample various surface chemical properties. Ellipses were calculated from 95% confidence intervals. Previously shown correlations are omitted.

Table S6. Correl	ation coefficie	nts for figure	S65

	Ha (kJ/mol)	Hb (kJ/mol)	Sa (J/mol*K)	Sb (J/mol*K)
Ha (kJ/mol)		0.14	0.99	-0.14
Hb (kJ/mol)	0.14		0.02	0.94
Sa (J/mol*K)	0.99	0.02		-0.22
Sb (J/mol*K)	-0.14	0.94	-0.22	
XPS total N- content (at%)	-0.22	-0.79	-0.064	-0.59
Pyridinic N- Content (at%)	-0.25	-0.76	-0.1	-0.56
Pyrrolic N-content (at%)	0.07	-0.87	0.22	-0.79
Pyridinic + Pyrrolic N-content (at%)	-0.14	-0.84	0.02	-0.67
Graphitic N- content (at%)	-0.49	-0.25	-0.42	-0.0013
Oxidic N-content (at%)	-0.44	-0.46	-0.33	-0.19
N/C XPS	-0.2	-0.78	-0.049	-0.59
N/C EA	-0.3	-0.8	-0.15	-0.59



**Figure S66.** Correlation plots between the dual site Langmuir fit parameters against sample various physical properties. Ellipses were calculated from 95% confidence intervals. Previously shown correlations are omitted.

#### Table S7. Correlation coefficients for figure S66

	Ha (kJ/mol)	Hb (kJ/mol)	Sa (J/mol*K)	Sb (J/mol*K)
Ha (kJ/mol)		0.14	0.99	-0.14
Hb (kJ/mol)	0.14		0.02	0.94
Sa (J/mol*K)	0.99	0.02		-0.22
Sb (J/mol*K)	-0.14	0.94	-0.22	
pore volume <1nm (cc/g)	-0.1	0.82	-0.24	0.74
pore volume 1-2nm (cc/g)	-0.56	0.62	-0.63	0.66
pore volume 2-50nm (cc/g)	-0.51	0.51	-0.57	0.52
BET Surface Area (m²/g)	-0.33	0.74	-0.44	0.71
d-spacing (Å)	0.17	0.85	0.025	0.72
Tau (Å)	-0.25	-0.66	-0.15	-0.49
Number of Sheets	-0.25	-0.68	-0.16	-0.51
La (Å)	0.27	0.65	0.16	0.46



**Figure S67.** Correlation plots between the thermodynamic values take at 0.1% coverage of  $CO_2$  against various chemical properties. Ellipses were calculated from 95% confidence intervals. Previously shown correlations are omitted.

Table S8. Correlation coefficients for figure S67

	-ΔHads (kJ/mol) (0.1% Cov	-ΔSads (J/mol*K) (0.1% cov)	ΔGads (kJ/mol) (0.1% cov, 30°C)
-∆Hads			
(kJ/mol)			
(0.1% Cov)		0.94	0.72
-ΔSads			
(J/mol*K)			
(0.1% cov)	0.94		0.44
-ΔGads			
(kJ/mol)			
(0.1% cov,			
`30°C) ∕	0.72	0.44	
XPS			
N-Content			
(at%)	0.63	0.34	0.97
Pyridinic N-			
Content			
(at%)	0.63	0.35	0.95
Pyrrolic N-			
Content			
(at%)	0.42	0.12	0.88
Pyridinic+			
Pyrrolic N-			
Content			
(at%)	0.58	0.27	0.97
Graphitic			
N-Content			
(at%)	0.65	0.54	0.63
Oxidic			
N-Content			
(at%)	0.69	0.48	0.82
N/C XPS	0.61	0.32	0.96
N/C EA	0.67	0.39	0.96



**Figure S68.** Correlation plots between the thermodynamic values take at 0.1% coverage of  $CO_2$  against various physical properties. Ellipses were calculated from 95% confidence intervals. Previously shown correlations are omitted.

	(kJ/mol) (0.1% Cov)	(J/mol*K) (0.1% cov)	(0.1% cov, 30°C)
-AHads		(012/0 001)	00 0,
(kl/mol)			
(0.1% Cov)		0.94	0.72
-ΔSads			
(J/mol*K)			
(0.1% cov)	0.94		0.44
-∆Gads			
(kJ/mol)			
(0.1% cov <i>,</i>			
30°C)	0.72	0.44	
pore volume			
<1nm			
(cc/g)	-0.53	-0.25	-0.88
pore volume			
1-2nm			
(cc/g)	-0.35	-0.15	-0.61
pore volume			
2-50nm			
(cc/g)	-0.27	-0.07	-0.57
BET			
Surface			
Area			
(m²/g)	-0.46	-0.22	-0.78
d-spacing			
(A)	-0.68	-0.42	-0.93
του (Å)	0.50	0.20	0.75
Tau (A)	0.56	0.36	0.75
Number of			
Sheets	0.57	0.37	0.76
0.10005	0.07	0.07	0.70
La (Å)	-0.49	-0.27	-0.73

-∆Gads (kJ/mol)

 Table S9. Correlation coefficients for figure S68

-∆Hads

-∆Sads



**Figure S69.** Correlations between different types of N-content a) pyridinic, b) pyrrolic, c) the sum of pyridinic and pyrrolic, d) graphitic, and e) oxidic measured by XPS and Henry's constant for N<sub>2</sub>.



**Figure S70.** Correlation between total N-content measured by XPS and selectivity for  $CO_2/N_2$  predicted by IAST at 15%  $CO_2$  and 30°C.



**Figure S71.** Predicted regeneration energy and working capacity as a function of desorption temperature for K-activated materials (a&d), Na-activated materials (b&e) and Li activated materials (c&f).



**Figure S72.** Working capacity per energy as a function of total working capacity, obtained by dividing the working capacity by regeneration energy at a specific temperature for a) K-activated samples, b) Na-activated samples, and c) Li-activated samples.



**Figure S73.** Entropy as a function of  $CO_2$  loading. The black line represents entropy loss of 1 translation degree of freedom from pure gas phase  $CO_2$  at 1 bar and 30C.



**Figure S74.** Gibbs energy of adsorption as a function of  $CO_2$  loading for a) potassium, b) sodium and c) lithium activated samples. The dotted line indicates the a the free energy required for a 90% capture rate from a feed stream of  $CO_2$  of 15%  $CO_2$  at 30°C.

All code used in the analysis of the N-rich carbons can be found at the following: https://github.com/jeeichler

#### References

1. M. G. Down, M. J. Haley, P. Hubberstey, R. J. Pulham and A. E. Thunder, J. Chem. Soc., Dalton Trans., 1978, 1407.