Electronic Supplementary Material (ESI) for Energy & Environmental Science

Strong and binder free structured zeolite sorbents with very high CO_2-over-N_2 selectivities and high capacities to adsorb CO_2 rapidly

Farid Akhtar,*[a,b] Qingling Liu,[a,c] Niklas Hedin,[a,b] Lennart Bergström*[a]

[a]Department of Materials and Environmental Chemistry, Stockholm University, Stockholm SE-10691, Sweden

[b]Berzelii Center EXSELENT on Porous Materials, Stockholm University, Stockholm 10691, Sweden

[c]Currently at Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716, United States

S1- Scanning electron micrographs of Na(K)A Powders, PCP-consolidated monoliths and X-ray diffraction data

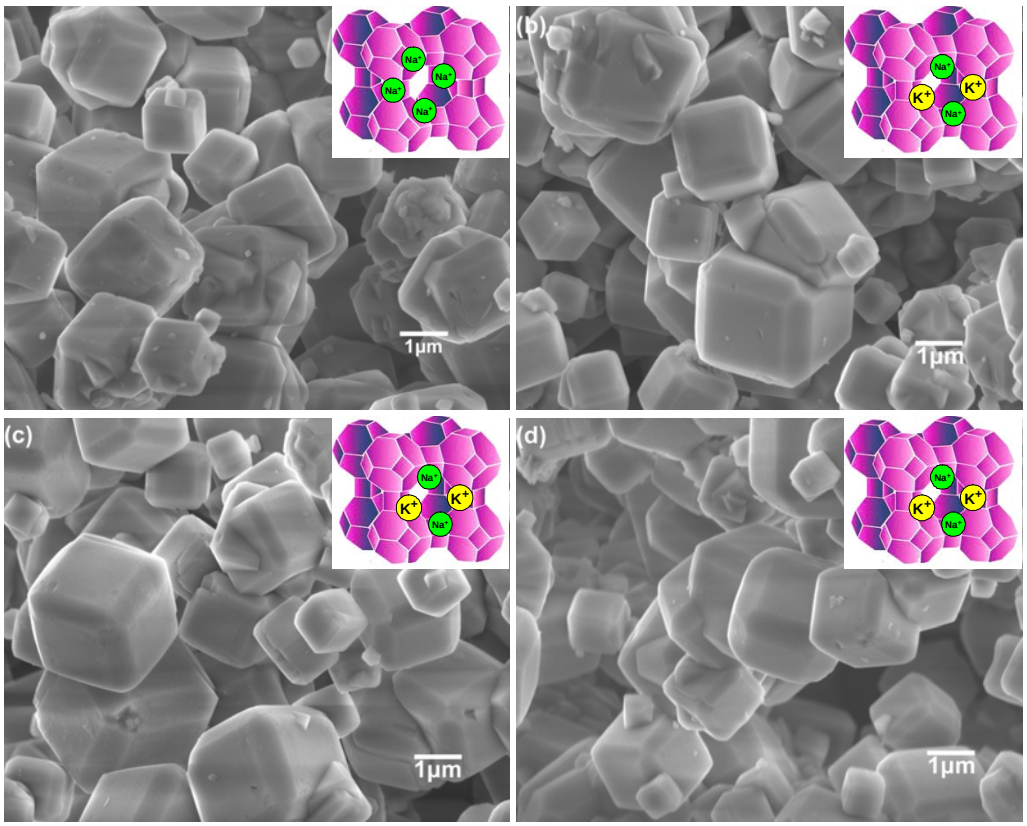

Figure 1S: Scanning electron micrographs a) NaA; b) NaK(17.3)A; c) NaK(24.6)A; d) NaK(37.4)A.

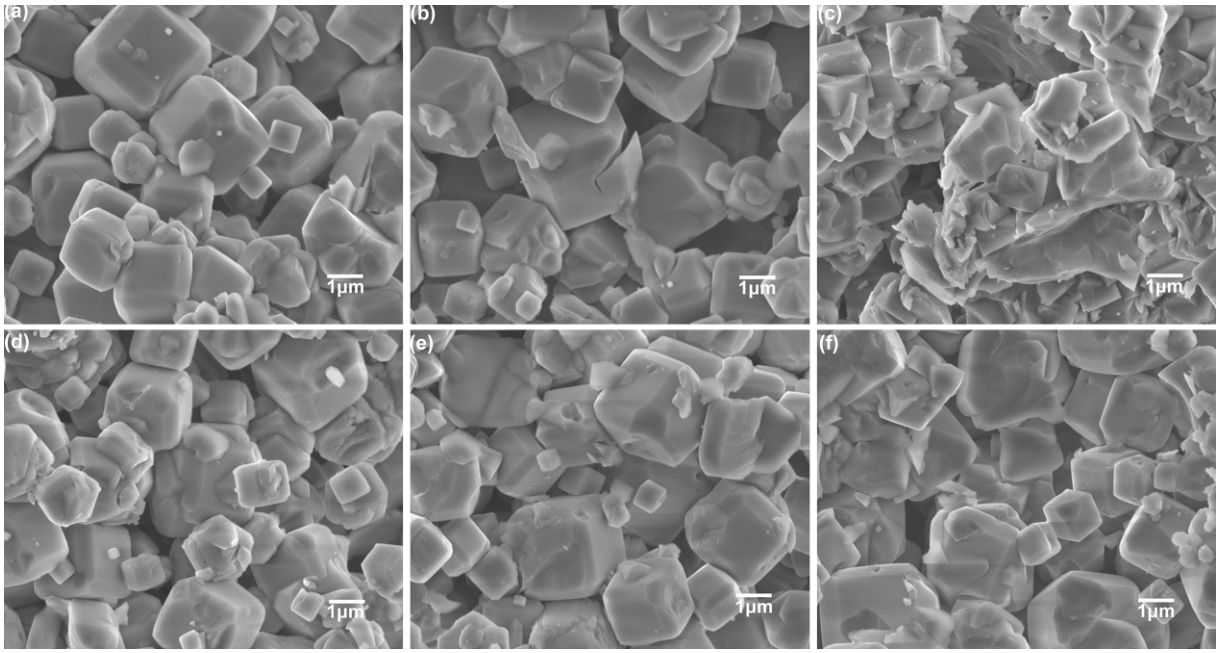

Figure 2S: a,b,c) Scanning electron micrographs of NaK(9.9)A consolidated by pulsed current processing (PCP) at a) 600 °C; b) 700 °C; c) 800 °C; d,e,f) Scanning electron micrograpahs of NaK(24.6)A consolidated by PCP at d) 600 °C; e) 700 °C; f) 800 °C.

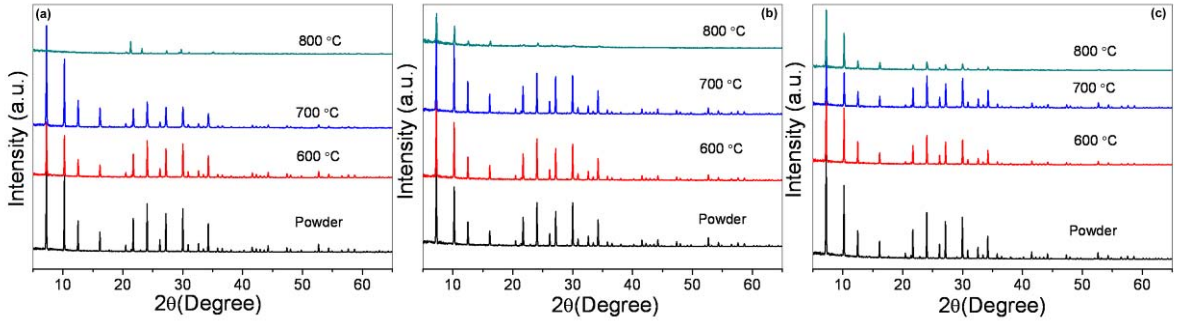

Figure 3S: Powder X-ray diffractograms of a) NaA powder and monoliths consolidated by pulsed current processing (PCP) at 600, 700 and 800 °C; b) NaK(9.9)A powder and monoliths consolidated by PCP at 600, 700 and 800 °C; c) NaK(24.6)A powder and monoliths consolidated by PCP at 600, 700 and 800 °C.

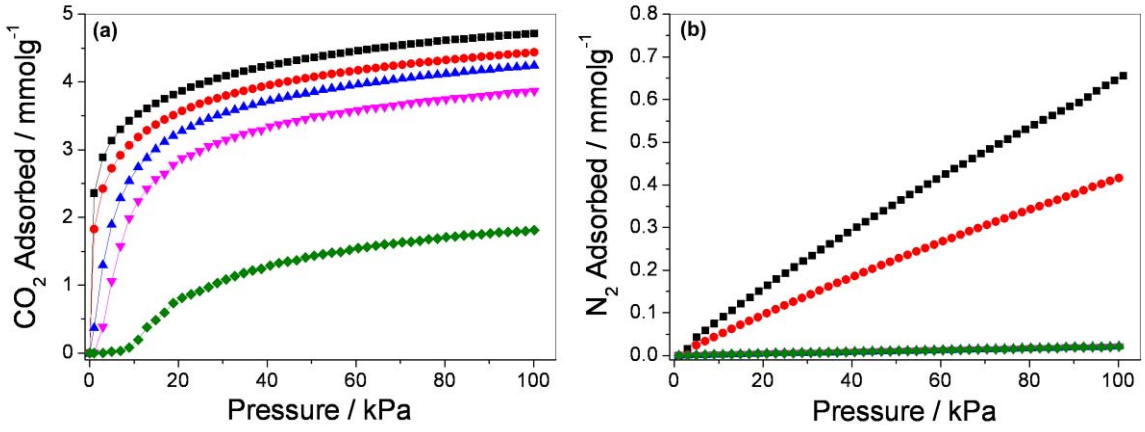

Figure 4S: The adsorption isotherms at 0 °C on NaKA with varying K^+ content (at. %); NaA (—■—), NaK(9.9)A (—●—), NaK(17.3)A (—▲—), NaK(24.6)A (—▼—), NaK(37.2)A (—◆—) a) CO_2 b) N_2.

S2- Langmuir model:

Langmuir model is used to describe the uptake of CO_2 and N_2. The traditional Langmuir isotherm model can be written as:[1]

$$q = \frac{q_m bP}{1+bP} \qquad (1)$$

where q and q_m are the uptake and the maximum uptake, respectively, b is equation constant and P is the equilibrium pressure.

S3- Toth model

The Toth isotherm describes well systems with sub-monolayer coverage and is a three parameter function: [1]

$$q = \frac{q_m bP}{(1+(bP)^t)^{1/t}} \qquad (2)$$

Here, q and q_m are the uptake and the maximum uptake, respectively, b is equation constant and P is the equilibrium pressure. The parameter t is usually less than unity and can be

interpreted as a characterization of the homogeneity of adsorption sites. Parameters b and t are specific for adsorbate-adsorbent pairs.

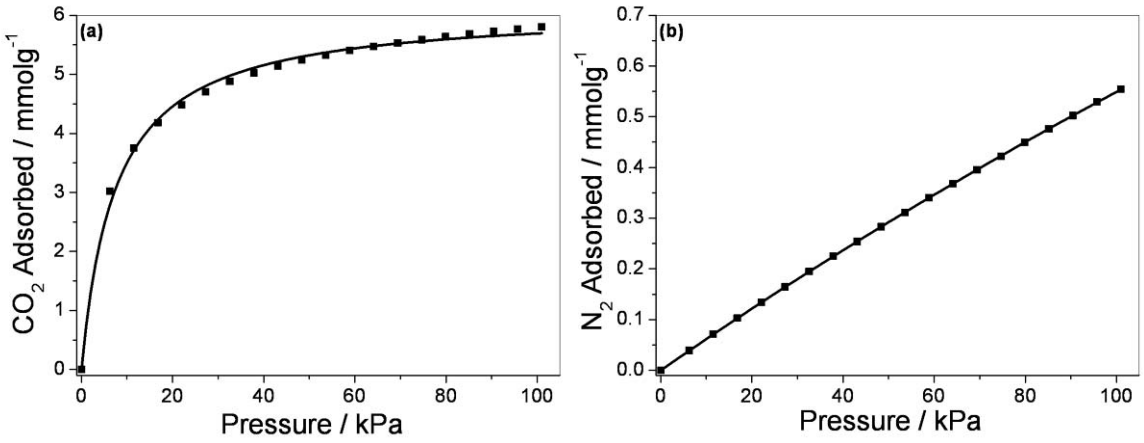

Figure 5S: Adsorption isotherms at 25 °C on 13X powder a) CO_2; b) N_2. The isotherms are fitted to a Langmuir model (□).

S4- Ideal adsorbed solution theory (IAST)

The IAS theory was used to predict binary adsorption isotherms using the adsorption isotherms of pure CO_2 and N_2. The IAS theory is analogous to Raoult's law and assumes an ideal solution between component gases at equilibrium. And at equilibrium the chemical potential of the adsorbed phase is estimated equal to the gas phase. For binary adsorption of constituents A and B, the conditions of IAS theory are[1-3]

$$xp_t = yp_A \qquad (2)$$

and/or $$(1-x)\,p_t = (1-y)\,p_B \qquad (3)$$

where x and y represents the molar fraction of constituent A in the gas phase and adsorbed phase, respectively. P_t,P_A and P_B are the total pressure, pressure of constituent A and B, respectively. The pressure of constituents A (P_A) and B (P_B) corresponds to the spreading pressure (π) of the binary mixture of constituent A and B and is expressed as[2]

$$\frac{A\pi}{RT} = \int_0^{P_1^0} \frac{q_{_1}}{P_1} dp_1 = \int_0^{P_2^0} \frac{q_{_2}}{P_2} dp_2 = \ldots = \int_0^{P_N^0} \frac{q_{_N}}{P_N} dp_1 = \int_0^{P} \frac{q}{P} dp \qquad (4)$$

where A, R, T and q are the specific surface area of the adsorbent, gas constant, temperature and the adsorbed amount at pressure P. The reduced spreading pressure (z) of the adsorbed phase is given as[2]

$$z = \frac{A\pi}{RT} = \int_0^{P_1^0} \frac{q_{_1}}{P_1} dp_1 = \int_0^{P_2^0} \frac{q_{_2}}{P_2} dp_2 = \ldots = \int_0^{P_N^0} \frac{q_{_N}}{P_N} dp_1 = \int_0^{P} \frac{q}{P} dp \qquad (5)$$

To calculate reduced spreading pressure (z), IAS theory is combined with the Langmuir model, and z can be calculated using equations 1 and 5 and its analytical solution is given as[2,3a]

$$z = q_t \ln(1 + \sum_{i=0}^{N} b_i p_i) = q_t \ln(1 + bp) \qquad (6)$$

At equilibrium, the reduced spreading pressure of each of the costituents (A and B) will be equal i.e. z_A=z_B and the molar fraction of constituent A in the adsorbed phase is deduced using equations 2, 3 and 6 and can be written as[3a]

$$q_{t,A} \ln\left(1 + \frac{b_A p_t y}{x}\right) - q_{t,B} \ln\left(1 + \frac{b_B p_t (1-y)}{1-x}\right) = 0 \qquad (7)$$

The parameter $q_{t,A}$ and b_A are obtained from the Langmuir model of the equilibrium isotherm of component A (CO_2) and $q_{t,B}$ and b_B are Langmuir parameters for component B (N_2). Matlab (version R2010b, The MathWorks, Inc.) was used to solve equations and integrals for x for fixed p_t and y values. Generally, the total adsorption could be determined based on IAS and expressed as[3b]

$$\frac{1}{n_t} = \sum_{i=0}^{N} \left[\frac{x_i}{n_i\,(P_i)} \right] \qquad (8)$$

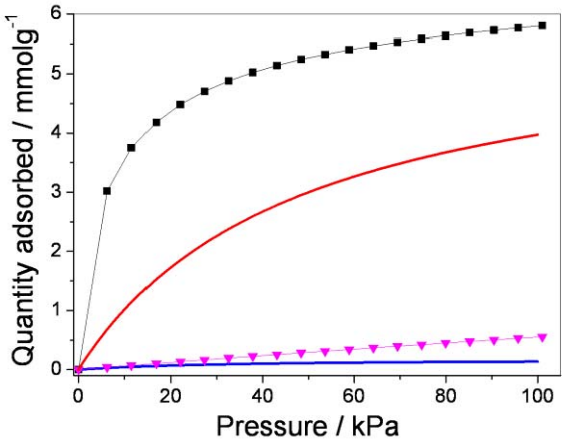

Figure 6S: Experimental single component CO_2 (—■—) and N_2 (—▼—) adsorption isotherms at 25 °C and ideal adsorbed solution (IAS) theory prediction of CO_2 (□) and N_2 adsorption (□) from binary 15 mol % CO_2 and 85 mol% N_2 mixture on 13X powder.

S5- Uptake kinetics

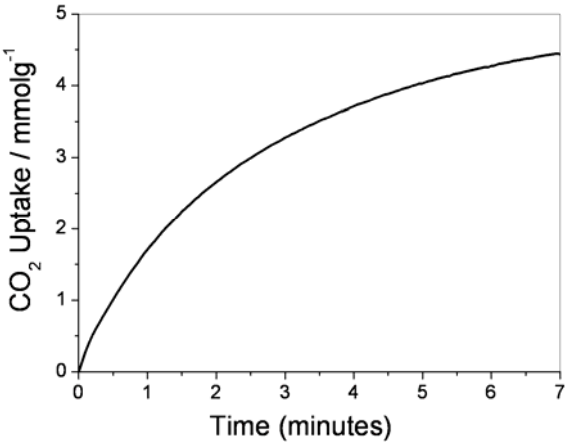

Figure 7S: CO_2 uptake kinetics on 13X powder.

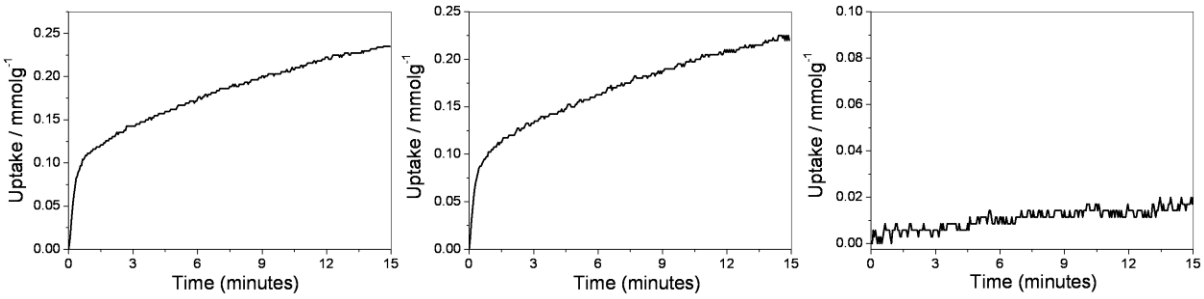

Figure 8S: Adsorption kinetics of N_2 at 25 °C on monoliths consolidated by Pulsed Current Processing (PCP) at 600 °C a) NaA monolith; b) NaK(9.9)A monolith; c) NaK(17.3)A.

Table 1S: EDX elemental analysis of NaA and partially K^+ exchanged NaKA powders.

Specimen	**Si (at. %)**	**Al(at. %)**	**O (at. %)**	**Na (at. %)**	**K (at. %)**	**K/(K+Na) (at. %)**
NaA	13.3	12.1	62.7	11.9	---	0.0
NaK(9.9)A	13.2	12.1	62.6	10.9	1.2	9.90
NaK(17.3)A	12.5	11.5	63.9	10.0	2.1	17.3
NaK(24.6)A	13.4	12.2	62.2	9.2	3.0	24.6
NaK(37.4)A	13.7	12.8	61.2	7.7	4.6	37.4

Table 2S: CO_2 and N_2 isotherm parameters obtained from Langmuir model for zeolite NaA.

Specimen	Treatment	Gas/Temperature	q_m	b	R^2
NaA	Powder	CO_2/25 °C	4.41362	0.37581	0.92448
NaA	PCP 600 °C	CO_2/25 °C	3.83398	0.23642	0.97622
NaA	PCP 700 °C	CO_2/25 °C	1.10548	0.17735	0.96018
NaA	Powder	N_2/25 °C	3.45355	0.00206	0.99972
NaA	PCP 600 °C	N_2/25 °C	462.97946	7.31668e-6	0.98552
NaA	PCP 700 °C	N_2/25 °C	0.16423	0.00529	0.99688

Table 3S: CO_2 and N_2 isotherm parameters obtained from Toth model for zeolite NaA.

Specimen	Treatment	Gas/Temperature	q_m	B	n	R^2
NaA	Powder	CO_2/25 °C	7.60444	159.62924	0.21803	0.99908
NaA	PCP 600 °C	CO_2/25 °C	4.62193	0.99617	0.4936	0.99604
NaA	PCP 700 °C	CO_2/25 °C	1.89442	4.39659	0.28904	0.99927
NaA	Powder	N_2/25 °C	3.31985	0.00214	1.01852	0.99972
NaA	PCP 600 °C	N_2/25 °C	---	---	---	---
NaA	PCP 700 °C	N_2/25 °C	4.36466	0.00035	0.3109	0.99792

Table 4S: CO_2 and N_2 isotherm parameters obtained from Langmuir model for NaK(9.9)A.

Specimen	Treatment	Gas/Temperature	q_m	b	R^2
NaKA	Powder	CO_2/25 °C	4.18041	0.29383	0.9474
NaKA	PCP 600 °C	CO_2/25 °C	4.2072	0.21012	0.9761
NaKA	PCP 700 °C	CO_2/25 °C	4.0216	0.23511	0.95848
NaKA	Powder	N_2/25 °C	2.35136	0.0019	0.99974
NaKA	PCP 600 °C	N_2/25 °C	1.54074	0.00296	0.99933
NaKA	PCP 700 °C	N_2/25 °C	254.84515	1.25512E-5	0.99548

Table 5S: CO_2 and N_2 isotherm parameters obtained from Toth model for NaK(9.9)A.

Specimen	Treatment	Gas/Temperature	q_m	b	n	R^2
NaKA	Powder	CO_2/25 °C	6.96906	35.68234	0.24774	0.99998
NaKA	PCP 600 °C	CO_2/25 °C	5.35128	1.20015	0.44356	0.99956
NaKA	PCP 700 °C	CO_2/25 °C	6.11799	6.52035	0.30645	0.99999
NaKA	Powder	N_2/25 °C	---	---	---	---
NaKA	PCP 600 °C	N_2/25 °C	---	---	---	---
NaKA	PCP 700 °C	N_2/25 °C	---	---	---	---

Table 6S: CO_2 and N_2 isotherm parameters obtained from Langmuir model for NaK(17.3)A.

Specimen	Treatment	Gas/Temperature	q_m	b	R^2
NaKA	Powder	CO_2/25 °C	3.79599	0.13224	0.99007
NaKA	PCP 600 °C	CO_2/25 °C	3.40927	0.06863	0.99879
NaKA	PCP 700 °C	CO_2/25 °C	0.90424	0.00742	0.99209
NaKA	Powder	N_2/25 °C	0.11821	0.00482	0.99787
NaKA	PCP 600 °C	N_2/25 °C	0.08394	0.00757	0.94492
NaKA	PCP 700 °C	N_2/25 °C	---	---	---

Table 7S: CO_2 and N_2 isotherm parameters obtained from Toth model for NaK(17.3)A.

Specimen	Treatment	Gas/Temperature	q_m	b	n	R^2
NaKA	Powder	CO_2/25 °C	4.65149	0.34831	0.54232	0.99952
NaKA	PCP 600 °C	CO_2/25 °C	3.53959	0.07456	0.90026	0.99901
NaKA	PCP 700 °C	CO_2/25 °C	---	---	---	---
NaKA	Powder	N_2/25 °C	1.82817	4.73067E-4	0.35989	0.99848
NaKA	PCP 600 °C	N_2/25 °C	---	---	---	---
NaKA	PCP 700 °C	N_2/25 °C	---	---	---	---

References

1- R. T. Yang, *Gas Separation by Adsorption Processes*, Imperial College Press, London, 1997.

2- D. D. Do, *Adsorption analysis: Equilibria and kinetics*, Imperial College Press: London, (2008).

3- J. Peng, H. Ban, X. Zhang, L. Song, Z. Sun, *Chem. Phys. Letts.*, 2005, 401, 94; b) A. L. Mayers, J. M. Prausnitz, AIChE J., 1965, 11, 121.