NaKA sorbents with high CO_2-over-N_2 selectivity and high capacity to adsorb CO_2

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Supplementary Information

Details of experimental techniques, SEM images, adsorption data, FTIR spectroscopy, XRD pattern, Rietveld refinements results, and computational computer modeling details.

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1. Experimental and computational details

A range of experimental and computational procedures were used to derive and study the properties of NaKA.

1.1 Ion exchange of zeolite NaA

The zeolite NaA powder was supplied by Sigma-Aldrich. Zeolite NaKA with mixed cations of Na^+ and K^+, with K^+/ (Na^+ +K^+) ranging from 0-97.0 atom%, were synthesized by a ion-exchange methods. The degree of K^+ exchange was controlled by changing the concentration of potassium chloride, the temperature, and the time for ion exchange. The final content of K^+ was determined by Energy Dispersive X-ray (EDX) analysis. The 9 kinds of NaKA zeolties were prepared as follow:

1. NaA (0 atom% K^+). The original zeolite powder supplied by Sigma-Aldrich.
2. NaKA (8.4 atom% K^+). 1 g of zeolite NaA was put in into a beaker and 100 ml of distilled water containing 0.075 g potassium chloride was added. The mixture was suspended by stirring for 30 minutes at 298.15 K. Thereafter the sample was washed with distilled water and dried at 383.15 K.
3. NaKA (17.4 atom% K^+). 1 g of zeolite NaA was put in into a beaker and 100 ml of distilled water containing 0.149 g potassium chloride was added. The mixture was suspended by stirring for 30 minutes at 298.15 K. Thereafter the sample was washed with distilled water and dried at 383.15 K.
4. NaKA (28.3 atom% K^+). 1 g of zeolite NaA was put in into a beaker and 100 ml of distilled water containing 0.298 g potassium chloride was added. The mixture was suspended by stirring for 30 minutes at 298.15 K. Thereafter the sample was washed with distilled water and dried at 383.15 K.
5. NaKA (39.4 atom% K^+). 1 g of zeolite NaA was put in into a beaker and 100 ml of distilled water containing 0.596 g potassium chloride was added. The mixture was suspended by stirring for 30 minutes at 298.15 K. Thereafter the sample was washed with distilled water and dried at 383.15 K.
6. NaKA (46.9 atom% K^+). 1 g of zeolite NaA was put in into a beaker and 100 ml of distilled water containing 0.746 g potassium chloride was added. The mixture was suspended by stirring for 30 minutes at 298.15 K. Thereafter the sample was washed with distilled water and dried at 383.15 K.

7. NaKA (58.5 atom% K^+). 1 g of zeolite NaA was put in into a beaker and 100 ml of distilled water containing 1.491 g potassium chloride was added. The mixture was suspended by stirring for 60 minutes at 298.15 K. Thereafter the sample was washed with distilled water and dried at 383.15 K.
8. NaKA (88.1 atom% K^+). 1 g of zeolite NaA was put in into a beaker and 100 ml of distilled water containing 2.895 g potassium chloride was added. The mixture was suspended by stirring for 60 minutes at 333.15 K. The supernatant liquid was decanted and another 100 ml portion of the same concentration of potassium chloride was added. The mixture was suspended by stirring for 60 minutes at 333.15 K. Then the sample was washed with distilled water and dried at 383.15 K.
9. NaKA (97.00 atom% K^+). 1 g of zeolite NaA was put in into a beaker and 100 ml of distilled water containing 4.47 g potassium chloride was added. The mixture was suspended by stirring for 60 minutes at 333.15 K. The supernatant liquid was decanted and another 100 ml. portion of the same concentration of potassium exchange solution was added. The process repeated for three times. Then the sample was washed with distilled water and dried at 383.15 K.

1.2 SEM/EDX

SEM micrographs and EDX spectra were obtained with a JEOL JSM-7000F scanning electron microscope equipped with a Link analytical system. The electron energy used was 15 keV. The zeolite powder was thinly spread onto a carbon film supported on a brass stud and carbon coated. Scanning electron microscope analysis showed that the crystals were nearly cubic in shape with a number-average size of 4μm. The zeolite size and morphology before and after ion-exchange is similar (see Figure S1).

1.3 Adsorption experiments

The adsorption capacities of the zeolite NaKA at different temperatures were measured by a slight modified Micromeritics Gemini TM 2375 device.[1] This volumetric adsorption device measures the gas uptake capacity under (quasi) equilibrium conditions at a given temperature and pressure. Before the experiments, each sample was treated under a flow of dry N_2 gas at a temperature of 623.15 K for 4 h. The adsorption temperature was controlled by a refrigerated and heated circulating bath (Huber MinistatTM 230) and a Dewar flask. A low-molecular-weight siloxane oligomer was used as the heat transfer medium, and the temperature was established in the Dewar flask by an external thermocouple and cross calibrated to that in the circulating bath.

1.4 FT IR spectroscopy

Fourier Transform Infrared (FTIR) spectra were recorded on a Varian 670-IR spectrometer, equipped with a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen. A thin slice of sample is prepared by pressing 35 mg zeolite powder together to a partly IR transparent self-supporting pellet with a diameter of 16 mm using a 20-ton pressing tool (International Crystal Laboratories, USA). The pellets were pressed with a pressure of 1 ton/cm^2 for 2 minutes. The pellet was then put a home-built stainless steel IR transmission cell with KBr windows. The cell was placed in the sample compartment of the IR spectrometer and was connected to a high vacuum system. The samples were prepared by heating the cell to 473.15 K (controlled by a PID temperature regulator) and subjected to conditions of dynamic vacuum (lower than 10^{-6} torr) for typically 6 hours. When the pellet was cooled down a background spectrum was recorded for the IR spectra. After which, the CO_2 gas was let into the cell and equilibrated to the proper pressure; spectra are recorded for the adsorption branch by increasing the pressure, the desorption branch is studied by decreasing the pressure. The sample is let to equilibrate. The equilibration is controlled by either the read out from the pressure transducers (in the low-pressure regime), or a monitoring of the actual spectrum. When the integral intensities in the spectrum stop to change the equilibrium spectrum is recorded for that given pressure. For each spectrum, 32 scans were accumulated at a spectral resolution of 4 cm^{-1}. The contributions from free gaseous CO_2 to the spectra were corrected for by subtracting the corresponding gaseous spectra measured separately with CO_2 in the cell at the same temperature as the sample measurement are carried out.

At low pressures chemisorbed species form first, there is no physisorption (Figure S6, spectrum b). At higher pressures the main form of the adsorption is physisorption, however the ν_3 absorption band of CO_2 is saturated fast, one can follow the physisorption quantitatively by the intensity of combination bands ($\nu_3+\nu_1$, $\nu_3+2\nu_2$) at 3714 and 3598 cm^{-1}. There is a little additional chemisorption in the pressure range (spectra d-f) over around 0.05 bar.

The majority of the physisorbed CO_2 removes during desorption, however to remove all physisorbed CO_2 simple evacuation is not enough: heating of the NaKA material needed. With the heat treatment all the phisysorbed CO_2 can be removed (Figure S7, spectrum g). The decrease in the chemisorbed species is not very significant during the desorption. Heating of the sample is necessary to remove the majority of the chemisorbed species. There are some remaining bands those cannot be removed even 4 hours heating of the sample at 473.15 K.

1.5 XRD and Rietveld refinements

The XRD patterns of the original zeolite NaA and ion-exchanged NaKA were obtained using a XPERT-PRO powder diffractometer (CuKa radiation, k = 1.5418A °) over the range of 2θ = 5.0–100.0 °. All the zeolite samples were first heated up and kept at 673.15 K for one hour in vacuum to remove any absorbed gas molecules and powder X-ray data were then collected at 673.15 K. During the Rietveld refinements, the K/Na ratios were restrained to be close to the EDS analysis results (see Table S1).

1.6 Computer modeling: Methods, models, results and discussion

1.6.1 Introduction

In order to provide a full picture of the dynamics involved in the separation of CO_2 and N_2 with the proposed Zeolite it is necessary to take into account both thermodynamic as well as kinetic effects. With Molecular Mechanical (MM) simulation techniques, the effects of these two properties in the system can potentially be modeled. When modeling the thermodynamic effects of gas adsorption Monte Carlo (MC) techniques are sufficient, although in order to take into account the kinetic effects, which are suggested to be decisive for the high CO_2/N_2 separation potential of the NaKA adsorbent, a Molecular Dynamics (MD) approach is needed. However, in this paper the modeling has been restricted to MC simulations, hence thermodynamic effects alone, in an attempt to show that these are not sufficient to describe the full separation retrieved from the experimental results, leaving the kinetic analysis for an upcoming paper.

Several μVT ensemble MC methods have been used, where molecules can be created, annihilated, translated or destroyed, in a 3D system with periodic boundary conditions. Equilibrium is reached when temperature and chemical potential (μ) outside and inside the framework are equal in the various steps of the procedure when computing the adsorption of CO_2 and N_2 in the NaKA structure, as a result of the thermodynamic effects of in the system. All calculations where performed with the Accelrys Materials Studio software. The procedure steps are explained below.

1.6.2 Methodology

The LTA framework was imported from the Materials Studio database into where the total of 96 extra-framework Na^+ and K^+ were inserted. The cation positions were optimized using the "locate task" of the SORPTION module utilizing the Canonical MC simulated annealing algorithm[,2] which provides a good approximation of the global minimum by slowly lowering the temperature of the system from an initial high. During the this procedure the geometry of the framework is kept fixed which is standard procedure as previous studies have shown it to be a good assumption as the framework flexibility, when loading small molecules, is generally negligible.[3] The framework atoms were assigned following partial charges; Si +2.4*e*, Al +1.7*e* and O -1.2*e* and the cations 0.7*e* in accordance with Maurin *et. al*[4] which results in a neutral system and the CVFF force field was used. Six NaKA structure models are in this manner created at $K^+/(K^++Na^+)$ ratios of 0, 0.2, 0.4, 0.6, 0.8 and 1. Computational details for calculations are found in appendix A, section 2.5.1. Further, the N_2 and CO_2 molecules geometry was optimized with the DMol3 module, at the DFT level of theory with functional GGA B3LYP and a DND basis set.

For the calculation of the adsorption isotherms for the two gases the *Adsorption Isotherm* task of the SORPTION module is used, utilizing the Grand Canonical MC (GCMC) method where the gas molecules are loaded, into the fixed NaKA structure, as a function of the gas fugacity at a fixed temperature. A series of fixed pressure simulations are performed separately starting with the configuration reached at the end of the previous simulation. An adsorption isotherm for the respective gases at fugacity intervals of 0.1 bar ranging from 0 to 1 bar at temperature 298.15 K is calculated. Segregation constraints were set on the calculations disallowing the gas molecules to be inserted into the sodalite cages as the windows entering these are to narrow for the gas molecules to pass. In the GCMC calculations the COMPASS force field was used for the gas-gas and gas-NaKA interactions, where the valence parameters and the atomic partial charges have been fitted to *ab-initio* data[5]. This is particularly important in this case as it allows for an elaborate calculation of the quadrupole moment N_2 which is crucial for accurate calculations of the adsorption related to the thermodynamics of this system. An isotherm was calculated for each of the six NaKA frameworks and gas, respectively.

As the focus of this study is the effect of the ion exchange, the computational results are compared with figure 1. Using the least squares fit method the computed isotherms at each $K^+ / (Na^+ + K^+)$ ratio was extrapolated to 0.85 bar (figure S10). The N_2 isotherms were fitted to a third degree curve while a first degree curve was fitted to the CO_2 isotherms in the range 0.6 to 1.0 bar as this range can be approximated to be linear.

1.6.3 Results and Discussion

From figure S11 it is clear that the MC simulations of the system result in significantly higher uptake of both gases compared with that which is experimentally measured. These overestimations fall in the line of our thesis that the kinetic effects play a significant role in the separation of the gases. A particular hint of this is the observation that the uptake of respective gases does not reach zero at 100% K^+ content as observed experimentally and should be expected as the kinetic diameters of both gases are larger than the pore openings and thus none of the molecules should be able to enter.

It is also clear that this thermodynamically based model provides a more continuous curve for both gas uptakes following the cation exchange and does not describe the different stages observed in experiment providing the “sweet spot” where the uptake of N_2 approaches zero as the uptake for CO_2 still remains high.

We are currently working with the MD simulations in order to measure the kinetic effects as well as *ab-initio* calculations at the specific adsorption sites of the gas molecules in the NaKA structure and hope to shortly present a work describing the full picture of the CO_2-over-N_2 selectivity, measured in the experiments.

2. Additional Figures

Here we present additional Figures to support the communicated findings. They include SEM, adsorption data, FTIR spectra, XRD, and computational results.

2.1 SEM images

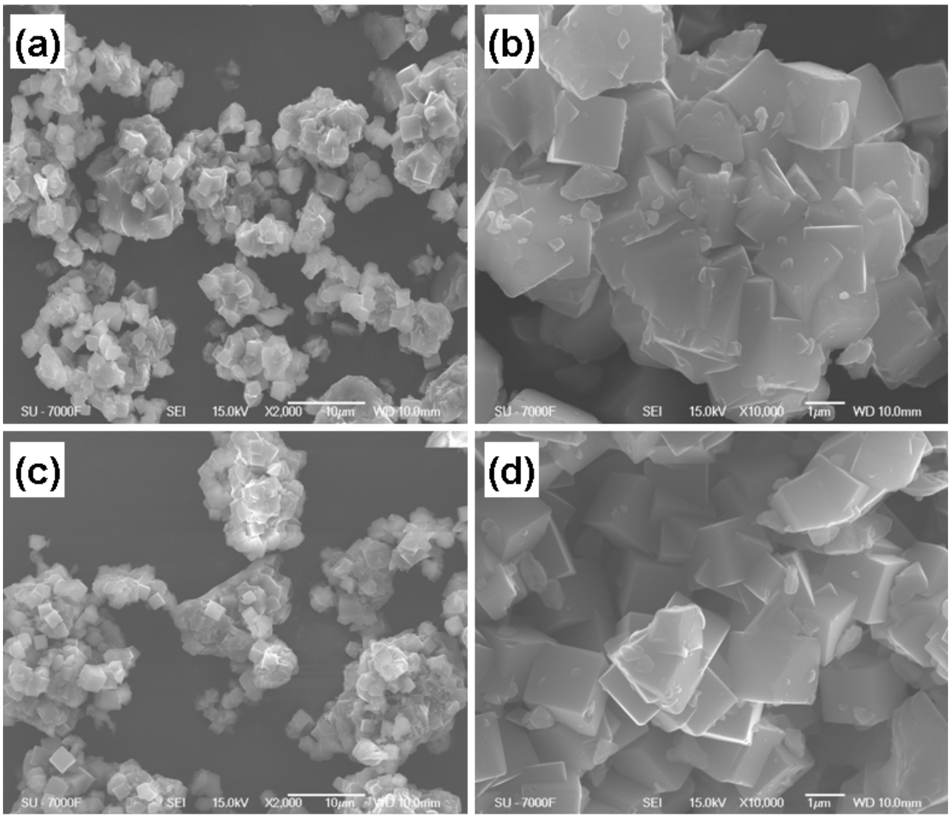


Figure S1. Low- and high-magnification SEM images of the original zeolite NaA (a) (b), and NaKA with 17.4 atom% K^+ (c) (d)

2.2 Adsorption data

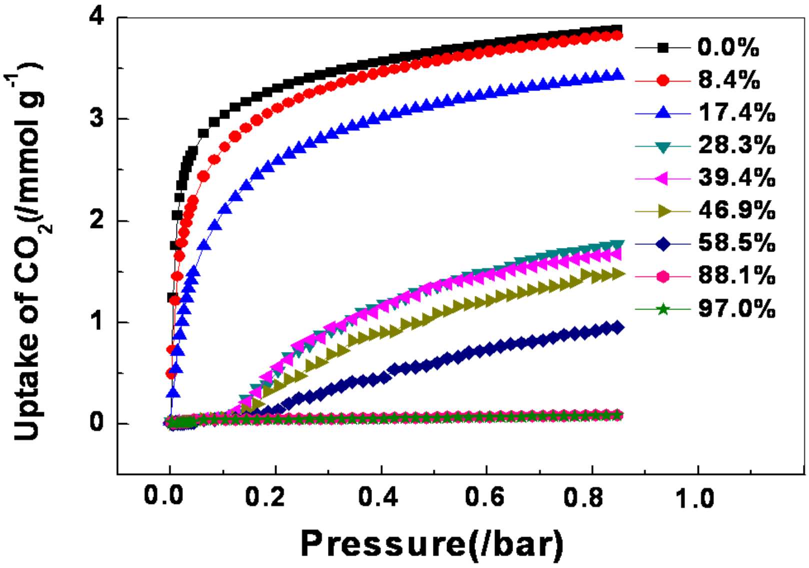


Figure S2. The adsorption isotherms of CO_2 on zeolite NaKA with different K^+ content (298.15 K)

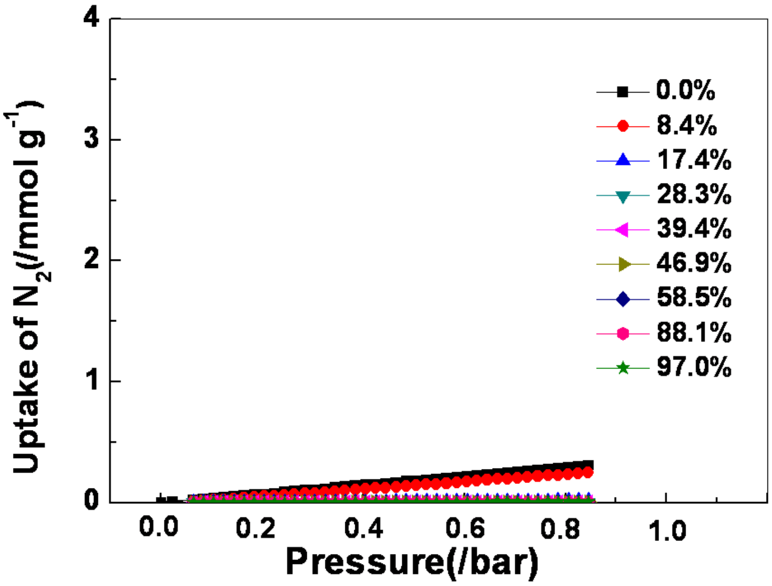


Figure S3. The adsorption isotherms of N_2 on zeolite NaKA with different K^+ content (298.15 K)

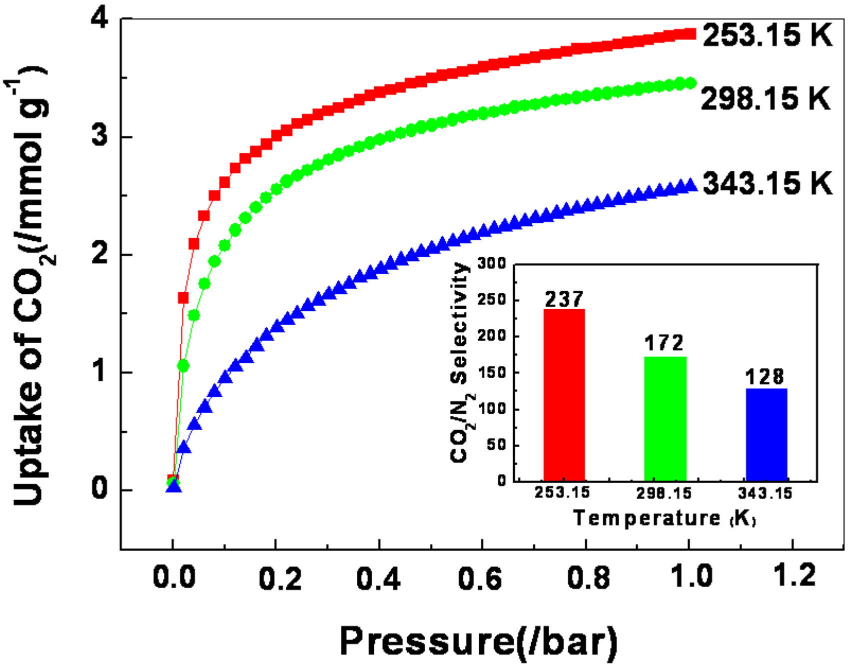


Figure S4. Adsorption isotherms for CO_2 in NaKA with $K^+/(Na^+ + K^+)$ equal 17.4 atom% at different temperatures

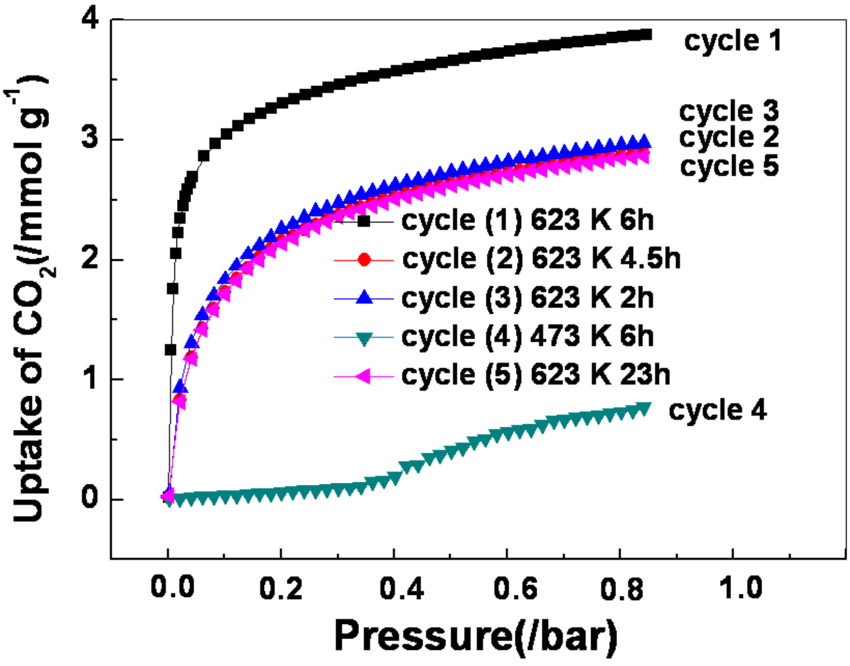


Figure S5. The adsorption isotherms of CO_2 in different cycles; measurement on zeolite NaKA with 17.4 atom % K^+; the sample was subjected to humid air after each cycle

2.3 FTIR spectra

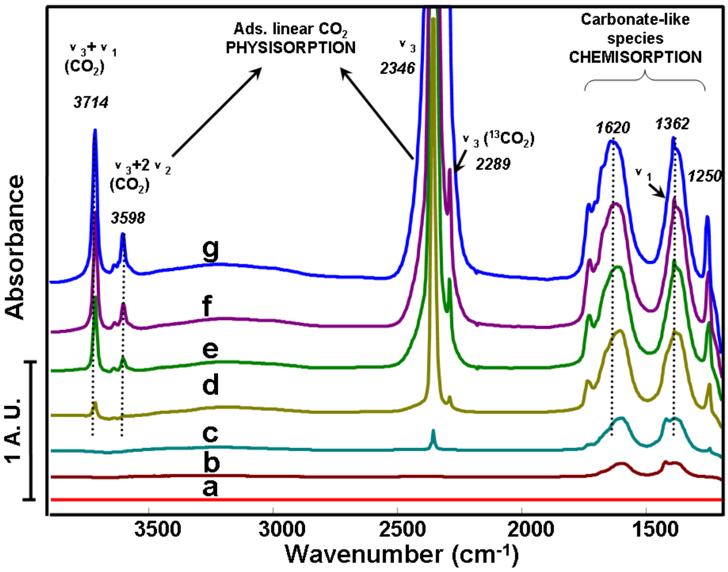


Figure S6. Infrared spectra of adsorption branch of CO_2 on NaKA with K^+ content of 17.4 atom% in the a) without CO_2 (background) and at CO_2 pressures of b) 1.3×10^{-5} bar c) 2.7×10^{-4} bar, d) 0.04 bar, e) 0.053 bar, f) 0.13 bar and g) 0.85 bar.

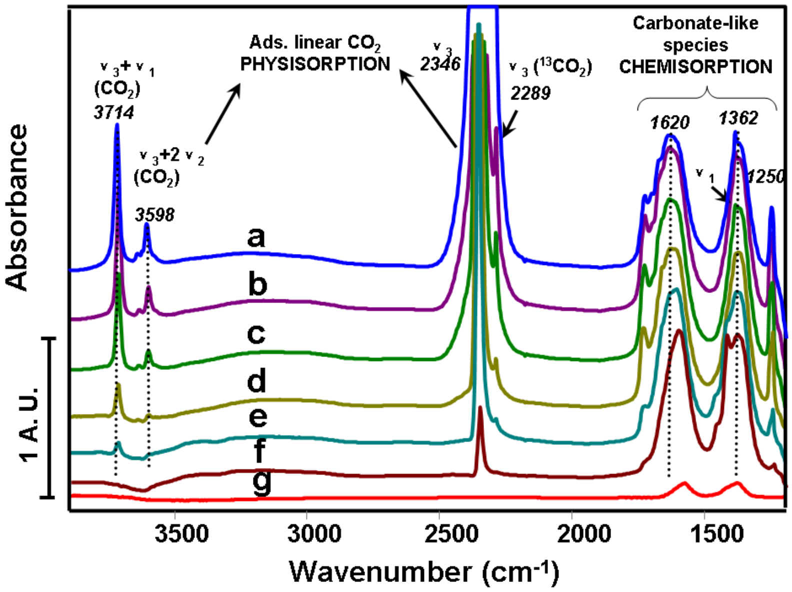


Figure S7. Infrared spectra of desorption branch of CO_2 on NaKA with K^+ content of 17.4 atom%, at pressures of a) 0.85 bar, b) 0.13 bar, c) 0.053 bar, d) 0.004 bar, e) 1.3×10^{-6} bar, f) 4 hours evacuation ($<10^{-8}$ bar) and g) heating 4 hours at 473.15 K.

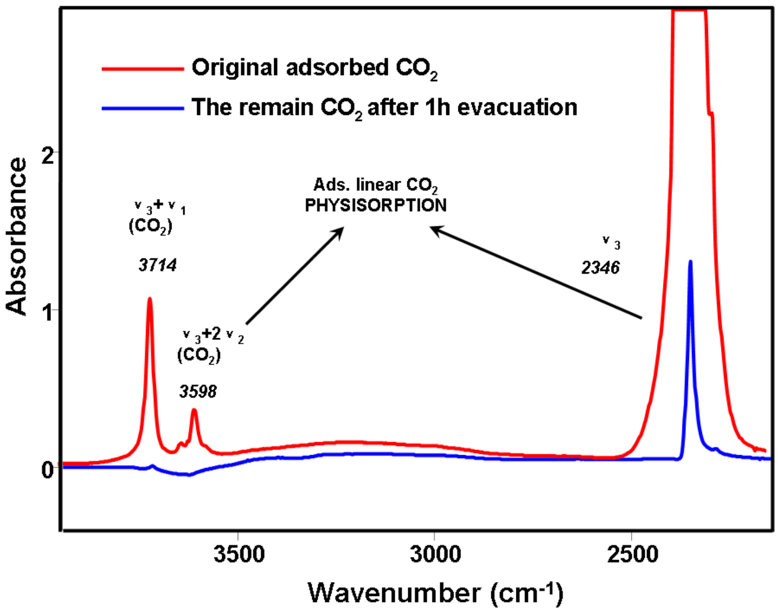
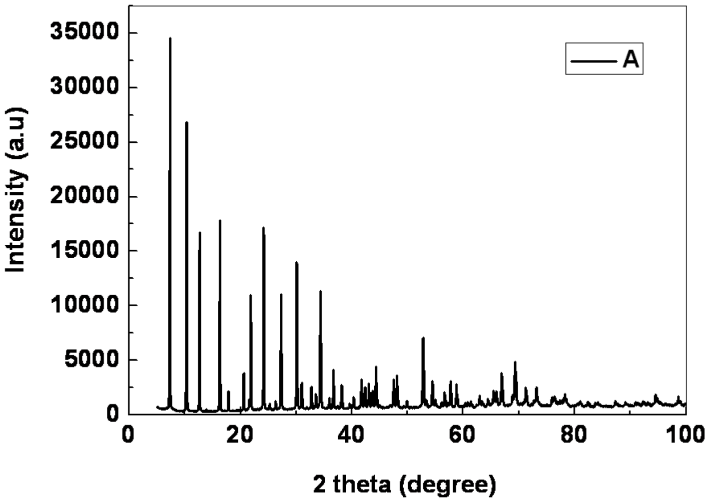
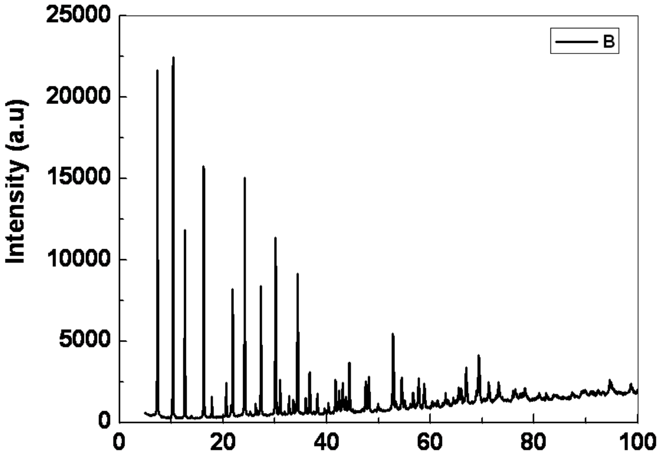


Figure S8. Infrared spectra of desorption branch of CO_2 on NaKA with K^+ content of 17.4 atom%, at pressures of 0.85 bar (red line), and after one hour evacuation (blue line). There is 1.7 vol.% CO_2 remains in the zeolite after 1h evacuation.

2.4 XRD patterns of NaKA

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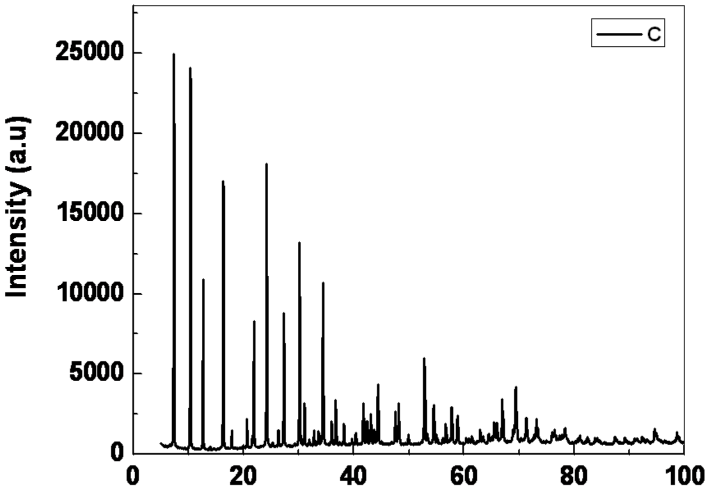
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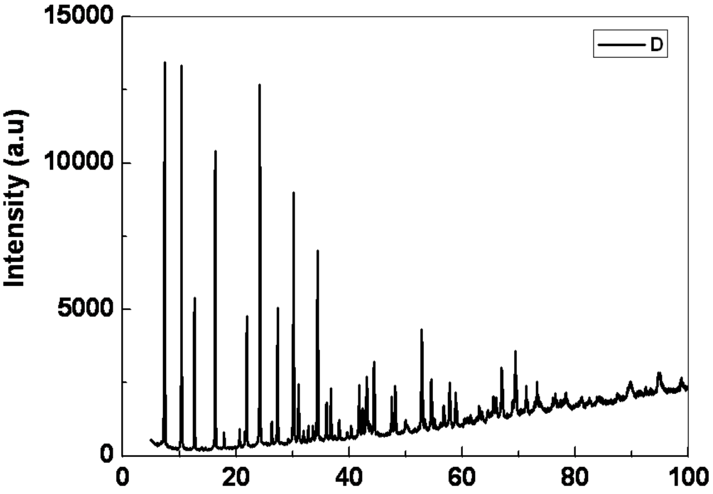
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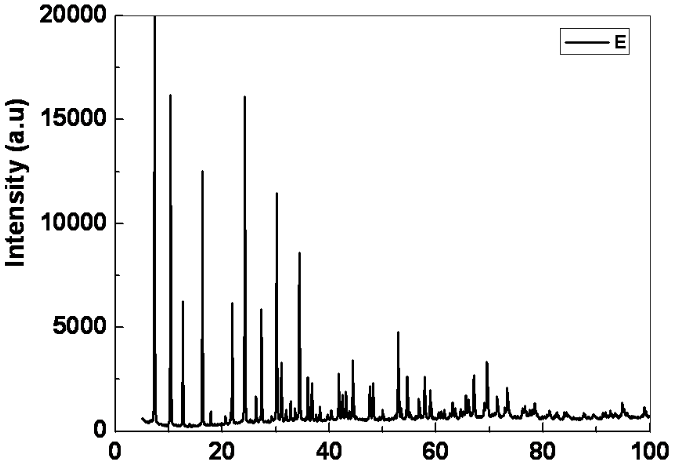
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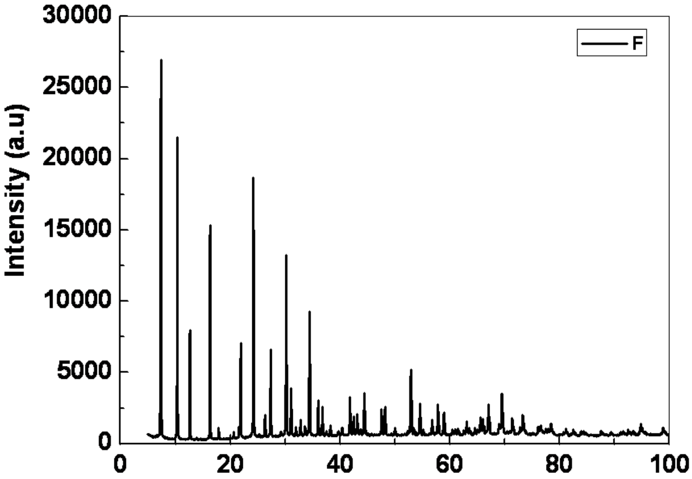
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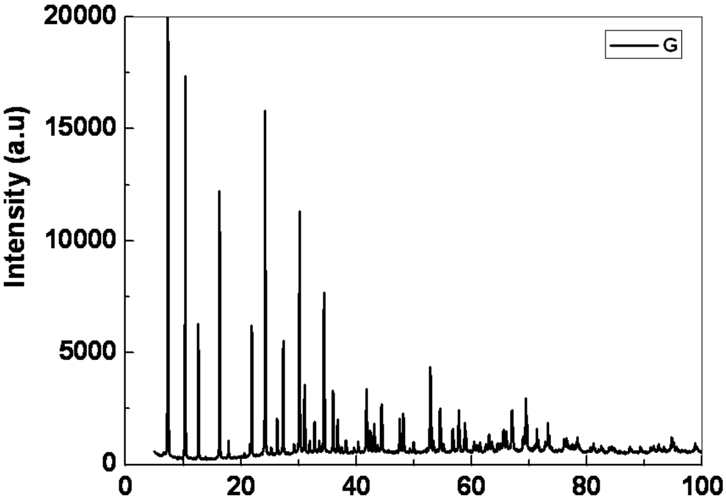
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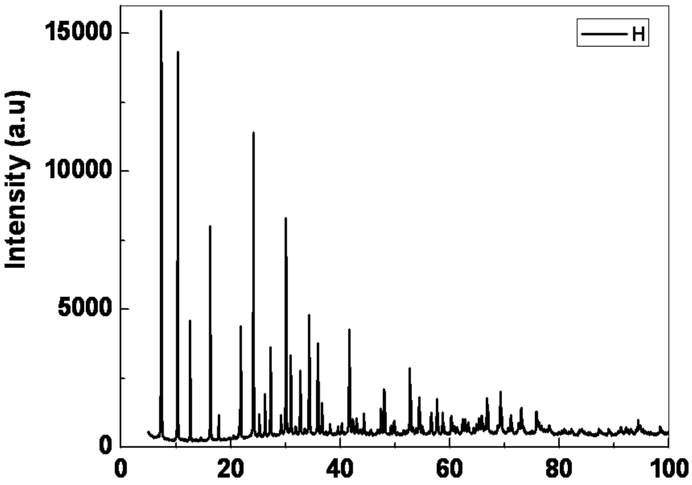

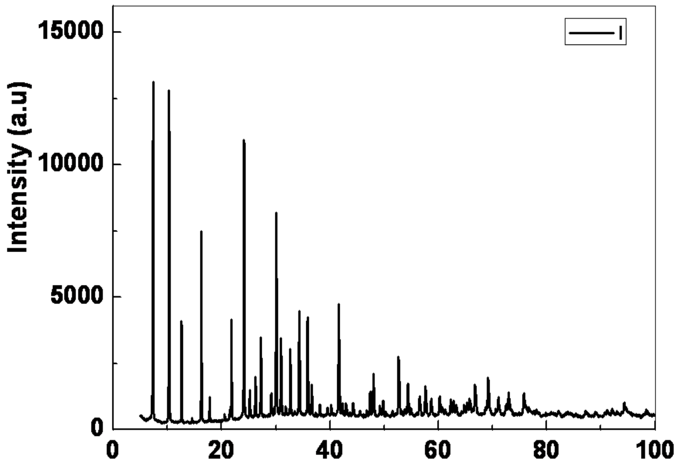

Figure S9. The XRD of the zeolite NaKA with different K^+ content. (A) 0 atom%. (B) 8.4 atom%. (C) 17.4 atom%. (D) 28.3 atom%. (E) 39.4 atom%. (F) 46.9 atom%. (G) 58.5 atom%. (H) 88.1 atom%. (I) 97.0atom%.

Table S1 The K^+ content measured from EDX and Rietveld refinements results of the zeolite NaKA

K^+ atom% (EDX)	K^+ atom% (Rietveld refinement)	Occupancy of Na^+			Rp
		occ1	occ2	occ3	
0.00	**0.0**	**1.000**	**0.25**	**0.083**	**8.2**
8.4	**10.4**	**1.000**	**0.228**	**0.001**	**7.9**
17.4	**17.5**	**1.000**	**0.152**	**0.006**	**7.4**
28.3	**28.4**	**0.992**	**0.046**	**0.009**	**5.7**

39.4	**39.4**	**0.878**	**0.015**	**0.006**	**6.8**
46.9	**46.9**	**0.792**	**0.002**	**0.001**	**6.9**
58.5	**57.7**	**0.634**	**0.000**	**0.000**	**7.2**
88.1	**84.7**	**0.230**	**0.000**	**0.000**	**7.9**
97.0	**92.9**	**0.107**	**0.000**	**0.000**	**8.2**

2.5 Computational results

2.5.1 Appendix A: Computational details

Cation Loading:

```
---- Locate calculation parameters ----

Loading steps                   :  100000
Production steps                :  1000000
Heating cycles                  :  15


---- Energy parameters ----

Forcefield                      : cvff
Electrostatic terms:
  Summation method              : Ewald
  Accuracy                      : 0.0001 kcal/mol
  Buffer width                  : 0.5 A

van der Waals terms:
  Summation method              : Atom based
  Truncation method             : Cubic spline
  Cutoff distance               : 15.5 A
  Spline width                  : 1 A
  Buffer width                  : 0.5 A
```

Adsorption Isotherms:

```
---- Fixed pressure calculation parameters ----

Equilibration steps             :  1000000
Production steps                :  10000000


---- Energy parameters ----

Forcefield                      : COMPASS26
Electrostatic terms:
  Summation method              : Ewald
  Accuracy                      : 0.001 kcal/mol
  Buffer width                  : 0.5 A

van der Waals terms:
  Summation method              : Atom based
  Truncation method             : Cubic spline
  Cutoff distance               : 12.5 A
  Spline width                  : 1 A
  Buffer width                  : 0.5 A

Sample interval                 : 50 steps

---- Metropolis Monte Carlo method parameters ----

 |                | Ratio       | Maximum     |
 |                |             | amplitude   |
```

```
|_______________________________________________
| Exchange          |        2.000 |             |
| Rotate            |        1.000 |  5 deg      |
| Translate         |        1.000 |  1 A        |
| Regrowth          |        0.100 |             |
```

2.5.2 Appendix B: Results in detail

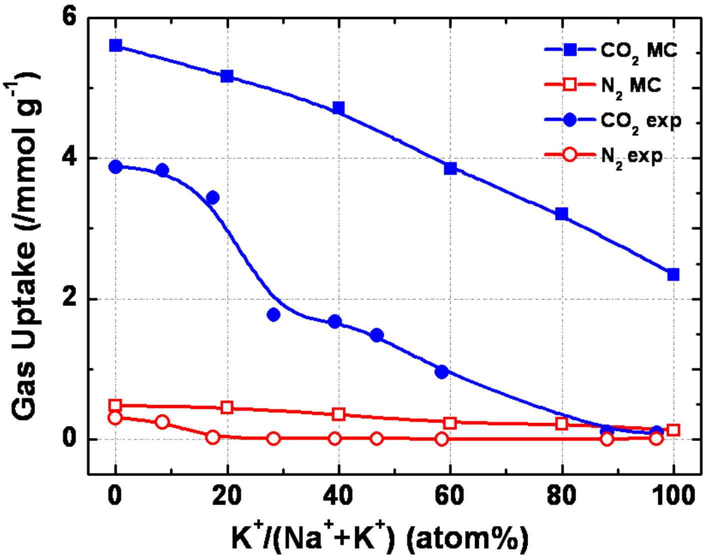

Figure S10. A Comparison of the computed uptake as a function of the K$^+$ content of the zeolite with that measured experimentally indicates that the thermodynamic effects are not sufficient to describe the CO_2/N_2 separation of the system.

Cation Loading

Na content [%]	Electrostatic Energy [kcal/mol]	Van der Waals Energy[kcal/mol]	Total energy [kcal/mol]
100	-6726.454	-222.837	-6949.291
80	-6243.650	-556.721	-6800.371
60	-5845.014	-808.511	-6653.526
40	-5370.651	-1126.593	-6497.244
20	-4816.364	-1397.093	-6213.457
0	-4185.398	-1760.562	-5945.960

100% Na

CO2 Fugacity [*kPa*]	CO2 Average Loading [*molecules/UC*]	Isosteric Heat (298*K*) [*kcal/mol*]	Average total energy [*kcal/mol*]
0.000	0	0.000	0.000

10.000	84.037	16.282	-1272.416
20.000	85.960	16.277	-1299.056
30.000	88.023	16.181	-1326.185
40.000	88.694	16.141	-1331.494
50.000	88.498	16.211	-1332.120
60.000	88.634	16.203	-1334.972
70.000	89.085	16.198	-1341.237
80.000	89.221	16.178	-1340.203
90.000	88.883	16.188	-1337.242
100.000	88.751	16.174	-1333.365

N2 Fugacity [*kPa*]	**N2 Average Loading [*molecules/UC*]**	**Average total energy [*kcal/mol*]**	**Isosteric Heat (298.15*K*) [*kcal/mol*]**
0.000	0	0.000	0.000
10.000	1.272	-5.118	4.600
20.000	2.282	-8.976	4.512
30.000	3.142	-12.140	4.445
40.000	3.897	-14.837	4.391
50.000	4.585	-17.206	4.338
60.000	5.176	-19.151	4.288
70.000	5.765	-21.113	4.251
80.000	6.275	-22.701	4.210
90.000	6.780	-24.345	4.184
100.000	7.289	-25.935	4.154

80% Na

CO2 Fugacity [*kPa*]	**CO2 Average Loading [*molecules/UC*]**	**Average total energy [*kcal/mol*]**	**Isosteric Heat (298.15*K*) [*kcal/mol*]**
0.000	0	0.000	0.000
10.000	78.738	16.576	-1224.858
20.000	79.425	16.565	-1234.417
30.000	81.306	16.474	-1259.272
40.000	80.322	16.584	-1250.286
50.000	81.695	16.381	-1260.641
60.000	80.736	16.530	-1253.005
70.000	83.627	16.297	-1280.795
80.000	84.512	16.223	-1288.021
90.000	83.148	16.359	-1278.455
100.000	82.920	16.396	-1277.468

N2 Fugacity [*kPa*]	**N2 Average Loading [*molecules/UC*]**	**Average total energy [*kcal/mol*]**	**Isosteric Heat (298.15*K*) [*kcal/mol*]**
0.000	0	0.000	0.000
10.000	1.199	4.614	-4.842
20.000	2.157	4.531	-8.528
30.000	3.000	4.481	-11.700
40.000	3.723	4.426	-14.308
50.000	4.369	4.373	-16.549
60.000	4.947	4.328	-18.508
70.000	5.482	4.293	-20.311
80.000	6.008	4.265	-22.080
90.000	6.526	4.235	-23.773
100.000	6.993	4.212	-25.301

60% Na

CO2 Fugacity	**CO2 Average Loading**	**Average total energy**	**Isosteric Heat (298.15*K*)**

[*kPa*]	**[*molecules/UC*]**	**[*kcal/mol*]**	**[*kcal/mol*]**
0.000	0	0.000	0.000
10.000	70.928	16.520	-1092.878
20.000	73.009	16.493	-1119.989
30.000	74.306	16.424	-1133.724
40.000	74.997	16.364	-1142.511
50.000	75.943	16.264	-1152.108
60.000	75.657	16.275	-1147.664
70.000	78.388	16.114	-1178.164
80.000	77.499	16.113	-1166.988
90.000	77.307	16.174	-1165.973
100.000	76.809	16.156	-1159.242

N2 Fugacity [*kPa*]	**N2 Average Loading [*molecules/UC*]**	**Average total energy [*kcal/mol*]**	**Isosteric Heat (298.15*K*) [*kcal/mol*]**
0.000	0	0.000	0.000
10.000	0.887	4.357	-5.983
20.000	1.621	4.269	-3.351
30.000	2.285	4.218	4.218
40.000	2.856	4.158	-10.215
50.000	3.381	4.116	-11.937
60.000	3.888	4.078	-13.577
70.000	4.361	4.048	-15.085
80.000	4.771	4.019	-16.356
90.000	5.211	3.994	-17.727
100.000	5.638	3.976	-19.064

40% Na

CO2 Fugacity [*kPa*]	**CO2 Average Loading [*molecules/UC*]**	**Average total energy [*kcal/mol*]**	**Isosteric Heat (298.15*K*) [*kcal/mol*]**
0.000	0	0.000	0.000
10.000	57.930	15.779	-853.937
20.000	60.035	15.681	-875.939
30.000	62.069	15.562	-898.442
40.000	61.224	15.644	-891.734
50.000	61.755	15.588	-896.225
60.000	65.224	15.322	-930.382
70.000	65.423	15.211	-930.298
80.000	64.994	15.261	-923.500
90.000	63.714	15.401	-913.551
100.000	63.671		

N2 Fugacity [*kPa*]	**N2 Average Loading [*molecules/UC*]**	**Average total energy [*kcal/mol*]**	**Isosteric Heat (298.15*K*) [*kcal/mol*]**
0.000	0.000	0.000	0.000
10.000	0.425	3.517	-1.251
20.000	0.840	3.524	-2.474
30.000	1.231	3.523	-3.624
40.000	1.627	3.530	-4.800
50.000	2.001	3.538	-5.917
60.000	2.364	3.548	-7.007
70.000	2.714	3.547	-8.038
80.000	3.069	3.550	-9.098
90.000	3.368	3.546	-9.963
100.000	3.704	3.558	-10.995

20% Na

CO2 Fugacity [*kPa*]	**CO2 Average Loading** [*molecules/UC*]	**Average total energy** [*kcal/mol*]	**Isosteric Heat (298.15*K*)** [*kcal/mol*]
0.000	0.000	0.000	0.000
10.000	49.099	14.893	-687.134
20.000	51.155	14.831	-710.974
30.000	51.296	14.825	-711.610
40.000	52.084	14.761	-719.306
50.000	52.788	14.655	-725.114
60.000	54.455	14.528	-741.107
70.000	53.587	14.619	-734.302
80.000	53.609	14.609	-733.383
90.000	55.186	14.358	-742.803
100.000	54.897	14.446	-743.092

N2 Fugacity [*kPa*]	**N2 Average Loading** [*molecules/UC*]	**Average total energy** [*kcal/mol*]	**Isosteric Heat (298.15*K*)** [*kcal/mol*]
0.000	0.000	0.000	0.000
10.000	0.492	4.123	-1.744
20.000	0.936	4.082	-3.280
30.000	1.316	4.024	-4.531
40.000	1.700	4.004	-5.819
50.000	2.067	3.977	-7.020
60.000	2.393	3.956	-8.073
70.000	2.726	3.944	-9.159
80.000	2.991	3.914	-9.956
90.000	3.306	3.906	-10.976
100.000	3.579	3.887	-11.809

0% Na

CO2 Fugacity [*kPa*]	**CO2 Average Loading** [*molecules/UC*]	**Average total energy** [*kcal/mol*]	**Isosteric Heat (298.15*K*)** [*kcal/mol*]
0.000	0.000	0.000	0.000
10.000	35.398	12.747	-420.132
20.000	37.214	12.605	-436.510
30.000	38.952	12.563	-455.719
40.000	38.910	12.555	-454.521
50.000	38.788	12.530	-452.112
60.000	39.643	12.500	-460.684
70.000	40.542	12.460	-469.919
80.000	40.389	12.406	-465.805
90.000	40.734	12.426	-470.596
100.000	40.802	12.429	-471.081

N2 Fugacity [*kPa*]	**N2 Average Loading** [*molecules/UC*]	**Average total energy** [*kcal/mol*]	**Isosteric Heat (298.15*K*)** [*kcal/mol*]
0.000	0.000	0.000	0.000
10.000	0.259	3.424	-0.739
20.000	0.506	3.424	-1.440
30.000	0.749	3.423	-2.132
40.000	0.982	3.426	-2.795
50.000	1.204	3.424	-3.425
60.000	1.418	3.428	-4.039
70.000	1.629	3.426	-4.636
80.000	1.831	3.427	-5.208
90.000	2.028	3.427	-5.768
100.000	2.207	3.426	-6.274

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