Electronic Supplementary Material (ESI) for Chemical Communications

SUPPLEMENTARY INFORMATION

Zeolite Rho: a highly selective adsorbent for CO2/CH4 separation induced by a structural phase modification

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Synthesis details of zeolite Rho.

The zeolite Rho employed in this work was synthesized following a similar procedure than that reported by Chatelain [Ref. 30 in main text]. The exact synthesis procedure was as follows:

0.94 g of crown ether 18-C-6, 0.705 g of CsOH and 0.34 g of NaOH were dissolved in 6.04 g of distilled water. Then, 1.32 g of sodium aluminate (54 wt% Al_2O_3, 39 wt% Na_2O) were added to the above solution and the resulting mixture was stirred until a clear solution was formed. Subsequently, 10.5 g of colloidal silica (Ludox AS-40) were added and the resulting reaction mixture was stirred at room temperature for 24 hours. The final gel composition was:

$$1.8\ Na_2O : 0.3\ Cs_2O : Al_2O_3 : 10\ SiO_2 : 0.5\ R : 100\ H_2O$$

where R is the crown ether 18-C-6.

All chemicals were purchased from Sigma-Aldrich Co except sodium aluminate that was supplied by Carlo Erba.

Zeolite crystallization was carried out in Teflon-lined stainless steel autoclaves at 398 K under rotation for 3 days. The zeolite Rho recovered after filtration, washing with water and drying at 373 K, was calcined at 773 K for 3 hours in order to remove the occluded organic material.

Characterization of zeolite Rho used in this study

Figure S1. X-Ray diffraction patterns of the zeolite Rho in its as-prepared and calcined forms. These X-Ray diffraction patterns were collected upon exposing the samples to ambient conditions. Routinary X-Ray Diffraction patterns (used only for phase identification) were measured in a Cubix'Pro diffractometer form Panalytical equipped with an X'Celerator detector and automatic divergence and reception slits (constant irradiated area of 3 mm).

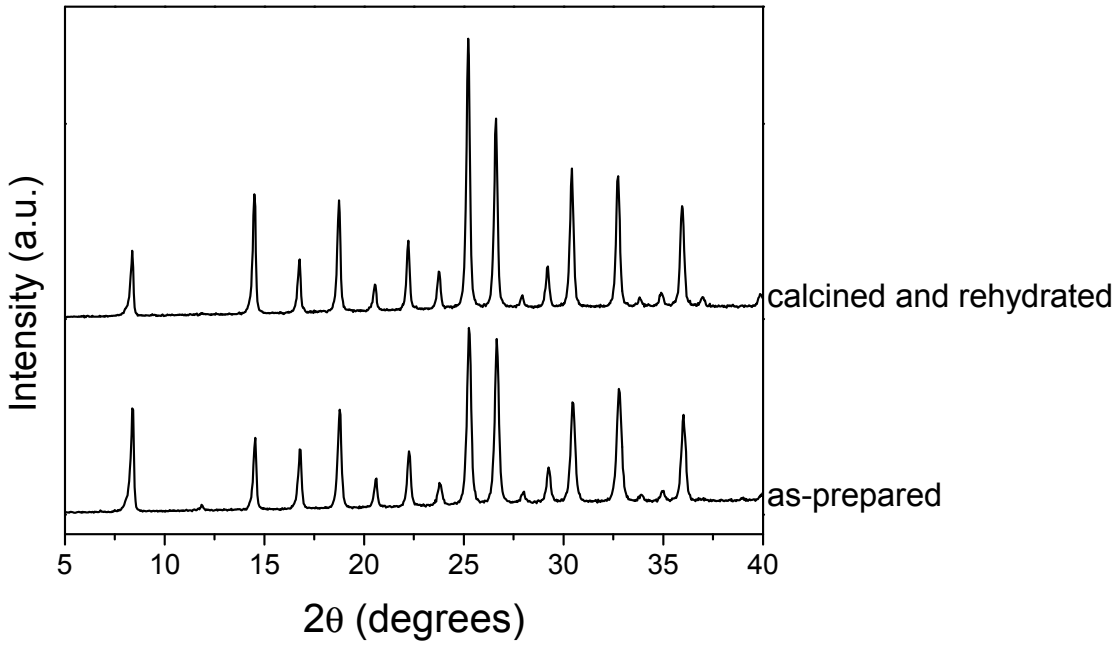


Table S1. Chemical composition of the zeolite Rho used in this work.

Zeolite	Si/Al	Na/Al	Cs/Al	Na/(Si+Al)	Cs/(Si+Al)
Rho	4.5	0.56	0.33	0.102	0.060

Chemical analysis was performed by ICP on a Varian 715ES spectrometer, after dissolving the sample in an 1:1 HF/HNO_3 solution (approx. 5 wt% acid solution in distilled water, MilliQ® quality). 100 mg of sample: 200 ml of acid solution).

Figure S2. Scanning electron microscopy images of zeolite Rho obtained on a JEOL JSM 5410 microscope.

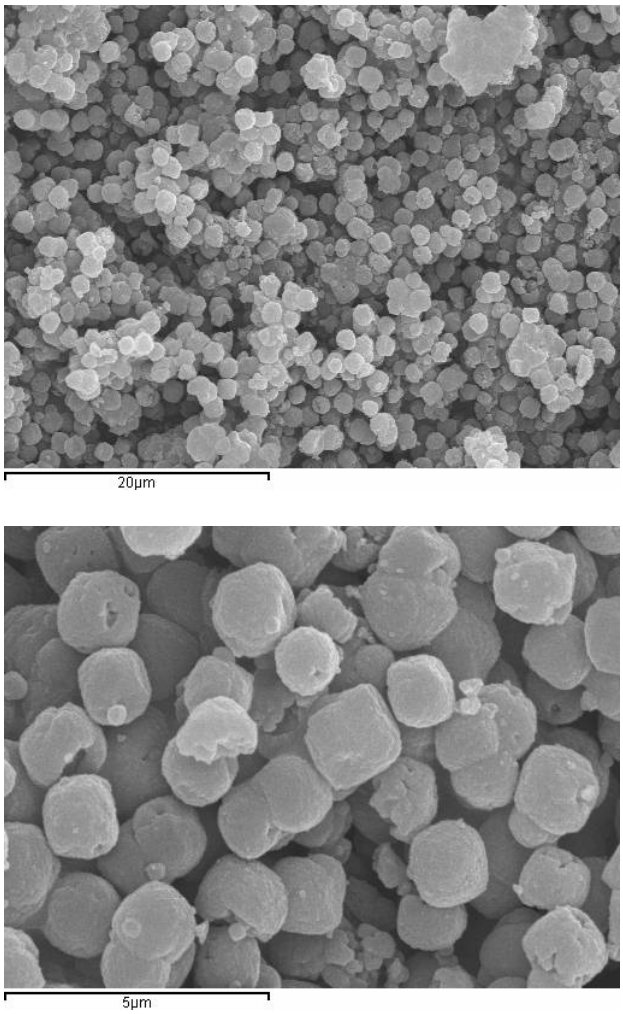
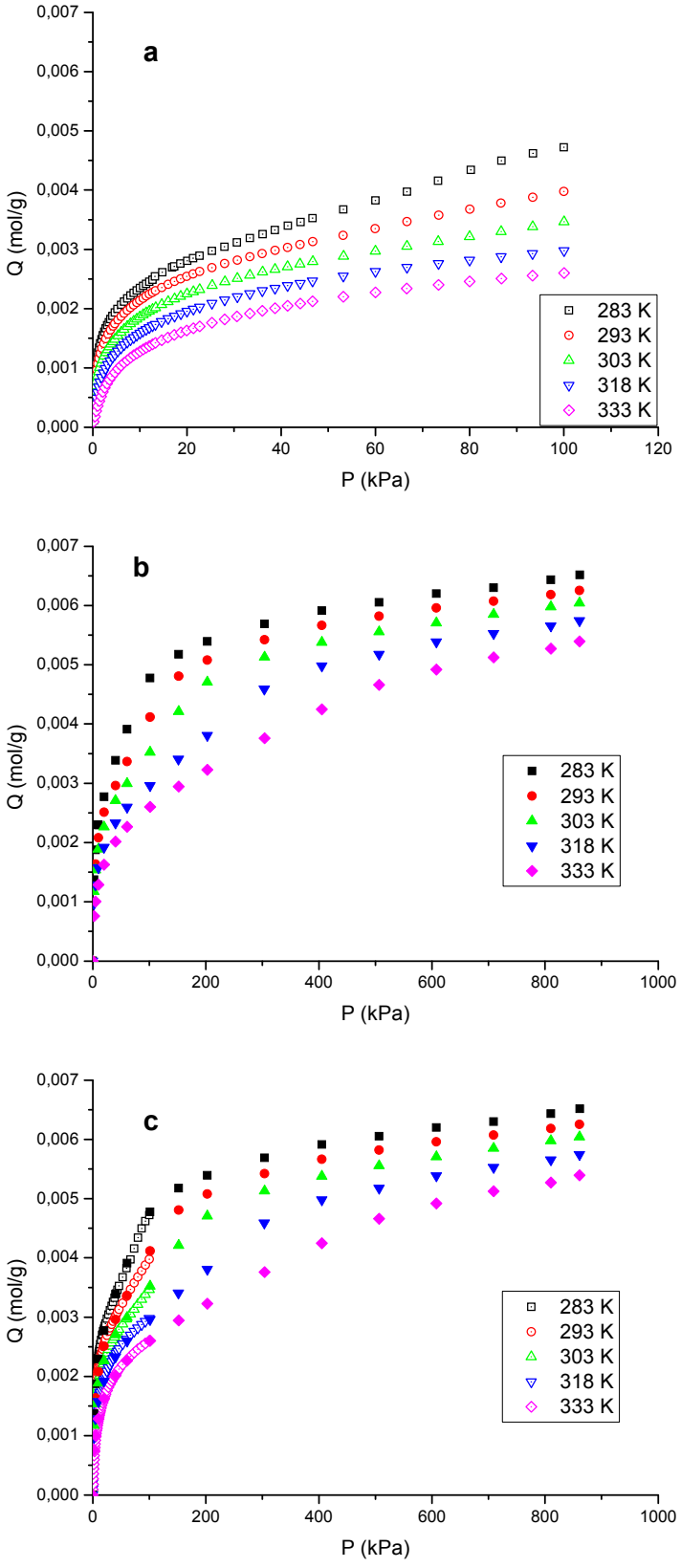


Figure S3. Low (a) and high (b) pressure CO_2 adsorption isotherms measured at different temperatures on zeolite Rho. (c) Combination of both sets of isotherms.



High resolution low pressure isotherms (up to 100 kPa) were measured at different temperatures in a Micromeritics ASAP 2010 volumetric instrument in order to get more reliable data in the low pressure range. Temperature was controlled by means of a thermostatic Julabo F32-HL bath.

High Pressure isotherms (up to 850 kPa) were measured at different temperatures on an IGA-3 gravimetric instrument from Hiden Isochema Ltd equipped with a thermostatic bath FP50-HE from Julabo.

Figure S4. Isosteric heat of adsorption (q_{st}) as a function of CO_2 loading in zeolite Rho.

The isosteric heat of CO_2 adsorption (q_{st}) was calculated from the corresponding set of combined high and low pressure isotherms measured at different temperatures showed in Figure S3c, and applying the Clausius-Clapeyron equation.

$$q_{st} = R \cdot T^2 \cdot \left[\frac{\partial(\ln P)}{\partial T}\right]_{Q_i} \equiv R \cdot \left[-\frac{\partial(\ln P)}{\partial(1/T)}\right]_{Q_i}$$

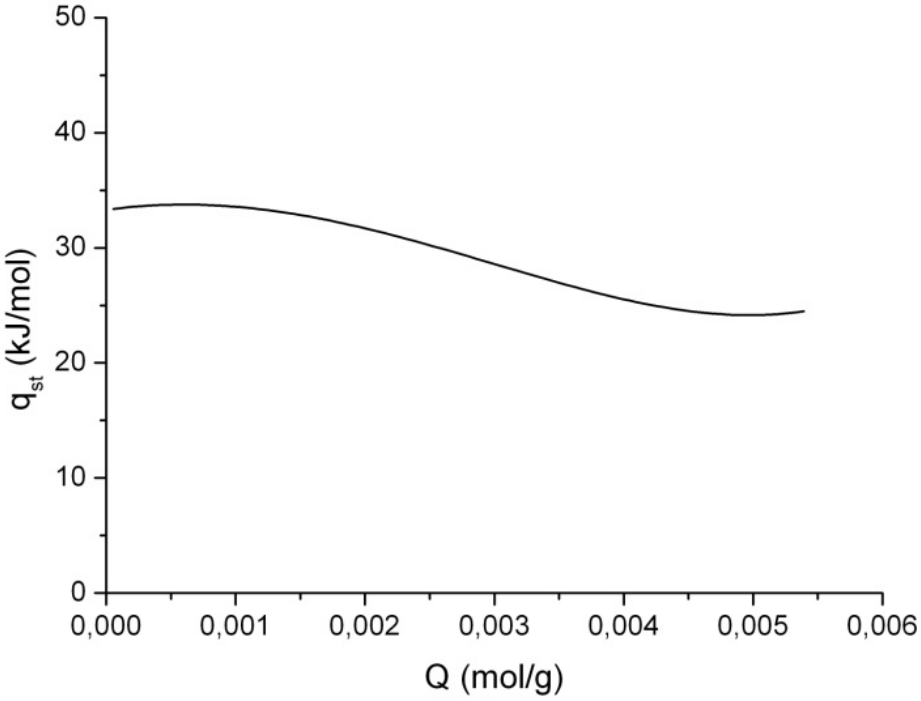
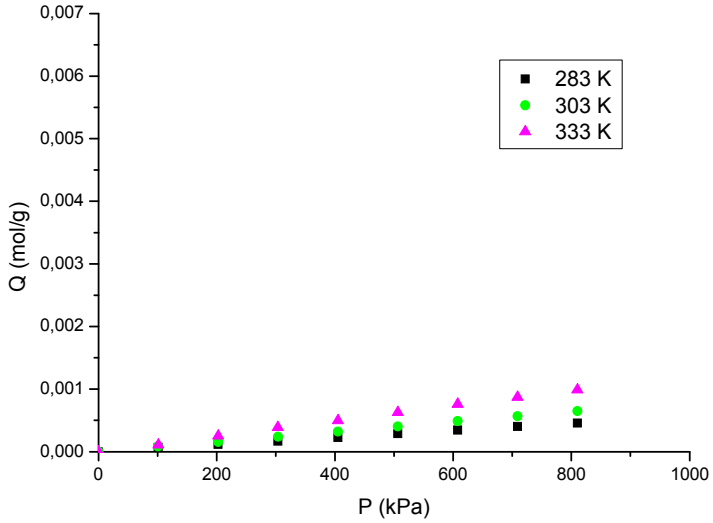
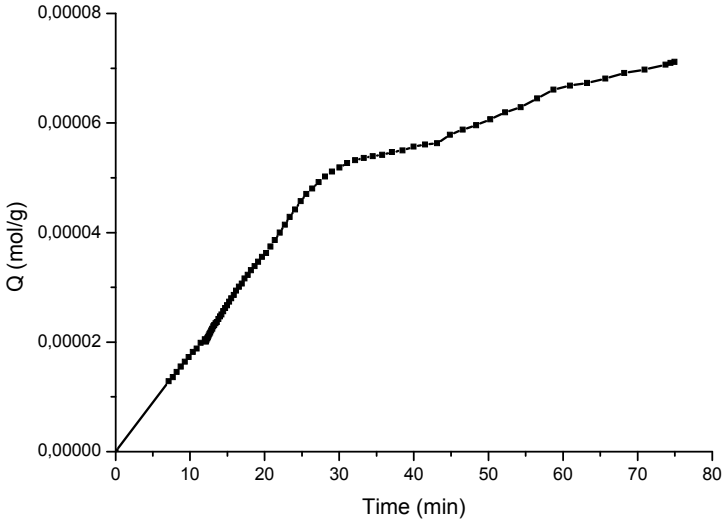


Figure S5. High pressure CH_4 adsorption isotherms measured at different temperatures on zeolite Rho.



Note that CH_4 adsorption capacity of zeolite Rho does not increase as the temperature decreases as expected. This is because equilibrium is not reached, as it is demonstrated in the kinetics shown in Figure S6 and, therefore, the calculation of thermodynamic parameters is meaningless.

Figure S6. Kinetics of the CH_4 adsorption measured at 303 K and 100 kPa on zeolite Rho.



X-ray diffraction measurements and Rietveld Refinements

X-ray powder diffraction (XRPD) data were collected using a Panalytical X'Pert PRO diffractometer with Bragg-Brentano geometry, using CuKα radiation (λ1=1.5406, λ2=1.5441Å, I2/I1=0.5; divergence slit: fixed = 1/16º; goniometer arm length: 240mm; detector: Panalytical X'Celerator; tube voltage and intensity: 45 kV, 40 mA; scan range: 3.0º to 75.0º (2θ), scan step size: 0.017º (2θ); counting time: 2440s/step).

In-situ dehydration at 500ºC under flow of N_2 and *in-situ* high pressure measurements under Nitrogen, CO_2 and CH_4 at 30ºC were performed in an Anton Parr XRK-900 reaction chamber attached to the diffractometer.

Profile fitting for determination of the cell parameters, as well as Rietveld refinement of the complete structures were performed using the program FullProf (J. Rodriguez-Carvajal, *Commission on Powder Diffraction (IUCr) Newsletter* **26** (2001) 12-19).

Crystallographic data

Dehydrated Rho under a dry N_2 atmosphere

Chemical composition: $|H_{0.9}Na_{4.9}Cs_{2.9}|\ [Si_{39.3}Al_{8.7}O_{96}]$
Refined composition: $|Na_{6.8}Cs_{3.2}|\ [Si_{48}O_{96}]$
Unit cell:
Space group I-43*m* (No. 217)
a = 14.6199(5) Å
b = 14.6199(5) Å
c = 14.6199(5) Å
V= 3124.86(19) $Å^3$
Background: visually estimated
Profile function: pseudo-Voigh
Peak range (number of FWHM) 25
Number of contributing reflections: 290
Number of geometric restraints: 4 (T-O)
dist (T-O): 1.63(1) Å
Refined 2θ range = 4.0-60.0º
Number of profile parameters: [a] 11
Number of structural parameters: 21
R_{exp} = 0.067
R_{wp} = 0.106
R_F = 0.066
R_B = 0.069
[a] Including unit cell parameters and zero-shift

Table S2: Atomic coordinates, thermal parameters and occupancy after Rietveld refinement of dehydrated zeolite Rho

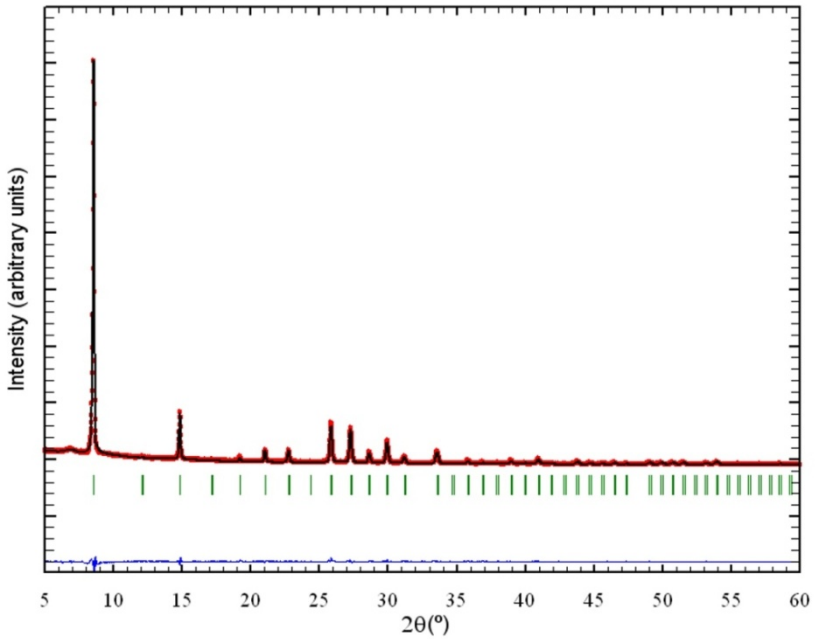
Atom	x	y	z	Uiso	Occupancy	Multiplicity & Wyckoff
Si1	0.2683(3)	0.1191(3)	0.4184(3)	0.047(2)	1	48h
O1	0.2119(6)	0.0287(4)	0.3859(5)	0.038(2) [a]	1	48h
O2	0.2093(6)	0.2093(5)	0.3945(10)	0.038(2) [a]	1	24g
O3	0.3645(5)	0.1209(8)	0.3645(5)	0.038(2) [a]	1	24g
Na1	0.3029(16)	0.3029(16)	0.3029(16)	0.04(3)	0.29(4)	8c
Na2	0.022(3)	0.022(3)	0.422(4)	0.08(2)	0.32(4)	24g
Cs1	0	0	½	0.065(9)	0.53(3)	6b

Space group *I*-43*m* (No. 217), a = 14.6199(5) Å, b = 14.6199(5) Å, c = 14.6199(5) Å, V= 3124.86(19) Å^3

Numbers in parentheses are the esd's in the units of the least significant digit given. Values without an esd were not refined. Coordinates given as 0 or 1/2 are fixed by symmetry and therefore have not been refined.

[a] Parameters with the same index are constrained to be equal.

Figure S7: Observed (red) and calculated (black) XRD patterns of dehydrated zeolite RHO, as well as difference profile (blue). The green short tick marks below the pattern give the positions of the Bragg reflections.



Rho + CH_4 (500 kPa)

Chemical composition: $|H_{0.9}Na_{4.9}Cs_{2.9}|$ $[Si_{39.3}Al_{8.7}O_{96}]$
Refined composition: $|Na_{7.1}Cs_{3.2}|$ $[Si_{48}O_{96}]$
Unit cell:
Space group I-43*m* (No. 217)
a = 14.6223(5) Å
b = 14.6223 (5) Å
c = 14.6223 (5) Å
V= 3126.43(18) $Å^3$
Background: visually estimated
Profile function: pseudo-Voigh
Peak range (number of FWHM) 25
Number of contributing reflections: 280
Number of geometric restraints: 4 (T-O)
dist (T-O): 1.63(1) Å
Refined 2θ range = 4.0-60.0º
Number of profile parameters: [a] 11
Number of structural parameters: 21
R_{exp} = 0.084
R_{wp} = 0.109
R_F = 0.059
R_B = 0.053
[a] Including unit cell parameters and zero-shift.

Table S3. Atomic coordinates, thermal parameters and occupancy after Rietveld refinement of zeolite Rho with CH_4 at 500 kPa

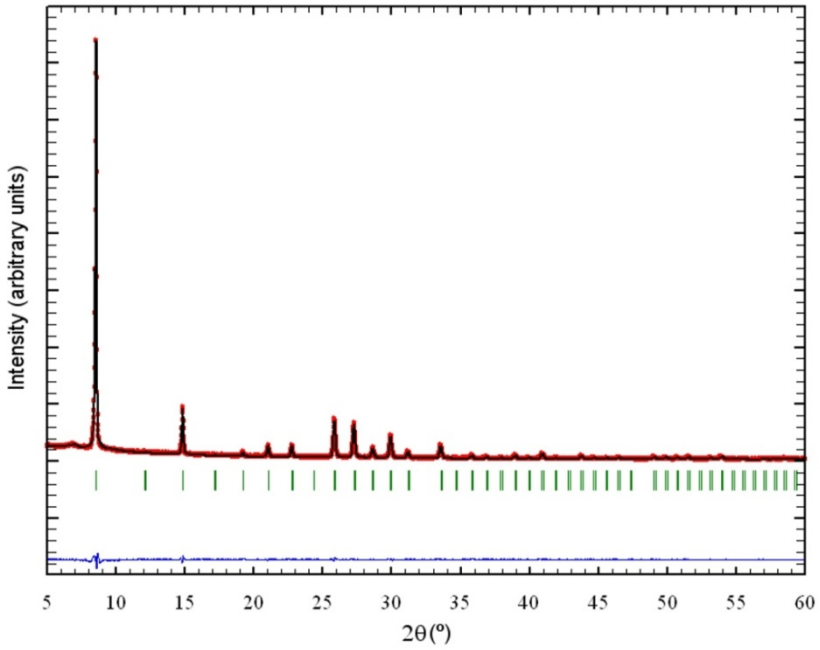
Atom	x	y	z	Uiso	Occupancy	Multiplicity & Wyckoff
Si1	0.2674(3)	0.1191(3)	0.4184(3)	0.049(2)	1	48h
O1	0.2114(6)	0.0294(4)	0.3858(5)	0.045(2) [a]	1	48h
O2	0.2101(6)	0.2101(6)	0.3926(10)	0.045(2) [a]	1	24g
O3	0.3648(5)	0.1205(8)	0.3648(5)	0.045(2) [a]	1	24g
Na1	0.2989(13)	0.2989(13)	0.2989(13)	0.05(3)	0.28(4)	8c
Na2	0.0226(19)	0.0226(19)	0.422(4)	0.09(2)	0.35(3)	24g
Cs1	0	0	½	0.051(8)	0.49(2)	6b

Space group *I*-43*m* (No. 217), a = 14.6223 (5) Å, b = 14.6223 (5) Å, c = 14.6223 (5) Å, V= 3126.43(18) $Å^3$

Numbers in parentheses are the esd's in the units of the least significant digit given. Values without an esd were not refined. Coordinates given as 0 or 1/2 are fixed by symmetry and therefore have not been refined.

[a] Parameters with the same index are constrained to be equal.

Figure S8: Observed (red) and calculated (black) XRD patterns of dehydrated zeolite RHO under CH_4 at 500 kPa, as well as difference profile (blue). The green short tick marks below the pattern give the positions of the Bragg reflections.



Rho + CO_2 (500 kPa)

Chemical composition: $|H_{0.9}Na_{4.9}Cs_{2.9}|\ [Si_{39.3}Al_{8.7}O_{96}].20CO_2$
Refined composition: [a] $|Na_{7.3}Cs_{3.2}|\ [Si_{48}O_{96}].18CO_2$
Unit cell:
Space group I*m*-3*m* (No. 229)
a = 14.9673(7) Å
b = 14.9673(7)Å
c = 14.9673(7)Å
V= 3353.0(3) $Å^3$
Background: visually estimated
Profile function: pseudo-Voigh
Peak range (number of FWHM) 25
Number of contributing reflections: 300
Number of geometric restraints: 4 (T-O)
dist (T-O): 1.63(1) Å
Refined 2θ range = 4.0-60.0º
Number of profile parameters: [b] 11
Number of structural parameters: 22
R_{exp} = 0.094
R_{wp} = 0.139
R_F = 0.109
R_B = 0.084

[a] Due to the large mobility of the adsorbed CO2 molecules at room temperature, they have been refined as single O atoms with large Uiso and the electrons corresponding of the whole molecule.

[b] Including unit cell parameters and zero-shift.

Table S4. Atomic coordinates, thermal parameters and occupancy after Rietveld refinement of zeolite Rho with CO_2 at 500 kPa

Atom	x	y	z	Uiso	Occupancy	Multiplicity & Wyckoff
Si1	¼	0.10402(16)	0.39598(16)	0.048(2)	1	48j
O1	0.2242(5)	0	0.3880(4)	0.037(2)[a]	1	48j
O2	0.1645(3)	0.1645(3)	0.3747(5)	0.037(2)[a]	1	48k
Na1	0.3145(7)	0.3145(7)	0.3145(7)	0.03(4)	0.453(7)	16f
Cs1	0	0	0.3514(15)	0.04(5)	0.262(8)	12e
$CO_2$1	0.0411(14)	0.1446(6)	0.1446(6)	0.19	0.503(5) [b]	48k
$CO_2$2	0.040(2)	0.040(2)	0.307(2)	0.19	0.351(14) [b]	48k
$CO_2$3	0	0	0.422(4)	0.19	0.75(7) [b]	12e

Space group I*m*-3*m* (No. 229), a = 14.9673(7) Å, b = 14.9673(7)Å, c = 14.9673(7)Å, V= 3353.0(3) $Å^3$
Numbers in parentheses are the esd's in the units of the least significant digit given. Values without an esd were not refined. Coordinates given as 0 or 1/4 are fixed by symmetry and therefore have not been refined.

Due to the large mobility of the adsorbed CO2 molecules at room temperature, they have been refined as single O atoms with large Uiso and the electrons corresponding of the whole molecule.

[a] Parameters with the same index are constrained to be equal.

[b] Occupancy of CO_2 has been refined as O atoms; then, it corresponds to an occupancy of 0.183, 0.128 and 0.273 CO_2, respectively.

Figure S9: Observed (red) and calculated (black) XRD patterns of dehydrated zeolite RHO under CO_2 at 500 kPa, as well as difference profile (blue). The green short tick marks below the pattern give the positions of the Bragg reflections.

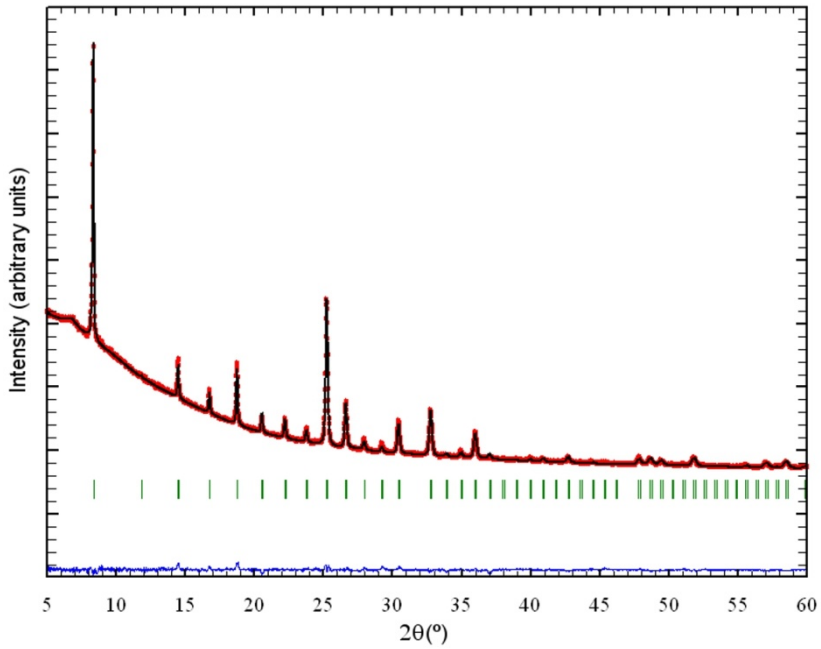
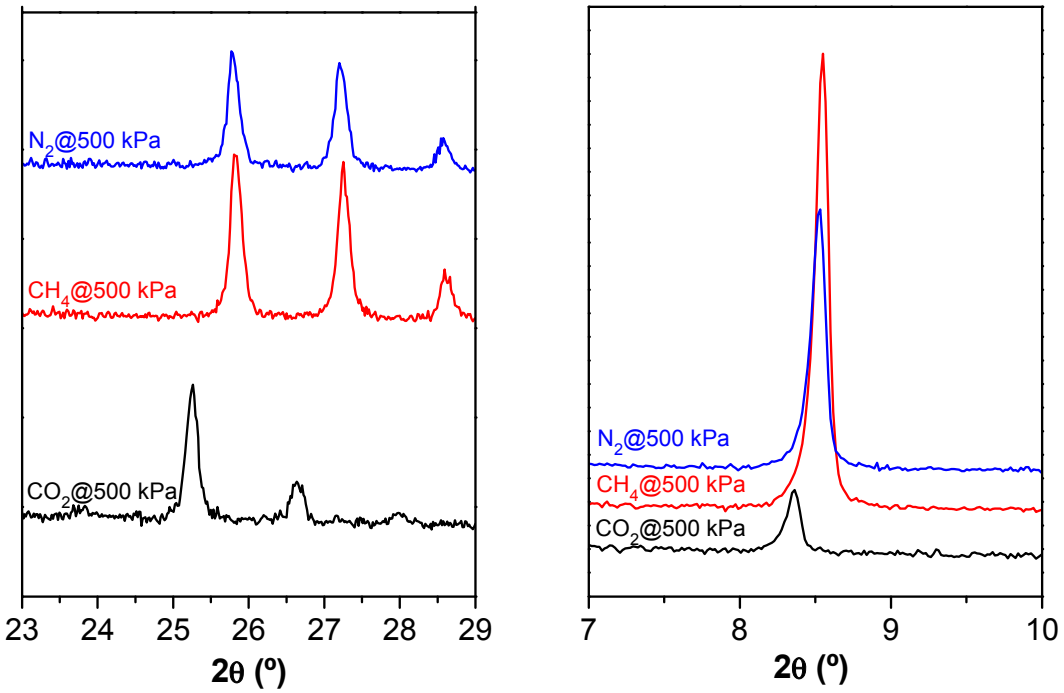


Figure S10. Selected areas of the X-Ray diffraction patterns of Zeolite Rho submitted to 500 kPa of pressure of CO_2, CH_4 and N_2.



The left figure evidences that no phase change occurs by applying pressure using CH_4 and N_2. Right figure shows the decrease of the low angle diffraction peak of zeolite Rho in presence of CO_2 (indicating the pore filling of its void space), on the contrary there is very little modification of its intensity when CH_4 is employed as pressure medium, evidencing that CH_4 does not diffuse inside of Zeolite Rho. Finally, N_2 shows an intermediate behaviour, indicating that N_2 (probably due to the highest saturation pressure of N_2) does not completely fill up the empty space of zeolite Rho.

Table S5. Comparison of bibliographic CO_2/CH_4 molar selectivities on different zeolites at approx. 100 kPa and at ambient temperature.

Adsorbent	P (kPa)	T (K)	α Selectivity (mol CO_2/mol CH_4)	Ref.
RHO	**100**	**303**	**75.1**[1]	**This work**
5A (LTA)	107	298	5.6	[1]
LTA (Si/Al=∞)[2]	100	303	4.2	[2]
LTA (Si/Al=5)[3]	100	303	8.8	[2]
LTA (Si/Al=3.5)[4]	100	303	10.9	[2]
LTA (Si/Al=2)[5]	100	303	8.5	[2]
LTA (Si/Al=1)[6]	100	303	6.6	[2]
SAPO-34 (CHA)	100	298	9.2	[3]
SAPO-34 (CHA)	100	297	5.8	[4]
Pure silica DD3R	100	298	3.2	[5,6]
Silicalite (MFI)	100	304-313	2.4-2.7	[7,8]
Na-ZSM-5 (MFI, Si/Al=30)	70	297	2.8	[9]
13X (FAU)	100	298	7.6-11.6	[9,10]
Na-MOR	500	293	1.9	[11]
H-MOR	500	293	1.8	[11]
H-Beta (BEA)	100	303	4.7	[12]
Na-Beta (BEA)	100	303	4.2	[12]

[1] Selectivity was calculated from volumetric high resolution isotherms.
[2] no cations were present in this zeolite.
[3] H^+/Na^+ ratio = 4.0
[4] H^+/Na^+ ratio = 1.6
[5] H^+/Na^+ ratio = 0.3
[6] H^+/Na^+ ratio = 0

References

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