Thermodynamic Analysis of Framework Deformation in Na,Cs-RHO Zeolite upon CO_2 Adsorption

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Figure & Table captions:

Figure S1. Free energy, enthalpy and entropy representations of CO_2 adsorption / desorption in Na,Cs-RHO in the temperature range 293-333 K. The dashed and straight curves correspond to the fittings using for the adsorption and desorption branches, respectively. The values for $\Delta F°$, $\Delta H°$ and $\Delta(TS°)$ are given in dimensionless form.

Figure S2. Evolution of the free energy, enthalpy and entropy representations for CO_2 adsorption (left) and desorption (right) isotherms on Na,Cs-RHO as a function of temperature.

Figure S3. Normalized free energy, enthalpy and entropy representations for CO_2 adsorption (left) and desorption (right) in Na,Cs-RHO in the temperature range 293-333 K. The dashed and straight curves correspond to the fittings for the adsorption and desorption branches, respectively.

Figure S4. Comparison of experimental and predicted normalized integral free energies, enthalpies and entropies relative to saturation for CO_2 adsorption / desorption in Na,Cs-RHO in the temperature range 283-333 K. The straight line corresponds to the parity curve.

Figure S5. Free energy, enthalpy and entropy differences between the adsorption and desorption branches in Na,Cs-RHO as a function of temperature.

Figure S6. On the left, fittings of Tóth isotherm for the Na,Cs-RHO_C phase together with the adjusted parameters in the temperature range 293-333 K; on the right, evolution of the surface potential for the adsorption / desorption isotherms and estimated curves for Na,Cs-RHO_A and Na,Cs-RHO_C phases. Tóth isotherm: $q = q_M K P / [1 + (K P)^n]^{1/n}$).

Table S1. Summary of the results of the pre-fittings of Eq. 18 to the experimental thermodynamic isotherm representation (free energy basis) for CO_2 adsorption in Na,Cs-RHO

Table S2. Summary of the results of the pre-fittings of Eq. 18 to the experimental thermodynamic isotherm representation (free energy basis) for CO_2 desorption in Na,Cs-RHO

Table S3. Summary of the results of the fittings of Eq. 18 and related equations to the experimental thermodynamic isotherm representation (free energy, enthalpy and entropy basis) for CO_2 adsorption in Na,Cs-RHO.

Table S4. Summary of the results of the fittings of Eq. 18 and related equations to the experimental thermodynamic isotherm representation (free energy, enthalpy and entropy basis) for CO_2 desorption in Na,Cs-RHO.

Glossary

$\bar{F}_a$	Integral free energy of the sorbate [J/mol]
F^o	Integral free energy of the sorbate at P° (Eq. 19) [-]
$\bar{H}_a$	Integral entropy of the sorbate [J/mol]
H°	Integral enthalpy of the sorbate at P° (Eq. 20) [-]
m	Energy heterogeneity parameter in Eq. 18
P°	Saturation pressure [Pa]
P	Pressure [Pa]
Q_{st}	Isosteric heat [J/mol]
q	Sorbate loading [mol/kg]
q_M	Saturation loading [mol/kg]
P_G	Gate opening pressure [Pa]
R	Gas constant [8.314 $J.mol^{-1}.K^{-1}$]
T	Temperature [K]
$T\bar{S}_a$	Integral entropy of the sorbate [J/mol]
TS°	Integral entropy of the sorbate at P° (Eq. 21) [-]
Z	1/-ln(Π) [-]
Z_i^α	Affinity parameter in Eq. 18 [-]

Greek symbols

α	Phase or adsorption site
$\Delta\bar{f}$	Differential free energy of the sorbate [J/mol]
$\Delta\bar{h}$	Differential heat of the sorbate [J/mol]
ΔF°	Integral free energy dissipated in an adsorption / desorption cycle (Eq. 22) [-]
ΔH°	Integral enthalpy dissipated in an adsorption / desorption cycle (Eq. 22) [-]
$T\Delta\bar{s}$	Differential entropy of the sorbate [J/mol]
TΔS°	Integral entropy dissipated in an adsorption / desorption cycle (Eq. 22) [-]
$\Delta F°_{ads\text{-}des}$	Integral free energy difference between the adsorption and desorption curves (Eq. S7) [J/kg]
$\Delta H°_{ads\text{-}des}$	Integral enthalpy difference between the adsorption and desorption curves (Eq. S8) [J/kg]
$T\Delta S°_{ads\text{-}des}$	Integral entropy difference between the adsorption and desorption curves (Eq. S9) [J/kg]
Φ	Surface potential of the sorbate [J/kg solid]
λ_i^α	$\left(Z/Z_i^\alpha\right)^{m_i^\alpha}$ (Eq. 1) [-]
μ	Chemical potential [J/mol]
$\mu_C\big\vert_{G\to P_G}$	Chemical potential of the solid/sorbate system (condensed phase) [J/kg]
Π	P/P^o [-]
θ	Surface coverage [-]
σ_b	Sorbate-induced stress
$\bar{\Phi}_{el,A\to C}$	Elastic energy involved in the Na,Cs-RHO_A → Na,Cs-RHO_C transition [J/kg].
Ψ_F	Integral free energy of adsorption or desorption relative to saturation [-]

Ψ_H	Integral enthalpy energy of adsorption or desorption relative to saturation [-]
Ψ_{TS}	Integral entropy energy of adsorption or desorption relative to saturation [-]

Subscript

1-4	First, second, third and fourth zones in the thermodynamic isotherm (Eq. 18)
a	Sorbate
ads	Adsorption
c	Condensed phase
comp	Compression
des	Desorption
el	Elastic
G	Starting point of deformation
v	Gas/vapor phase
S	Solid

Acronyms

A	Acentric phase
C	Centric phase
MIL	Matériau Institut Lavoisier
ZIF	Zeolite Imidazolate Framework

Conversion between dimensionless and standard energies

Integral free energy of adsorption / desorption: $\Delta\bar{F}_{a,el}\left(J/g\right)=-q_M\,RT\left(F°-\frac{\Psi_F}{RT}\right)$ (S1)

Integral enthalpy of adsorption / desorption: $\Delta\bar{H}_{a,el}\left(J/g\right)=-q_M\,RT\left(H°-\frac{\Psi_H}{RT}\right)$ (S2)

Integral entropy of adsorption / desorption: $T\Delta\bar{S}_{a,el}\left(J/g\right)=-q_M\,RT\left(TS°-\frac{\Psi_{TS}}{RT}\right)$ (S3)

Maximum free energy dissipated in an adsorption / desorption cycle (absolute values):

$\Delta\bar{F}°\left(J/g\right)=q_M\,RT\,\Delta F°$ (S4)

Maximum enthalpy dissipated in an adsorption / desorption cycle (absolute values):

$\Delta\bar{H}°\left(J/g\right)=q_M\,RT\,\Delta H°$ (S5)

Maximum entropy dissipated in an adsorption / desorption cycle (absolute values):

$T\Delta\bar{S}°\left(J/g\right)=q_M\,RT\left(T\Delta S°\right)$ (S6)

Free energy difference between the adsorption and desorption branches:

$$\Delta\bar{F}^{o}_{ads-des}\left(J/g\right)=-\Delta\bar{F}_{ads-des}=\Delta\bar{F}_{a,el}\Big|_{des}-\Delta\bar{F}_{a,el}\Big|_{ads}=q_M\,RT\left[\left(F°-\frac{\Psi_F}{RT}\right)\Big|_{ads}-\left(F°-\frac{\Psi_F}{RT}\right)\Big|_{des}\right] \quad \text{(S7)}$$

Enthalpy difference between the adsorption and desorption branches:

$$\Delta\bar{H}^{o}_{ads-des}\left(J/g\right)=-\Delta\bar{H}_{ads-des}=\Delta\bar{H}_{a,el}\Big|_{des}-\Delta\bar{H}_{a,el}\Big|_{ads}=q_M\,RT\left[\left(H°-\frac{\Psi_H}{RT}\right)\Big|_{ads}-\left(H°-\frac{\Psi_H}{RT}\right)\Big|_{des}\right] \quad \text{(S8)}$$

Entropy difference between the adsorption and desorption branches:

$$T\Delta\bar{S}^{o}_{ads-des}\left(J/g\right)=-T\Delta\bar{S}_{ads-des}=T\Delta\bar{S}_{a,el}\Big|_{des}-T\Delta\bar{S}_{a,el}\Big|_{ads}=q_M\,RT\left[\left(TS°-\frac{\Psi_{TS}}{RT}\right)\Big|_{ads}-\left(TS°-\frac{\Psi_{TS}}{RT}\right)\Big|_{des}\right] \quad \text{(S9)}$$

Conversion between dimensionless and standard energies

Integral free energy of adsorption / desorption: $\Delta\overline{F}_{a,el}\left(J/g\right)=-q_M\,RT\left(F°-\frac{\Psi_F}{RT}\right)$ (S15)

Integral enthalpy of adsorption / desorption: $\Delta\overline{H}_{a,el}\left(J/g\right)=-q_M\,RT\left(H°-\frac{\Psi_H}{RT}\right)$ (S16)

Integral entropy of adsorption / desorption: $T\Delta\overline{S}_{a,el}\left(J/g\right)=-q_M\,RT\left(TS°-\frac{\Psi_{TS}}{RT}\right)$ (S17)

Maximum free energy dissipated in an adsorption / desorption cycle:

$$\Delta F^{\circ}\left(J/g\right)=-q_M\,RT\,\Delta F^{\circ} \tag{S18}$$

Maximum enthalpy dissipated in an adsorption / desorption cycle:

$$\Delta H^{\circ}\left(J/g\right)=-q_M\,RT\,\Delta H^{\circ} \tag{S19}$$

Maximum entropy dissipated in an adsorption / desorption cycle:

$$T\Delta S^{\circ}\left(J/g\right)=-q_M\,RT\left(T\Delta S^{\circ}\right) \tag{S20}$$

Free energy difference between the adsorption and desorption branches:

$$\Delta\overline{F}^{o}_{ads-des}\left(J/g\right)=-\Delta\overline{F}_{ads-des}=\Delta\overline{F}_{a,el}\Big|_{des}-\Delta\overline{F}_{a,el}\Big|_{ads}=q_M\,RT\left[\left(F^{\circ}-\frac{\Psi_F}{RT}\right)\Big|_{ads}-\left(F^{\circ}-\frac{\Psi_F}{RT}\right)\Big|_{des}\right] \tag{S21}$$

Enthalpy difference between the adsorption and desorption branches:

$$\Delta\overline{H}^{o}_{ads-des}\left(J/g\right)=-\Delta\overline{H}_{ads-des}=\Delta\overline{H}_{a,el}\Big|_{des}-\Delta\overline{H}_{a,el}\Big|_{ads}=q_M\,RT\left[\left(H^{\circ}-\frac{\Psi_H}{RT}\right)\Big|_{ads}-\left(H^{\circ}-\frac{\Psi_H}{RT}\right)\Big|_{des}\right] \tag{S22}$$

Entropy difference between the adsorption and desorption branches:

$$T\Delta\overline{S}^{o}_{ads-des}\left(J/g\right)=-T\Delta\overline{S}_{ads-des}=T\Delta\overline{S}_{a,el}\Big|_{des}-T\Delta\overline{S}_{a,el}\Big|_{ads}=q_M\,RT\left[\left(TS^{\circ}-\frac{\Psi_{TS}}{RT}\right)\Big|_{ads}-\left(TS^{\circ}-\frac{\Psi_{TS}}{RT}\right)\Big|_{des}\right] \tag{S23}$$

Fitting details

Parameters m^{α} and Z^{α} included in the λ-terms in Eq. 18 in the main text for the free energy and related equations for enthalpy and entropy were fitted using a least-square non-linear optimization method based on the Levenberg-Marquardt algorithm by comparison of predicted and experimental integral free energies and enthalpies of adsorption. All the parameters were fitted simultaneously for the different zones. The critical pressure of CO_2 was used as reference pressure (i.e. P_0=7344 kPa).

The relevant parameters in the Tóth equation (see caption of Figure S5) were also fitted using a least-square non-linear optimization method based on the Levenberg-Marquardt algorithm by comparison of predicted and experimental CO_2 loadings each phase. In these fittings, the saturation loading, q_M, was kept constant at the value 7.5 mmol/g.

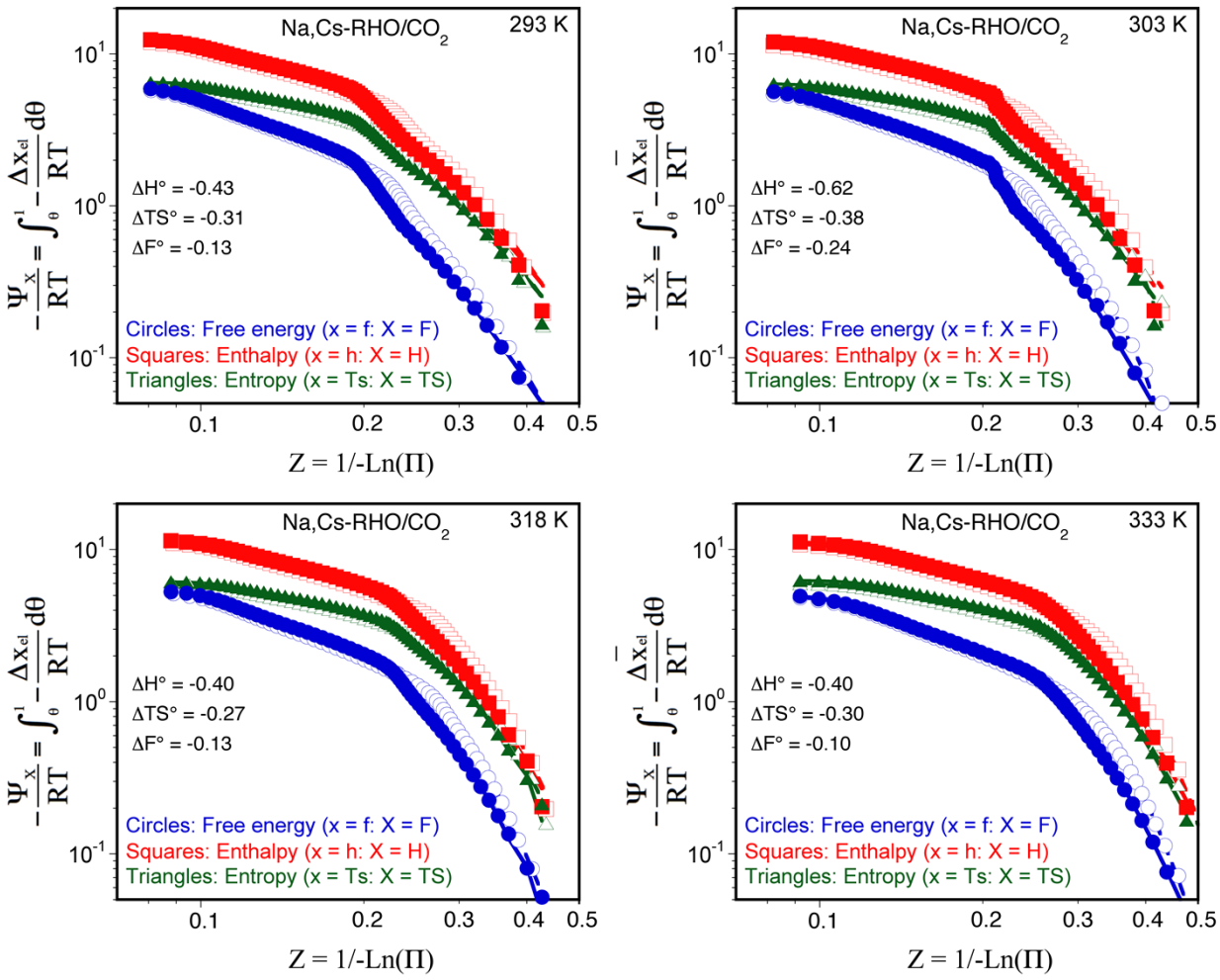

Figure S1. Free energy, enthalpy and entropy representations of CO_2 adsorption / desorption in Na,Cs-RHO in the temperature range 293-333 K. The dashed and straight curves correspond to the fittings using for the adsorption and desorption branches, respectively. The values for *ΔF°*, *ΔH°* and *Δ(TS°)* are given in dimensionless form.

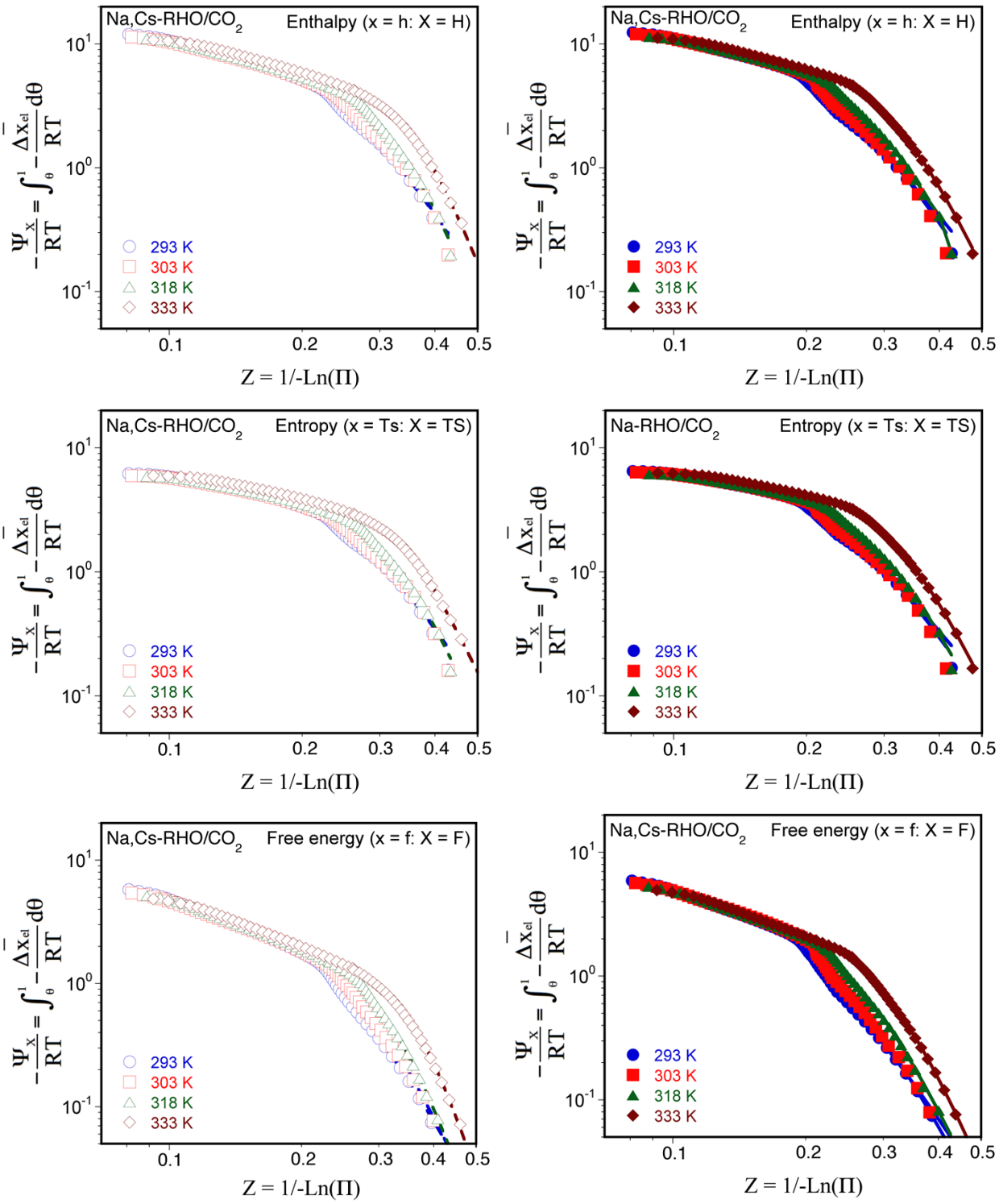

Figure S2. Evolution of the free energy, enthalpy and entropy representations for CO_2 adsorption (left) and desorption (right) isotherms on Na,Cs-RHO as a function of temperature.

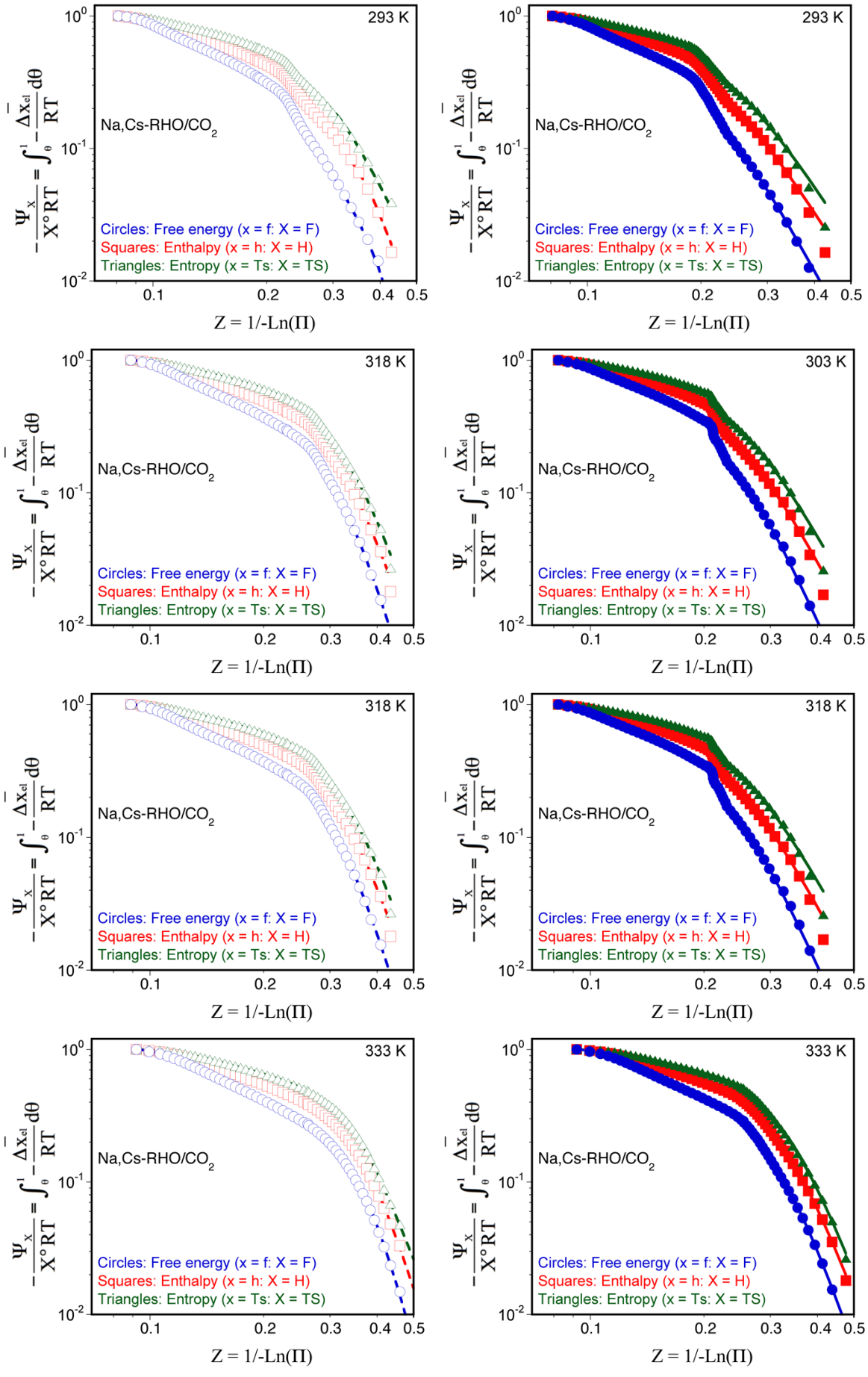

Figure S3. Normalized free energy, enthalpy and entropy representations for CO_2 adsorption (left) and desorption (right) in Na,Cs-RHO in the temperature range 293-333 K. The dashed and straight curves correspond to the fittings for the adsorption and desorption branches, respectively.

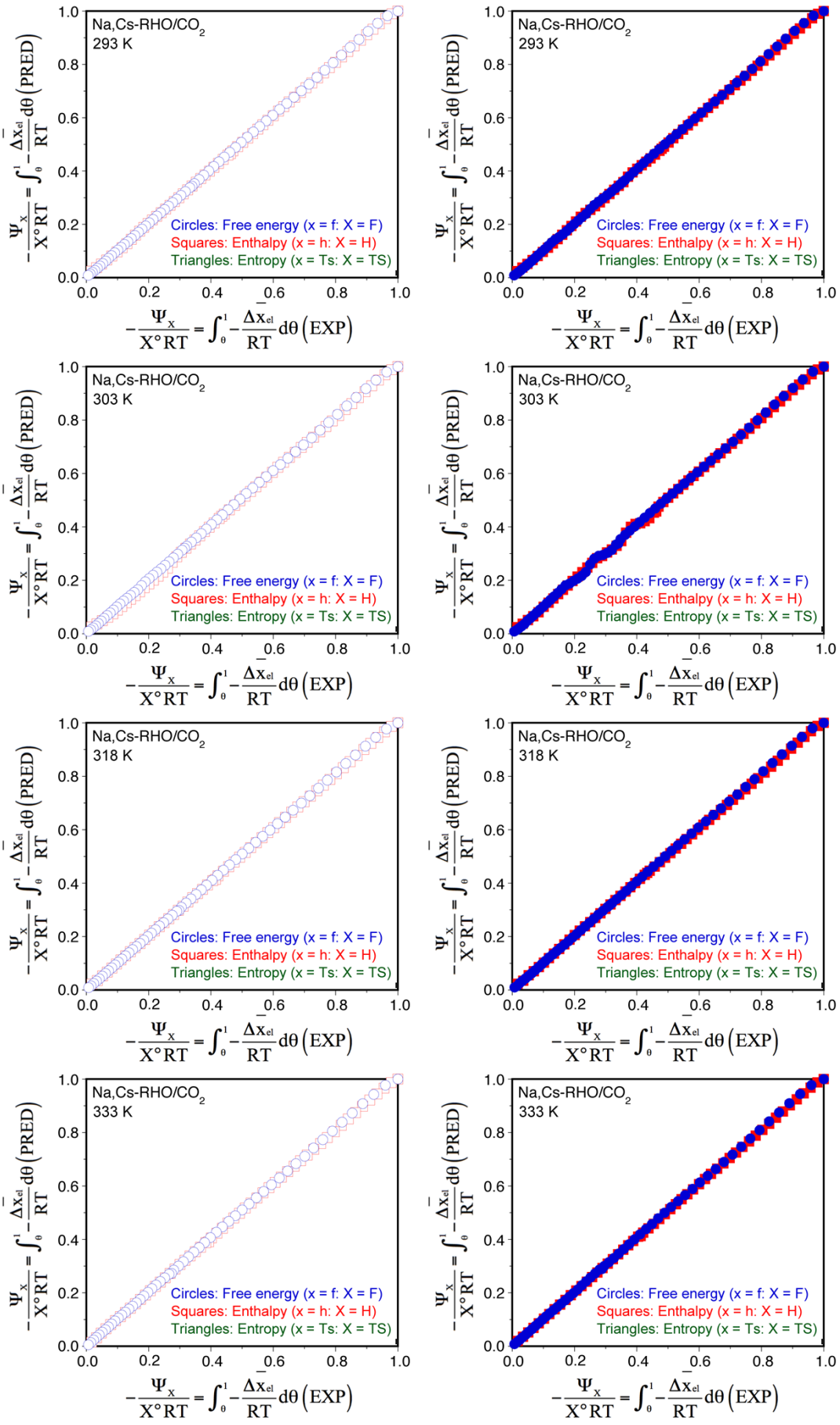

Figure S4. Comparison of experimental and predicted normalized integral free energies, enthalpies and entropies relative to saturation for CO_2 adsorption / desorption in Na,Cs-RHO in the temperature range 283-333 K. The straight line corresponds to the parity curve.

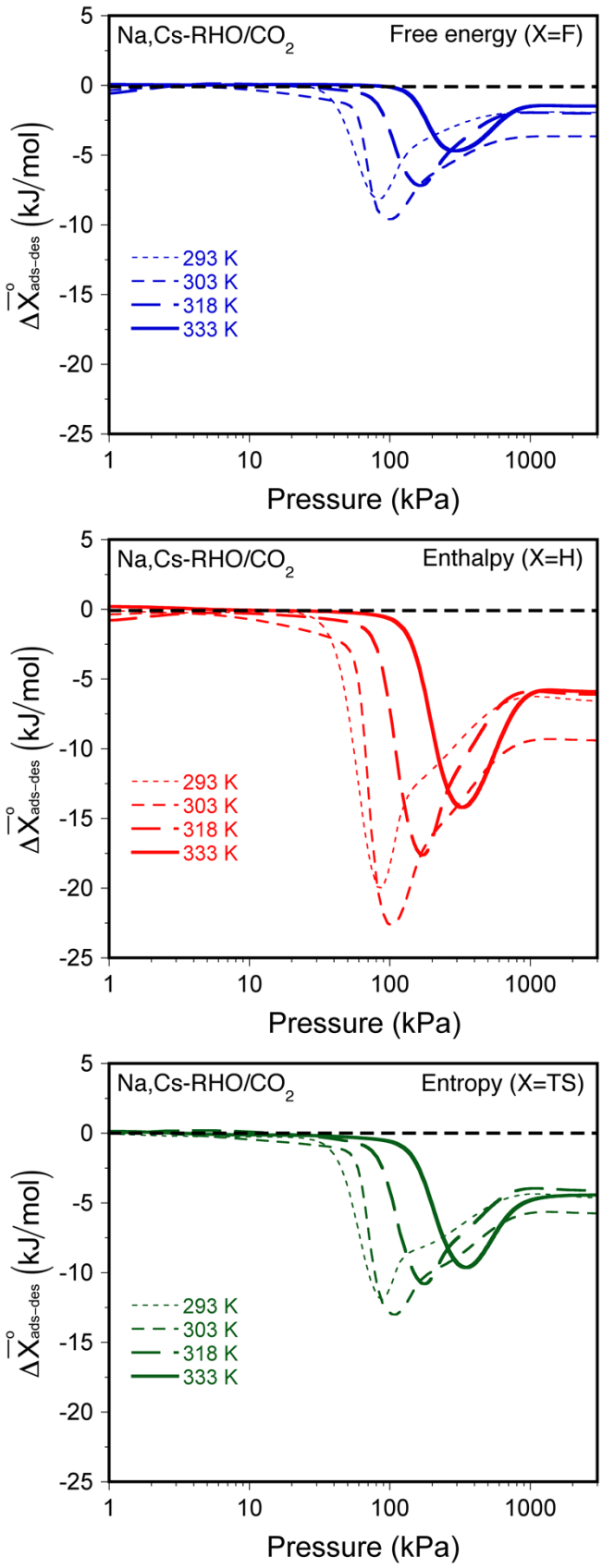

Figure S5. Free energy, enthalpy and entropy differences between the adsorption and desorption branches in Na,Cs-RHO as a function of temperature.

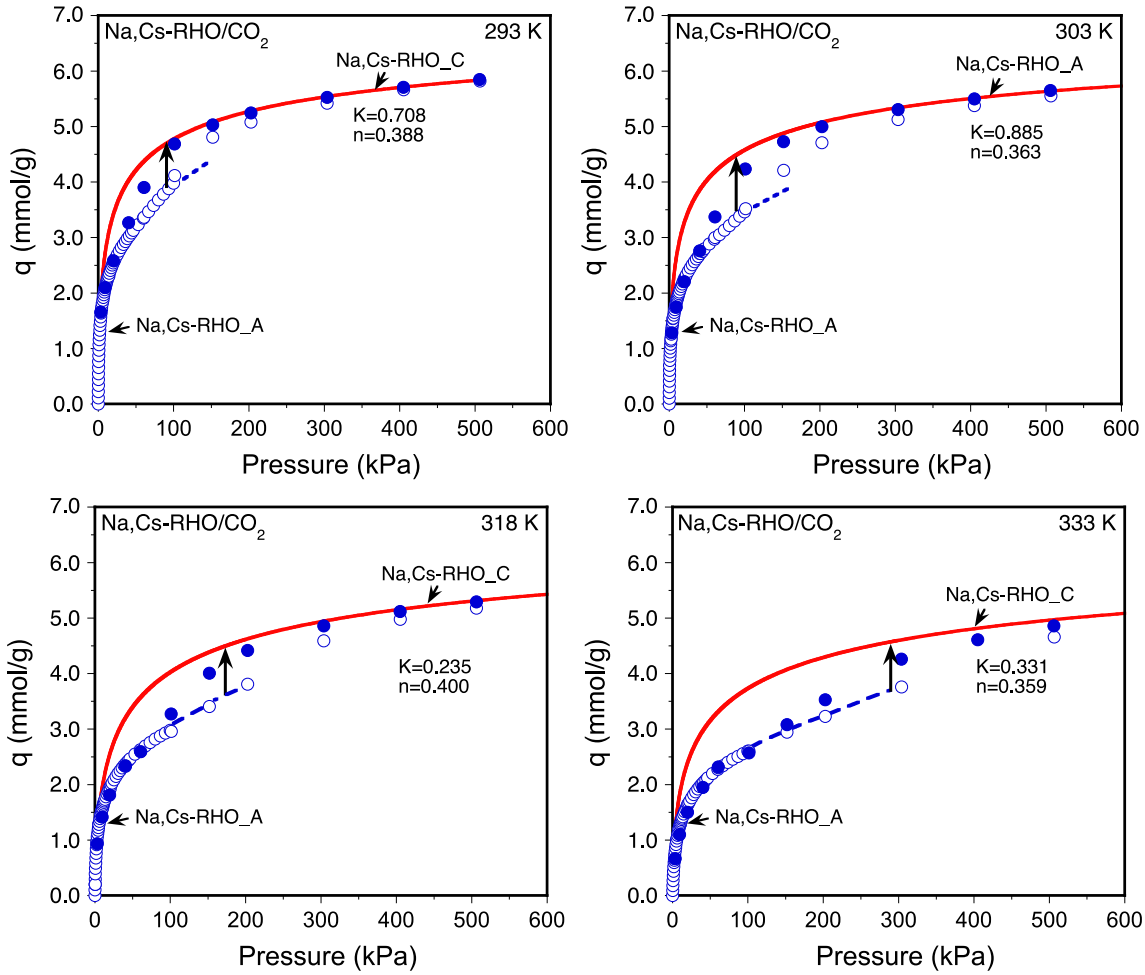

Figure S6. On the left, fittings of Tóth isotherm for the Na,Cs-RHO_C phase together with the adjusted parameters in the temperature range 293-333 K; on the right, evolution of the surface potential for the adsorption / desorption isotherms and estimated curves for Na,Cs-RHO_A and Na,Cs-RHO_C phases. Tóth isotherm: $q = q_M K P / [1 + (K P)^n]^{1/n}$).

Table S1. Summary of the results of the pre-fittings of Eq. 18 to the experimental thermodynamic isotherm representation (free energy basis) for CO_2 adsorption in Na,Cs-RHO.

T (K)	X°	First zone		Second zone		Third zone		Fourth zone	
		m_1^1	Z_1^1 x10^2	m_2^1	Z_2^1 x10^2	m_2^2	Z_2^2 x10^2	m_2^2	Z_2^2 x10^2
293	5.9	12.9 ± 0.2	10.6 ± 0.1	2.48 ± 0.02	14.6 ± 0.1	35 ± 4	23.2 ± 0.1	5.6 ± 0.3	20.9 ± 0.1
303	5.6	12.0 ± 0.3	10.9 ± 0.1	2.45 ± 0.02	15.2 ± 0.1	37 ± 6	24.8 ± 0.1	6.3 ± 0.4	22.9 ± 0.1
318	5.2	12.9 ± 0.6	11.9 ± 0.1	2.38 ± 0.05	16.1 ± 0.1	36 ± 10	27.9 ± 0.1	8 ± 1	26 ± 1
333	4.9	10.0 ± 0.2	12.9 ± 0.1	2.27 ± 0.03	16.8 ± 0.1	34 ± 12	29 ± 1	11.7 ± 0.9	31.4 ± 0.1

Table S2. Summary of the results of the pre-fittings of Eq. 18 to the experimental thermodynamic isotherm representation (free energy basis) for CO_2 desorption in Na,Cs-RHO.

T (K)	X°	First zone		Second zone		Third zone		Fourth zone	
		m_1^1	Z_1^1 x10^2	m_2^1	Z_2^1 x10^2	m_2^2	Z_2^2 x10^2	m_2^2	Z_2^2 x10^2
293	6.0	12.8 ± 0.5	10.7 ± 0.1	2.42 ± 0.06	14.7 ± 0.1	37 ± 5	20.3 ± 0.1	4.9 ± 0.3	18.1 ± 0.1
303	5.8	12.9 ± 0.5	10.8 ± 0.1	2.54 ± 0.04	15.6 ± 0.1	80 ± 8	20.9 ± 0.1	5.8 ± 0.2	20.4 ± 0.3
318	5.4	12.4 ± 0.6	11.8 ± 0.1	2.37 ± 0.02	16.4 ± 0.1	35 ± 11	23.7 ± 0.1	6.2 ± 0.7	22.9 ± 0.9
333	5.0	9.9 ± 0.2	13.0 ± 0.1	2.18 ± 0.04	17.1 ± 0.1	30 ± 5	26.8 ± 0.1	7.6 ± 0.4	26 ± 5

Table S3. Summary of the results of the fittings of Eq. 18 and related equations to the experimental thermodynamic isotherm representation (free energy, enthalpy and entropy basis) for CO_2 adsorption in Na,Cs-RHO.

Material	T (K)	X°	First zone		Second zone		Third zone		Fourth zone	
			m_1^1	Z_1^1 x10^2	m_2^1	Z_2^1 x10^2	m_2^2	Z_2^2 x10^2	m_2^2	Z_2^2 x10^2
Free energy (X=F)	293	5.8	14.4 ± 0.3	10.6 ± 0.1	2.58 ± 0.02	14.6 ± 0.1	40 ± 3	23.2 ± 0.1	6.8 ± 0.2	21.8 ± 0.2
	303	5.4	13.7 ± 0.3	10.9 ± 0.1	2.54 ± 0.02	15.4 ± 0.1	36 ± 4	24.6 ± 0.1	7.8 ± 0.3	24.0 ± 0.3
	318	5.1	14.1 ± 0.3	11.9 ± 0.1	2.47 ± 0.02	16.2 ± 0.1	40 ± 5	27.5 ± 0.1	9.7 ± 0.4	27.0 ± 0.3
	333	4.8	11.3 ± 0.3	12.9 ± 0.1	2.36 ± 0.03	17.2 ± 0.1	33 ± 10	29.8 ± 0.1	10.9 ± 0.6	31.5 ± 0.1
Enthalpy (X=H)	293	12.0	14.3 ± 0.3	11.0 ± 0.1	2.46 ± 0.02	17.8 ± 0.1	46 ± 3	23.6 ± 0.1	6.2 ± 0.1	24.8 ± 0.1
	303	11.4	13.5 ± 0.3	11.4 ± 0.1	2.46 ± 0.02	18.8 ± 0.1	35 ± 3	25.1 ± 0.1	7.0 ± 0.2	26.3 ± 0.2
	318	11.0	14.3 ± 0.2	12.3 ± 0.3	2.40 ± 0.01	19.8 ± 0.1	38 ± 2	28.0 ± 0.1	8.7 ± 0.1	28.7 ± 0.1
	333	10.8	11.3 ± 0.2	13.7 ± 0.1	2.25 ± 0.03	21.5 ± 0.1	21 ± 3	31.0 ± 0.1	9.4 ± 0.5	32.6 ± 0.1
Entropy (X=TS)	293	6.2	15.1 ± 0.6	11.6 ± 0.1	2.64 ± 0.03	21.3 ± 0.1	53 ± 6	23.7 ± 0.1	6.3 ± 0.1	27.1 ± 0.1
	303	6.0	14.2 ± 0.6	12.1 ± 0.1	2.69 ± 0.03	22.2 ± 0.1	37 ± 4	25.4 ± 0.1	7.0 ± 0.2	28.3 ± 0.1
	318	5.9	15.1 ± 0.3	12.9 ± 0.1	2.60 ± 0.01	23.5 ± 0.1	39 ± 2	28.4 ± 0.1	8.6 ± 0.1	30.1 ± 0.1
	333	6.0	11.9 ± 0.3	14.6 ± 0.1	2.38 ± 0.03	25.8 ± 0.1	14 ± 2	33.2 ± 0.1	7 ± 1	31 ± 2

Table S4. Summary of the results of the fittings of Eq. 18 and related equations to the experimental thermodynamic isotherm representation (free energy, enthalpy and entropy basis) for CO_2 desorption in Na,Cs-RHO.

Material	T (K)	X°	First zone		Second zone		Third zone		Fourth zone	
			m_1^1	Z_1^1 x10^2	m_2^1	Z_2^1 x10^2	m_2^2	Z_2^2 x10^2	m_2^2	Z_2^2 x10^2
Free energy (X=F)	273	5.9	14.2 ± 0.4	10.7 ± 0.1	2.50 ± 0.04	14.9 ± 0.1	31 ± 2	20.4 ± 0.1	5.7 ± 0.2	18.7 ± 0.3
	303	5.7	14.3 ± 0.6	10.8 ± 0.1	2.59 ± 0.05	15.8 ± 0.1	74 ± 10	21.4 ± 0.1	6.8 ± 0.2	20.8 ± 0.3
	308	5.3	13.9 ± 0.3	11.8 ± 0.1	2.50 ± 0.03	16.5 ± 0.1	42 ± 3	23.4 ± 0.1	7.6 ± 0.2	23.5 ± 0.1
	323	4.9	11.4 ± 0.3	13.0 ± 0.1	2.32 ± 0.04	17.5 ± 0.1	33 ± 4	26.9 ± 0.1	8.3 ± 0.3	27.5 ± 0.1
Enthalpy (X=H)	273	12.4	14.1 ± 0.4	11.1 ± 0.1	2.38 ± 0.02	18.3 ± 0.1	31 ± 2	20.9 ± 0.1	5.0 ± 0.1	21.3 ± 0.1
	303	12.0	13.7 ± 0.8	11.4 ± 0.1	2.49 ± 0.06	19.2 ± 0.1	63 ± 7	21.6 ± 0.1	5.9 ± 0.2	22.9 ± 0.1
	308	11.4	13.9 ± 0.3	12.3 ± 0.3	2.38 ± 0.02	20.2 ± 0.1	40 ± 2	23.8 ± 0.1	7.1 ± 0.1	25.8 ± 0.1
	323	11.2	11.4 ± 0.2	13.7 ± 0.1	2.21 ± 0.03	22.1 ± 0.1	29 ± 2	27.5 ± 0.1	7.7 ± 0.1	29.2 ± 0.1
Entropy (X=TS)	273	6.5	14.9 ± 0.8	11.7 ± 0.1	2.57 ± 0.06	22.0 ± 0.1	32 ± 2	21.2 ± 0.1	5.0 ± 0.1	23.5 ± 0.1
	303	6.4	14 ± 1	12.3 ± 0.1	2.67 ± 0.09	22.2 ± 0.1	61 ± 7	21.8 ± 0.1	5.7 ± 0.1	24.7 ± 0.1
	308	6.1	14.9 ± 0.4	12.9 ± 0.1	2.65 ± 0.02	23.8 ± 0.1	40 ± 2	24.1 ± 0.1	7.1 ± 0.1	27.4 ± 0.1
	323	6.3	12.4 ± 0.2	14.5 ± 0.1	2.40 ± 0.02	26.4 ± 0.1	28 ± 1	28.0 ± 0.1	7.6 ± 0.1	30.6 ± 0.1