Supporting Information:

Synthesis and properties of pure and intergrown CHA/PHI zeolites from inorganic multi-cation colloidal suspensions

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Additional figures and tables

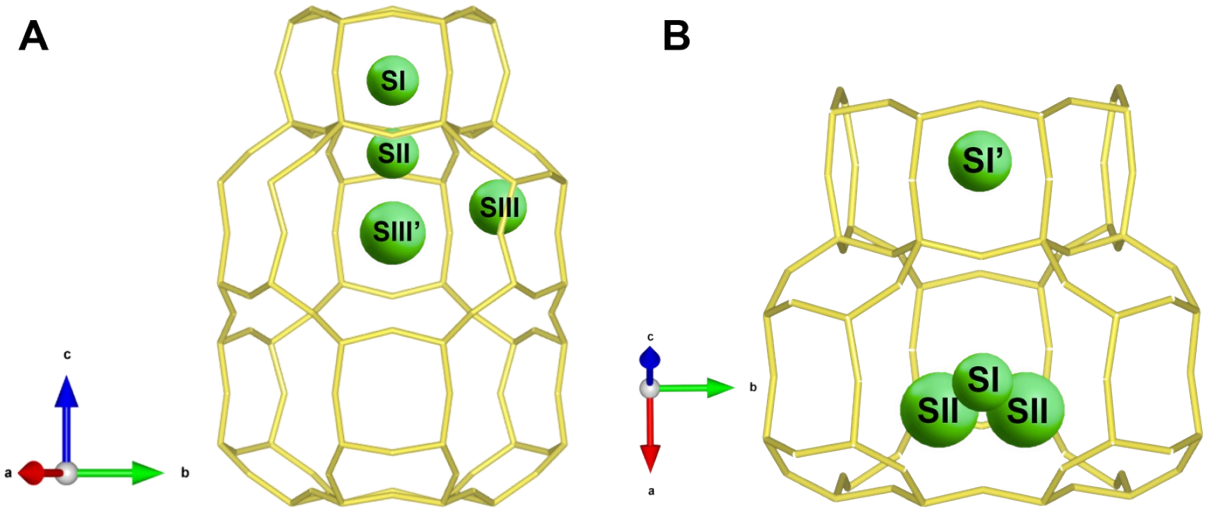


Figure S1. Extra-framework cations site location in the chabazite (A) and in the phillipsite (B). The structures are viewed as a projection along [$\bar{1}$00].

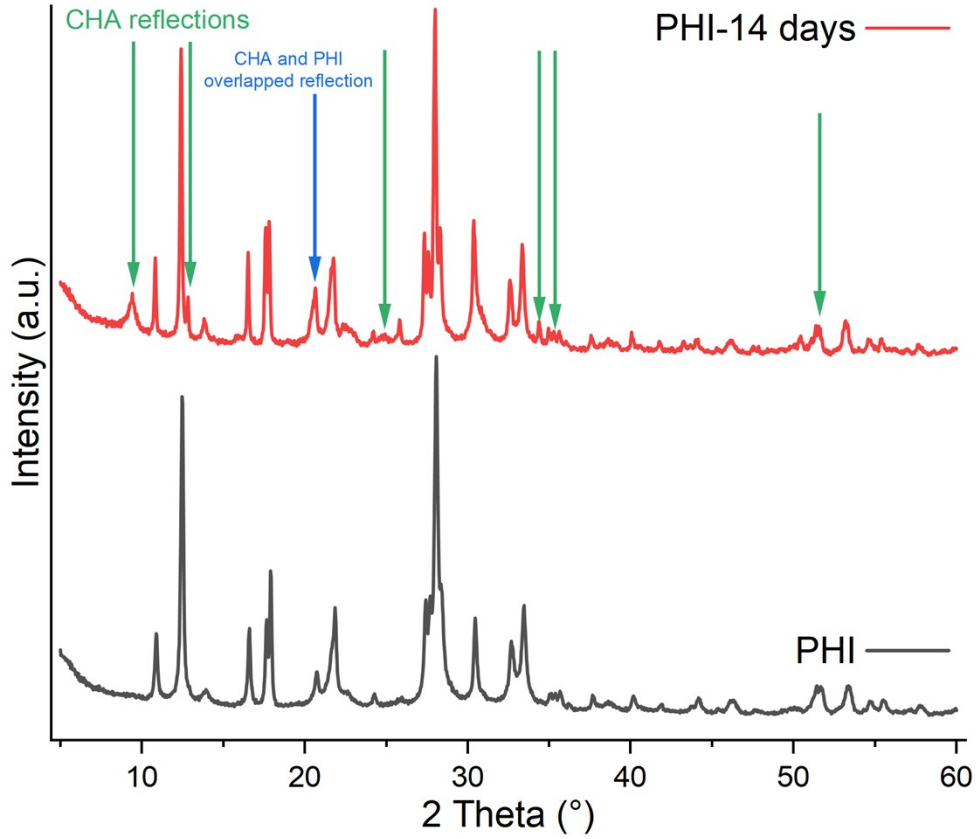


Figure S2. Powder XRD pattern of a chabazite/phillipsite zeolite compared to the pattern of a pure phillipsite pattern. The green arrows indicate peaks attributed to the CHA phase and the blue arrow indicates an overlapped CHA and PHI peak.

Table S1. Screening of the synthesis parameters yielding pure CHA, PHI and intergrown zeolites.

	Chemical composition								Crystallisation		Zeolitic product	
	Cs_2O	K_2O	Na_2O	BaO	CaO	SiO_2	Al_2O_3	H_2O	Ageing time (days)	HT time (h)	XRD phase	CHA/PHI
(1) CHA[42]	0.2	1.5	6	-	-	16	0.7	140	7	7	CHA	1
(2) Chabazite[40]	0.15	1.35	6	-	-	16	0.6	120	12	8	CHA	1
(3) CHA-Na,Cs-1.3K,0.2Ba[42]	0.2	1.3	6	0.2	-	16	0.7	140	7	7	CHA	1
(4) CHA-Na,K,Cs-0.2Ca[42]	0.2	1.5	6	-	0.2	16	0.7	140	7	10	CHA	1
(5) CHA-Na,K,Cs-0.2Ba[42]	0.2	1.5	6	0.2	-	16	0.7	140	7	4	CHA	1
(6) CHA-Na,K	-	1.5	6	-	-	16	0.7	140	7	7	CHA	1
(7) CHA-Na,Cs-1.3K,0.2Ca[42]	0.2	1.3	6	-	0.2	16	0.7	140	7	7	CHA & PHI	0.81
(8) CHA-Na,K,Cs-0.50Al	0.2	1.5	6	-	-	16	0.5	140	7	7	CHA & PHI	0.74
(9) CHA-Na,K,Cs-0.25Al	0.2	1.5	6	-	-	16	0.25	140	7	7	CHA & PHI	0.69
(10) CHA-Na,K,Cs-0.5Ba	0.2	1.5	6	0.5	-	16	0.7	140	7	4	CHA & PHI	0.59
(11) CHA-Na,K,Cs-1.0Ba	0.2	1.5	6	1	-	16	0.7	140	7	4	CHA & PHI	0.42
(12) PHI	-	1.5	6	-	0.2	16	0.7	140	7	7	PHI	0
(13) PHI-14 days *	-	1.5	6	-	0.2	16	0.7	140	14	7	CHA & PHI	0.29

* The suffix "14 days" refers to the ageing time that was prolonged for fourteen days instead of seven

Table S2A. Scherrer crystalline domain size calculation of the PHI-14 days sample. The Miller indices were chosen to average out over crystal orientation and not overlap with those of chabazite.

h,k,l	B obs. [° 2θ]	B std. [° 2θ]	Peak pos. [° 2θ]	B struct. [° 2θ]	Crystallite size [Å]
100	0.121	0.003	10.806	0.118	676
020	0.148	0.003	12.392	0.145	551
120	0.108	0.003	16.505	0.105	765
22-1	0.144	0.003	21.855	0.141	574
14-2	0.18	0.003	32.566	0.177	468
34-2	0.108	0.003	37.57	0.105	799
					average: 64±13 nm

Table S2B. Scherrer crystalline domain size calculation of the PHI sample.

h,k,l	B obs. [° 2θ]	B std. [° 2θ]	Peak pos. [° 2θ]	B struct. [° 2θ]	Crystallite size [Å]
100	0.144	0.003	10.879	0.141	566
020	0.18	0.003	12.476	0.177	452
120	0.144	0.003	16.581	0.141	569
22-1	0.144	0.003	21.855	0.141	574
14-2	0.252	0.003	32.632	0.249	332
34-2	0.18	0.003	37.65	0.177	474
					average: 49±10 nm

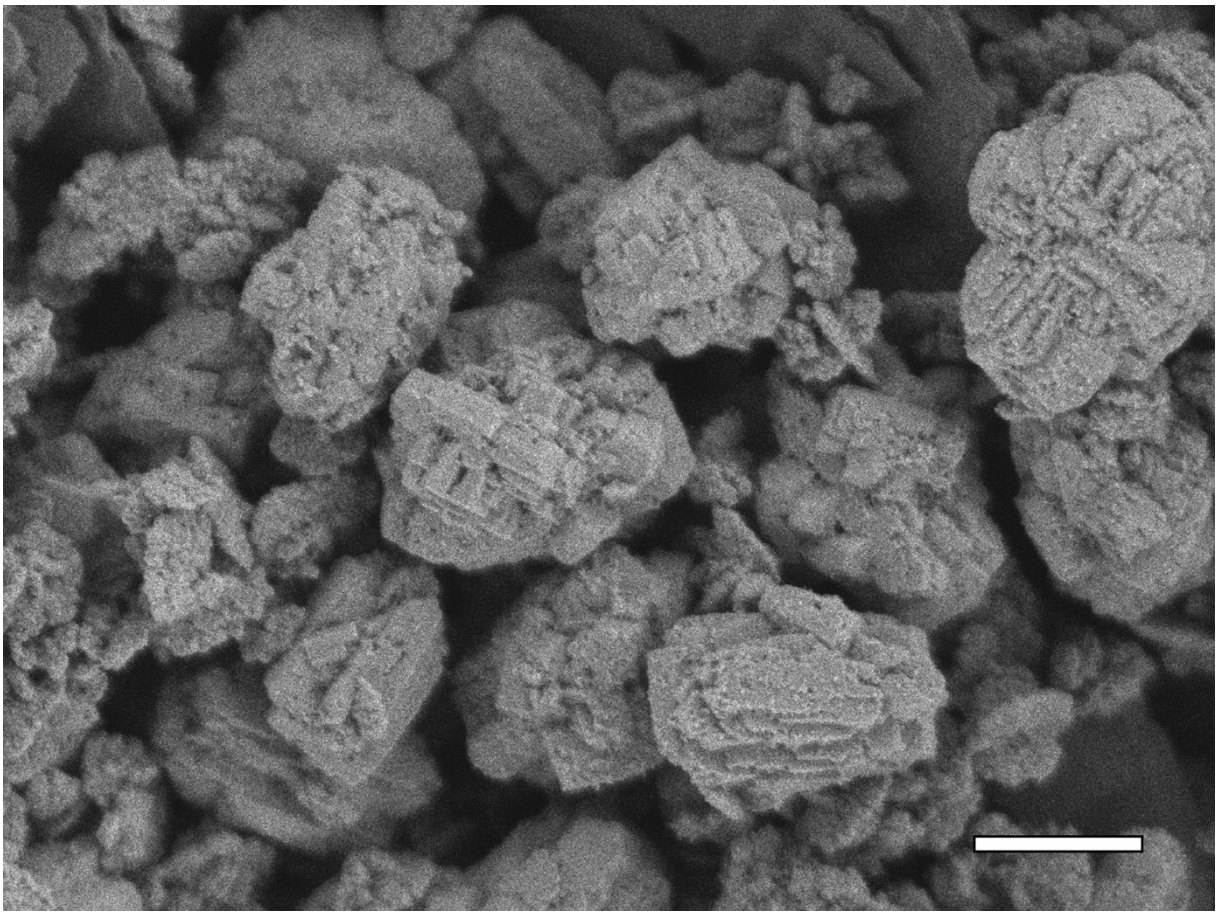


Figure S3. SEM images of PHI-14 days. Scale bar is 500 nm.

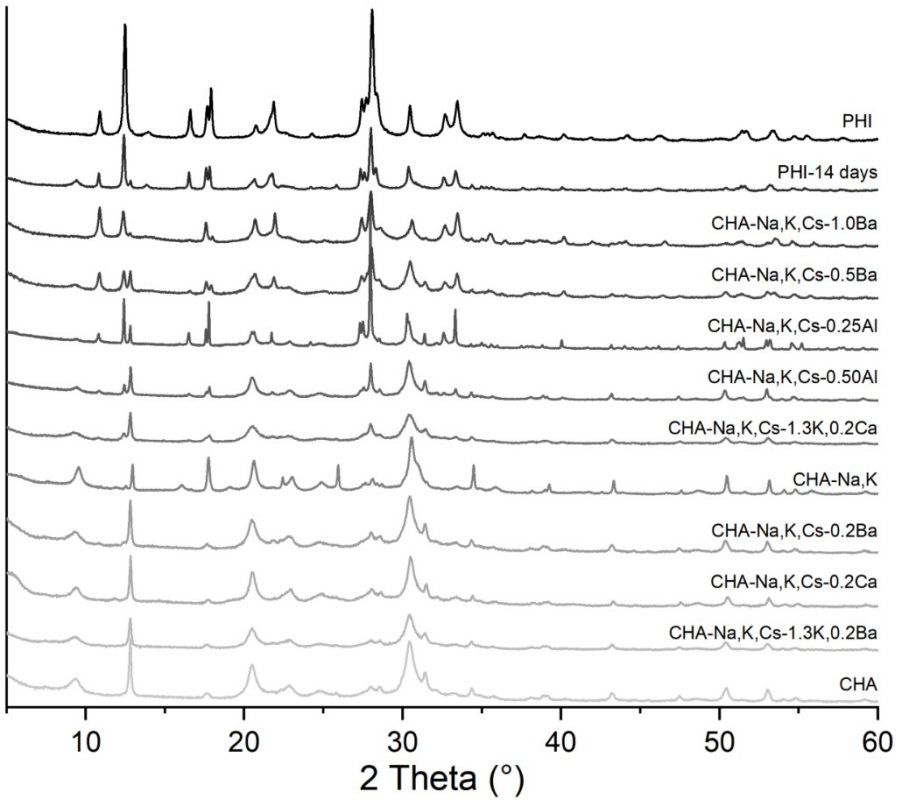


Figure S4. Powder XRD patterns of all zeolite samples.

Sample	Phase	GOF	wR (%)	reduced X^2	a (Å)	b (Å)	c (Å)	beta (°)	Volume ($Å^3$)
CHA	CHA	3.42	9.683	11.67	13.835607	-	15.184503	-	2517.258
CHA-Na,Cs-1.3K,0.2Ba	CHA	3.39	9.847	11.46	13.800795	-	15.163165	-	2501.086
CHA-Na,K,Cs-0.2Ca	CHA	3.76	8.906	14.14	13.779192	-	15.086180	-	2480.604
CHA-Na,K,Cs-0.2Ba	CHA	3.92	8.717	15.40	13.803514	-	15.118306	-	2494.670
CHA-Na,K	CHA	4.44	11.506	19.70	13.823164	-	15.082600	-	2495.869
CHA-Na,Cs-1.3K,0.2Ca	CHA	3.05	8.807	9.28	13.777796	-	15.074650	-	2478.206
	PHI				9.943584	14.187387	8.678807	124.8448	1004.827
CHA-Na,K,Cs-0.50Al	CHA	3.14	8.691	9.85	13.799675	-	15.086954	-	2488.112
	PHI				9.957733	14.202910	8.702450	124.8743	1009.740
CHA-Na,K,Cs-0.25Al	CHA	4.51	12.294	20.32	13.830740	-	15.083669	-	2498.783
	PHI				9.985948	14.261571	8.739134	125.2619	1016.232
CHA-Na,K,Cs-0.5Ba	CHA	2.89	6.596	8.38	13.841154	-	15.052657	-	2497.402
	PHI				9.886988	14.214983	8.705141	124.9366	1002.967
CHA-Na,K,Cs-1.0Ba	CHA	2.56	5.887	6.56	13.829992	-	15.052693	-	2493.381
	PHI				9.870288	14.210071	8.727031	124.8026	1005.081
PHI-14 days	CHA	3.29	11.004	10.84	13.822081	-	15.069711	-	2493.345
	PHI				9.927806	14.204983	8.713394	124.9560	1007.115
PHI	PHI	3.08	7.252	9.5	9.916595	14.202499	8.717479	125.0690	1004.884

Table S3. Le Bail refined unit cell parameters of the chabazite and phillipsite zeolites.

Table S4. Chemical composition of the chabazite and phillipsite nanozeolites determined by ICP-MS. *Due to the co-existence of $Ca(OH)_2$ precipitates the amount of Ca^{2+} cations present in the CHA unit cell was estimated (see *Advanced Sustainable Systems* **2024**, *8* (1), 2300326).

	ICP-MS Chemical composition								
	Cs	K	Na	Ba	Ca	Si	Al	Si/Al	CHA/PHI
CHA	3.1	5.7	2.5	-	-	24.7	11.3	2.2	1.00
Chabazite[60]	6.6	3.6	2.4	-	-	23.4	12.6	1.9	1.00
CHA-Na,Cs-1.3K,0.2Ba	3.7	5.2	1.5	0.3	-	24.9	11.1	2.2	1.00
CHA-Na,Cs-1.3K,0.2Ca	3.3	5.2	1.7	-	0.4	25.0	11.0	2.3	1.00
CHA-Na,K,Cs-0.2Ca	2.7	6.0	1.8 *	-	0.6 *	24.3	11.7	2.1	1.00
CHA-Na,K,Cs-0.2Ba	3.2	5.6	1.6	0.5	-	24.6	11.4	2.2	1.00
CHA-Na,K	-	7.7	3.5	-	-	24.5	11.2	2.2	1.00
CHA-Na,K,Cs-0.50Al	3.1	5.6	2.4	-	-	23.8	11.1	2.1	0.74
CHA-Na,K,Cs-0.25Al	2.3	5.6	3.1	-	-	24.0	11.0	2.2	0.69
CHA-Na,K,Cs-0.5Ba	2.3	4.4	0.9	1.6	-	23.5	10.8	2.2	0.59
CHA-Na,K,Cs-1.0Ba	1.4	2.1	-	3.4	-	23.2	10.3	2.3	0.42
PHI-14 days	-	6.1	3.2	-	0.7	22.6	10.7	2.1	0.29
PHI	-	5.8	3.3	-	0.7	21.6	10.5	2.1	0.00

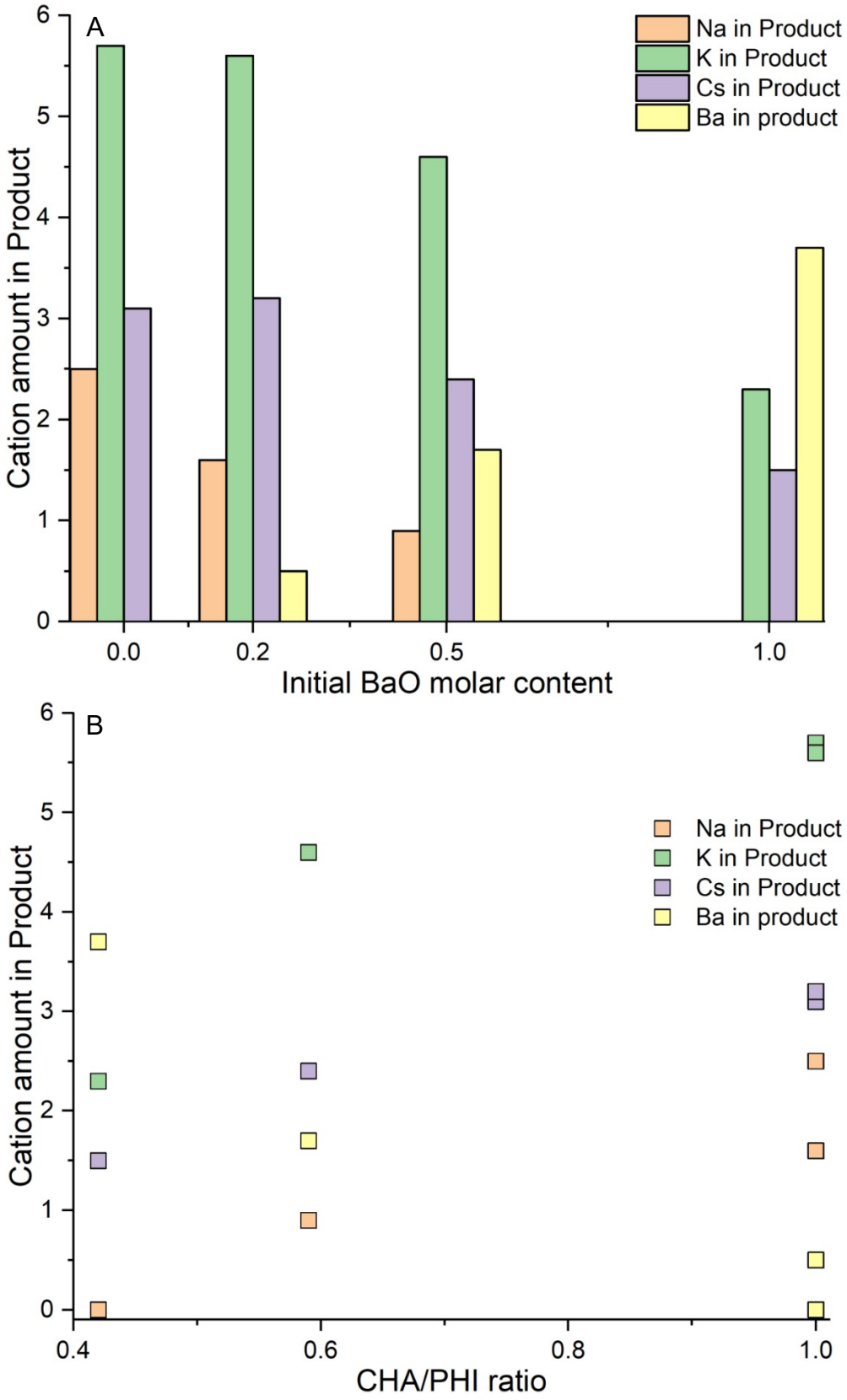


Figure S5. Plot of Cs, K, Na, Ba amount over the initial BaO molar content (A) or the CHA/PHI ratio (B), for samples CHA, CHA-Na,K,Cs-0.2Ba, CHA-Na,K,Cs-0.5Ba and CHA-Na,K,Cs-1.0Ba.

Table S5. Detailed molar ratio and coordinates of samples presented in the ternary phase diagram.

	CHA:PHI ratio	molar ratio			%		
		Al + K	Ca or Ba	Cs	Al + K	Ca or Ba	Cs
CHA	1.00	2.20	0.00	0.20	0.92	0.00	0.08
Chabazite[60]	1.00	1.95	0.00	0.15	0.93	0.00	0.07
CHA-Na,Cs-1.3K,0.2Ba	1.00	2.00	0.20	0.20	0.83	0.08	0.08
CHA-Na,Cs-1.3K,0.2Ca	0.81	2.00	0.20	0.20	0.83	0.08	0.09
CHA-Na,K,Cs-0.2Ca	1.00	2.20	0.20	0.20	0.85	0.08	0.08
CHA-Na,K,Cs-0.2Ba	1.00	2.20	0.20	0.20	0.85	0.08	0.08
CHA-Na,K	1.00	2.20	0.00	0.00	1.00	0.00	0.00
CHA-Na,K,Cs-0.50Al	0.74	2.00	0.00	0.20	0.91	0.00	0.09
CHA-Na,K,Cs-0.25Al	0.69	1.76	0.00	0.20	0.90	0.00	0.10
CHA-Na,K,Cs-0.5Ba	0.59	2.20	0.50	0.20	0.76	0.17	0.07
CHA-Na,K,Cs-1.0Ba	0.42	2.20	1.00	0.20	0.65	0.29	0.06
PHI*	0.00	2.20	0.20	0.00	0.92	0.08	0.00

*PHI-14 days is not included as its precursor chemical composition is the same as PHI

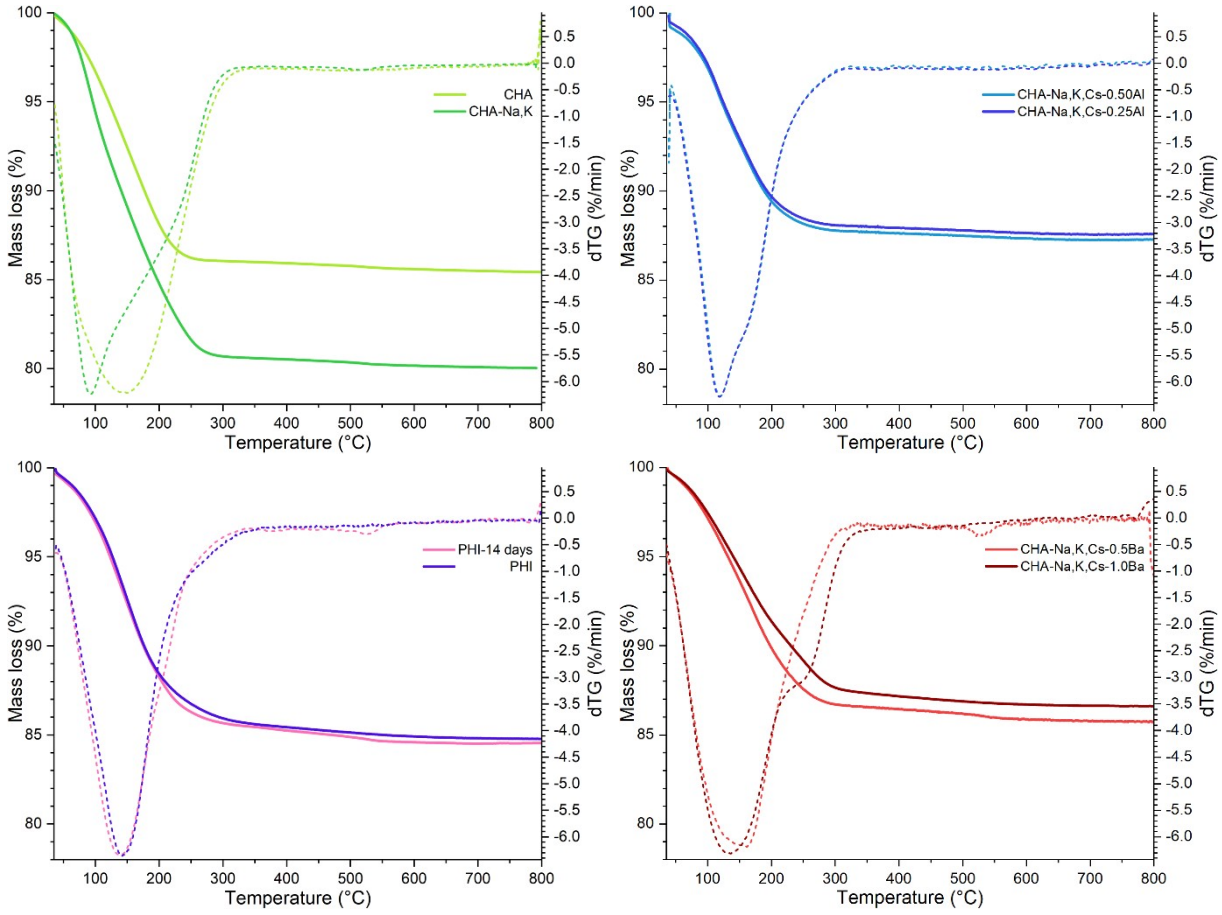


Figure S6. Thermogravimetric (solid) and differential thermogravimetic (dotted) curves of all zeolite samples.

Table S6. Mass loss at 800 °C of all nanosized zeolites calculated from thermogravimetric analysis.

	Mass loss at 800 °C
CHA*	14.5 %
CHA-Na,Cs-1.3K,0.2Ba*	14.3 %
CHA-Na,Cs-1.3K,0.2Ca*	14.7 %
CHA-Na,K,Cs-0.2Ca*	14.3 %
CHA-Na,K,Cs-0.2Ba*	14.7 %
CHA-Na,K	19.9 %
CHA-Na,K,Cs-0.50Al	12.8 %
CHA-Na,K,Cs-0.25Al	12.4 %
CHA-Na,K,Cs-0.5Ba	14.3 %
CHA-Na,K,Cs-1.0Ba	13.4 %
PHI-14 days	15.4 %
PHI	15.2 %

* Samples described in *Advanced Sustainable Systems* **2024**, *8* (1), 2300326.

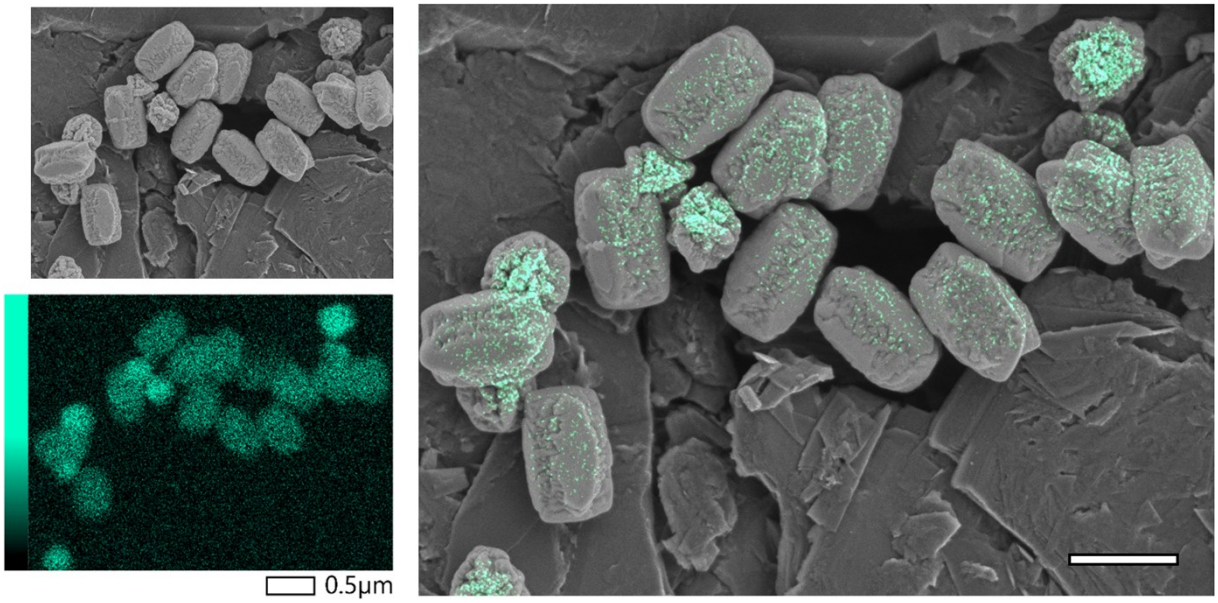


Figure S7. SEM picture and EDS mapping of caesium in the sample CHA-Na,K,Cs-0.25Al (left), overlay of the SEM and EDS pictures highlighting the greater amount of caesium in chabazite crystals (right). Scale bar is 500 nm.

Table S7. BET specific surface areas and microporous volumes of the synthesised nanozeolites from N_2 adsorption isotherms recorded at −196°C.

	BET specific surface areas (m^2/g)	Microporous volumes (cm^3/g)
CHA*	136	0.04
CHA-Na,Cs-1.3K,0.2Ba*	155	0.04
CHA-Na,Cs-1.3K,0.2Ca*	172	0.04
CHA-Na,K,Cs-0.2Ca*	290	0.07
CHA-Na,K,Cs-0.2Ba*	169	0.05
CHA-Na,K	233	0.06
CHA-Na,K,Cs-0.50Al	83	0.02
CHA-Na,K,Cs-0.25Al	24	0.00
CHA-Na,K,Cs-0.5Ba	98	0.03
CHA-Na,K,Cs-1.0Ba	66	0.02
PHI-14 days	86	0.03
PHI	60	0.00

* Samples described in *Advanced Sustainable Systems* **2024**, *8* (1), 2300326.

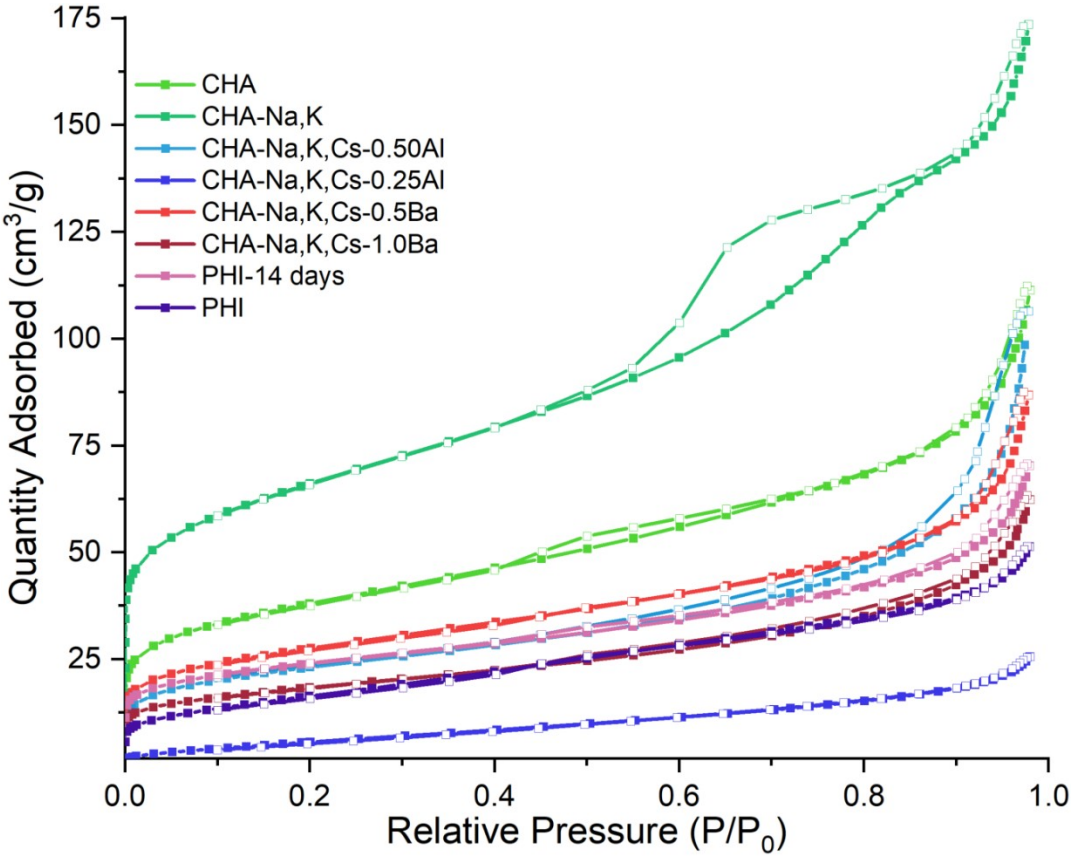
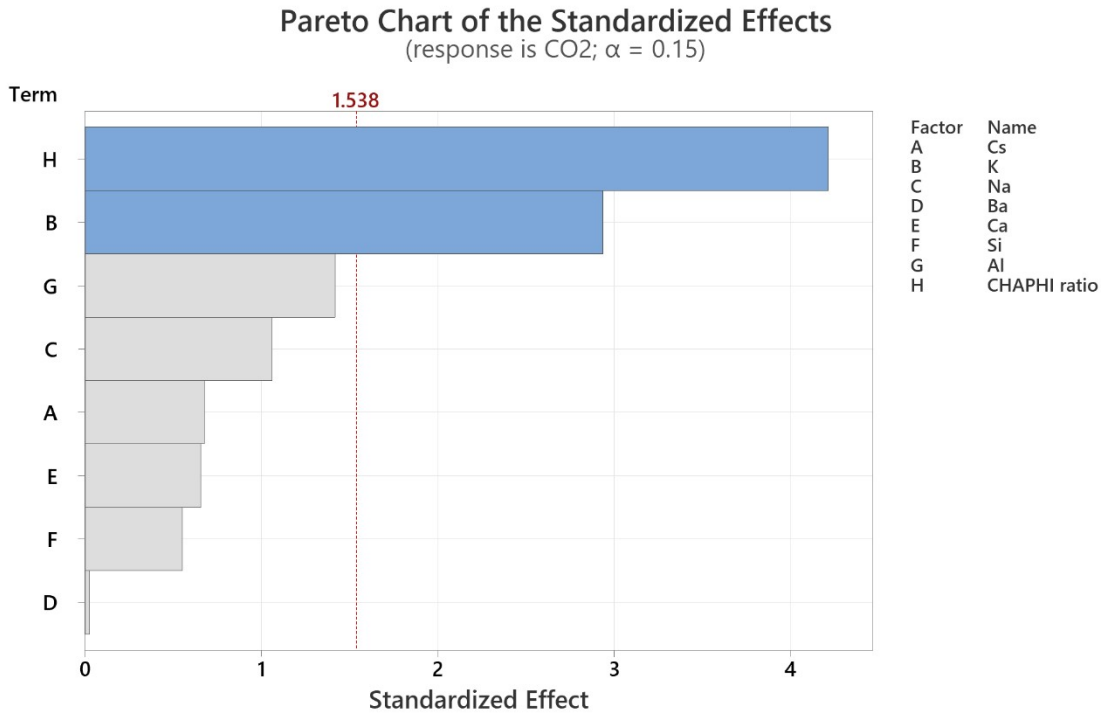


Figure S8. N_2 adsorption (full symbols) and desorption (empty symbols) isotherms of all zeolite samples measured at −196 °C.



A gray bar represents a term not in the model.

Coded Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	2.267	0.252	8.99	0.000	
K	1.275	0.434	2.93	0.013	1.13
CHAPHI ratio	1.201	0.285	4.21	0.001	1.13

Figure S9. Pareto chart of the standardised effects of elements from ICP-MS and CHA/PHI ratio from RiR method on the CO_2 adsorption capacity at 90 kPa. Based on a screening design model, parameters H and B are statistically significant at the 15% threshold (CHA/PHI ratio uncertainty) using the terms of the current model, computed by Minitab.