Supporting Information

Additive-free Synthesis of House-of-Card Faujasite Zeolite by Utilizing Aluminosilicate Gel Memory

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S1. Materials and Methods

S1.1 House-of-Card Faujasite zeolite synthesis

Example: synthesis of sample R (Fig. S4). An initial gel of composition 1 Al_2O_3:3.5 SiO_2:4 Na_2O:180 H_2O (gel A) was prepared followed by change in composition to 1 Al_2O_3:3.5 SiO_2:6 Na_2O:214 H_2O (gel B) after aging. Gel A was prepared from silica and alumina solutions as follows. The silica solution was prepared by dissolving 0.98 g NaOH in 8.8 g water before adding it dropwise to 2.46 g LUDOX® HS-40. The resulting turbid silica solution was then stirred for 5 min and heated at 80 °C in an oven until it became clear. The alumina solution was prepared by dissolving 0.87 g sodium aluminate in 4.71 g water. The prepared silica and alumina solutions were then kept in ice bath for 1 h before adding the alumina solution dropwise to the silica solution, resulting in gel A. Gel A was then aged at room temperature for 24 h while continuously stirring. Next, a solution of 0.79 g NaOH dissolved in 2.83 g water was added dropwise to gel A to modify its composition to gel B. Gel B was stirred for 1 h at room temperature before heating in an oven at 60 °C for 48 h. Finally, the product was washed several times by centrifugation and re-dispersion until the pH dropped to 7-8 and the collected solid was then dried overnight at 80 °C.

S1.2 Material characterization

X-ray Diffraction (XRD) patterns were acquired using a PANalytical X'Pert PRO MPD X-ray diffractometer, operated at 40 kV and 40 mA, equipped with a Cu source. Data was collected for 2θ range 5 -35°.

Scanning Electron Microscopy (SEM) images were collected using FEI Quanta 250 FEG scanning microscope operated at 3 kV. Samples were prepared by dusting the zeolite powder onto double sided carbon tape, mounted on an Aluminum stub. Samples were not coated. Si/Al ratios were obtained from Energy Dispersive X-ray (EDX) analysis from 4-5 different locations on the samples and the average is reported. No calibration standard was used.

Samples for Transmission Electron Microscopy (TEM) studies were prepared by applying a few drops of a zeolite suspension in ethanol onto a copper grid coated with Lacey Carbon (Agar scientific) and leaving it to dry at room temperature. TEM imaging was performed on FEI Tecnai 20 TEM operating at 200 kV. All TEM images were captured using a CCD camera.

Nitrogen adsorption (77 K) was performed using a commercially available automatic manometric sorption analyzer (Micromeritics 3-Flex). Prior to adsorption measurements, the samples were outgassed at 300 °C for 3 h under turbomolecular pump vacuum. Pore size distribution curves were calculated from the adsorption branch of the isotherm according to the MicroActive software (version 4.06) DFT kernel for Nitrogen at 77 K in cylindrical oxide surface pores. The t-plot method was employed to quantify the micropore volume and external surface area. CO_2 adsorption was also performed on the same instrument at 25 °C and up to 1 bar.

S2. Supplementary text

S2.1 Effect of Na_2O content in the synthesis sol for direct syntheses

In addition to the effect of water (presented in Fig. 1), the effect of Na_2O content in the synthesis sol was also studied for composition 1 Al_2O_3: 3.5 SiO_2: X Na_2O: 214 H_2O (Fig. S1). Slightly increasing the amount of Na_2O in the synthesis sol decreases the particle size, sheet thickness, and branching frequency (sample P). At higher amounts of Na_2O, nucleation is enhanced, and nanoparticles are formed (sample A). Despite the increase in EMT content for samples crystallized from higher Na_2O content sols, the decrease in particle size prevents the development of HCF morphology.

S2.2 Effect of aging time

For samples synthesized using a combination of trajectories, the timing of composition change can be critical. This was studied for an initial composition of 1 Al_2O_3:3.5 SiO_2: 4 Na_2O: 180 H_2O followed by change in composition to 1 Al_2O_3:3.5 SiO_2: 6 Na_2O: 214 H_2O after aging at room temperature for 0, 1, 2 and 5 days (Fig. S9). Results show that, for the composition studied, the particle size is not very sensitive to the aging time. In general, longer aging time resulted in bigger particles. It should be noted that this observation cannot be generalized; the aging time could be more important for other compositions, as observed by Khaleel at al [32]. This depends on the kinetics of the development of the initial gel structure.

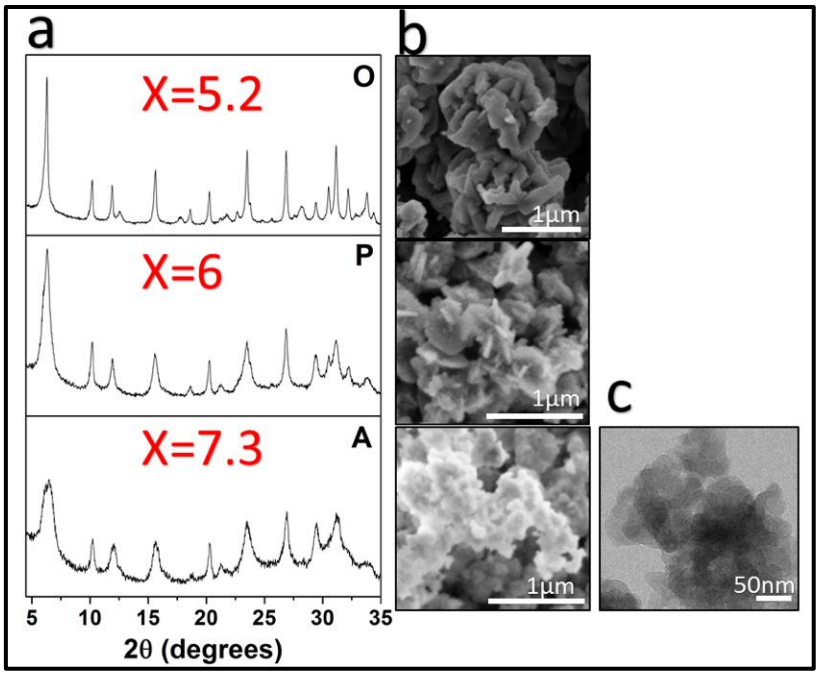

Figure S 1. a) XRD patterns, and b) SEM, and c) TEM images for samples crystallized at 60 °C from sols with compositions 1 Al_2O_3: 3.5 SiO_2: X Na_2O: 214 H_2O, where X is inset in the figure. The heating time is 2 days.

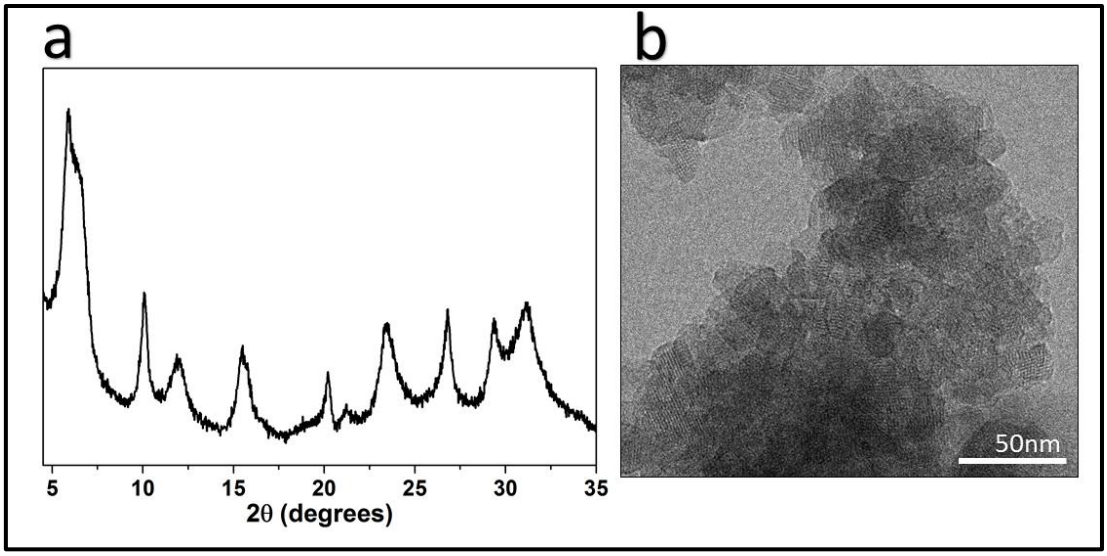

Figure S 2. a) XRD pattern and b) TEM image for sample synthesized by first mixing at 1 Al_2O_3: 3.5 SiO_2: 4 Na_2O: 180 H_2O and then changing the composition to 1 Al_2O_3:10 SiO_2: 12 Na_2O: 220 H_2O after 24h aging at room temperature. Sample is heated for 24h at 60 °C. There is no evidence of the initial gel structure in the final particle size.

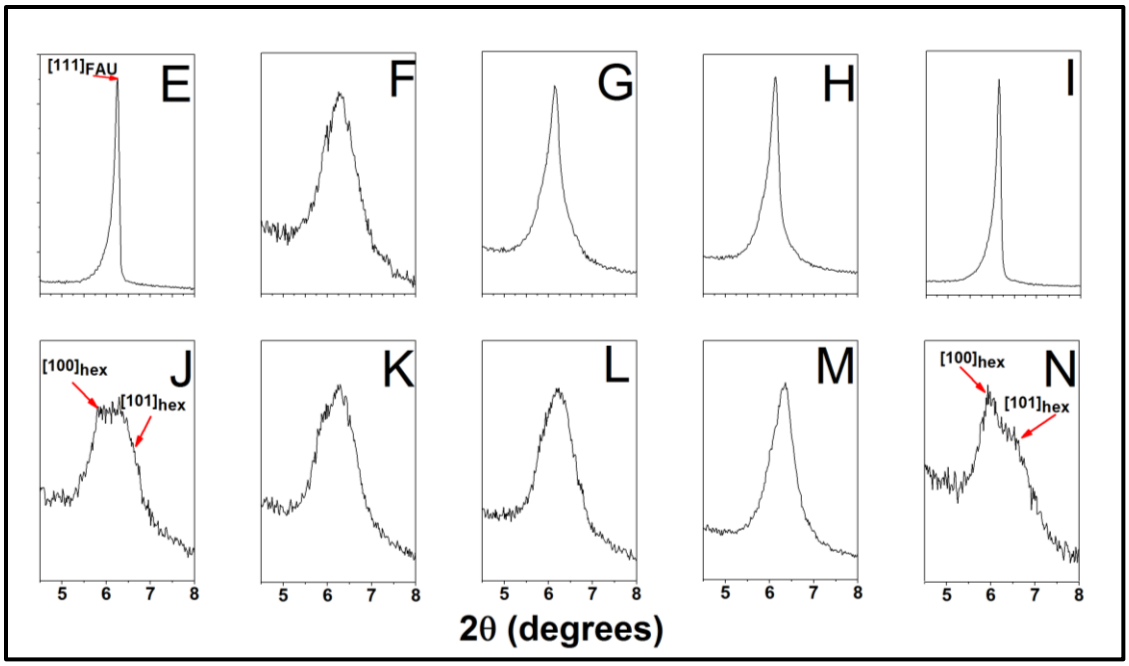

Figure S 3. Closer view at the FAU [111] peak in the XRD patterns for samples E-N presented in Fig. 2, showing the effect of synthesis mixture composition on crystallite size and faulting signified by peak broadening and the appearance of shoulder peaks (FAU/EMT intergrowths). The heating time is 5 days for sample E, 1 day for sample F, 3 days for sample G, 2 days for samples H- M, and 6 days for sample N.

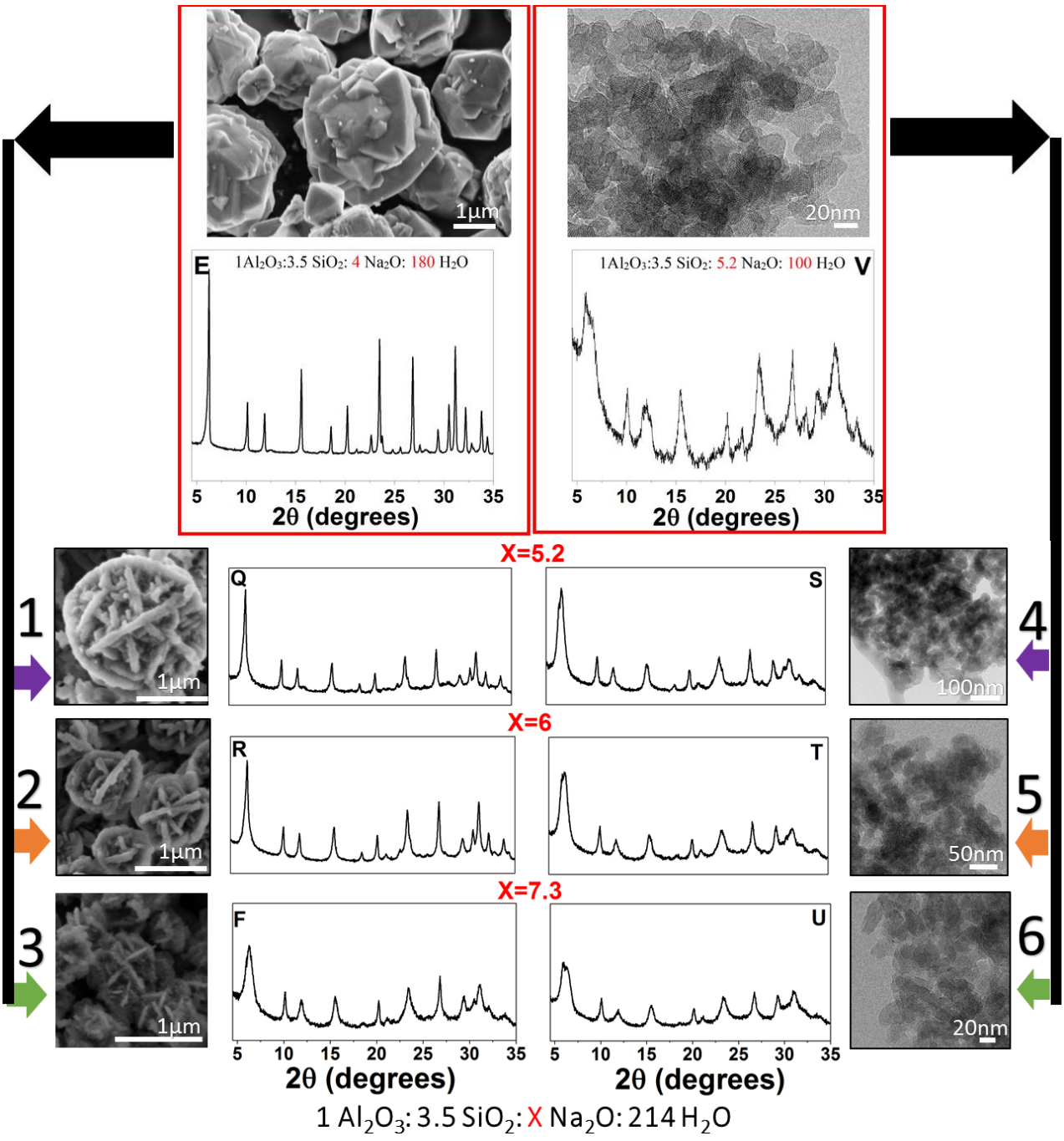

Figure S 4. XRD patterns, and SEM and TEM images for Faujasite samples crystallized at 60 °C from different combinations of trajectories with different starting and ending compositions. Samples E and V are directly synthesized from sols with compositions 1 Al_2O_3:3.5 SiO_2:4 Na_2O:180 H_2O and 1 Al_2O_3:3.5 SiO_2:5.2 Na_2O:100 H_2O, respectively. Samples F, Q and R are crystallized starting from composition 1 Al_2O_3:3.5 SiO_2:4 Na_2O:180 H_2O followed by a change in composition to 1 Al_2O_3:3.5 SiO_2:X Na_2O:214 H_2O (X: 5.2→ 7.3) after 24h aging at room temperature. Samples S, T and U are crystallized following the same procedure but starting from composition 1 Al_2O_3:3.5 SiO_2:5.2 Na_2O:100 H_2O. The heating time is 5 days for sample E, 1 day for sample F, 2 days for sample Q, 28h for sample R, 2 days for samples S-U, and 3 days for sample V.

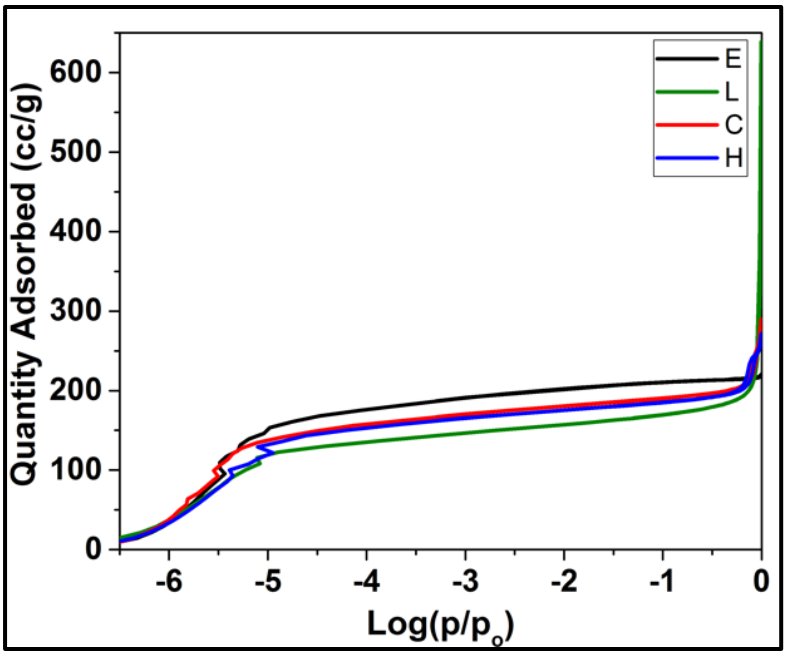

Figure S 5. Nitrogen adsorption/desorption isotherms plotted on logarithmic scale for zeolite samples prepared from compositions and trajectories shown in Fig. 1 and 2.

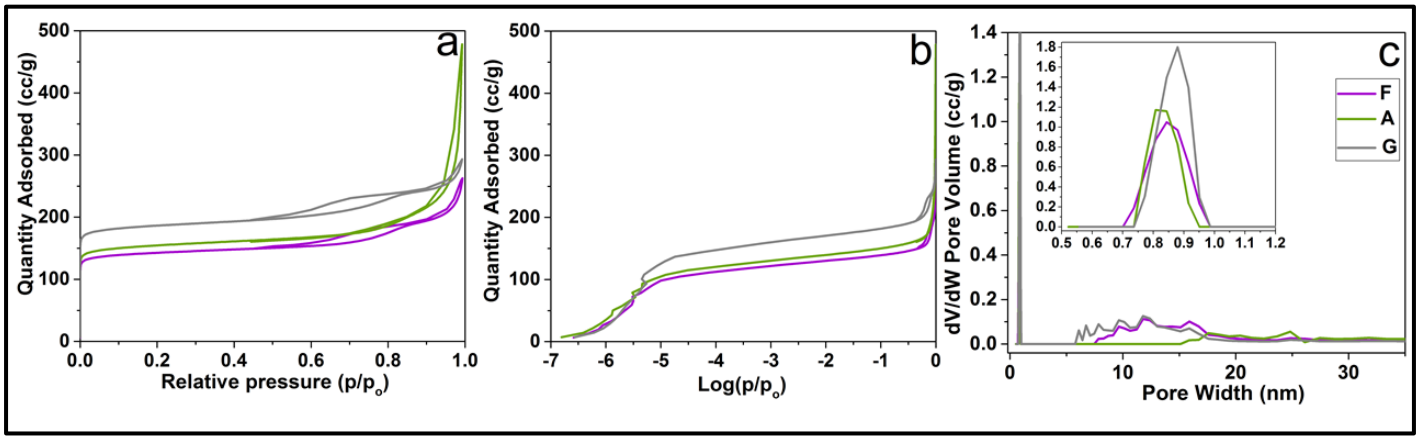

Figure S 6. Nitrogen adsorption/desorption isotherms plotted on a) linear and b) logarithmic scales, and c) pore size distributions for zeolite samples (presented in Fig. 1 and 2) prepared from direct synthesis (sample A) and a combination of trajectories (samples F and G). Using a proper combination of initial and final compositions can enhance Faujasite branching and reduce mesopore size.

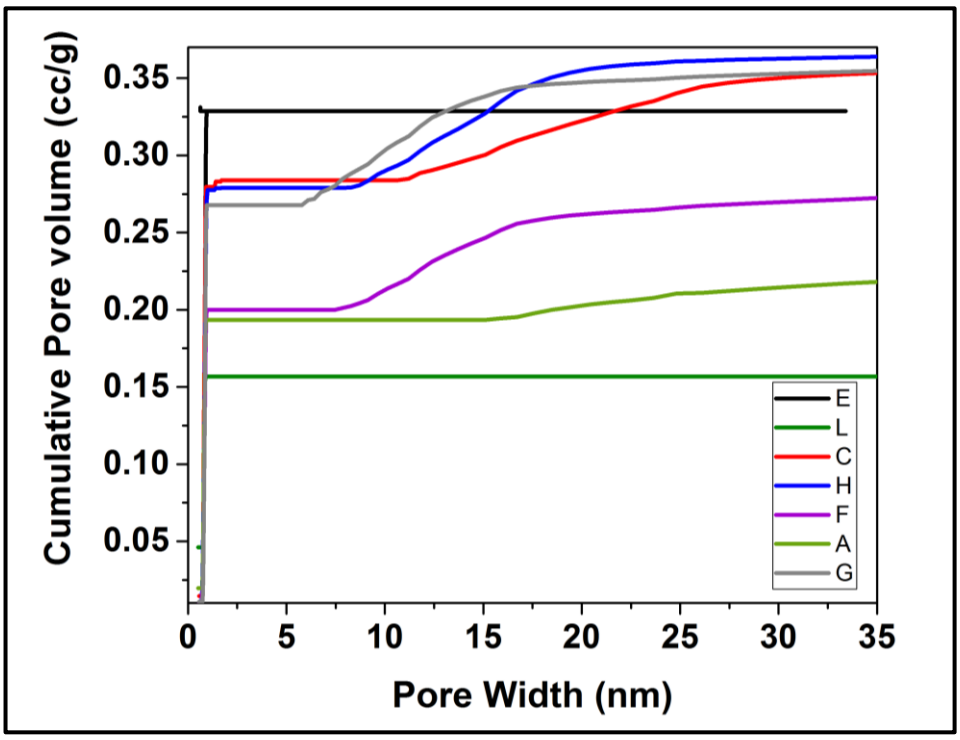

Figure S 7. Cumulative pore volumes for zeolite samples prepared from compositions and trajectories shown in Fig. 1 and 2.

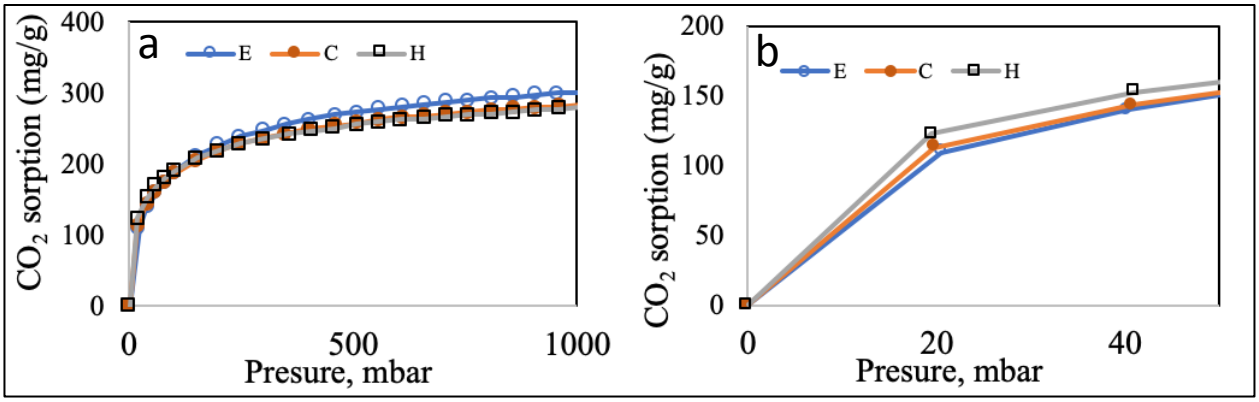

Figure S 8. CO_2 adsorption isotherms at 25 °C for samples E, C and H shown in Fig. 1 and 2.

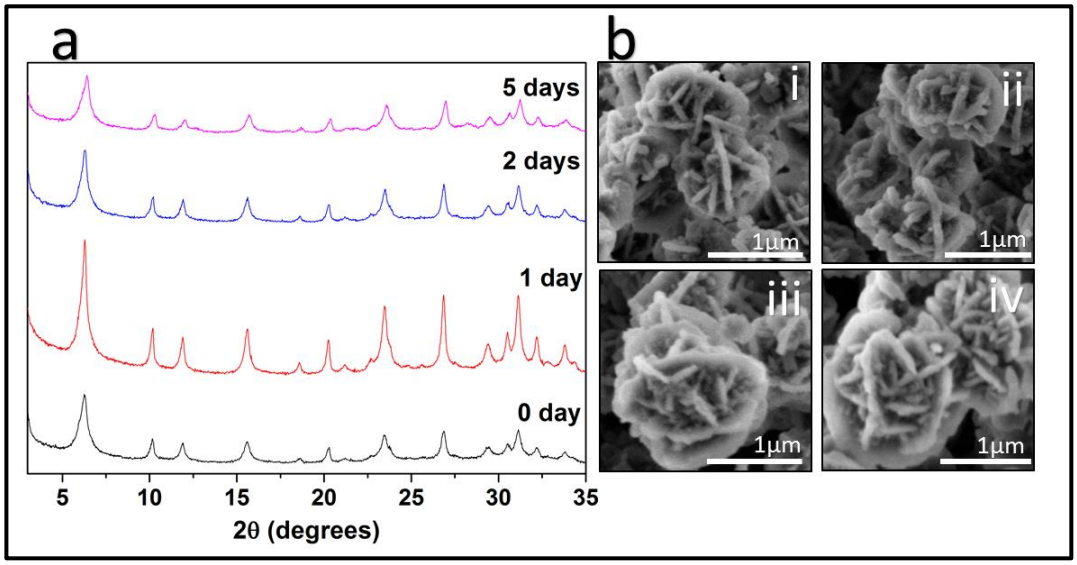

Figure S 9. a) XRD patterns and b) SEM images for zeolite samples prepared by initially mixing at 1 Al_2O_3:3.5 SiO_2: 4 Na_2O: 180 H_2O and then changing the composition to 1 Al_2O_3:3.5 SiO_2: 6 Na_2O: 214 H_2O after aging at room temperature for i) 0, ii) 1, iii) 2 and iv) 5 days. Heating duration is 28h at 60 °C.

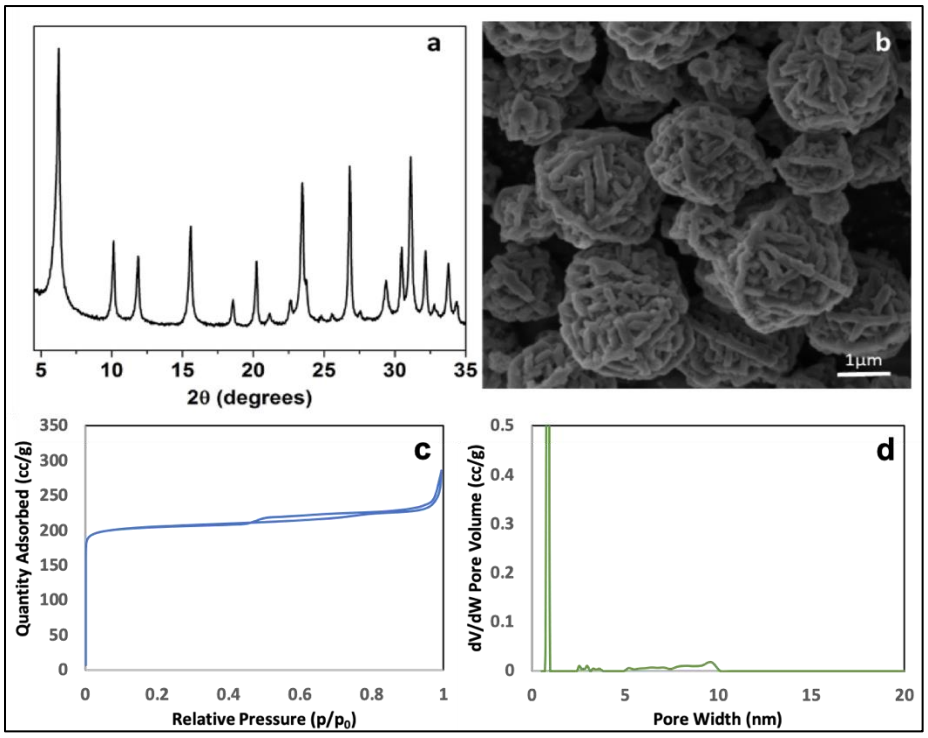

Figure S 10. a) XRD pattern, b) SEM image, c) nitrogen isotherm plotted on linear scale, and d) pore size distribution for zeolite sample crystallized by mixing the initial sol at 3.5 SiO_2: 1 Al_2O_3: 4 Na_2O: 180 H_2O, followed by aging for 24 h at room temperature, and a second aging stage for 24 h at 60 °C (no stirring), and finally modifying the composition to 3.5 SiO_2: 1 Al_2O_3: 7.3 Na_2O: 300 H_2O, and heating the sol at 60 °C for 24h. The resulting particles are bigger in size, show a higher degree of sheet interpenetration, less mesoporosity, and smaller mesopores (< 10 nm) compared to sample H (Fig. 2), which was only aged for 24 h at room temperature before changing the composition.

Table S1: A summary of the synthesis conditions for all presented samples. Aging is done at room temperature unless otherwise stated.

Sample	Initial Composition	Final Composition	Aging time (h)	Heating time (days)	Heating temperature (^oC)
A	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 214 H_2O	-	24	2	60
B	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 260 H_2O	-	24	3	60
C	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 300 H_2O	-	24	3	60
D	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 400 H_2O	-	24	3	60
E	1 Al_2O_3: 3.5 SiO_2: 4 Na_2O:180 H_2O	-	24	5	60
F	1 Al_2O_3:3.5 SiO_2:4 Na_2O:180 H_2O	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 214H_2O	24	1	60
G	1 Al_2O_3:3.5 SiO_2:4 Na_2O:180 H_2O	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 260 H_2O	24	3	60
H	1 Al_2O_3:3.5 SiO_2:4 Na_2O:180 H_2O	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 300 H_2O	24	2	60
I	1 Al_2O_3:3.5 SiO_2:4 Na_2O:180 H_2O	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 400 H_2O	24	2	60
J	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 150 H_2O	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 214H_2O	24	2	60
K	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 150 H_2O	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 260 H_2O	24	2	60
L	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 150 H_2O	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 300 H_2O	24	2	60
M	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 150 H_2O	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 400 H_2O	24	2	60
N	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 150 H_2O	-	24	6	60
O	1 Al_2O_3: 3.5 SiO_2: 5.2 Na_2O: 214 H_2O	-	24	2	60
P	1 Al_2O_3: 3.5 SiO_2: 6 Na_2O: 214 H_2O	-	24	2	60
Q	1 Al_2O_3: 3.5 SiO_2: 4 Na_2O: 180 H_2O	1 Al_2O_3: 3.5 SiO_2: 5.2 Na_2O: 214H_2O	24	2	60

R	1 Al_2O_3: 3.5 SiO_2: 4 Na_2O: 180 H_2O	1 Al_2O_3: 3.5 SiO_2: 6 Na_2O: 214 H_2O	24	28	60
S	1 Al_2O_3: 3.5 SiO_2: 5.2 Na_2O: 100 H_2O	1 Al_2O_3: 3.5 SiO_2: 5.2 Na_2O: 214H_2O	24	2	60
T	1 Al_2O_3: 3.5 SiO_2: 5.2 Na_2O: 100 H_2O	1 Al_2O_3: 3.5 SiO_2: 6 Na_2O: 214 H_2O	24	2	60
U	1 Al_2O_3: 3.5 SiO_2: 5.2 Na_2O: 100 H_2O	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 214 H_2O	24	2	60
V	1 Al_2O_3: 3.5 SiO_2: 5.2 Na_2O: 100 H_2O	-	24	3	60
Effect of temperature	1 Al_2O_3:3.5 SiO_2: 4 Na_2O: 180 H_2O	1 Al_2O_3:3.5 SiO_2: 6 Na_2O: 214 H_2O	24	2	50
				2	60
				1	70
				1	80
Effect of aging time	1 Al_2O_3: 3.5 SiO_2: 4 Na_2O: 180 H_2O	1 Al_2O_3:3.5 SiO_2: 6 Na_2O: 214 H_2O	0	28	60
			24		
			48		
			120		
Fig. S2	1 Al_2O_3:3.5 SiO_2: 4 Na_2O: 180 H_2O	1 Al_2O_3: 10 SiO_2: 12 Na_2O: 220 H_2O	24	1	60
Fig. S10	1 Al_2O_3:3.5 SiO_2: 4 Na_2O: 180 H_2O	1 Al_2O_3: 3.5 SiO_2: 7.3 Na_2O: 300 H_2O	24 h at RT followed by 24 h at 60 ^oC	1	60

Table S2: Textural properties from nitrogen isotherms for samples E, C, and H presented in Figs. 1 and 2.

Textural property	Sample E	Sample C	Sample H
Micropore volume (cc/g)	0.33	0.28	0.27
BET area (m^2/g)	874	781	759
External surface area (m^2/g)	7	52	57

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