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Framework Stabilization of Si-Rich LTA Zeolite Prepared in Organic-Free Media

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1. Materials and Methods

1.1 Zeolite Crystallization. LUDOX AS-40 colloidal silica (40%), LUDOX SM-30 colloidal silica (30%), silica fumed powder (7 nm), and sodium hydroxide (98%) were purchased from Sigma Aldrich. Sodium aluminate (technical grade) was purchased from Alfa Aesar. All reagents were used as received without further purification. All zeolite growth solutions were prepared using deionized water (DI, 18.2 MΩ) purified with an Aqua Solutions purification system (RODI-C-12A).

Zeolite growth solutions with molar compositions x SiO_2:y Al_2O_3:10 NaOH:z H_2O were prepared by first mixing sodium aluminate and sodium hydroxide in DI water. The solutions were stirred for 1 hour prior to the addition of the silica source. For these studies, LUDOX AS-40 was used unless otherwise specified. The mixture was aged for 24 hours at room temperature and then transferred to Teflon-lined stainless steel autoclaves (Parr Instruments). Syntheses were performed in a ThermoFisher Precision oven at either 65°C or 100°C. For these studies, the nominal time for hydrothermal treatment was 7 days (unless otherwise specified). The products were collected by three cycles of centrifugation and washing (with DI water) using a Sorvall RC-5B refrigerated centrifuge (13,000 rpm for 45 min). Isolation of the crystalline product was performed by filtration using a fluted VWR 410 qualitative filter membrane. Samples were dried in air at ambient conditions prior to characterization.

1.2 Zeolite Characterization. Zeolite samples were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and inductively-coupled plasma optical emission spectrometry (ICP-OES). Powder XRD patterns were collected on a Siemens D5000 X-ray diffractometer using CuKα radiation (λ = 1.54 Å) with a Ni filter. SEM microscopy was conducted with a FEI-235 Dual-Beam Focused Ion Beam microscope. Samples for SEM analysis were mounted to an aluminum stub using a conductive carbon tape, and were then coated with a layer of gold prior to analysis. EDS was conducted with a JEOL JSM 6330F Field Emission scanning electron microscope. ICP-OES was performed at the UH ICP Analytical Laboratory and Agilent Facility Center (University of Houston). Thermogravimetric analyses (TGA) were performed on a TA Q600 SDT system. Powders placed in alumina pans were heated to 800°C at 1°C/min ramp rate under N_2 flow after an isothermal step for 10 min at 30°C.

The CO_2 and N_2 adsorption isotherms of the zeolites Na-LTA and Na-HOU-2 were measured using a Micromeritics HPVA100 static volumetric analyzer at the setting temperature. Prior to the gas adsorption experiment, the zeolite samples were activated at 200 °C for a period of 12 h under vacuum and then slowly cooled down to 25 °C before admitting the gas. For low pressure (1bar) sorption experiment, 100 mbar of the gas was introduced into the sample chamber containing dehydrated zeolite for every 15 min. The volume adsorbed per gram of material was plotted against the pressure. After the desorption experiment, the material was degassed for 60 min before introducing the next set of experiments with the second gas. Similarly, high pressure sorption experiments were performed for both CO_2 and N_2 gases while monitoring the volume adsorbed per gram of zeolite sample.

2. Summary of LTA Framework Materials in the Literature

Table S1. Representative aluminosilicate materials with an LTA topology and their reported SAR values

LTA Zeolites	SAR	Reference
Linde Type A (zeolite A)	1.0	*J. Am. Chem. Soc.,* 78, 5972-5977 (1956)[1]
High silica LTA Materials (prepared with OSDA, by seeding and/or dealumination)		
ITQ-29	∞	*Nature*, 431, 287-290 (2004)[2]
UZM-9	3.5 – 6	*Stud. Surf. Sci. Catal.*, 154B, 364-372 (2004)[3]
ZK-4	1.0-1.7	*Inorg. Chem.*, 5, 1537-1539 (1966)[4]
ZK-21/22	1.1 – 1.8	*Inorg. Chem.*, 10, 2488-2495 (1971)[5]
Zeolite Alpha	3.1	US Patent 4,191,663[6] US Patent 3,375,205[7]
LTA (by seeding)	100 – 2400	*Chem. Mater.*, 19, 652-654 (2007)[8]
LTA (with OSDAs)	2 – 5	*Langmuir*, 26(3), 1910-1917 (2010)[9]

Zeotypes with an LTA-type framework have been reported in the literature. These include $AlPO_4$-LTA,[10-14] [Ge-Si]-LTA,[2] [Al-Ge-O]-LTA,[15] [Ga-P-O]-LTA,[11, 16] $[(H_2O)_4Cu_{12}S_{12}O_{48}]$-LTA,[17] and SAPO-42.[18] Several organic SDAs have been used for the synthesis of various LTA-type materials that include tetramethylammonium,[2-9] tetraethylammonium,[9] supramolecular 4-methyl-2,3,6,7-tetrahydro-1H-5H-pyrido[3.2.1-ij]quinolinium,[2, 8, 9] diethyl-dimethylammonium hydroxides,[9] diethanolamine,[10] crown ether Kryptofix 222,[11, 12] n-propylamine,[13] triquaternary imidazolinium,[14] 4-methylpyridine,[16] and polyamidoamine dendrimer.[19]

3. Powder X-Ray Diffraction (XRD)

Na-HOU-2 formation was studied at varying crystallization time at a synthesis temperature of 100 °C in order to monitor the evolution of the crystalline phase and any structural transformations to polymorphs at prolonged time. Figures S1 shows the XRD patterns of zeolites extracted at various times from a growth solution with molar composition C2. This study clearly shows a phase transformation from HOU-2 (LTA type) to gismondine (GIS type) after 7 days of heating.

The effect of the silica source on Na-HOU-2 formation was tested for three different reagents. The particle size of the amorphous silica precursor was altered by switching to a smaller colloidal silica source (LUDOX SM-30), which has an average diameter of 8 nm. Here we followed the same procedure that was used to prepare Na-HOU-2 in the presence of LUDOX AS-40 (i.e., 23 nm diameter silica particles). Figure S2 displays the XRD pattern of the FAU crystal phase that was obtained using LUDOX SM-30.

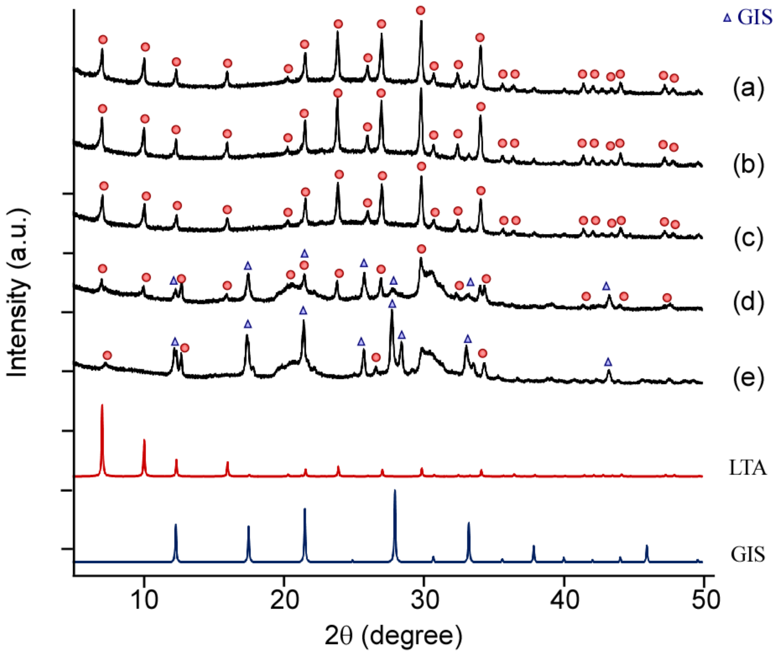

Figure S1. Powder XRD patterns of samples heated at 100°C with molar composition C2 (i.e., 18 SiO_2:3.9 Al_2O_3:5 Na_2O:173 H_2O). Samples were isolated from the synthesis solution at different crystallization times: (a) 1 day; (b) 3 days; (c) 5 days; (d) 8 days; and (e) 14 days. Simulated LTA and GIS patterns from the International Zeolite Association (IZA) database[20] are also included for identification of the crystalline phases present in the sample.

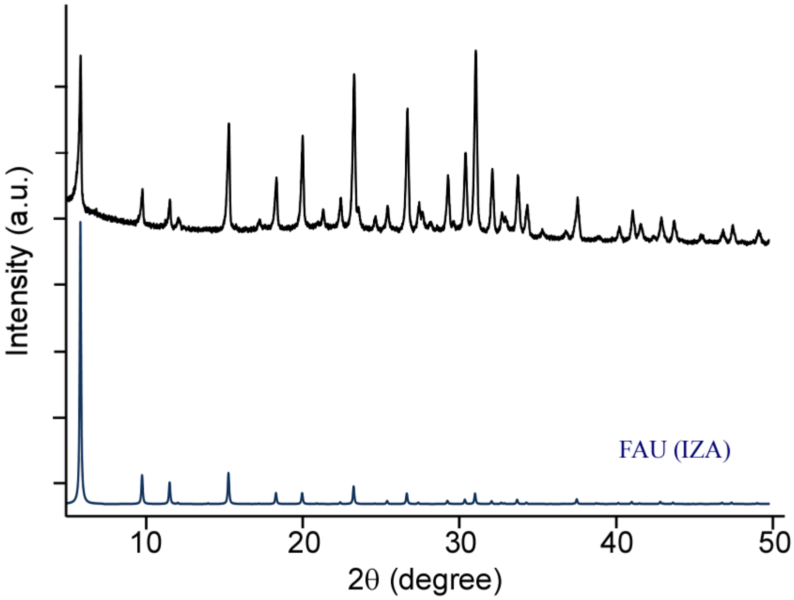

Figure S2. Powder XRD pattern of sample heated for 7 days at 100 °C with molar composition 18 SiO_2:3.9 Al_2O_3:5 Na_2O:173 H_2O using LUDOX SM-30 (8nm diameter colloidal silica). A simulated FAU pattern (bottom) from the IZA database[20] is included for identification of the crystalline phase.

4. Measuring the Chemical Composition of Na-HOU-2

4.1 Energy Dispersive Spectroscopy (EDS). The silicon-to-aluminum molar ratio (SAR) of the samples was determined using SEM-EDS. At least 30 points from five different imaging areas across the sample were measured for their Si and Al content. Figures S3 – S5 show that there is very little variation in measured Si and Al content for each sample. The samples were prepared at different water content using growth solutions with molar composition 18 SiO_2: 3.9 Al_2O_3:5 Na_2O: z H_2O ($z = 173$, 250, and 500).

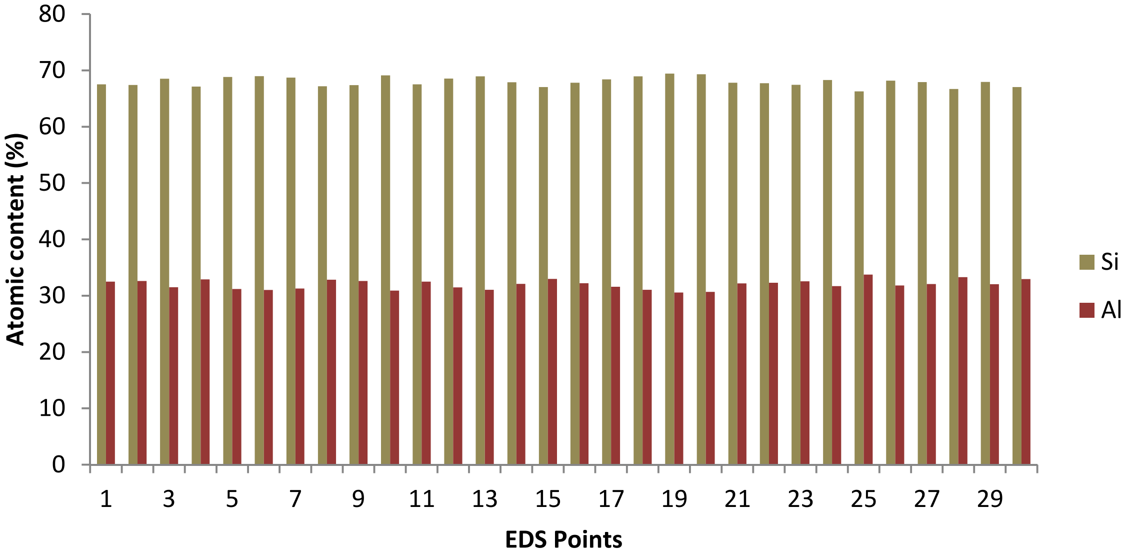

Figure S3. EDS measurements of the Si (brown) and Al (red) content of a Na-HOU-2 sample that was heated for 7 days at 100 °C with molar composition 18 SiO_2:3.9 Al_2O_3:5 Na_2O:173 H_2O. The average SAR for this experiment is 2.14 ± 0.09.

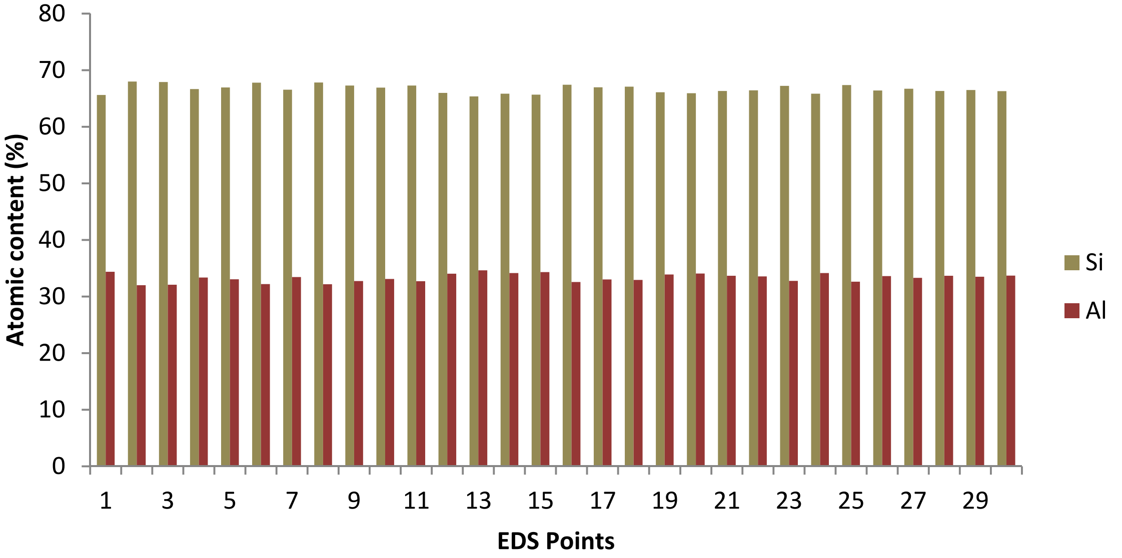

Figure S4. EDS measurements of the Si (brown) and Al (red) content of a Na-HOU-2 sample that was heated for 7 days at 100 °C with molar composition 18 SiO_2:3.9 Al_2O_3:5 Na_2O:250 H_2O. The average SAR for this experiment is 2.0 ± 0.1.

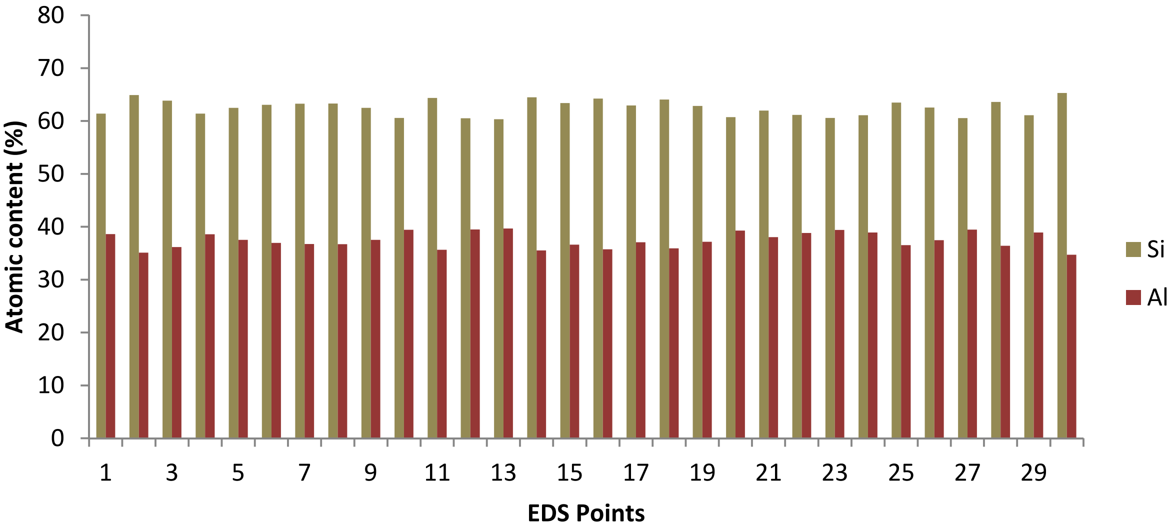

Figure S5. EDS measurements of the Si (brown) and Al (red) content of a Na-HOU-2 sample that was heated for 7 days at 100 °C with molar composition 18 SiO_2:3.9 Al_2O_3:5 Na_2O:500 H_2O. The average SAR for this experiment is 1.7 ± 0.2.

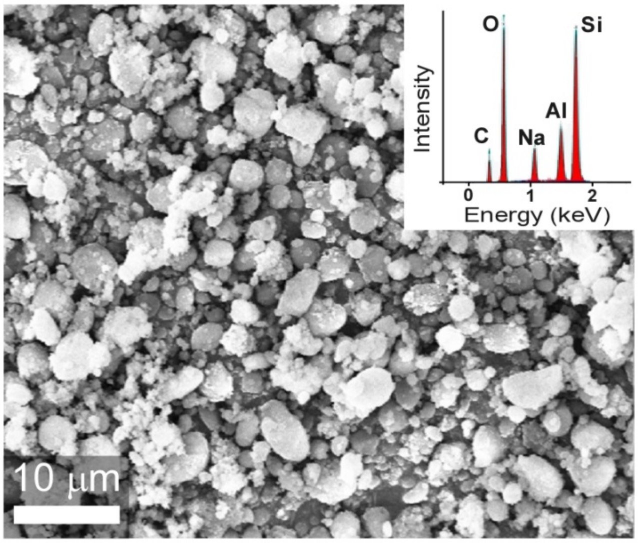

Figure S6. Scanning electron micrograph of Na-HOU-2 prepared with composition C1 (see Table 1). (inset) The representative EDS spectrum reveals that the sample has an SAR of approximately 2.

4.2 Elemental Analysis of Na-HOU-2 and Na-LTA. ICP-OES analysis was conducted to benchmark the accuracy of EDS measurements. The latter is a surface-biased technique wherein the X-rays only penetrate a certain distance into the zeolite crystals. In order to obtain the bulk SAR for Na-HOU-2 (i.e., average composition of the entire crystal) we prepared a sample for ICP-OES using composition C2 (18 SiO_2: 3.9 Al_2O_3: 5 Na_2O: 173 H_2O). This sample was heated for 7 days at 100°C and was extracted into a powder and dried in air prior to ICP-OES analysis. Table S2 shows the results of the analysis performed at the ICP Analytical Laboratory and Agilent Facility Center (University of Houston). The values obtained by EDS and ICP-OES are nearly identical.

Table S2. ICP-OES analysis of Na-HOU-2 and Na-LTA

	Na-HOU-2	Na-LTA
Si (ppm)	242650	147576
Al (ppm)	108700	152874
Si/Al (molar)	**2.14**	**1.00**

4.3 Empirical Calculation of the SAR for HOU-2. Lechert[21] provided a generalized formula to predict Si/Al ratios of zeolites based on the starting gel composition and an empirical fitting parameter *b*. This model agrees was shown to effectively estimate the composition of select zeolites, such as mordenite (MOR), beta (BEA), and OSDA-free preparation of ZSM-5 (MFI). Details of this model can be found in the original paper. Here we present the pertinent equations and a sample calculation.

For these calculations we refer to the generalized molar composition of the synthesis batch, $MAlO_2$: n ($M_mH_{4-m}SiO_4$): pH_2O, where M^{n+} is an alkali or alkaline earth cation. For Na-HOU-2 with a composition of $NaAlO_2$: 2.308 ($Na_{0.1222}H_{3.8778}SiO_4$) : 173 H_2O (compositions C1 and C2) the following equations were used to estimate the SAR of the crystalline product.

$$Free\ hydroxide\ m = \frac{[MeOH]-[MeAlO_2]}{[SiO_2]} = 0.1222 \qquad (S1)$$

$$SAR_{initial\ batch}\ n = \frac{Si}{Al} = 2.308 \qquad (S2)$$

$$Fitting\ paramter\ (empirically\ derived), b\ \approx 2 \qquad (S3)$$

$$Estimated\ SAR_{product} \approx \frac{(b+m)n}{(b+nm)} \approx 2.146 \qquad (S4)$$

5. Thermogravimetric Analysis and Gas Adsorption

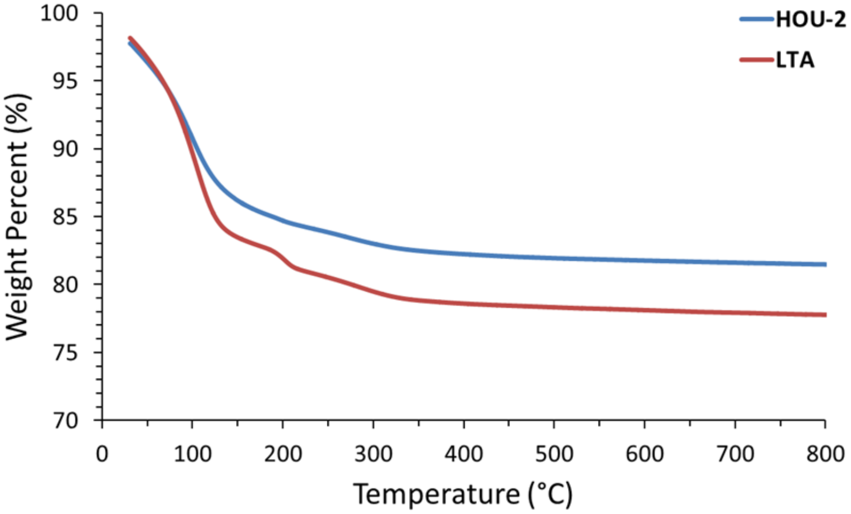

Figure S7. TGA curves showing fractional weight loss for as synthesized HOU-2 and LTA samples.

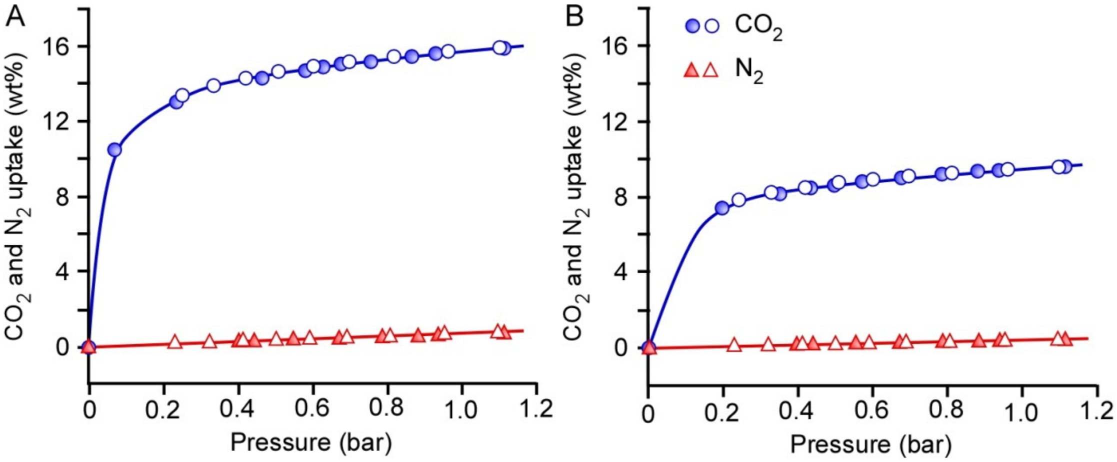

Figure S8. Gas sorption studies for (A) Na-LTA (SAR = 1.0) and (B) Na-HOU-2 (SAR = 2.1) at low pressure. Experiments were performed separately with CO_2 (blue) and N_2 (red). The adsorption data (closed symbols) and desorption data (open symbols) show no evidence of hysteresis. This data was converted to mol CO_2 per mol Al using the molecular weight for a single binding site in Na-LTA ($NaSiAlO_4$, Mw = 142 g/mol) and Na-HOU-2 ($NaSi_{2.1}AlO_{6.2}$, Mw = 208 g/mol).

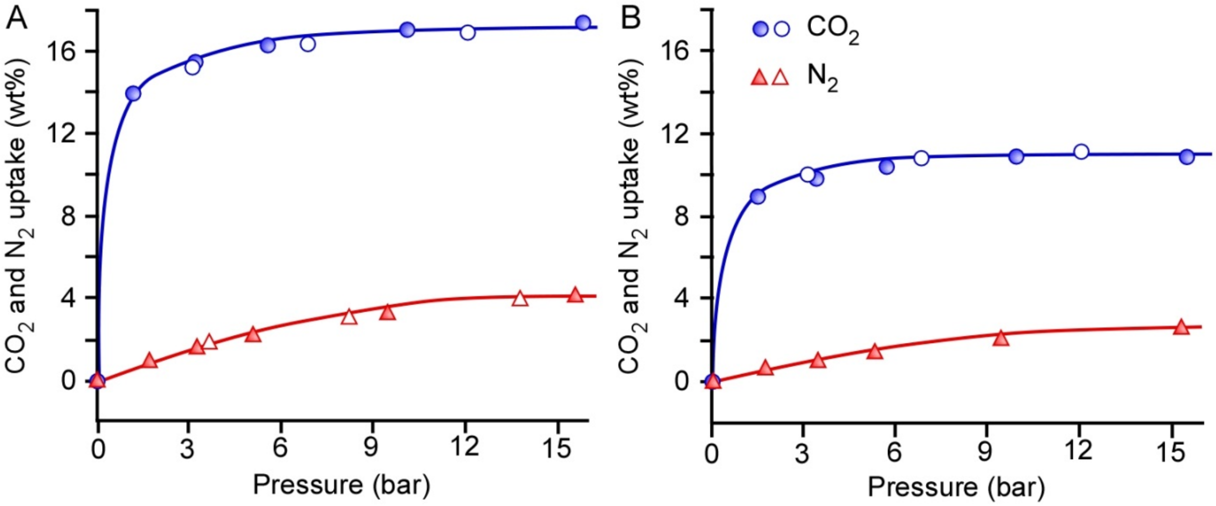

Figure S9. Gas sorption studies for (A) Na-LTA (SAR = 1.0) and (B) Na-HOU-2 (SAR = 2.1) at high pressure. Experiments were performed separately with CO_2 (blue) and N_2 (red). The adsorption data (closed symbols) and desorption data (open symbols) show no evidence of hysteresis.

6. Supporting References

1. D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, *J Am Chem Soc*, 1956, **78**, 5963-5971.
2. A. Corma, F. Rey, J. Rius, M. J. Sabater and S. Valencia, *Nature*, 2004, **431**, 287-290.
3. G. J. Lewis, M. A. Miller, J. G. Moscoso, B. A. Wilson, L. M. Knight and S. T. Wilson, *Stud Surf Sci Catal*, 2004, **154**, 364-372.
4. G. T. Kerr, *Inorg Chem*, 1966, **5**, 1537-1539.
5. G. H. Kuhl, *Inorg Chem*, 1971, **10**, 2488-2495.
6. *United States Pat.* 4 191 663, 1980.
7. *United States Pat.* 3 375 205, 1968.
8. Y. Bouizi, J. L. Paillaud, L. Simon and V. Valtchev, *Chem Mater*, 2007, **19**, 652-654.
9. M. Palomino, A. Corma, F. Rey and S. Valencia, *Langmuir*, 2010, **26**, 1910-1917.
10. L. Sierra, C. Deroche, H. Gies and J. L. Guth, *Microporous Mater*, 1994, **3**, 29-38.
11. A. S. Huang and J. Caro, *Micropor Mesopor Mat*, 2010, **129**, 90-99.
12. L. Schreyeck, F. Dagosto, J. Stumbe, P. Caullet and J. C. Mougenel, *Chem Commun*, 1997, 1241-1242.
13. X. T. Xu, J. P. Zhai, Y. P. Chen, I. L. Li, H. Y. Chen, S. C. Ruan and Z. K. Tang, *J Cryst Growth*, 2014, **407**, 1-5.
14. J. E. Schmidt, S. I. Zones, D. Xie and M. E. Davis, *Micropor Mesopor Mat*, 2014, **200**, 132-139.
15. R. M. Barrer, J. W. Baynham, F. W. Bultitude and W. M. Meier, *J Chem Soc*, 1959, 195-208.
16. F. S. Yu, C. Y. Xi, H. M. Yuan and J. S. Chen, *Studies in Surface Science and Catalysis*, 2001, **135**, 1680-1687.
17. X. J. Zhang, Y. H. Xing, J. Han, M. F. Ge and S. Y. Niu, *Z Anorg Allg Chem*, 2007, **633**, 2692-2694.
18. B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannan and E. M. Flanigen, *J Am Chem Soc*, 1984, **106**, 6092-6093.
19. L. Bonaccorsi, D. Lombardo, A. Longo, E. Proverbio and A. Triolo, *Macromolecules*, 2009, **42**, 1239-1243.
20. International Zeolite Association, www.iza-online.org.
21. H. Lechert, *Micropor Mesopor Mat*, 2000, **40**, 181-196.