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Electronic Supplementary Information

An ethylenediamine-grafted Y zeolite: a highly regenerable carbon dioxide adsorbent via temperature swing adsorption without urea formation

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Synthesis of ETS-10

For the synthesis of ETS-10, colloidal silica was used as a Si source, and titanium oxide was used as a Ti source. 2.0 g TiO₂ was dispersed in 25.3 g distilled water, to which 3.0 g NaOH and 1.1 g KF were added. After 1 h stirring, 18.8 g colloidal silica was added into the mixture while stirring vigorously. The stirring was continued for 6 h. The solution was transferred into a Teflon-lined autoclave, and heated at 215 °C for 72 h under static condition. After cooling the autoclave to room temperature, the crystals were collected by centrifugation at 3600 rpm and washed with distilled water.

Synthesis of SGU-29

For the synthesis of SGU-29, 6.6 g of sodium silicate solution (10.6 % Na₂O, and ~26.5% SiO₂, Sigma-Aldrich) was mixed with 0.2 g NaOH, 2.0 g KCl, 3.1 g NaCl and 10.0 g of distilled water. Cu precursor solution was prepared by dissolving 1.5 g CuSO₄ and 0.2 g H_2SO_4 in 5.0 g distilled water. The Cu solution was added dropwise into the Si precursor solution with vigorous stirring and aged at room temperature for 15 h. The pH of the resulting solution was controlled to 10.2. Small amount of ETS-10 seed, ~ 17 mg was added to the solution and the mixture was transferred into a Teflon-lined autoclave, and heated at 230 °C for 24 h under static condition. After cooling the autoclave to room temperature, the crystals were collected by centrifugation at 3600 rpm and washed with distilled water. The resultant zeolite was ion exchanged in 1 M NaCl solution for 2 h at 70 °C. Subsequently it was filtered and washed with distilled water. The ion exchange was repeated three times.

Note: For the synthesis of the SGU-29 sample, pre-made ETS-10 is used as a seed crystal (they share closely related crystal structures). For the ETS-10 synthesis, in the present work, we used a hydrothermal synthesis method which was reported in earlier work (Ref. 54, Xinsheng Liu and J. Kerry Thomas, *Chem. Commun.*, 1996, 1435–1436), as the method used in the Ref. 41 is not easily reproduced (sensitive to the batch size and impurities). For the SGU-29 crystallization step, we used a gel composition almost identical to that reported in Ref. 41 (we slightly decreased the amount of NaOH to increase the phase purity). We used the 1.00SiO₂: 5.78Na₂O: 2.50K₂O: 1.11CuO: 199.0H₂O gel composition (1.00SiO₂: 5.82Na₂O: 2.50K₂O: 1.11CuO: 199.0H₂O was originally reported in the Ref. 41).

Characterization of ETS-10 and SGU-29

For the characterization of ETS-10 and SGU-29 zeolites, scanning electron micrographs were obtained using a HITACHI S-4700 (Hitachi, Japan) operating at 25 kV after Pt coating. Elemental analysis was performed with an energy dispersive X-ray microanalyser (Oxford, England). The powder X-ray diffraction (XRD) spectra were recorded using a D/MAX Ultima III (Rikagu, Japan), operated at 40 kV and 40 mA with Cu K α radiation, for determination of phase purity and the crystallinity of the sample. Data were collected with a fixed divergence slit (0.50°) and Soller slits (incident and diffracted = 0.04 rad). N₂ BET adsorption-desorption isotherm was measured at -196 °C three times in order to ensure the reliability using both ASAP2020 instrument (Micromeritics) and Belsorp-Mini II instrument (BEL, Japan), after the sample was evacuated for 4 h at 300 °C.

Material	EDA-Y
Unit cell composition	
Chemical analysis	Na _{12.6} EDA _{40.1} [Si ₁₃₇ Al _{54.9} O ₃₈₄]
Refined structure	Na _{12.1} EDA _{47.1} (H ₂ O) ₂₆₉ [T ₁₉₂ O ₃₈₄]
Crystal system	Cubic
Space group	Fd ³ m (No. 227)
Cell parameters, a (Å)	24.6923(4)
Cell volume (Å ³)	15055.1(5)
Diffractometer	Rigaku D/MAX Ultima 3
Diffraction geometry	Bragg-Brentano
X-ray source	Cu K _{1,2} radiation (1.5046, 1.5441 Å)
2θ scan range (°)	2 – 100
Scan step size (°)	0.02
Duration time per step (sec)	10
Data collection temperature (°C)	25
Number of contributing reflections	413
Number of structural parameters	56
Number of geometric restraints	4
Profile function	pseudo-Voigt/FCJ Asym
R _p (%)	9.59
R _{wp} (%)	10.61
Goodness of Fit	1.21

 Table S1 XRD data collection and crystallographic parameters for EDA-Y.

atom	X	У	Z	occupancy	U _{iso} (Ų)	multiplicity
Si1	0.0356 (2)	0.1242 (2)	0.3048 (2)	1	0.0210 (9)	192
01	0.0000	0.3932 (3)	0.6068 (3)	1	0.0171 (14)	96
O2	0.3235 (3)	0.3235 (3)	0.0275 (4)	1	0.0171 (14)	96
O3	0.2508 (3)	0.2508 (3)	0.1470 (4)	1	0.0171 (14)	96
O4	0.0679 (3)	0.0679 (3)	0.3215 (4)	1	0.0171 (14)	96
Na1	0.2500	0.2500	0.00000	0.3916	0.051 (13)	16
Na2	0.0840 (20)	0.1660 (20)	0.0840 (20)	0.1801	0.051 (13)	32
Ow1	0.7153 (5)	0.3241 (5)	-0.0095 (8)	0.5207	0.105 (7)	192
Ow2	0.9870 (7)	0.9427 (11)	0.2630 (7)	0.4961	0.105 (7)	96
Ow3	0.6379 (8)	0.6121 (8)	0.6121 (8)	0.5445	0.105 (7)	32
Ow4	0.1250	0.1250	0.0577 (19)	0.4173	0.105 (7)	48
Ow5	1.0040 (2)	1.0040 (2)	0.2460 (20)	0.2655	0.105 (7)	32
Ow6	0.0772 (8)	0.0772 (8)	0.0772 (8)	0.6387	0.105 (7)	32
Ow7	0.7620 (19)	0.2620 (19)	-0.0120 (19)	0.3360	0.105 (7)	32
Ow8	0.9841 (6)	0.8860 (8)	0.2659 (6)	0.8209	0.127 (9)	96
			TLS refinement ^a			
N1a	0.595 (8)	0.696 (4)	0.8320 (11)	0.283 (3)	0.248 (16)	192
C1a	0.584 (3)	0.658 (3)	0.7879 (11)	0.283 (3)	0.248 (16)	192
C2a	0.635 (3)	0.625 (3)	0.7758 (11)	0.283 (3)	0.248 (16)	192
N2a	0.623 (8)	0.587 (4)	0.7316 (11)	0.283 (3)	0.248 (16)	192

Table S2 Atomic coordinates, displacement, and population parameters for EDA-Y.

^aEthylenediamine was initially considered as a rigid body, and then it was subjected to the TLS refinement because of the low electron density and also the limited number of contributing reflections.

 Table S3 Selected bond lengths for EDA-Y.

Bond length (Å)			
Si1-O1	1.626 (7)		
Si1-O2	1.732 (8)		
Si1-O3	1.691 (9)		
Si1-O4	1.654 (9)		
O1-N1a	2.34 (11)		
O4-N1a	2.50 (6)		
N1a-C1a	1.47 (9)		
C1a-C2a	1.49 (10)		
C2a-N2a	1.47 (9)		
N2a-N2a	3.21 (10)		
N2a-N2a	3.32 (10)		

Table S4 Elemental analysis results of ETS-10 and SGU-29 by SEM-EDX.^a

ETS-10		SGU-29		
Element	Atomic%	Element	Atomic%	
Na	5.73±0.54	Na	5.36±0.56	
Ti	6.89±1.04	Cu	6.53±0.85	
Si	26.18±2.26	Si	26.42±1.64	
к	2.65±0.52	к	2.95±0.46	
О	58.55±3.04	Ο	58.74±2.31	

^a The obtained elemental compositions for ETS-10 and SGU-29 were $Na_{1.10}K_{0.51}Ti_{1.32}Si_5O_{14.2}$ and $Na_{1.02}K_{0.55}Cu_{1.24}Si_5O_{14.1}$, respectively based on the cation content.

Material	ETS-10	SGU-29	
Crystal system	Monoclinic	Monoclinic	
Space group	C2/c (No. 15)	<i>C2/c</i> (No. 15)	
Cell parameters, a (Å)	21.1593 (4)	21.6071 (13)	
b (Å)	21.1523 (4)	21.5168 (12)	
c (Å)	14.6424 (6)	14.4443 (8)	
β(°)	111.2162 (33)	110.4094 (29)	
Cell volume (Å ³)	6109.3 (4)	6293.8 (6)	
Diffractometer	Rigaku D/MAX Ultima 3		
Diffraction geometry	Bragg-Brentano		
X-ray source	Cu K _{1,2} radiation		
2θ scan range (°)	2 – 100		
Scan step size (°)	0.02		
Duration time per step (sec)	10		
Collection temperature (°C)	25		
Profile function	pseudo-Voigt/FCJ Asym pseudo-Voigt/FCJ Asyr		
R _p (%)	6.51	4.84	
R _{wp} (%)	9.37	8.95	

Table S5 Results of profile refinement for ETS-10 and SGU-29.

Table S6 Comparison of the CO₂ uptake amounts under a wet flue gas (15% CO₂, 3% H₂O, and N₂ balance at 40 $^{\circ}$ C), measured by two different experimental setups.

	EDA-Y	PEI/SiO ₂	NaX	ETS-10	SGU-29
CO ₂ uptake (mmol g ⁻¹ , TGA-MS)	1.6	3.3	0.23	0.17	0.18
CO ₂ uptake (mmol g ⁻¹ , breakthrough)	1.5	3.5	0.21	0.17	0.16



Fig. S1 ¹³C CP-MAS solid-state NMR spectra of EDA-Y with different temperatures (25 and -90 °C).



Fig. S2 N₂ adsorption-desorption isotherms of ETS-10 (red) and SGU-29 (blue) obtained at -196 $^{\circ}$ C. The isotherm for SGU-29 was offset by 100 cm³ g⁻¹.



Fig. S3 Scanning electron micrographs of (a) SGU-29 [from the reference 41] (b) ETS-10, and (c, d) SGU-29 crystals synthesized in the present work.



Fig. S4 Powder X-ray diffraction patterns of (a) as-made ETS-10 and (b) SGU-29.



Fig. S5 Schematic diagram of the thermogravimetric analyser (Sinco, TGA N1500) combined with a mass spectrometer (Pfeiffer Vacuum, Omnistar GSD 320). The temperature of water-saturator was maintained at 25 °C.

Measurement of CO₂ and H₂O uptakes using a TGA-MS setup

The water concentration of incoming gas stream was calibrated with a high-sensitivity humidity sensor (EE31, E+E Electronik). The absolute humidity of the H_2O -saturated gas stream was in the range of 3.0 - 3.1% when the external temperature of water-saturator was set to 25 °C. Because the water-saturator was set to 25 °C which is close to room temperature, water condensation in the lines could be minimized. All the tubing located after the water-saturator was wrapped with heating tape and gently heated to inhibit water condensation. To obtain a stable MS signal, the MS system was stabilized at least for 1 day after turning it on, before starting the CO₂ adsorption measurements. After the stabilization, MS signals of H₂O and Ar showed highly reliable cyclic patterns over 20 consecutive TSA cycles (adsorption: 15% CO₂, 3% H₂O, 2% Ar, and N₂ balance at 40 °C/ desorption: 100% CO₂ at 130 °C) without significant fluctuations (Fig. S6). Ar was used as an internal standard because its adsorption on the adsorbents is negligible. Integration of peak area for H₂O can be carried out from the time of the Ar breakthrough in the MS signal (Ar was also used to find t=0). The difference in H₂O signals with and without an adsorbent (an empty sample pan was used) is due to the adsorption/desorption of H₂O by the adsorbent. The integrated blue area (Fig. S7a) was used for calculating the amount of adsorbed H₂O amount during the adsorption condition, and the integrated red area was used for calculating the amount of desorbed H₂O amount during the desorption condition. The plot of the integrated area (i.e., adsorbed/desorbed H₂O amount) vs the time gives time-dependent H₂O adsorption-desorption profiles (blue line in Fig. S7b). TGA can detect the overall mass change of adsorbent due to the uptake of both H₂O and CO₂ (grey line). Therefore, if the H₂O adsorption-desorption profiles determined from MS signal (blue line) is subtracted from the overall mass change profiles determined from TGA (grey line), the CO₂ adsorption-desorption profiles (red line) can be determined.



Fig. S6 Mass signal profiles of H₂O (m/z=18) and Ar (m/z=40) obtained without an adsorbent (using an empty sample pan) over 20 consecutive TSA cycles (adsorption: 3% H₂O, 15% CO₂, 2% Ar and N₂ balance at 40 °C/ desorption: 100% CO₂ at 130 °C).



Fig. S7 (a) MS signal profiles of H_2O (*m/z*=18) and Ar (*m/z*=40) in the TSA cycle with a wet flue gas (adsorption: 3% H_2O , 15% CO_2 , 2% Ar, and N_2 balance at 40 °C/ desorption: 100% CO_2 at 130 °C) in the presence and absence of an adsorbent (EDA-Y). (b) Gas uptake curves measured using a TGA-MS setup. The overall mass increase of an adsorbent by the adsorptions of both CO_2 and H_2O was measured using a TGA. H_2O uptake was calculated from the MS profile as demonstrated in (a). The adsorbed amount of CO_2 can be selectively calculated by subtracting the adsorbed amount of H_2O from the overall mass change due to the adsorptions of CO_2 and H_2O .



Fig. S8 Schematic diagram of the breakthrough experimental setup equipped with TCD detector (Autochem II 2920). CO_2 adsorption was carried out using a simulated wet flue gas containing 15% CO_2 , 3% H₂O and N₂ balance at 40 °C. The temperature of water-saturator was maintained at 25 °C.



Fig. S9 CO_2 concentration profiles of the outlet gas stream in the presence (solid line) and the absence (dashed line) of an adsorbent measured by TCD detector of the breakthrough equipment (Fig. S8).



Fig. S10 CO₂ uptake profiles of the adsorbents under a wet flue gas (3% H₂O, 15% CO₂, and N₂ balance, 40 °C), measured with the breakthrough experimental setup shown in Fig. S8. The profiles for NaX, ETS-10, and SGU-29 were offset by 4, 5, and 6 mmol g⁻¹, respectively.



Fig. S11 CO₂ (solid line) and H₂O (dashed line) uptake profiles of (a) EDA-Y, (b) NaX, (c) ETS-10 and (d) SGU-29 under a wet flue gas (3% H₂O, 15% CO₂, 2% Ar, and N₂ balance, 40 °C), which were measured with TGA-MS.



Fig. S12 CO₂ adsorption-desorption profiles of adsorbents (a) without pre-humidification (identical to Fig. 5a in the main text) and (b) with pre-humidification in the first TSA cycle with a wet flue gas (adsorption: 3% H₂O, 15% CO₂, 2% Ar, and N₂ balance at 40 °C/ desorption: 100% CO₂ at 130 °C). The profiles for NaX, ETS-10, and SGU-29 were offset by 4, 5, and 6 mmol g⁻¹, respectively.



Fig. S13 CO_2 adsorption-desorption profiles of EDA-Y (a) without pre-humidification (identical to Fig. 6a in the main text) and (b) with pre-humidification with 3% H₂O over 20 consecutive TSA cycles with a wet flue gas (adsorption: 3% H₂O, 15% CO₂, 2% Ar, and N₂ balance at 40 °C/ desorption: 100% CO₂ at 130 °C).



Fig. S14 Cyclic CO₂ working capacities of EDA-Y under TSA cycles with a dry flue gas (adsorption: 15% CO₂, 2% Ar and N₂ balance at 40 °C/ desorption: 100% CO₂ at 130 °C).



Fig. S15 Temperature-programmed desorption (TPD) profiles of (a) CO_2 and (b) H_2O . For the TPD experiments, EDA-Y is activated under N_2 flow (50 cm³ min⁻¹) for 2 h at 130 °C. After the temperature is reduced to 40 °C, the gas flow was switched to pure CO_2 (50 cm³ min⁻¹) or 3% H_2O/N_2 (50 cm³ min⁻¹) and kept for 30 min for the adsorption step. Desorption was carreid out under pure N_2 (50 cm³ min⁻¹) with a temperature ramp of 5 °C min⁻¹). All of the initially adsorbed CO_2 and H_2O could be fully desorbed at temperatures higher than 130 °C, inidicating that the adsorptions of both CO_2 and H_2O are completely reversible.



Fig. S16 CO₂ uptake profiles of pre-humidified (a) MEA/NaX and (b) TEPA/NaX under a wet flue gas (15% CO₂, 3% H₂O balanced with N₂). Profiles for as-synthesized MEA/NaX and TEPA/NaX samples are shown in solid lines, and those for the samples after prolonged thermal treatment (130 °C, 24 h under N₂ flow) are shown in dashed lines.