Supplementary Information for
Confinement Effects Facilitate Low Concentration Carbon Dioxide Capture with Zeolites

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Supplementary Information Text

S1. Chemicals

All materials for synthesizing zeolites were used as-received without further purifications from the stated vendors. The moisture contents of the solid sources were determined by thermogravimetric analysis (TGA). Ludox-AS40 (40 wt% silica dispersed in water, Sigma-Aldrich), fumed silica (Cab-O-sil M-5, Sigma-Aldrich), tetraethyl orthosilicate (TEOS, 99+%, Alfa Aesar, Lot R31E031) were used as silica source. The aluminum source was sodium aluminum oxide (tech., Alfa Aesar, Lot Q07G052). The organic structure-directing agents (OSDAs) were: pyrrolidine (99%, Aldrich), piperidine (99%, Sigma-Aldrich), pyridine (99.8%, anhydrous, Sigma-Aldrich) azepane (99%, Sigma-Aldrich), piperazine (99%, Sigma-Aldrich), 1,4-diazabicyclo[2,2,2]octane (DABCO, ≥99%, Sigma-Aldrich), 4-methylpiperidine (98+, Alfa Aesar), tetramethy lammonium hydroxide (25 wt% in water, Sigma-Aldrich), tetraethylammonium hydroxide (35 wt% in water, Alfa Aesar), tetrabutylammonium bromide (TBABr, 99+%, Acros Organics). The alkaline aqueous solution was NaOH (50 wt%, Sigma-Aldrich). The salt used for ion exchange was sodium nitrate (high purity, 99%, VWR). The gases used were all from Airgas Inc.: 400 ppm CO2/400 ppm Ar (internal standard)/He, 400 ppm CO2/20% O2/ 1% Ar (internal standard)/N2, CO2 (ultrahigh purity), He (ultrahigh purity), Ar (ultrahigh purity).

S2. Synthesis of materials

MOR-type zeolites. MOR-type zeolites with Si/Al=6.5 (CBV10A, Zeolyst) were used as received.

MOR-type zeolites with Si/Al=5 were synthesized by modifying the recipe reported in (1) using different OSDAs. Typically, sodium hydroxide (50wt% aqueous solution, Sigma-Aldrich), silica (Ludox-40, Sigma-Aldrich), sodium aluminate and water were mixed in a Teflon liner. After 30 min stirring, the OSDA (pyrrolidine, piperidine, azepane, piperazine, DABCO, 4-Methylpiperidine) was added, and the mixture was stirred for 60 min. Then ca. 5 wt% (silica based) seeds (CBV10A) were added before charging into Teflon-lined Parr autoclaves. The molar composition of the synthesize gel was: 1 SiO2: 0.067 Al2O3: 0.23 OSDA: 0.75 Na2O: 11 H2O. The autoclaves were loaded into a preheated static convection oven at 170 ºC for 3 days.

The procedure for the synthesis of OSDA-free MOR zeolites followed (2). Silica, sodium aluminate, sodium hydroxide and water were mixed and stirred for 30 min. Then ca. 5 wt% (silica based) seeds (CBV10A) were added before charging into Teflon-lined Parr autoclaves. The molar composition of the synthesize gel was: 1 SiO2: 0.1 Al2O3: 0.2 Na2O: 26 H2O. The autoclaves were loaded into a preheated rotatory convection oven at 170 ºC for 7 days.

Large MOR-type zeolite crystals were synthesized following (3). Silica (Ludox-40, Sigma-Aldrich), sodium aluminate, sodium hydroxide (50 wt% aqueous solution, Sigma-Aldrich) and water were mixed and stirred for 30 min. Then ca. 5 wt% (silica based) seeds (CBV10A, Zeolyst) were added before charging into Teflon-lined Parr autoclaves. The molar composition of the synthesize gel was: 1 SiO2: 0.052 Al2O3: 0.23 Na2O: 3.42 H2O. The autoclaves were loaded into a preheated rotatory convection oven at 170 ºC for 7 days.

Omega-1 (MAZ). Omega-1 zeolites were synthesized following (4). The OSDA (TMAOH, Sigma-Aldrich) was first mixed with water. Then sodium hydroxide and sodium aluminate were added. To the solution silica (Ludox-40, Sigma-Aldrich) was added and stirred for 30 min. The molar composition of the resulting solution was: 10 SiO2: 1.0 Al2O3: 1.6 TMAOH: 3.2 Na2O: 160 H2O. The solution was charged into a polypropylene bottle and heated to 95 °C for 10 days.

*BEA. *BEA-type zeolites were synthesized following (5). Sodium aluminate, the OSDA (TEAOH, Sigma-Aldrich) and water were mixed. Then silica (Carbosol M5) was added and stirred for 120 min. The molar composition of the resulting gel was: 1 SiO2: 0.1 Al2O3: 1.0 TEAOH: 0.1 Na2O: 6.2 H2O. The thick gel was charged into Teflon-lined Parr autoclaves and put in a preheated static convection oven at 170 ºC for 3 days.
**MEL (ZSM-11).** ZSM-11 zeolites with Si/Al=15 were synthesized following (6). Silica (TEOS) and the OSDA (TBA Br) were mixed. Then aluminum sulfate and sodium hydroxide were added and stirred for 60 min to obtain a solution. The molar composition of the resulting solution was: 1 SiO₂: 0.025 Al₂O₃: 0.18 TBA Br: 0.14 Na₂O: 42.35 H₂O. The solution was charged into Teflon-lined Parr autoclaves and put in a rotatory convection oven at 150 °C for 3 days.

**MFI, FER and LTL.** FER-type (CP914C, NH₄-form) with Si/Al=10 and MFI-type (CBV2314, NH₄-form ZSM-5) with Si/Al=12 zeolites were obtained from Zeolyst. LTL-type zeolite (HSZ500, K-form) with Si/Al=3 was obtained from Tosoh. The LTL-type zeolite was converted to NH₄-form by ion exchange with 1M NH₄NO₃ for three times (72 h in total) at 80 °C.

**Calcination of zeolites.** After the synthesis was completed, the resulting solids were washed three times with distilled water. The materials synthesized with OSDAs were further washed by acetone. To remove the OSDAs from zeolites, the obtained solids were then dried at 80 °C before calcining in a flow air furnace at 580 °C for 8 h, with a ramp rate of 1.0 °C/min. Crystallinity of the materials was examined using lab based X-ray diffraction (XRD).

**Aqueous-phase Ion-Exchange of Zeolites.** Na-type zeolites were prepared by ion exchange of calcined or as received zeolites with 1M aqueous NaNO₃ solution. Typically, 600 mg of zeolites were added to 30 mL of salt solutions, which were then stirred at 80 °C for 24 h. The exchanged crystals were dried at 100 °C in ambient air in a free convention oven overnight.

A similar ion exchange procedure was used to prepare samples for the preparation of MOR-type zeolites with varying Na⁺ loading. The MOR6 zeolites (CBV10A, Zeolyst, 4# in Table 1) were first fully converted to ammonium form after two times (48 h in total) ion exchange using 1 M NH₄NO₃ aqueous solution at 80 °C. Depending on the targeting Na⁺ exchange level, 30 mL of 0.002 M to 5 M aqueous NaNO₃ solution were used as the precursor. The materials were recovered by centrifugation and washed 6 times with copious amount of distilled water. The exchanged crystals were dried at 100 °C overnight. The Na- and H- density were measured using energy-dispersive X-ray spectroscopy (EDS) and solid state ¹H nuclear magnetic resonance (NMR) spectroscopy, respectively.

**Pyridine-modification of zeolites.** A previously reported method was followed for pyridine modification of the MOR-type zeolites, denoted as py-MOR. Briefly, Na-MOR was dehydrated at 170 °C under vacuum (0.1 mbar) overnight. The sample was cooled to room temperature and flushed with ultra-high purity Ar before dosing pyridine into MOR zeolites with an amount of ca. 0.5 mL pyridine/mg zeolites. The py-MOR zeolites were heated to 300 °C and kept for 19 h to remove the water and excess pyridine prior to the CO₂ adsorption measurements at 30 °C in the dynamic column fixed bed system.

**S3. Characterizations**

**X-ray diffraction.** The crystallinity of the materials was examined using powder X-ray diffraction (XRD). The XRD patterns were collected using a Rigaku Miniflex II desktop instrument with a Cu radiation source, Kα = 1.5418 Å.

**Scanning electron microscopy.** The morphology of the materials was measured using scanning electron microscopy (SEM, ZEISS 1550 VP FESEM). The SEM was equipped with an Oxford X-Max SDD. Energy dispersive X-ray spectroscopy (EDS) used for determining the element contents of each sample.

**Solid-state, magic-angle spinning nuclear magnetic resonance.** Solid-state, magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were obtained on a Bruker AVANCE 500 MHz (11.2 T) spectrometer using a 4 mm zirconia rotor with a Kel-F cap. ¹H MAS NMR spectroscopy was measured to quantify the residue H-density of Na⁺ exchanged MOR-type zeolites as a function of Na⁺ loading. NH₄-form materials were used to avoid the dealumination through ion exchange and dehydration. The samples were loaded in the rotor and dehydrated under vacuum (10⁻² Torr) at 400 °C for 12 h in a Schlenk manifold. The spectra were acquired at 500.1 MHz with a 90° pulse length of 4 μs and a spinning rate of 12 kHz, and then were deconvoluted using DMFit software. The number of framework NH⁺ site (mmol/g) was measured by referencing the signal intensities to hexamethyl benzene and normalizing by the sample mass, followed by
dividing by 4, that is the number of protons per NH$_4^+$. The residual NH$_4$ site density of Na-exchanged MOR zeolites was then quantified with the same procedure as a function of Na loading. To examine the state of aluminum in Na-exchanged MOR zeolites, the $^{27}$Al MAS NMR spectra were also recorded on the same samples without undergoing dehydration at 130.2 MHz with a 10° pulse length of 0.5 μs, a cycle delay time of 0.5 s, and a spin rate of 12 kHz.

**Fourier transform infrared spectroscopy.** Fourier transform infrared (FTIR) spectra were collected on zeolite samples using a Nexus 470 FTIR spectrometer equipped with a deuterated, L-alanine doped triglycine sulfate (DTGS) detector. Catalyst samples (ca. 10-12 mg) were pressed into a self-supporting wafer (ca. 1.2 cm in diameter) and placed in a custom-built FTIR cell. The wafers were treated in flowing dry air at 723 K for 120 min, and then cooled to RT for CO$_2$ adsorption under flowing dry air for 30 min. Spectra were collected with a resolution of 4 cm$^{-1}$ and averaged over 64 scans.

**Single-crystal X-ray diffraction.** Single-crystal X-ray diffraction was performed at 100 K on a Bruker D8Venture CCD diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å). Crystal was mounted on Mitegen MicroMount. A multi-scan absorption correction was applied to the collected reflections. The structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. All non-hydrogen atoms were refined anisotropically. The figures were exported using Olex2.
4. CO$_2$ adsorption kinetics

The adsorption kinetics of MOR-type zeolites for CO$_2$ adsorption was examined using TGA (Perkin Elmer STA6000). For the TGA measurements, 49.54 mg 13X and 57.19 mg MOR-type zeolites were used to obtain comparable volumes (ca. 0.10 mL). The loaded sample was activated at 600 ºC for 20 h with a 70 mL/min He flow. After the temperature was cooled to 30 ºC, the gas was switched to a 70 mL/min 400ppm CO$_2$/He flow. Desorption was performed with a ramp rate of 10 ºC/min to 600 ºC with a 70 mL/min He flow. The weight of the sample was recorded as a function of time on stream.

5. Isosteric heat of adsorption

The isotherms measured at different temperatures were first fitted using the Langmuir-Freundlich (LF) isotherm model:

\[ q = \frac{a \cdot b \cdot p^n}{1 + b \cdot p^n} \quad (1) \]

where "a" is the saturation uptake (mmol/g), "b" is the corresponding adsorption equilibrium constant showing the affinity coefficient, "n" is the deviation from the ideal homogeneous surface, "p" is the equilibrium pressure.

The heat of adsorption was calculated from the Clausius-Clapeyron equation:

\[ \ln \frac{p_2}{p_1} = -\frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2) \]

where "p" is the pressure (bar), "\Delta H" is the changing in enthalpy (kJ/mol), "R" is the universal gas constant (8.314 J/K/mol), and "T" is the temperature (K).

The function can be simplified to:

\[ \ln p = -\frac{\Delta H}{R} \left( \frac{1}{T} \right) + c \quad (3) \]

for the calculation of \( \Delta H \) (isosteric heat of adsorption).
Fig. S1. X-ray diffraction patterns of the MOR-type zeolites synthesized (5#-13#) with the pattern from the commercial zeolite (4#, CBV10A) as the reference. Sample codes are listed in Table S1.
Fig. S2. SEM images of commercial MOR-type zeolites (1-4#) and the samples synthesized with organic-directing agents (5-13#). Sample codes are listed in Table S1.
Fig. S3. CO$_2$ adsorption isotherms up to 1 bar at 25 °C for MOR-type zeolites synthesized with different organic structure-directing agents (5# - 13#) as well as commercial zeolites, i.e., HSZ620 (1#) and CBV10A (4#). Sample codes are listed in Table S1.
Fig. S4. Bar graphs comparison of the capacity for 400 ppm CO$_2$ over MOR-type zeolites, including commercial samples, zeolites synthesized with and without organic-structure directing agents (OSDAs). The data are obtained from 0.0004 bar from isotherms measured up to 1 bar at 25 ºC. Sample codes are listed in Table S1.
Fig. S5. Schematic of the deconvolution of the OH stretching region of MOR-type zeolites. The spectra were deconvoluted using a Voigt function, with contributions from Gaussian and Lorentz functions.
Fig. S6. Correlation of Na\textsuperscript{+} at the 8MR side-pocket of MOR-type zeolites (Si/Al=5-7) synthesized with different OSDAs (5#-13#) as well as commercial zeolites, i.e., HSZ620 (1#) and CBV10A (4#). Details of the data are summarized in Table S2.
Fig. S7. CO\textsubscript{2} isotherms of the organic structure-directing agents free MOR-type zeolites measured at 25 °C. 14*# is the MOR-type zeolites (14#) after Na\textsuperscript{+} ion exchange. The results show that high CO\textsubscript{2} adsorption capacity can be obtained directly from the as-prepared MOR-type zeolites without further ion exchange. Moreover, the CO\textsubscript{2} adsorption capacity can be adjusted by varying the Al content through OSDA-free synthesis. The OSDA-free MOR-type zeolites (14#) shows a capacity of 1.14 mmol/g, comparable to that of OSDA-directed material (7#). This would lead to a cost-efficient, environmentally friendly preparation of MOR-type zeolites with high capacity in large industrial scale, offering opportunities for lowering the cost of the DAC technique.
Fig. S8. The adsorption and desorption kinetics of MOR-type zeolites (7#) measured by TGA: a) Uptake profiles during adsorption at 30 °C with a gas flow of 70 mL/min 400ppm CO₂/He. b) Desorption profiles with a gas flow of 70 mL/min pure He with a ramp rate of 10 °C/min.
Fig. S9. Comparison of adsorption behavior of 13X and MOR-type (4#) zeolites. Column breakthrough profiles of 13X and MOR7(4#) zeolites for the adsorption of dry CO$_2$ at 30 ºC. The composition of the CO$_2$ gas for adsorption under is ca. 400 ppm CO$_2$/400 ppm Ar (internal standard)/ He.
Fig. S10. The FTIR spectra of MOR-type (4#) zeolites for the CO$_2$ physisorption (a) and chemisorption (b) regions. The results show that CO$_2$ adsorbed in MOR-type zeolites exclusively in the form of physisorption as no apparent absorption peaks of carbonates were observed in the chemisorption region.
Fig. S11. Non-linear curve fits for the CO$_2$ sorption of MOR-type zeolite (7#) at different temperatures in the low-pressure range of 0-0.008 bar obtained from volumetric CO$_2$ isotherms.
Fig. S12. Isosteric heat of adsorption of a representative MOR-type zeolite (7#) in the low-pressure range of 0-0.008 bar obtained from volumetric CO$_2$ isotherms.
**Fig. S13.** Mass spectra profiles from temperature programmed desorption of: a) parent and b) pyridine-modified MOR-type (4#) zeolites after being saturated with 400 ppm CO\textsubscript{2} at 30 °C. The adsorption gas was 400ppm CO\textsubscript{2}/400 ppm Ar (internal standard)/He. The components detected are CO\textsubscript{2} (red), H\textsubscript{2}O (black) and pyridine (blue). Both materials were activated at 300 °C. The data show that the strongly adsorbed pyridine remained in the MOR-type zeolites after activation at 300 °C.
Fig. S14. Bar graphs of breakthrough and saturation capacities from pyridine adsorbed and parent MOR zeolites after activation at 300 ºC. The capacities are compared to the values obtained from isotherms at 400 ppm CO$_2$ as well as parent MOR-type (4#) zeolites activated at 550 ºC. The results show that ca. 85% of the capacity maintained with pyridine adsorption in the 12MR main channel of the MOR framework, compared to the parent material. The results suggest that the adsorption sites in the 8MR side-pocket are responsible for the high capacity of MOR-type zeolites. It should be noted that the slight increase of CO$_2$ uptake of MOR-type zeolites after 300 ºC compared to that after 550 ºC can be attributed to the trace amount of water in the former. It has been previously shown that the presence of trace amount of water can enhance the CO$_2$ adsorption.(7)
Fig. S15. Volumetric CO$_2$ isotherms up to 1 bar of MOR-type (7#) measured at different temperatures. The results show that the inflection pressures are independent on the measurement temperatures. Moreover, the CO$_2$ capacity increases with the decrease of temperatures.
**Fig. S16.** CO₂ adsorption isotherms up to 1 bar at 25 °C in linear scale (left) and logarithm scale (right) for the MOR-type (4# in NH₄⁺ form) as a function of Na⁺ loading.
Fig. S17. FTIR spectra of the OH stretching region for the MOR-type (4# in NH$_4^+$ form) samples with various Na$^+$ loading. The spectra were deconvoluted using a Voigt function, with contributions from Gaussian and Lorentz functions. Note that the spectra were not normalized based on weight, thus the area only qualitatively reflect the consumption of BAS with the loading of Na$^+$ cations.
Fig. S18. $^1$H NMR spectra of the MOR-type (4# in NH$_4^+$ form) samples with various Na$^+$ loading. The spectra were deconvoluted using a Voigt function, with contributions from Gaussian and Lorentz functions. Note that the spectra were not normalized based on weight.
Fig. S19. $^{27}\text{Al}$ NMR spectra of the MOR-type (4# in $\text{NH}_4^+$ form) with various Na$^+$ loading. The results show that all materials were free of extraframework Al$^{3+}$, although small OH stretching bands attributed to extraframework Al$^{3+}$ were observed for some samples from FTIR (Fig. S17).
Fig. S20. FTIR spectra of the asymmetric stretching of CO$_2$ for the MOR-type (4# in NH$_4^+$ form) samples as a function of Na$^+$ loading. Right panel shows the zoom in spectra of the 2380-2440 cm$^{-1}$ region in those in the left panel. The bands at 2348, 2359, and the band between 2400-2430 cm$^{-1}$ indicates the gas phase, the C-O stretching and Na-O stretching of linearly adsorbed CO$_2$ molecules, respectively.
Fig. S21. Scanning electron microscopic image of large crystals for single-crystal X-ray diffraction measurements. The sizes of the crystals are 30-40 µm.
Fig. S22. Visualization of the sittings of Na\(^+\) cations in Na-MOR-type zeolites as a function of Na\(^+\) loadings. 
a) Four distinct extraframework cations sites, namely N1, N2, N3, N4, were found in the MOR-type framework. Oxy represents the oxygen atom connected to Tx and Ty sites. The extraframework cations in the N1 and N3 sites are located at the center of the 8MRs in the side-pocket and in the intersection between the side-pocket and 12MR channel, respectively. Those in the N2 site are located at the 8MR side-pocket balancing the O33. Those in the N4 site are located at the 12MR channel balancing the O44. Na&N represents the site partially exchanged by Na\(^+\). b-e) Results from samples (A-D) highlighted in Fig. 2c, respectively. Panel b) shows that sample A had Na\(^+\) cations in the N1 site. Panel c) shows that sample B had Na\(^+\) cations in the N1 and N2 sites. Panel d) shows that sample C had both N1 and N2 sites fully occupied by Na\(^+\) cations, while the N3 site was partially occupied by Na\(^+\) cations. Panel e) shows that the occupancy of sample D is similar to that of sample C, with extra Na\(^+\) cations added to N4 site. The details of the occupancy for each site are summarized in Tables S7-S10.
Fig. S23. X-ray diffraction patterns of the zeolites tested with different framework topologies.
Fig. S24. X-ray diffraction patterns of the ZSM-5 (MFI) and ZSM-11 (MEL) zeolites. The MEL and MFI phases were identified by the arrows based on the MEL and MFI reference peaks from the International Zeolite Structure Database.
It has been demonstrated in the present work that the side-pockets of LTL-, MAZ-, MOR-type frameworks are responsible for the adsorption of 400 ppm CO₂. The longest dimension of the side pockets of these zeolites were used to define the confined space. Similar concept was used for the FER-type framework due to the structural similarity between the MOR- and FER-type frameworks. The sizes are measured via VESTA, and the values are 5.2, 6.7, 6.3, and 9.7 Å for the LEL-, MAZ-, MOR-, and FER-type zeolites, respectively. It should be noted that a larger size was obtained for the FER-type zeolites than that for the MOR-type zeolites. This is due to the “antenna” structure as well as the larger size of the swelling shape of the side-pocket of FER-type framework, compared to the side-pocket of MOR-type framework. For Na-MFI-type zeolites, it was shown by simulation that CO₂ molecules preferentially adsorbs in the intersection of the two channels.(9) Thus, the size of the intersection of MFI-type framework was applied for defining its confined space. Similar concept was used for MEL-type framework due to the similarity between MFI- and MEL-type frameworks. The intersection for *BEA-type zeolites is a large and open space. Thus, we surmise that the confinement in BEA is likely from the 12MR channel, where the largest dimension is 7.7 Å. For FAU-type zeolites, α-cage is the only accessible space for CO₂ molecules as the 6MR window (2.5 Å) for the β-cage (sodalite cage) is too small for CO₂ molecules (3.3 Å). The sizes of the confined space of FAU-, MFI-, MEL-type zeolites are 11.2, 6.4, and 7.7 Å, as indicated by the maximum sphere that can be included shown in the IZA website (http://www.iza-structure.org/databases/).

Fig. S25. Visualization of the confined space in zeolites with different frameworks.
**Fig. S26.** CO$_2$ isotherms of zeolites with different framework topologies measured at 25 ºC.
Fig. S27. Mass spectra profiles from temperature programmed desorption of a) CO₂ and b) H₂O from pyridine dosed (py-MAZ, red) and parent (MAZ, black) MAZ zeolites after being saturated at 30 ºC with 400 ppm CO₂, i.e., 400 ppm CO₂/400 ppm Ar (internal standard)/He. Both materials were activated at 280 ºC. The results show that the amount of CO₂ adsorbed in the MAZ and py-MAZ materials are comparable. As the pyridine molecules selectively shield the 12MR channels(10), the 8MR side-pocket is the only accessible channel in the py-MAZ material. Therefore, these data suggest that the 8MR side-pocket is responsible for the adsorption of 400 ppm CO₂ in MAZ-type zeolites.
Fig. S28. Comparison of the capacities for CO₂ and N₂ measured from single-component isotherms and simulated air real time breakthrough experiments. The simulated air is 400 ppm CO₂/1 Ar% (internal standard)/20% O₂/N₂. The results show that the capacities for CO₂ and N₂ decreased for simulated air measurements compared to those from the single-component isotherms. This suggests the competitive adsorption of CO₂ and N₂. The higher CO₂/N₂ molar selectivity for the breakthrough experiments than that from the isotherms demonstrated the preferential adsorption of CO₂ compared to N₂.
Fig. S29. The performance of commercially available MOR-type zeolites (4#, CBV10A) obtained from real time breakthrough experiments under simulated conditions for direct air capture. a) Comparison of the breakthrough and saturation capacities of MOR zeolites (4#, CBV10A) with different gas mixtures at 30 ºC. CO₂/He indicates 400 ppm CO₂/400 ppm Ar (internal standard)/He, CO₂/N₂ indicates 400 ppm CO₂/20% Ar (internal standard)/N₂, CO₂/N₂/O₂ indicates 400 ppm CO₂/1% Ar (internal standard)/20%O₂/N₂. b) The adsorption-desorption recyclability over MOR-type zeolites (4#, CBV10A) with a gas flow of CO₂/N₂/O₂. The first cycle was obtained after activation of the material at 550 ºC for 20 h. Then the material was regenerated at 60 ºC and 100 ºC for 2h for each cycle before a 2h deep regeneration at 550 ºC for three cycles. The results show that the material exhibit high recyclability even at temperature as low as 60 ºC.
### Supplementary Information Tables S1-S12

**Table S1.** Physicochemical properties of MOR-type zeolite samples.

| Sample code | Sample source          | Adsorbent     | Si/Al ratio<sup>a</sup> | Na/Al<sup>a</sup> | Fraction of Na<sup>+</sup> in the 8MR side-pocket (%)<sup>b</sup> |
|-------------|------------------------|---------------|--------------------------|------------------|---------------------------------------------------------------|
| 1           | Commercial             | Na-HSZ620     | 7.36                     | 0.93             | 49.0                                                          |
| 2           | 9.19                   | Na-HSZ640     | 0.67                     |                  |                                                               |
| 3           | 12.79                  | Na-HSZ660     | 0.83                     |                  |                                                               |
| 4           | CBV10A                 | 5.81          | 1.03                     | 54.3             |                                                               |
| 5           | 5.30                   | Pharmaceutical | 0.91                     | 65.3             |                                                               |
| 6           | 5.67                   | OSDA-directed synthesis | 0.95                  | 61.3             |                                                               |
| 7           | 5.04                   | OSDA-directed synthesis | 0.89                  | 66.5             |                                                               |
| 8           | 5.35                   | OSDA-directed synthesis | 0.86                  | 73.7             |                                                               |
| 9           | 5.37                   | OSDA-directed synthesis | 0.83                  | 64.3             |                                                               |
| 10          | 5.51                   | OSDA-directed synthesis | 0.82                  | 63.8             |                                                               |
| 11          | 5.10                   | OSDA-directed synthesis | 0.81                  | 60.1             |                                                               |
| 12          | 5.72                   | OSDA-directed synthesis | 0.90                  | 65.9             |                                                               |
| 13          | 4.89                   | OSDA-directed synthesis | 0.98                  | 58.4             |                                                               |
| 14          | 4.38                   | OSDA-free synthesis | 0.75                   |                  |                                                               |
| 15          | 9.46                   | OSDA-free synthesis | 1.03                   |                  |                                                               |
| 16          | 13.47                  | OSDA-free synthesis | 0.94                   |                  |                                                               |

<sup>a</sup> Elemental analysis was performed using EDS.

<sup>b</sup> Values were determined from the deconvolution of the OH stretching from the FTIR spectra.
Table S2. The capacities of MOR-type zeolites for 400 ppm CO$_2$ as well as the number of Na$^+$ cations in the 8MR side-pocket for each MOR unit cell.

| Sample code | CO$_2$ capacity (mmol/g)$^a$ | Na$^+$ in 8MR side-pocket per unit cell$^b$ |
|-------------|-----------------------------|-------------------------------------------|
| 1           | 0.49                        | 2.62                                      |
| 4           | 0.77                        | 3.94                                      |
| 5           | 0.88                        | 4.53                                      |
| 6           | 0.91                        | 4.19                                      |
| 7           | 1.15                        | 4.70                                      |
| 8           | 0.98                        | 4.79                                      |
| 9           | 0.85                        | 4.02                                      |
| 10          | 0.85                        | 3.86                                      |
| 11          | 0.90                        | 3.83                                      |
| 12          | 0.89                        | 4.24                                      |
| 13          | 1.00                        | 4.66                                      |

Note: a. The CO$_2$ capacity obtained at 0.0004 bar from the isotherms measured at 30 °C.
b. The number of Na$^+$ cations in the 8MR side-pocket for each MOR unit cell was calculated from the FTIR results in the OH stretching region and the elemental analysis from EDS.
Table S3. CO$_2$ adsorption results from the MOR-type (4# in NH$_4^+$ form) zeolites as a function of Na$^+$ loadings.

| Sample code | Samples | Capacity (mmol/g) |   |   |
|-------------|---------|------------------|--|--|
|             |         | 400 ppm | 1 bar | CO$_2$/U.C. |
| 17          | H-MOR7  | 0.02     | 2.92   | 0.06 |
| 18          | 0.002Na | 0.03     | 2.82   | 0.09 |
| 19          | 0.005Na | 0.04     | 2.90   | 0.12 |
| 20          | 0.01Na  | 0.05     | 2.89   | 0.15 |
| 21          | 0.05Na  | 0.09     | 2.93   | 0.27 |
| 22          | 0.1Na   | 0.16     | 3.07   | 0.46 |
| 23          | 0.2Na   | 0.33     | 3.26   | 0.97 |
| 24          | 0.5Na   | 0.49     | 3.38   | 1.47 |
| 25          | 1Na     | 0.62     | 3.36   | 1.84 |
| 26          | 2Na     | 0.60     | 3.33   | 1.81 |
| 27          | 3Na     | 0.65     | 3.30   | 1.98 |
| 28          | 4Na     | 0.68     | 3.48   | 2.20 |
| 29          | 5Na     | 0.75     | 3.30   | 2.26 |
**Table S4.** Proton densities and Na⁺ distributions in the MOR-type (4# in NH₄⁺ form) zeolites as a function of Na⁺ loadings.

| Sample code | Proton density ² | Na/U.C. ³  | Na @ 8MR ³  | Na @ 12 MR ³  |
|-------------|------------------|-----------|-------------|--------------|
| 17          | 5.82             | 0.00      | 0.00        | 0.00         |
| 18          | 5.64             | 0.18      | 0.17        | 0.01         |
| 19          | 5.21             | 0.60      | 0.55        | 0.05         |
| 20          | 4.94             | 0.87      | 0.84        | 0.03         |
| 21          | 4.30             | 1.50      | 1.47        | 0.03         |
| 22          | 3.91             | 1.89      | 1.72        | 0.18         |
| 23          | 3.30             | 2.50      | 2.18        | 0.32         |
| 24          | 1.97             | 3.83      | 2.43        | 1.40         |
| 25          | 1.76             | 4.04      | 2.66        | 1.37         |
| 26          | 1.24             | 4.56      | 3.04        | 1.52         |
| 27          | 1.18             | 4.62      | 2.99        | 1.62         |
| 28          | 1.00             | 4.80      | 2.97        | 1.83         |
| 29          | 0.88             | 4.92      | 3.16        | 1.76         |

Note:

a. The values were obtained from ¹H NMR.

b. The values were calculated based on the proton density from ¹H NMR.

c. The values were calculated based on the proton density from ¹H NMR and the deconvolution of the OH stretching from FTIR spectra of corresponding samples.
Table S5. Assignments of IR bands of CO₂ in Na-form zeolites.

| Wavenumbers/cm⁻¹ | Vibration mode | Physical meaning | ref |
|------------------|----------------|------------------|-----|
| 656              | ν₂             | Deformation mode | (11) |
| 1382             | ν₁             | Symmetric stretching | (11) |
| 1365 and 1700 pair |                | Carbonate-like | (12) |
| 1425 and 1485 pair |                | Carbonate-like | (12) |
| 2290             | ν₃ of ^1³CO₂   | Asymmetric stretching of isotope ^1³CO₂ | (13) |
| 2349             | ν₃             | Asymmetric stretching of gas phase CO₂ in zeolites | (12) |
| 2350-2360        | ν₃             | Asymmetric stretching of linearly adsorbed, end on form of CO₂ | (11, 12, 14) |
| 2360-2370        | Unassigned     |                  |     |
| 2422             | ν₂+ ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν₁⁺ν� | (15) |
| 3598-3725        | ν₃+ν₁ and ν₃+2ν₂ |                  | (12) |
Table S6. Compositions of MOR-type zeolite large crystals for single-crystal X-ray diffraction measurements.

| Sample code | Si/Al ratio | Na/Al | Al$^{3+}$/U.C. | Na$^+$/U.C. |
|-------------|-------------|-------|----------------|-------------|
| 30          | 5.51        | 0.12  | 7.37           | 0.88        |
| 31          | 5.48        | 0.35  | 7.41           | 2.59        |
| 32          | 5.47        | 0.59  | 7.42           | 4.38        |
| 33          | 5.52        | 0.81  | 7.36           | 5.96        |

Note: The compositions were measured using EDS.
Table S7. Single crystal X-ray structure data and refinement conditions for MOR (30#).

| Identification code   | cu_V22151_0m          |
|-----------------------|------------------------|
| Empirical formula     | Al0.46 N0.43 Na0.05 O6.12 Si2.54 |
| Formula weight        | 189.11                 |
| Temperature           | 100(2) K               |
| Wavelength            | 1.54178 Å              |
| Crystal system        | Orthorhombic           |
| Space group           | Cmcm                   |
| Unit cell dimensions  | a = 18.116(2) Å, α = 90° |
|                       | b = 20.4326(17) Å, β = 90° |
|                       | c = 7.4962(5) Å, γ = 90° |
| Volume                | 2774.8(4) Å³           |
| Z                     | 16                     |
| Density (calculated)  | 1.811 Mg/m³            |
| Absorption coefficient| 6.092 mm⁻¹             |
| F(000)                | 1507                   |
| Crystal size          | 0.040 x 0.030 x 0.020 mm³ |
| Theta range for data collection | 3.260 to 74.455°. |
| Index ranges          | -19<=h<=22, -25<=k<=25, -9<=l<=9 |
| Reflections collected | 15027                  |
| Independent reflections| 1585 [R(int) = 0.0652] |
| Completeness to theta | 67.679° 100.0 %        |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7538 and 0.6167 |
| Refinement method     | Full-matrix least-squares on F² |
| Data / restraints / parameters | 1585 / 0 / 126 |
| Goodness-of-fit on F² | 1.100                  |
| Final R indices [I>2sigma(I)] | R1 = 0.0616, wR2 = 0.1983 |
| R indices (all data)  | R1 = 0.0817, wR2 = 0.2075 |
| Extinction coefficient| n/a                    |
| Largest diff. peak and hole | 1.570 and -0.446 e.Å⁻³ |
| Property                           | Value                                           |
|-----------------------------------|------------------------------------------------|
| **Identification code**           | cu_V22152_0m                                   |
| **Empirical formula**             | Al0.46N0.30 Na0.16 O6.12 Si2.54                |
| **Formula weight**                | 189.75                                         |
| **Temperature**                   | 100(2) K                                       |
| **Wavelength**                    | 1.54178 Å                                      |
| **Crystal system**                | Orthorhombic                                   |
| **Space group**                   | Cmcm                                           |
| **Unit cell dimensions**          | a = 18.0770(15) Å, α = 90°.                    |
|                                   | b = 20.438(3) Å, β = 90°.                      |
|                                   | c = 7.5007(8) Å, γ = 90°.                      |
| **Volume**                        | 2771.2(6) Å³                                   |
| **Z**                             | 16                                             |
| **Density (calculated)**          | 1.819 Mg/m³                                    |
| **Absorption coefficient**        | 6.156 mm⁻¹                                     |
| **F(000)**                        | 1512                                           |
| **Crystal size**                  | 0.040 x 0.030 x 0.020 mm³                      |
| **Theta range for data collection**| 3.264 to 72.233°                               |
| **Index ranges**                  | -22<=h<=22, -25<=k<=25, -9<=l<=8               |
| **Reflections collected**         | 14071                                          |
| **Independent reflections**       | 1524 [R(int) = 0.1051]                         |
| **Completeness to theta = 67.679°**| 99.9 %                                         |
| **Absorption correction**         | Semi-empirical from equivalents                |
| **Max. and min. transmission**    | 0.7536 and 0.6220                              |
| **Refinement method**             | Full-matrix least-squares on F²                |
| **Data / restraints / parameters**| 1524 / 0 / 113                                 |
| **Goodness-of-fit on F²**         | 1.132                                          |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0859, wR2 = 0.2356                       |
| **R indices (all data)**          | R1 = 0.1267, wR2 = 0.2793                      |
| **Extinction coefficient**        | n/a                                            |
| **Largest diff. peak and hole**   | 1.739 and -0.631 e.Å⁻³                         |
Table S9. Single crystal X-ray structure data and refinement conditions for MOR (32#).

| Identification code   | cu_v22156_0m             |
|-----------------------|--------------------------|
| Empirical formula     | Al0.45N0.17 Na0.28 O6.12 Si2.55 |
| Formula weight        | 190.66                   |
| Temperature           | 100(2) K                |
| Wavelength            | 1.54178 Å               |
| Crystal system        | Orthorhombic            |
| Space group           | Cmcm                     |
| Unit cell dimensions  | a = 18.0490(19) Å, α = 90°. |
|                       | b = 20.4300(19) Å, β = 90°. |
|                       | c = 7.5003(8) Å, γ = 90°. |
| Volume                | 2765.7(5) Å³            |
| Z                     | 16                       |
| Density (calculated)  | 1.832 Mg/m³             |
| Absorption coefficient| 6.238 mm⁻¹              |
| F(000)                | 1518                     |
| Crystal size          | 0.040 x 0.030 x 0.020 mm³|
| Theta range for data collection | 3.267 to 74.757°. |
| Index ranges          | -22<=h<=22, -24<=k<=24, -9<=l<=9 |
| Reflections collected | 28102                    |
| Independent reflections| 1579 [R(int) = 0.0508]   |
| Completeness to theta | 67.679°                  |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7538 and 0.6606       |
| Refinement method     | Full-matrix least-squares on F² |
| Data / restraints / parameters | 1579 / 0 / 113       |
| Goodness-of-fit on F² | 1.160                    |
| Final R indices [I>2sigma(I)] | R1 = 0.0727, wR2 = 0.2313 |
| R indices (all data)  | R1 = 0.0827, wR2 = 0.2505 |
| Extinction coefficient| n/a                     |
| Largest diff. peak and hole | 1.501 and -0.539 e.Å⁻³  |
Table S10. Single crystal X-ray structure data and refinement conditions for MOR (33#).

| Identification code   | cu_v22159_0m          |
|-----------------------|-----------------------|
| Empirical formula     | Al0.26 N0.05 Na0.21 O3.50 Si1.44 |
| Formula weight        | 109.16                |
| Temperature           | 100(2) K              |
| Wavelength            | 1.54178 Å             |
| Crystal system        | Orthorhombic          |
| Space group           | Cmcm                  |
| Unit cell dimensions  | a = 18.034(2) Å, α = 90°. |
|                       | b = 20.451(3) Å, β = 90°. |
|                       | c = 7.5111(8) Å, γ = 90°. |
| Volume                | 2770.2(6) Å³          |
| Z                     | 28                    |
| Density (calculated)  | 1.832 Mg/m³           |
| Absorption coefficient| 6.244 mm⁻¹            |
| F(000)                | 1520                  |
| Crystal size          | 0.040 x 0.030 x 0.020 mm³ |
| Theta range for data collection | 3.267 to 74.267°. |
| Index ranges          | -16<=h<=22, -25<=k<=23, -9<=l<=9 |
| Reflections collected | 12659                 |
| Independent reflections| 1570 [R(int) = 0.2170] |
| Completeness to theta | 67.679°               |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7538 and 0.5884 |
| Refinement method     | Full-matrix least-squares on F² |
| Data / restraints / parameters | 1570 / 0 / 113 |
| Goodness-of-fit on F²  | 1.140                 |
| Final R indices [I>2sigma(I)] | R1 = 0.0953, wR2 = 0.2781 |
|                       | R1 = 0.1838, wR2 = 0.3061 |
| Extinction coefficient | n/a                  |
| Largest diff. peak and hole | 1.879 and -0.930 e.Å⁻³ |
Table S11. Physicochemical properties of the zeolite samples.

| Adsorbent | Framework | Si/Al ratio<sup>a</sup> | Na/Al<sup>a</sup> | Micropore volume (cm<sup>3</sup>/g) |
|-----------|-----------|------------------------|------------------|-----------------------------------|
| 34        | FAU       | 1.22                   | 0.82             | 0.28                              |
| 35        | LTL       | 2.79                   | 0.84             | 0.16                              |
| 36        | MAZ       | 3.15                   | 0.78             | 0.05                              |
| 37        | *BEA      | 4.31                   | 0.93             | 0.21                              |
| 38        | MOR       | 5.81                   | 1.03             | 0.17                              |
| 39        | FER       | 10                     | 0.98             | 0.11                              |
| 40        | MFI       | 9.84                   | 1.00             | 0.13                              |
|           | MEL       | 15.49                  | 0.98             | 0.11                              |

a. Elemental analysis was performed using EDS.

b. The micropore volumes of zeolites studied are consistent with the reported values of 0.30 cm<sup>3</sup>/g for FAU(16), 0.15 cm<sup>3</sup>/g for LTL(17), 0.05 cm<sup>3</sup>/g for MAZ(18), 0.21 cm<sup>3</sup>/g for *BEA(19), 0.16 cm<sup>3</sup>/g for MOR(2), 0.11 cm<sup>3</sup>/g for FER(20), 0.13 cm<sup>3</sup>/g for MFI(21), 0.13 cm<sup>3</sup>/g for MEL(22).
| Sample code | Framework | Samples             | 400 ppm | 1 bar |
|-------------|-----------|---------------------|---------|-------|
|             |           |                     | Capacity (mmol/g) | Ads. Efficiency (CO₂/Na⁺) | Capacity (mmol/g) |
| 34          | FAU       | FAU1 (13X)          | 0.41     | 0.06  | 5.64  |
| 35          | LTL       | LTL3                | 0.02     | 0.01  | 2.39  |
| 36          | MAZ       | MAZ3 (Omega-1)      | 0.65     | 0.22  | 4.06  |
| 37          | *BEA      | BEA5                | 0.23     | 0.08  | 3.13  |
| 4           | MOR       | MOR6                | 0.77     | 0.32  | 3.32  |
| 14          | MOR       | MOR4 (OSDA free)    | 1.13     | 0.49  | 3.57  |
| 38          | FER       | FER10 (ZSM-35)      | 0.11     | 0.08  | 2.12  |
| 39          | MFI       | MFI12 (ZSM-5)       | 0.57     | 0.38  | 2.78  |
| 40          | MEL       | MEL15 (ZSM-11)      | 0.17     | 0.17  | 2.39  |

Table S12. Capacity of zeolites with different framework topologies as measured by isotherms at 25 °C.
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