Supporting Information

**Controlled Synthesis of Metal-Organic Frameworks in Scalable Open-Porous Contactor for Maximizing Carbon Capture Efficiency**

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(i) Bulk gas phase
(ii) Micropore phase in porous supports
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### Ergun Equation

\[
\frac{\Delta P}{L} = \frac{150\mu(1 - \varepsilon)^2u_0}{\varepsilon^4d_p^2} + \frac{1.75(1 - \varepsilon)\rho u_0^2}{\varepsilon^3d_p}
\]

\(\Delta P = \) Pressure drop  
\(u_0 = \) Superficial velocity of the fluid  

| Module Length (L) | Dynamic viscosity \(\mu\) [kg/m/s] | Void fraction \(\varepsilon\) [%] | Particle size \(d_p\) [m] | Fluid density \(\rho\) [kg/m\(^3\)] |
|-------------------|-----------------------------------|-------------------------------|-----------------|------------------|
| 0.12              | \(1.8 \times 10^{-5}\)            | 49                            | 0.0001, 0.0002  | 1.17             |
| # of fiber sorbents | 9   | 10  | 11  | 12  |
|--------------------|-----|-----|-----|-----|
| Void fraction (%)  | 49  | 43  | 38  | 31  |
| CO₂ capacity (mmol/g-fiber) | 2.56 | 3.05 | 3.57 | 3.77 |

**Figure S29.** a-d) Dry CO₂ breakthrough curves for diamine-Mg₂(dobpdc)/PEI modules loaded with a various number of fiber sorbents at 15% CO₂, 35 °C, and 30 sccm. e) Breakthrough capacities and void fraction of the modules depending on the number of fiber sorbents. Inlet feed composed of 15%/15%/70% CO₂/He/N₂ at 30 sccm. He trace (black); CO₂ (red).
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Supporting Tables:

Table S1. Dope composition of (50 & 300 nm) MgO/PEI precursor fibers and the amount of loaded MgO in the fiber matrix.

| Sample | PEI (wt %) | NMP (wt %) | H₂O (wt %) | LiNO₃ (wt %) | MgO (wt %) | Size of MgO (nm) | Loading MgO calculated by TGA (wt %) |
|--------|------------|------------|-------------|--------------|-------------|------------------|------------------------------------|
| #1     | 14         | 78         | 1           | 1            | 6           | 50               | 25                                 |
| #2     | 14         | 76         | 1           | 1            | 8           | 50               | 33                                 |
| #3     | 13         | 73         | 1           | 1            | 12          | 50               | 46                                 |
| #4     | 12         | 68         | 1           | 1            | 18          | 50               | 48                                 |
| #5     | 12         | 68         | 1           | 1            | 18          | 50               | 58                                 |
| #6     | 11         | 61         | 1           | 1            | 26          | 50               | 66                                 |
| #7     | 11         | 61         | 1           | 1            | 26          | 50               | 69                                 |
| #8     | 11         | 43         | 0.5         | 0.5          | 45          | 50               | 71                                 |
| #9     | 11         | 43         | 0.5         | 0.5          | 45          | 300              | 73                                 |
Table S2. Spinning parameters of (50 & 300 nm) MgO/PEI precursor fibers.

| Spinning parameters of MgO/PEI fiber precursors               |       |
|--------------------------------------------------------------|-------|
| Bore fluid composition (wt%)                                  | NMP/water 90/10 |
| Core fluid flow rate (mL/h)                                  | 240-400 |
| Bore fluid flow rate (mL/h)                                  | 0-80   |
| Air gap (cm)                                                 | 3      |
| Drum take-up rate (m/min)                                   | 10-20  |
| Spinning temperature (ºC)                                   | 25     |
| Quench bath temperature (ºC)                                | 50     |
Table S3. CO2 working capacities of the di-/tetraamine-Mg:(dobpdc)/PEI from 46 wt% of 50 nm MgO at various ranges of operating temperature and pressure.

| Range of temperature | Pressure | 25 – 100 °C (mmol/g-fiber) | 25 – 125 °C (mmol/g-fiber) | 25 – 150 °C (mmol/g-fiber) |
|----------------------|----------|-----------------------------|-----------------------------|-----------------------------|
| Diamine insertion    | 150 mbar | 1.60                         | 2.65                         | 2.69                         |
|                      | 1013 mbar| 1.50                         | 2.39                         | 3.42                         |
| Tetraamine insertion | 150 mbar | 0.02                         | 0                            | 1.72                         |
|                      | 1013 mbar| 0.17                         | 0.18                         | 1.49                         |
Table S4. Elemental analysis of crosslinked MgO/PEI precursor fibers obtained by varying chemical crosslinking methods.

| Sample                      | Element  | H (%) | C (%) | N (%) |
|-----------------------------|----------|-------|-------|-------|
| Pristine fiber              |          | 4.66  | 71.90 | 5.41  |
| Batch crosslinked fiber      |          | 4.98  | 65.11 | 6.08  |
| Continuous flow crosslinked fiber |       | 6.25  | 66.86 | 6.61  |
Table S5. Bed breakthrough capacities of 11 diamine-Mg$_2$(dobpdc)/PEI module.

| Composition of mixed feed gas |  | Capacity of the diamine sample (mmol CO$_2$/g-fiber) [mass = 0.2398 g] |
|------------------------------|---|-----------------|
|                              |  | Cycle 1 | Cycle 2 | Cycle 3 | Cycle 4 | Cycle 5 |
| 15 % CO$_2$ / 15% He / 15% N$_2$ balance / RH 100% | 30 mL / min | 3.58 | 3.41 | 3.33 | 3.32 | 3.31 |
|                              | 60 mL / min | 2.91 |  |  |  |  |
|                              | 90 mL / min | 2.73 |  |  |  |  |
| 400 ppm CO$_2$ / 400 ppm He / N$_2$ balance | 30 mL / min | 4.41 | 4.10 | 3.87 | 3.83 | 3.8 |
|                              |  | 0.70 |  |  |  |  |
Table S6. Bed breakthrough capacities of 11 tetraamine-Mg$_2$(dobpdc)/PEI module.

| Composition of mixed feed gas                  | Capacity of the tetraamine sample (mmol CO$_2$/g-fiber) [mass = 0.280 g] |
|-----------------------------------------------|-------------------------------------------------------------------|
| **15 % CO$_2$ / 15% He 15% / N$_2$ balance**  | Cycle 1 | Cycle 2 | Cycle 3 | Cycle 4 | Cycle 5 |
| **30 mL / min**                               | 2.49    | 2.31    | 2.27    | 2.24    | 2.23    |

| **15 % CO$_2$ / 15% He / N$_2$ balance / RH 100%** | Cycle 1 | Cycle 2 | Cycle 3 | Cycle 4 | Cycle 5 |
| **30 mL / min**                                  | 4.12    | 3.97    | 3.91    | 3.85    | 3.81    |

| **400 ppm CO$_2$ / 400 ppm He / N$_2$ balance**   | **60 mL / min** | **1.99** |
Table S7. Performance comparison of the reported structured sorbents.

| Porous sorbents          | Support               | T (°C) | P (bar) | RH (%) | CO₂ (%) | CO₂ capacity† (mmol/g-fiber) | Ref. |
|--------------------------|-----------------------|--------|---------|--------|---------|-----------------------------|------|
| Zeolite 13X              | Cellulose acetate     | 45     | 1       | 100    | Dry     | 2.4†                        | 4    |
| PEI-impregnated silica   | Poly(amide-imide)     | 35     | 1       | 14     | 100     | 0.85‡                       | 5    |
| HKUST-1                  | Cellulose acetate     | 35     | 1       | 12.50  | Dry     | 0.15                        | 6    |
| PEI-impregnated silica   | Cellulose acetate     | 35     | 1       | 10     | 100     | 0.58                        | 7    |
| PEI-impregnated silica   | Cellulose acetate     | 35     | 1       | 380 ppm| 85      | 0.43                        | 8    |
| PEI-impregnated silica   | Poly(amide-imide)     | 35     | 1       | 14     | 100     | 0.85                        | 9    |
| -                        | PEI-functionalized    | 35     | 0.1     | 10     | 100     | 1.4‡                        | 10   |
| Diamine-Mg₂(dobpdc)※     | Honeycomb cordierite  | 25     | 1       | 10     | Dry     | 2.37‡                       | 1    |
|                          | monolith              |        |         |        |         | 3.58                        |      |
| Diamine-Mg₂(dobpdc)      | Polyetherimide        | 35     | 1       | 15     | 100     | 4.41                        |      |
| Tetraamine-Mg₂(dobpdc)   | Polyetherimide        | 35     | 1       | 15     | 100     | 4.12                        |      |

†CO₂ capacities are based on breakthrough experiments except for ref. 8, 9, 13, and 14
‡Gravimetric sorption capacity
※Thin film on monolith
Materials:

Magnesium oxide (MgO) (99.95%, 50 nm and 99.5%, 300 nm) as solid sorbent precursors and polyetherimide (PEI) as polymer matrix (melt index 9 g/10 min) were purchased from Korea nanomaterials and Sigma-Aldrich, respectively. 4,4’-Dihydroxybiphenyl (97%), potassium bicarbonate (≥ 99.95% trace metals basis, 99.7-100.5% dry basis), and 1,2,4-trichlorobenzene (anhydrous, ≥ 99%) were purchased from Sigma-Aldrich and used as sources of H₄(dobpdc) linker. N-Methyl-2-pyrrolidone (NMP) (99.5%) was purchased from Daeyeung Chem and used as the solvent in the dope solution. Lithium nitrate (LiNO₃) (anhydrous, 99%) was purchased from Alfa Aesar used as the pore-former to construct the open-porous structure of the polymer matrix. Methanol (ACS Reagent, 99.8%) and n-hexane (ACS Reagent, > 98.5%) were used in the solvent-exchange processes for removing residual NMP and water in as-spun fibers and purchased from Sigma-Aldrich and Baker Inc., respectively. Ethylenediamine (EDA) and p-xylylenediamine (XDA) (> 99.0%) were purchased from JUNSEI and Tokyo Chemical Industry (TCI), respectively, and used as the crosslinkers to improve the chemical stability of the polymer matrix. All the other chemicals, solvents, and non-solvents were purchased from Sigma-Aldrich and used as received without further purification or modification. Potassium chloride (KCl) purchased from Sigma-Aldrich was used to prepare a saturated solution using deionized (DI) water at 35°C for a humid CO₂ breakthrough test. Single-/multi-component gases were purchased from special gas co. as ultrahigh-purity (UHP) grade. Ar and N₂ as sweep and bubbling gas were purchased from special gas co. as 99.999% grade. A mixture composed of 15% CO₂/N₂ balance was used for comparing the sorption capacity and kinetics on the pressure decay system (PDC). A mixture composed of 15% CO₂/ 15% He/ N₂ balance was used for breakthrough CO₂ adsorption experiments from flue gas compositions. A mixture composed of 400 ppm of CO₂/ 408 ppm of He/ N₂ balance was used for breakthrough adsorption experiments for direct air capture.

Syntheses:

Synthesis of H₄(dobpdc) linker

KHCO₃ (4.00 g, 40.0 mmol), 4,4’-dihydroxybiphenyl (2.32 g, 12.48 mmol), 1,2,4-trichlorobenzene (6 mL) and dry ice (3 g) were added to a Teflon-lined stainless-steel autoclave and heated at 250 °C for 17 h. After a solvothermal reaction, the mixture was washed with diethyl ether and filtered. The collected crystal samples were immersed in deionized water (600 mL) for 12 h and again filtered. To the filtrate, hydrochloric acid was added drop-wise until it was pH 2 by using a syringe, resulting in the formation of white precipitates, and then the precipitates were assembled by filtration. The resulting material was recrystallized overnight at 4 °C in acetone/deionized water solution (50/50 mL) per gram of the material. Figure S4 shows a ¹H NMR (300 MHz, DMSO-d₆) of the successfully synthesized H₄(dobpdc) linker. In the data, there were three solvent and five proton peaks: δ = 14.04 (br, 2H) 11.25 (br, 2H), 7.93 (s, 2H), 7.80 (d, 2H), 7.05 (d, 2H).

Diamine-Mg₂(dobpdc) synthesis from commercial MgO powder

Mg₂(dobpdc) nano-/microcrystals were synthesized from 50 nm and 300 nm MgO powder via a solvothermal reaction. A 10 mL glass vial was filled with DMF (2 mL) and H₄(dobpdc) (274 mg, 1 mmol) and was heated to 120 °C in a forced convection oven until there was the complete dissolution of the ligand, with the result that the color of ligand solution became transparent. Then, the MgO powder (2 mmol) was added to the ligand solution, and the solution was maintained at 120 °C for 6 hours for complete conversion to Mg₂(dobpdc) powder. After the reaction
mixture cooled to room temperature, DMF was added to the vial, and the MOF powders were washed two times via a centrifuge. Methanol was further added into the vial and washed three times to perform solvent exchange with the residual DMF. The Mg$_2$(dobpdc) powders were activated to remove the residual moiety present in the MOF pores at 120 °C for 12 h in a vacuum oven. To insert the diamine functional group into the inside of the MOF, the 30 mg of the Mg$_2$(dobpdc) powders were soaked for 4 h in a solution that contained 1 ml of N,N'-Dimethylethylenediamine (mmen, diamine), and 9 mL of anhydrous hexane. Next, the samples were rinsed with fresh hexane and dried in a vacuum. Porosimetry and adsorption properties of the samples were carried out immediately after activation to minimize the MOF’s exposure to air.

**Dope preparation and spinning process for MgO/PEI precursor fibers**
Composites of spinning dope included polyetherimide (PEI) (polymer), MgO (solid sorbent precursor), NMP (solvent), water (non-solvent), and lithium nitrate (LiNO$_3$) (pore former) which used to promote the formation of well-defined macropores in the polymer phase. To remove adsorbed water, the PEI and LiNO$_3$ were dried under vacuum at 100 °C for 12 h. In Table S1, all dope compositions used in this experiment were listed. A week before making the dope solution, a prime dope consisting of 20 wt% of the total PEI, NMP, DI water, and LiNO$_3$ is mixed in a sealed glass jar (50 mL) and mixed on a roller at 60 °C and 24 h. The prime dope solution can abruptly enhance the viscosity of the primary dope solution as well as attach a polymer chain on the surface of the MgO particles, which improves the dispersion of the particles in the solution.

The primary dope preparation is as follows. First, 100% of MgO is added to a solution corresponding to 80% of the total NMP, DI water, and LiNO$_3$ mixtures which are completely single-phase solutions. Second, until the MgO particles are sufficiently mixed in the solution, the dope solution is dispersed via an impeller and ultra-sonication horn, alternatively. Third, when the prime dope is added, the dope solution must be mixed immediately to prevent the local aggregation of sorbent particles. Fourth, we slowly insert the remaining 80% of the polymer and mechanically disperse the solution at 60 °C until the polymer is completely dissolved. During mixing, a closed system of the container should be realized to stop the change of the dope compositions by evaporation of the volatile solvent or nonsolvent. For an additional mixing process, the dope solution is dispersed via a roller at 60 °C for 12 h, which can prevent aggregated or undissolved particles from forming as well as clogging of the orifice spinneret. Finally, after the dope solution is transferred to a syringe pump (Teledyne Isco), the loaded dope is degassed at 60 °C for 3 h to reduce gravity settling of the sorbent materials in the solution. According to the spinning parameters listed in Table S2, Supporting Information, the various MgO/PEI monolithic and hollow precursor fibers are spun via a dry-jet/wet-quench spinning process. Finally, after the spinning process, the precursor fibers are subjected to solvent exchange with DI water (x2)/methanol (x3)/hexane (x3) to prevent pore collapse of the polymer matrix.

**Crosslinking of as-spun precursor fibers**
In order to increase chemical resistance toward DMF, the MgO/PEI precursor fiber was thermally crosslinked in a tube furnace and heated at 270 °C and 12 h in an Ar atmosphere. For another way, the precursor fibers can be chemically crosslinked with diamine groups such as ethylenediamine (EDA) and p-xylylenediamine (XDA) in two different reactors. In a batch reactor, the precursor fibers were immersed for 12 h in a 100 mL methanol solution that contained 1.5 g of EDA and 3.5g of XDA and rinsed with fresh methanol to remove the residual crosslinkers. In a continuous flow module system, the MgO/PEI precursor fibers modulated into the 1/4” line were chemically crosslinked by flowing the amine solution to the module at 1 mL/min for 12 h via a peristaltic pump. To effectively disperse the crosslinkers during the reaction, the solution in a liquid reservoir was stirred by a magnetic bar at 400 rpm. After the reaction, the fresh methanol was flowed to the module for washing at 1 mL/min for 1 h.
**Synthesis of amine-appended Mg(dobpdc)/PEI fiber sorbents (batch synthesis)**

To convert the MgO/PEI precursor fibers (46 wt% with 50 nm MgO) to Mg(dobpdc)/PEI, 187 mg of H(dobpdc) linker (0.68 mmol) and 2.7 mL of DMF were added into a glass pressure vessel (35 mL) as a batch reactor and heated at 120 °C until the ligand was completely dissolved. The molar concentration of the ligand solution was 0.25 M. After that, 120 mg of the monolithic or hollow MgO/PEI precursor fibers corresponding to 55 mg of MgO (= 1.36 mmol of MgO) was placed in the reactor and maintained in a synthetic oven at 120 °C for 6 h. In other samples (i.e., 25 – 73 wt% MgO), MgO/PEI precursor fibers in which the loaded MgO became 1.36 mmol were added. Finally, the resulting Mg(dobpdc)/PEI fiber sorbents were washed with DMF (20 mL x5) and methanol (20 mL x5) and activated at 120 °C overnight in a vacuum. Fully activated the MOF/PEI fiber sorbents were soaked in anhydrous hexane solution containing N,N’-dimethylethlenediamine (mmen, diamine) for 4 h, while maintaining 1 and 9 mL of diamine and hexane, respectively, per 30 mg of the Mgz(dobpdc) which were loaded in the polymer matrix. Next, the amine-appended fiber sorbents were rinsed with hexane (20 mL x3) and dried under a vacuum. In the case of the N,N’-bis(3-aminopropyl)-1,4-diaminobutane (tetraamine), the activated the MOF/PEI fiber sorbents were soaked in an anhydrous toluene solution containing tetraamine for 4 h, while maintaining 2 and 8 mL of tetraamine and toluene, respectively, per 20 mg of the Mgz(dobpdc) which were loaded in the polymer matrix. Because the melting point of the tetraamine is 30 °C, the amine source was melted in an oven at 60 °C before the preparation of the amine solution. In addition, the sample was left at 60 °C for 24 h and washed with toluene (3 × 20 mL), and dried at 100 °C.

The dry CO2 isotherms (Figure S15) of the diamine-Mgz(dobpdc)/PEI generated from three different precursors (46 wt% with 50 nm MgO, 46 wt% with 300 nm MgO, and 73 wt% with 300 nm MgO) were compared with the diamine-Mgz(dobpdc) synthesized from the MgO powders. The amine-appended MOF fiber sorbent synthesized from the 73 wt% precursors with 300 nm MgO showed only a 5% difference in equilibrium CO2 uptake at 298K to an ideal case of MOF prepared from MgO powder. As the MgO loading in the precursor fiber decreased (73 wt% to 46 wt%), the CO2 uptake of the analogous MOF fiber sorbent decreased to 3.74 mmol/g-fiber, which corresponded to a 15% loss in CO2 sorption capacity. Notably, MOF fiber sorbents synthesized from 46 wt% precursor fiber showed similar CO2 uptake regardless of the MgO particle size. The final loading amount of MOF in the fiber sorbents prepared from different MgO loadings was calculated via 77K N2 physisorption (Figure S16). As the MgO loading in the precursor fiber increased (25 wt% to 46 wt%), the increment in the Brunauer–Emmett–Teller (BET) surface area was almost linear, confirming that complete MOF conversion was achieved in these fibers. However, the Mgz(dobpdc)/PEI prepared from the 73 wt% precursor fiber showed less increase in the BET surface area, indicating the incomplete MOF conversion of the MgO precursors. Furthermore, the CO2 uptakes measured at 298K of diamine-Mgz(dobpdc)/PEI had a similar trend, illustrating that only partial MOF conversion occurred in 73 wt% fiber precursors (Figure S17). Based on the CO2 sorption and BET surface area, only 60% of the MgO was expected to be converted into MOF in the 73 wt% precursor fiber, which revealed that severe delamination and MgO aggregation affected the optimal synthesis of the MOF fiber sorbent.

**Preparation of amine-appended fiber sorbent module (flow synthesis)**

The amine-appended Mgz(dobpdc)/PEI monolithic fiber module was prepared from a module filled with 11 MgO/PEI crosslinked precursor fibers in a continuous flow system. All connections in the system were PTFE 1/8” tubing excluding the module which used stainless 1/4” fitting and tubing (Swagelok®). In all steps on the synthesis, the solution in a liquid reservoir was flowed through the module to 1 mL/min via a peristaltic pump and flushed before reaction with the solvent used in the next step. Since the length of the fiber sorbents becomes longer due to the volume expansion of the crystal after MOF conversion, it is recommended to load MgO/PEI fiber precursors that are about 1
cm shorter than the length of the module. Before the MOF conversion step, a H$_2$(dobpdc) linker solution is sealed in a liquid reservoir and placed in a convection oven at 120 °C until the color of the solution becomes transparent. During the MOF conversion reaction, the ligand solution was continuously circulated into the system at 120 °C for 6 h and the liquid reservoir and fiber module were located in a convective oven to prevent precipitation of the ligand solution into particles at room temperature. After the reaction, an Mg$_2$(dobpdc)/PEI module was washed and flushed with DMF (20 mL x2) and methanol (20 mL x2) for 20 mins per step. The following procedure was used to insert amine functional groups such as diamine and tetraamine into the MOF through a continuous flow system. In the case of diamine insertion, the solution consisted of anhydrous hexane containing 10% v/v N,N'-dimethylethylenediamine which was flowed into the module for 4 hours at room temperature. Then the samples were washed with hexane (20 mL x2) for 10 mins and dried at 100 °C in a vacuum. Similarly, for tetraamine insertion, anhydrous toluene containing 20% v/v N,N’-bis(3-aminopropyl)-1,4-diaminobutane flowed to the Mg$_2$(dobpdc)/PEI module for 24 h at 60 °C. The tetraamine solution exists as a solid at room temperature, so all equipment must be placed in an oven. In all drying processes of the sample, the temperature should be slowly raised from room temperature to the target temperature to minimize deformation of the fiber shape due to evaporation of the solvent.

Material Characterizations:

**Thermogravimetric Analysis (TGA)**
TGA of the fiber sorbents was performed in the temperature range from 30 °C to 750 °C with a heating rate of 10 °C/min in the air via a TG209 F1 Libra.

**Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS)**
SEM and EDS of the samples were performed on a NOVA 230 (FEI) with a cold field emission gun at an accelerating voltage of 10 kV and an emission current of 0.64 mA with a working distance of 5 mm. The samples were sputtered using a SPT-20, COXEM sputter with Au target.

**X-ray Diffraction (XRD)**
Powder XRD of the samples was tested on a RIGAKU Smart Lab diffractometer with a Cu Kα anode (λ= 0.1542 nm) operating at 35 kV and 40 mA. The diffraction patterns were plotted in the range of 2 theta from 3 to 50 ° with a step size of 0.01° per step. In the case of the fiber sorbents, the samples were ground and sampled using a mortar for the powder XRD.

**Nitrogen Physisorption and CO$_2$ Sorption Measurements**
N$_2$ physisorption at 77 K was conducted in ASAP 2020 HD (Micromeritics) to determine the Brunauer-Emmett-Teller (BET) surface area and type of isotherm adsorption of the powders and fiber sorbents. Fibers were cut into lengths of 1 ~ 1.5 cm and inserted into the sample analysis tube to fully activate the samples. CO$_2$ Sorption performance of the samples was performed under a pressure range of 0 to 1 bar and operating temperature of 25 to 150 °C at 100 % CO$_2$. Isosteric heat of sorption was calculated based on isotherm data obtained from three different operating temperatures.

**Fourier Transform-Infrared Spectrometer (FT-IR)**
FT-IR (Nicolet iS50, Thermo Fisher Scientific Instrument) was carried out to demonstrate and compare the chemical structure of fiber sorbents over a spectrum area from 4000 to 500 cm$^{-1}$.

**Elemental Analysis (EA)**
EA of the samples was performed by Flash EA 1112, Thermo Finnigan, Italia. The fiber sorbents were activated at 120 °C for 2 hours before analysis.

**Mercury Porosimeter**
Mercury porosimetry of the samples was performed via a Micromeritics AutoPore IV 9520 up to 60,000 psi, corresponding to an intrusion pore diameter from 900 to 0.003 µm.

**CO₂ Breakthrough Experiments:**
Breakthrough experiments of the packed-fiber module were performed in an in-house building breakthrough system (Figure S25) and connected to an Omnistar mass spectrometer (MS) (Pfeiffer Vacuum). The flow rate of the feed gas and He tracer to the fiber module were controlled by a mass flow controller (MFC) and the real-time CO₂ concentration at the outlet was transiently measured by MS. The amine-appended Mg₂(dobpdc)/PEI module was activated in the breakthrough system in a vacuum at 120 °C for 12 h and cooled down to 35 °C under Ar flow before adsorption. Breakthrough curves were measured under various feed flow rates (30 – 90 sccm), molar compositions (400 ppm, 15 % CO₂), and humidity (0, 100 RH %) at 35 °C and 1 bar. In the experiment for the humid cycle, the fiber module was pre-humidified with wet N₂ before the adsorption until the H₂O signal was in equilibrium. In addition, the chamber and all lines were heated at 60 °C to prevent water condensation in the system. In the experiment for the humid cycle stability in realistic conditions, the diamine-/tetraamine-Mg₂(dobpdc)MOF/PEI were additionally performed to long-term cyclic CO₂ adsorption/desorption up to 200 cycles without the pre-humidification step. The cycles proceeded in the humid conditions (100 % RH %) mentioned above, and the adsorption capacity of the sample was measured every 50 cycles. The pressure drop of the module was derived from two pressure transducers which were attached to each end of the module at various inlet velocities of N₂. In empty cells, there was little difference in pressure drop in the range of the inlet velocity (20-200 sccm), so losses due to friction drag, stainless steel tubing, or fittings could be ignored.⁸
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