Supporting Information for:

Amine-dependent CO₂ Sorption on Amine-Impregnated Mg₂(dobpdc) MOF under Humid Conditions

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1. Linear PEI (LPEI) synthesis

Materials

Anhydrous acetonitrile (>99.8%) and calcium hydride (~93%) was acquired from Thermo Scientific. Ethylenediamine (\geq 99%), 2-ethyl-2-oxaoline (\geq 99%), methanol (\geq 99.8%), and sodium hydroxide (\geq 97%) were obtained from Sigma Aldrich. Methyl p-toluenesulfonate (\geq 98%) and hydrochloric acid (37%) were purchased from VWR. Ammonium hydroxide solution (14.8 M) was purchased from Fisher Scientific.

Synthesis

The synthesis of linear PEI (LPEI) was adapted from previous methods.^{1,2} To synthesize poly(2ethyl-2-oxazoline), anhydrous acetonitrile and 2-ethyl-2-oxaoline were respectively stirred overnight with calcium hydride and vacuum distilled. A Schlenk flask capped with a septum was evacuated and purged with argon several times. While Ar was flowed through the neck of the Schlenk flask, 2-ethyl-2-oxaoline (8.14 g, 8.29 mL, 0.082 mol) and acetonitrile (62 mL, 1.19 mol) were added to the flask by injection through the septum and stirred for 5 min. Additionally, methyl p-toluenesulfonate (1.28 g, 6.72×10⁻³ mol) was added while stirring at room temperature and the reaction mixture was bubbled with Ar for another 30 min. Subsequently, the reaction mixture was heated at 80 °C in an oil bath for 48 h. The reaction was quenched by injecting ethylenediamine (0.81 g, 0.90 mL, 1.34×10⁻² mol) and stirring overnight at room temperature. Acetonitrile and excess ethylenediamine were removed by rotary evaporation at 50 °C to obtain crude poly(2-ethyl-2-oxazoline), the LPEI prepolymer. Hydrolysis of the prepolymer was performed by adding 5M HCl (163 mL) and stirring under reflux at 110 °C for 48 h to remove the side chain. After cooling to room temperature, excess water and acid were removed by rotary evaporation. The pH of the solution was adjusted to 14 by adding concentrated NaOH solution (10 M) while stirring in an ice bath. The slurry was centrifuged, and the resulting supernatant was poured off. The precipitate was washed twice with ammonium hydroxide solution and once with D.I. water, centrifuging and disposing of the supernatant after each wash. The final precipitate was dissolved in methanol then

filtered using a syringe filter (0.22 μ m, PTFE). The solution was dried by rotary evaporation (50°C) to remove methanol then dried under vacuum (<20 mTorr) at room temperature overnight.



Figure S1. Proton (¹H) NMR (500 MHz) spectra of as synthesized LPEI and molecular weight calculation in CD_3OD .

2. Amine appended Mg₂(dobpdc) for DAC and the failure of CO₂ insertion mechanism under DAC conditions

In this section, we report our observation that m-2-m-Mg₂(dobpdc) showed a higher adsorption capacity at low pressure (20 ppm) from CO₂ isotherm at 0 °C compared to 25 °C. While the increase of CO₂ uptake in isotherms can lead to the enhanced adsorption capacity and carbon capture fraction of fixed bed experiment, the measured breakthrough results under 400 ppm CO₂. /N₂ at temperatures from -20 to 25 °C indicated similar CO₂ adsorption capacities at different temperatures without a sign of shock-wave breakthrough profiles likely due to the failure in CO₂ insertion mechanism.

Amine-appended Mg₂(dobpdc) adsorbents showed S-shaped step isotherms with high CO₂ adsorption capacity.³⁻⁶ While this material class has shown promising results in applications with high CO₂ concentrations such as post-combustion CO₂ capture, their performance in direct air capture (DAC) has been less stellar because their step pressures are higher than or close to atmospheric CO₂ pressures (0.4 mbar).⁷ Two ways of controlling their adsorption-onset-pressures are to use different amines, thereby changing the interaction between amine and magnesium open metal sites, or changing the adsorption temperature.⁵ One of the lowest onset step pressures reported in the literature was near 0.4 mbar for the m-2-m-Mg₂(dobpdc) composition, yet this material's distinct "slip-shock-wave" type breakthrough profile in a fixed bed led to a low CO₂ capture fraction of only 44%.⁷ Darunte et. al demonstrated that the low capture fraction and transient zone of for m-2-m-Mg₂(dobpdc) are associated with the shape of its isotherm, causing stretched concentration fronts.⁷ We hypothesized that the long transient zone can be shortened if

the step pressure is well below adsorption pressure (i.e. 0.4 mbar), which might be achieved by lowering the adsorption temperature. To this end, we evaluated the potential of this material class for cold temperature DAC.

Successful synthesis of the Mg₂(dobpdc) parent framework was confirmed by X-ray diffraction and its high surface area derived from nitrogen physisorption, as shown in Fig. S2. The high surface area (3750 m²/g) of the parent Mg₂(dobpdc) suggests its merit for use in gas adsorption. Four amines (m-2, m-2-m, ee-2, ii-2) with a wide range of onset step pressures were selected to test our hypothesis. In Fig. S3, the equilibration time for each dose was optimized, as slow CO₂ adsorption kinetics for this material class can result in inaccurate step pressures. S-shaped isotherms (25 °C) and their onset pressure (Fig. S4) evidence the successful synthesis of four different amine-appended Mg₂(dobpdc) adsorbents, as previously reported by Siegelman et al.⁵ To demonstrate a step pressure shift at lower temperatures, isotherms at 0 °C were measured, as shown in Fig. S5. Only one isotherm point could be obtained at 0 °C from the m-2-Mg₂(dobpdc) and m-2-m-Mg₂(dobpdc) samples over three weeks of equilibration, which shows their slow CO_2 adsorption kinetics. However, the measured 0.4 and 1.7 mmol/g of CO_2 adsorption at 20 ppm (for m-2-m and m-2, respectively) demonstrate that the onset pressure can be moved to lower pressures at colder temperatures, suggesting the potential for use of these amine appended MOFs for coldtemperature DAC. For further study, m-2-m-Mg₂(dobpdc) was chosen due to its low onset step pressure and relatively lower desorption temperature (determined from its pure CO₂ isobar) among different candidate amines compared to its boiling temperature, providing limited evaporation of amines during regeneration (Table S1). Breakthrough experiments for m-2-m-Mg₂(dobpdc) were conducted in a fixed bed under dry conditions at -20, 0, and 25 °C (Fig. S6) to explore the CO₂ capture fraction at colder temperatures in a dynamic adsorption environment. Unexpectedly,

relatively sharp breakthrough profiles were observed, as opposed to the distinct shock-wave type profiles reported in other studies.^{3, 7} We surmise that the CO₂ insertion mechanism did not occur due to the slow kinetics and low concentration driving force at DAC conditions. The adsorption mechanism of amine-appended Mg₂(dobpdc) is considered to occur by pre-step ammonium carbamate formation by reversible CO₂ physisorption and ammonium carbamate chain formation by CO₂ insertion (chemisorption).^{8, 9} For the successful CO₂ insertion reaction, physisorption of CO₂ to amines, C-N bond formation, proton transfer, metal oxygen bond formation, and charge stabilization of the neighboring ammonium are all required.^{8, 9} With this multi-step reaction pathway, the low concentration of reactant (CO₂) can result in failure of the reaction due to the decreased kinetics and thermodynamic driving force. Indeed, Martell et al. reported longer CO₂ adsorption (15% CO₂/N₂) induction periods for m-2-m-Mg₂(dobpdc) at temperatures close to the step adsorption temperature in isobars and attributed this to the increase in entropic penalty to form adsorption intermediate species.^{8,9} Although Darunte et. al observed the shock-dispersive wave profile of m-2-m-Mg₂(dobpdc) under DAC conditions, the use of He balanced 400 ppm CO₂ in his study might facilitate the insertion step by removing competitive adsorption between CO_2 (400 ppm) and N₂ (79%).^{7, 8} We measured the pseudo equilibrium CO₂ capture capacities (95% C/C₀) of m-2-m-Mg₂(dobpdc) from dynamic breakthrough experiments, achieving similar uptakes at various temperatures (1.29, 1.38, and 1.16 mmol/g at -20, 0, and 25 °C, respectively). However, these uptake values (~0.25 mol CO_2 / mol diamine) were much lower than its isotherm capacity (2.9 mmol/g at 0.4 mbar and 25 °C) and far below the theoretical amine efficiency (1 mol CO₂/mol diamine). This is likely due to the failure of the CO₂ insertion mechanism to operate at the 400 ppm CO₂ concentration, regardless of adsorption temperature. Therefore, we sought to explore another amine functionalization strategy to develop Mg₂(dobpdc)-based DAC sorbents.



Figure S2. XRD patterns and N₂ physisorption results for the as-synthesized Mg₂(dobpdc). Langmuir surface area of the synthesized Mg₂(dobpdc) was 3750 m²/g. The pore volume of as-synthesized Mg₂(dobpdc) at 0.93 P/P₀ was 1.33 mL/g.



Figure S3. CO_2 isotherms for ii-2-Mg₂(dobpdc) at 25 °C with different equilibration times seeking to locate the step pressure precisely by removing kinetic effects.



Figure S4. CO₂ isotherms for diamine-appended Mg₂(dobpdc) samples at 25 °C.



Figure S5. CO_2 isotherms for diamine-appended Mg₂(dobpdc) at 0 °C. More isotherm points for m-2 and m-2-m-Mg₂(dobpdc) could not be measured due to the slow equilibration (over three weeks for the first isotherm point).

Materials	Adsorption Temp, °C	Desorption Temp, °C	Boling Point, °C
3-4-3 tetra amine ⁴	120	160	308
2-ampd ³	90	140	67
m-2 ⁵	140	150	115
m-2-m ⁵	125	135	118
mm-2 ⁵	60	100	105
dmpn ⁶	60	93	152
ee-2 ⁵	60	80	145
ii-2 ⁵	30	70	170

Table S1. Adsorption, desorption, and boiling temperatures of amine-appended $Mg_2(dobpdc)$ from literature.

* Adsorption and desorption temperatures were based on pure CO₂ isobar.



Figure S6. Breakthrough profiles for m-2-m-Mg₂(dobpdc) under dry 400 ppm CO_2/N_2 at temperatures from -20 to 25 °C. Before each experiment, the sample was desorbed at 110 °C for 2 h until the outlet CO_2 concentration was lower than 5 ppm under 40 sccm of N_2 . The adsorption flow rate was 22 sccm.

3. CO₂ adsorption behavior of oligomeric and polymeric amine-impregnated Mg₂(dobpdc) under dry DAC conditions

Our preliminary study about the originally developed amine appended Mg₂(dobpdc) showed the failure of its CO₂ insertion mechanism at cold temperatures,⁵ leading to lower amine efficiency (0.25 mol CO₂/ mol diamine) than its theoretical value (1.0 mol CO₂/ mol diamine). In this section, to tackle obstacles stemming from the CO₂ insertion mechanism, we employed the amine impregnation method and observed the successful removal of the CO₂ step-isotherm.

Amine impregnation, whereby amine is progressively added to mostly or completely fill the pore space of a support material, has been extensively studied for CO2 capture.^{10, 11} One of the advantages of this method is it loads a large amount of amine compared to stochiometric functionalization methods, like open-coordination site titration (referred to here as amineappended samples). Although this method may cause a mass transfer resistance if used for materials with small pore size, the impregnation method should result in a material that removes the step adsorption behavior in the CO₂ isotherms due to the presence of several layers of amines in the Mg_2 (dobpdc) pores, thereby increasing the carbon capture fraction (captured CO₂/flowed CO_2) of the amine-functionalized Mg₂(dobpdc) under DAC conditions. To test this hypothesis, the Mg₂(dobpdc) framework was functionalized by tetraethylenepentaamine (TEPA) and molecular weight 800 branched poly(ethyleneimine) (BPEI) at different weight loadings by the wet impregnation method. Isotherms (25 °C) shown in Fig. S7 demonstrate the removal of the step adsorption behavior. However, the isotherms show unique trends and offer differing isotherm shapes. The lowest amine loaded samples yielded the highest CO₂ uptakes at high CO₂ partial pressures, which is unusual compared to amine-impregnated oxide (e.g. silica, alumina) supports.^{12, 13} The higher loading samples, with 50% or 70% wt TEPA or BPEI, also gave unusual

isotherm shapes, independent of CO₂ pressure over the range tested. At low CO₂ pressures (Fig. S7c,d), the 30%wt and 50%wt samples had similar uptakes, whereas the 70%wt samples offered much higher capacities. These results can be rationalized based on the mechanism of pore filling with amines and the resulting mass transfer resistance. Compared to typical oxide supports with pores ranging from 5 to 20 nm in diameter, Mg₂(dobpdc) MOFs have smaller pore openings (2.1 nm),¹¹ which hinder the incorporation of larger amines like TEPA or BPEI into the pore space. In fact, the radius of gyration for BPEI with 800 Da is estimated to be ~ 1.4 nm (2.8 nm in diameter), which is comparable to the 2.1 nm of the pore diameter of Mg₂(dobpdc).^{5, 14} The support can likely accommodate some of the amines in the pores at low total amine loadings (30%wt), producing isotherms that are qualitatively like those produced using the same amines on oxide supports. But at higher amine loadings, the pores become clogged with amine (50%wt) and films of excess PEI coating the outer surface of the MOF particles develop (70%wt). The larger amount of amine in this external film, which can quickly adsorb CO₂ at low pressure, leads to higher uptake for the higher loaded samples (Fig. S7c,d) at low CO₂ pressure.¹⁵ Taking BPEI as an example, based on the pore volume of Mg₂(dobpdc) (1.33 mL/g at 0.93 P/P₀) and the density of BPEI (1.05 g/mL), the estimated pore filling fractions for BPEI 30, 50, and 70% wt Mg₂(dobpdc) samples are 31, 72, and 167%v/v, respectively, assuming all the amines entered the MOF pores. Also, the nitrogen and carbon ratio (N/C) at the sorbent surface by X-ray photoelectronic spectroscopy (XPS) and bulk composition by elemental analysis (EA) are similar for BPEI(30)-Mg₂(dobpdc) (0.28 and 0.25) while the ratios for BPEI(70)-Mg₂(dobpdc) are different, with the surface higher than the bulk (0.56 and 0.46; **Table S2**). Additionally, the XPS peak for Mg was undetectable for BPEI(70)-Mg₂(dobpdc), likely due to the thick BPEI surface layers, further suggesting the existence of an amine film on the outside surface of the BPEI(70)-Mg₂(dobpdc) particles. This pore

clogging/overfilling phenomena in higher loading samples (50 and 70%wt) can also explain the flat isotherm uptake trend at higher pressure (> 10 mbar); a significant mass transfer resistance by pore clogging limits further interaction of amines inside Mg₂(dobpdc) and CO₂ gas molecules. Additionally, increasing viscosity of amines upon adsorption of CO₂ has been reported in the literature.¹⁶

Fig. S8 presents breakthrough profiles under dry conditions at different DAC temperatures. Overall, the breakthrough profiles of amine impregnated Mg₂(dobpdc) show no evidence of shockwave breakthrough profiles previously observed for amine-appended samples,⁷ thereby leading to higher CO₂ capture fractions.^{3, 7} All samples except for BPEI(30)-Mg₂(dobpdc) displayed higher CO₂ capacities at higher temperatures, suggesting significant impacts of pore clogging or blocking by amines, with diffusion limitations partially alleviated by increased amine mobility at higher temperatures, outweighing the thermodynamic decrease in adsorption capacity at higher temperature associated with the exothermic nature of adsorption (Fig. S8 and Table S3). A similar breakthrough time but a longer mass transfer zone (i.e., the zone between breakthrough and the pseudo equilibrium point) was observed for BPEI(30)-Mg₂(dobpdc) at lower temperatures (Fig. S8), resulting in higher CO₂ adsorption capacities at colder temperatures for this material. This suggests that although the mass transfer rate of CO₂ through the amine domain is slower at colder temperatures, the adsorption capacity still increased due to the higher thermodynamic driving force, providing evidence of the existence of amines in the pores that are accessible to CO₂ at this lower amine loading. The higher PEI loading negatively affects pseudo equilibrium capacities at cold temperatures (-20 and 0 °C) due to the congested pores, thereby reducing the accessibility of CO₂ to amines but increasing the capacities measured at 25 °C thanks to the more mobile nature of the amines. Contrarily, TEPA-impregnated samples showed the lower adsorption capacities at

50%wt. A possible explanation is that TEPA tends to fill the Mg₂(dobpdc) pores at 50%wt rather than coating the pore outer surface, endowing a mass transfer resistance in the pores compared to PEI, which the pore and develops films on the outer pore surface at the same time due to its comparable size to the Mg₂(dobpdc) pore.^{5, 14} As a consequence, TEPA samples showed higher CO₂ capture capacities than PEI analogues at 30%wt loading, probably due to the relatively compact size of TEPA, the absence of tertiary amines, improved chain mobility, and a more favorable distribution of the amines in the Mg₂(dobpdc) pores. However, the trend is reversed at 50%wt as PEI tends to develop films on the outer pore surface more than TEPA due to its size, and the outer amine films are more accessible to CO₂ than pore-confined amines.



Figure S7. Isotherms for amine-impregnated $Mg_2(dobpdc)$ at 25 °C. (a) and (b) are for PEI and TEPA with different amine weight loading fractions, respectively. (c) and (d) are the same isotherms with magnification in the lower pressure range.

Sample	C, wt%	H, wt%	N, wt%	O, wt%	Mg, wt%	N/C ratio
PEI30-Mg ₂ (dobpdc) by XPS	58.2	-	16.6	19.2	6.0	0.28
PEI70-Mg ₂ (dobpdc) by XPS	60.3	-	34	5.7	-	0.56
PEI30-Mg ₂ (dobpdc) by EA	48	6.7	11.9	33	.4*	0.25
PEI70-Mg ₂ (dobpdc) by EA	49.6	9.3	22.7	18	.4*	0.46

Table S2. The chemical composition of PEI-impregnated $Mg_2(dobpdc)$ from XPS and EA

* The weight fraction of O and Mg from EA analysis cannot be deconvoluted since the analysis was only sensitive to C, H, and N.



Figure S8. Breakthrough profiles for PEI-Mg₂(dobpdc) and TEPA-Mg₂(dobpdc) under dry 400 ppm CO₂/N₂ at temperatures from -20 to 25 °C. (a), (c), and (e) represent PEI 30, 50, 70%wt Mg₂(dobpdc) and (b) and (d) show TEPA 30 and 50%wt Mg₂(dobpdc). The samples were desorbed at 80 °C for 3 h under 40 sccm of N₂. The flow rate was 22 sccm and particles between 125 and 425 μ m were sieved and used for the experiments. The sample weight used during the fixed bed experiments was 60 mg (wet).

	B.T.* capacity, mmol/g	P.E.* capacity, mmol/g	Amine efficiency**,
Materials	at -20, 0, 25 °C	at -20, 0, 25 °C	CO ₂ /amine at 25 °C
PEI(30)	0.18, 0.14, 0.17	0.56, 0.43, 0.3	0.05
PEI(50)	0.1, 0.25, 0.38	0.23, 0.39, 0.59	0.05
PEI(70)	0.07, 0.26, 0.66	0.1, 0.3, 0.79	0.06
		, ,	
TEPA(30)	0.05, 0.14, 0.32	0.27, 0.47, 0.8	0.12
		, ,	
TEPA(50)	0.09, 0.2, 0.37	0.2, 0.33, 0.54	0.05
	· · ·	· · ·	

Table S3. CO2 capture performance of amine-impregnated Mg2(dobpdc) from dry fixed bed experiments at different temperatures.

*B.T. and P.E. represent breakthrough and pseudo equilibrium, respectively **P.E. was used to calculate amine efficiency

*** 70% wt TEPA impregnated-Mg₂(dobpdc) was excluded from discussion due to its unstable nature during regeneration. See constant loss of weight during thermal cycles between 30-80 °C in **Fig. S12**.

4. Significant increase in CO₂ uptake of oligomeric and polymeric amine-impregnated Mg₂(dobpdc) at 25 °C and 70% RH.

In this section, both oligomeric and polymeric amine-impregnated Mg₂(dobpdc) that showed a significant increase in their CO₂ uptakes under humid DAC conditions are discussed. Poor mass transfer was observed with long mass transfer zones at temperatures <25 °C (70% RH). However, sharp breakthrough curves at 25 °C and 70% RH with more than two-fold increase of amine efficiency implies that mass transfer resistances can be overcome at the given condition. Breakthrough experiments with oligomeric amine-impregnated Mg₂(dobpdc) at different flow rates demonstrated the removal of the flow rate dependence that was observed by amine-appended Mg₂(dobpdc) in the literature,⁷ again showing how these materials differ from the classic amine-appended materials.

 CO_2 adsorption in the presence of humidity is a critical factor to examine, since all real feeds are humid for DAC. Furthermore, humidity can be advantageous for CO_2 adsorption on aminefunctionalized sorbents because it can increase the amine efficiency (ratio of captured CO_2 to the number of amines) and improve CO_2 diffusion by opening new modes of CO_2 sorption by altering the CO_2 -amine adsorption chemistry and/or releasing amine-amine hydrogen bonds, creating more free amine binding sites.^{17, 18, 19} In parallel, at high levels of humidity, water can compete with CO_2 for pore space and binding sites, reducing the efficacy of the sorbents. Breakthrough profiles of BPEI and TEPA-impregnated samples under 70% RH at a range of temperatures (-20 to 25 °C) were measured and are provided in **Fig. S9** and **Table S3**. The breakthrough profiles at cold temperatures (< 25 °C) display long mass transfer zones even under humid conditions. This indicates that the impregnated amines in the narrow (2.1 nm) and one-dimensional Mg₂(dobpdc) pores create prominent mass transfer limitations for CO_2 adsorption at cold temperatures. The low value of T_2 (spin-spin or transverse relaxation time) in ¹H T_1 - T_2 correlation NMR spectra, as shown in section 5 in below, also corroborates the low mobility of the amines in Mg₂(dobpdc) compared to the reported bulk amine behavior (BPEI and TEPA) or trends for BPEI impregnated SBA-15 samples reported by Moon et al.²⁰ Further discussion of ¹H T_1 - T_2 correlation NMR results can be found in section 5 or our previous literature.^{15, 20, 21}

At 25 °C, relatively sharp breakthrough profiles are observed under humid conditions due to the increased amine mobility, providing enhanced diffusion of CO₂ into the amine domains. While amines with good accessibility to CO₂ aids CO₂ adsorption, there is a potential disadvantage of having such highly exposed amines - their potential volatility during regeneration. Indeed, TEPA(70)-Mg₂(dobpdc) showed increasing weight loss over cycling compared to TEPA(50)-Mg₂(dobpdc) during TGA cycles between 30 and 80 °C, attributed to the state and location of the amines, with excess amines on the external MOF surface more susceptible to evaporation (**Fig. S11**). Therefore, we decided to focus on the 30 and 50%wt amine-impregnated samples at 25 °C for further studies.

A summary of column breakthrough results is presented in **Fig. S12**. Under humid conditions, it is noteworthy that the amine efficiency (AE) of the 50%wt loaded BPEI was almost two times lower than that of the 50%wt loaded TEPA sample, suggesting that BPEI chains are harder to unravel than TEPA chains due to the greater polymer entanglement and/or amine-amine hydrogen bonding points within the BPEI chains. In both dry and humid cases, higher amine loadings showed equal or lower AE than lower amine loadings regardless of the types of amine, implying less CO_2 accessibility to the amines in the higher loading samples. Comparing dry and humid (70% RH) breakthrough experiments, the humidity enhanced both the CO_2 adsorption capacity and AE for all samples by more than a factor of two. Given the theoretical maximum amine efficiency increase is by two from dry (carbamate, AE: 0.5) to humid conditions (bicarbonate, AE: 1.0),^{22, 23, 24} it can be hypothesized that the diffusion of CO₂ is the main cause of the observed improvement, with water enhancing amine chain mobility, rather then a change from carbamate to bicarbonate stoichiometry alone. Among the samples, BPEI(30)-Mg₂(dobpdc) and TEPA(50)-Mg₂(dobpdc) showed the best adsorption capacities at 25 °C under humid DAC conditions. Therefore, they were subjected to further analyses and discussion in the main body of the paper. Finally, the flow rate dependence of TEPA(50)-Mg₂(dobpdc) was evaluated, as shown in **Fig. S15**, since a lower CO₂ capture fraction at higher flow rates using m-2-m-Mg₂(dobpdc) reduced its efficacy for practical DAC application. ⁷ As expected, the use of TEPA(50)-Mg₂(dobpdc) removed the flow rate dependence that originated from the slow kinetics of the CO₂ insertion mechanism of amine appended Mg₂(dobpdc).



Figure S9. Breakthrough profiles for PEI-Mg₂(dobpdc) and TEPA-Mg₂(dobpdc) under humid (70% RH) 400 ppm CO₂/N₂ at temperatures from -20 to 25 °C. (a) and (c) represent PEI(30)-Mg₂(dobpdc) and PEI(50)-Mg₂(dobpdc). (b) and (d) show TEPA(30)-Mg₂(dobpdc) and TEPA(50)-Mg₂(dobpdc). The samples were desorbed at 80 °C for 3 h under 40 sccm of N₂. The flow rate of 400 ppm CO₂/N₂ was 22 sccm and particles between 125 and 425 μ m were sieved and used for the experiments. The sample weight used during the fixed bed experiments was 60 mg (wet). Unusual curve shapes at 0 °C are discussed in **Fig. S10**, below.



Figure S10. CO₂ and water breakthrough profiles for (a) PEI(50)-Mg₂(dobpdc) and TEPA(50)-Mg₂(dobpdc) at 0 °C and 70% RH. The sudden dip in CO₂ breakthrough profiles occurred right after the water breakthrough. This suggests that the saturation of the samples with water results in more adsorption sites becoming available, for example, by untangling amines in the pores with hydration or creating a basic, amine-water liquid pocket. At -20 °C or 25 °C, water did not break through during the CO₂ adsorption period or did so almost immediately due to the low (0.73 mmol/mol) or high (21.9 mmol/mol) water concentration, respectively (**Fig. S9**). Therefore, a sudden jag in the breakthrough curves, as observed at 0 °C in the humid breakthrough experiments, was not observed.

Table S4. CO_2 capture performance of amine-impregnated Mg₂(dobpdc) from humid (70% RH) fixed bed experiments at different temperatures.

Materials	B.T.* capacity,	P.E.* capacity, mmol/g	Amine efficiency**,

	mmol/g at -20, 0, 25	at -20, 0, 25 °C	CO ₂ /amine at 25 °C
	°C		
PEI(30)	0.32, 0.43, 1.48	0.73, 2.45, 2.5	0.39
PEI(50)	0.19, 0.29, 0.72	0.35, 1.05, 1.86	0.16
TEDA(20)	0 10 0 42 1 52	076 245 287	0.42
IEPA(50)	0.19, 0.43, 1.32	0.70, 2.43, 2.87	0.42
TEPA(50)	0.18, 0.3, 3.18	0.32, 3.37, 3.9	0.33
()	, -,	,)	

*B.T. and P.E. represent breakthrough and pseudo equilibrium, respectively **P.E. was used to calculate amine efficiency



Figure S11. Weight profiles of (a) TEPA(70)-Mg₂(dobpdc) and (b) TEPA(50)-Mg₂(dobpdc) during dry CO₂ adsorption (30 °C for 1 h) and desorption (80 °C for 1 h) cycles in TGA. Initially, desorption was conducted at 80 °C for 4 h under dry N₂.



Figure S12. Summary of breakthrough experiment results; (a) pseudo equilibrium capacity and (b) amine efficiency at 25 °C and 400 ppm CO_2/N_2 under dry or 70% RH conditions.



Figure S13. The effect of flow rate in breakthrough profiles for TEPA(50)-Mg₂(dobpdc) under 70% RH and 400 pm CO_2/N_2 flow without presaturation. The samples were desorbed at 80 °C for 3 h under 40 sccm of N₂. The flow rates were 22 and 44 sccm (400 ppm CO_2/N_2), resulting in 3.3 and 3.2 mmol/g respectively. Particles between 125 and 425 μ m were sieved and used for the experiments. Sample weight used during the fixed bed experiments was 60 mg (wet). TEPA(50)-Mg₂(dobpdc) 70% RH at 25 °C showed the elimination of dependency on flow rate.

5. Proton T₁-T₂ correlation experiments

The ¹H T_1 - T_2 correlation experiment involves encoding the signal with T_1 relaxation, achieved through an inversion recovery experiment with a variable delay t1 prior to the acquisition of a CPMG rf pulse train, which measures the relaxation time T_2 . By executing the experiment with varied delays t1, a two-dimensional dataset was generated, with T₂ relaxation in the direct dimension and T_1 relaxation in the indirect dimension. A total of 32 inversion times (t₁) were chosen to logarithmically spread between 1 ms and 5 s. A repetition time of 5 s was set to ensure complete magnetization equilibration between signal acquisitions. Optimization for short T₂ relaxation was pursued by utilizing the minimum feasible echo time of 60 µs between the 180° pulses of the CPMG train, each pulse lasting 6 µs. A total of 256 echoes were generated, allowing for full magnetization decay observation, with maximum echo intensity sampled at the midpoint between 180° pulses. Subsequently, two-dimensional data underwent processing through a program for 2D inverse Laplace transformation (ILT), implemented in MATLAB based on the regularized non-negative least squares (NNLS) method.²⁵ Consistency in instrumental settings and parameter sets ensured comparability among all T_1-T_2 correlation spectra measured in this study. For reference, previously reported bulk TEPA and PEI T_1 - T_2 plots are shown in Fig. S14. When the T_1 and T_2 values of a material are close to the parity line ($T_1=T_2$), its mobility is considered to be liquid-like. Especially given that T₂ is proportional to the "molecular tumbling rate," the lower T₂ values of amine-impregnated Mg₂(dobpdc) (Fig. S15) compared to that of reported amineimpregnated SBA-15 (~10⁻²-10⁻⁴ sec) suggest comparably low mobility of amines in Mg₂(dobpdc) pores. 20,26



Figure S14. Solid state proton NMR T_1 - T_2 correlation for bulk TEPA and PEI. Reprinted with permission from the literature.²⁰ Copyright 2023 American Chemical Society



Figure S15. Solid state proton NMR T_1 - T_2 correlation for TEPA(50)-Mg₂(dobpdc) (a) before and (b) after 5 humid adsorption/desorption and PEI(30)-Mg₂(dobpdc) (c) before and (d) after 5 humid adsorption/desorption cycles. A similar T_1 - T_2 plot before and after humidity exposure suggests minimal changes in the mobility of amine after particle collapse.

6. Supporting information for the main text



Figure S16. Breakthrough profiles for (a) PEI(30)-Mg₂(dobpdc) and (b) TEPA(50)-Mg₂(dobpdc) under different humidities (30-70% RH) without presaturation at 25 °C and 400 pm CO₂/N₂ flow. The samples were desorbed at 80 °C for 3 h under 40 sccm of dry N₂. The flow rate was 22 sccm (400 ppm CO₂/N₂) and particles between 125 and 425 μ m were sieved and used for the experiments. The sample weight used during the fixed bed experiments was 60 mg (wet).



Figure S17. *In situ* IR spectra for TEPA(50)-Mg₂(dobpdc) during 400 ppm CO₂ adsorption at -20 °C under (a) dry (b) 70% RH (H₂O/CO₂ co-adsorption) conditions. Both carbamic acid and carbamate formation were observed.



Figure S18. Breakthrough profiles for TEPA(50)-Mg₂(dobpdc) under 30-70% RH and 400 pm CO_2/N_2 flow with presaturation using a humid N₂ stream. The samples were desorbed at 80 °C for 3 h under 40 sccm of dry N₂. The flow rate was 22 sccm (400 ppm CO_2/N_2) and particles between 125 and 425 μ m were sieved and used for the experiments. The sample weight used during the fixed bed experiments was 60 mg (wet). The breakthrough profiles show the CO_2 adsorption behavior of TEPA(50)-Mg₂(dobpdc) has a strong dependence on the relative humidity.



Figure S19. Temperature programmed desorption (TPD) experiments at different ramping rates using TEPA(50)-Mg₂(dobpdc). The disappearance of the seemingly separate peaks observed at the slower ramping rate (< 0.5 °C/min) suggests that the separate peaks are derived from kinetic and/or diffusion limitation rather than different heat of desorption. The particle size of the adsorbent was 125-425 μm . The amount of the sample loaded in the fixed bed was 30 mg. Before TPD experiments, the bed was saturated with 40 sccm of humid (70% RH at 25 °C) 400 ppm CO₂/N₂ more than 12 h. The saturation of the bed was confirmed by monitoring outlet CO₂ and water concentration. During the TPD experiments, 40 sccm of dry N₂ was used as a purge gas.



Figure **S20**. TPD experiments with different particle sizes of TEPA(50)-Mg₂(dobpdc). The delayed and lengthened CO₂ desorption peaks with larger particle size indicate a significant intra mass transfer resistance. The amount of the sample loaded in the fixed bed was 30 mg. Before TPD experiments, the bed was saturated with 40 sccm of humid (70% RH at 25 °C) 400 ppm CO₂/N₂ more than 12 h. The saturation of the bed was confirmed by monitoring outlet CO₂ and water concentration. During the experiments, 40 sccm of dry N₂ was used as a purge gas. The ramping rate was fixed at 0.5 °C/min.



Figure S21. (a) TGA profiles of amine-impregnated Mg₂(dobpdc) samples before and after humid adsorption/desorption cycles and (b) *in situ* IR spectra of PEI(30)-Mg₂(dobpdc) during humid adsorption/desorption cycles. Adsorption and desorption conditions were 30 °C and 50% RH for 2 h with 400 ppm CO₂/N₂ and 80 °C and dry N₂ for 2 h, respectively. Relative absorbance for the *in situ* IR spectra represents the spectrum after the first activation subtracted from the spectrum after cycles of adsorption and activation.



Figure S22. XRD patterns for the fresh and 7 days of air exposed (a) $PEI(30)-Mg_2(dobpdc)$ and (b) TEPA(50)-Mg_2(dobpdc). Samples were kept for 7 days in a laboratory environment (22 °C and 50% RH).



Figure S23. BET surface area analysis results from N_2 physisorption (77K) for various amineimpregnated Mg₂(dobpdc) samples before and after 7 days of air exposure. Samples were kept for 7 days in a laboratory environment (22 °C and 50% RH).



Figure S24. Cyclic breakthrough experiment profiles for (a) BPEI(40)-Mg₂(dobpdc) and (b) LPEI(40)-Mg₂(dobpdc) at 25 °C. Desorption was conducted at 80 °C for 2 h under dry N₂. During the first 70% RH experiment, the CO₂ concentration profile showed a small peak before the breakthrough point (C/C₀=0.05), probably due to the improved CO₂ uptake when the amines are unraveled by water. After the first humid run, the area (CO₂ capacity) between y=1.0 and the breakthrough curves decreased significantly due to the degradation of the material.



Figure S25. SEM images of (a) mmen-Mg₂(dobpdc), (b) PEI(40)-Mg₂(dobpdc), and (c) TEPA(40)-Mg₂(dobpdc) after 40 humid adsorption/desorption cycles using TGA. Adsorption and desorption conditions were 30 °C and 50% RH for 1 h with 400 ppm CO_2/N_2 and 80 °C and dry N₂ for 1 h, respectively. Perforation on the surface of the (a) mmen-Mg₂(dobpdc) and (b) PEI(40)-Mg₂(dobpdc) is notable.



Figure S26. Thermal decomposition profiles of $Mg_2(dobpdc)$ samples under (a) N_2 and (b) air (21% O_2/N_2). The weight fractions of amines in amine-functionalized $Mg_2(dobpdc)$ was calculated based on the ratio of the weight loss between the amine-functionalized $Mg_2(dobpdc)$ and bare $Mg_2(dobpdc)$.



Figure S27. Breakthrough profiles for BPEI(40)-Mg₂(doppdc) at 25 °C under 400 ppm CO₂/N₂ and 20% RH for (a) CO₂ up to 6 cycles and (b) both CO₂ and H₂O during the first cycle. Even under the low humidity (20% RH), BPEI impregnated Mg₂(dobpdc) materials showed degradation of the CO₂ adsorption capacity upon cycling (the area between y=1 and breakthrough curves). However, it should be noted that the degradation at 20% RH is less prominent than degradation at 70% RH shown in **Fig. S24(a)**.



Figure S28. XPS survey spectrum of PEI-impregnated $Mg_2(dobpdc)$ samples.

Materials	Dry CO_2 uptake (mmol g ⁻¹)	Humid CO_2 uptake (mmol g ⁻¹)	Method	Reference
MOF-808-Lys	0.56 at 25 °C	1.2 at 25 °C and 50% RH	Fixed bed	27
MOF-808-TAPA	0.45 at 25 °C	0.87 at 25 °C and 50% RH	Fixed bed	27
MEA-MIL- 101(Cr)	1.5 at 25 °C	2.15 at 25 °C and 80% RH	Fixed bed	28
Ed-Mg ₂ (dobpdc)	0.75 at 25 °C	1.1 at 25 °C and 63% RH	Fixed bed	29
mmen- Mg ₂ (hob)/PVDF	1.26 at 25 °C	1.54 at 25 °C and 40% RH	TGA desorption	30
2-UIO-EDA	0.04 at 25 °C	0.44 at 25 °C and 30% RH	Fixed bed	31
TEPA- impregnated MIL-101(Cr)	0.11 at 25 °C	0.38 at 25 °C and 70% RH	Fixed bed	32
TEPA- impregnated Mg ₂ (dobpdc)	0.54 at 25 °C	3.9 at 25 °C and 70% RH	Fixed bed	This work
PEI-impregnated Mg ₂ (dobpdc)	0.3 at 25 °C	2.5 at 25 °C and 70% RH	Fixed bed	This work
PEI-impregnated Mg0.55Al-CO ₃	1.2 at 25 °C	2.0 at 25 °C and 70% RH	Fixed bed	33
TEPA- impregnated Al ₂ O ₃	1.1 at 25 °C	1.33 at 25 °C and 70% RH	Fixed bed	32
In-situ polymerized PEI- meso porous silica foam	1.46 at 20 °C	2.45 at 20 °C and 60% RH	Fixed bed	34
APTMS-boron modified SBA-15	0.79 at 25 °C	0.88 at 25 °C and 60% RH	Fixed bed	35
Triamine grafted silica gel	0.48 at 25 °C	1.1 at 25 °C and 60% RH	Fixed bed	36

Table S5. Summary of relevant CO₂ uptake results under dry and humid DAC conditions from the literature

Amine grafted resin	0.75 at 28 °C	0.9 at 28 °C and 60% RH	Fixed bed	37
PEI-impregnated resin	2.45 at 25 °C	2.95 at 25 °C and 25% RH, ^a 2.2 at25 °C and 75% RH	Fixed bed	38
PEI film 10 nm	2.1 at 27 °C	2.5 at 27 °C and 80% RH	QCM	39
PEI film 100 nm	2.3 at 27 °C	5.7 at 27 °C and 80% RH	QCM	39

* Materials above dashed line are MOF-based sorbents
a: Decrease in CO₂ uptake under humid conditions was reported due to the amine loss

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