

Supporting Information

Discerning Molecular-Level CO₂ Adsorption Behavior in Amine-Modified Sorbents within a Controlled CO₂/H₂O Environment towards Direct Air Capture

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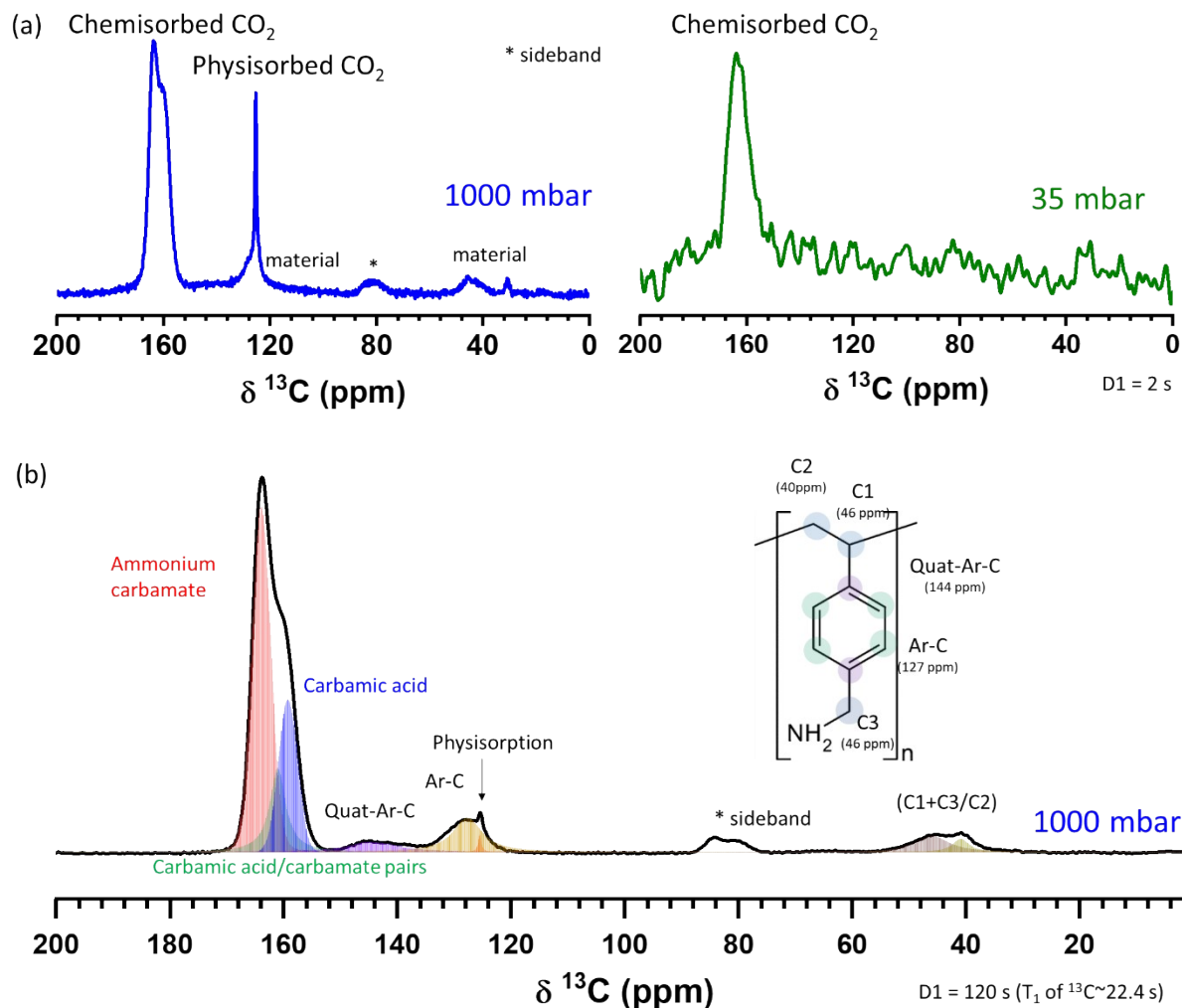


Fig. S1 ¹³C direct polarization with (a) 2 s and (b) 120 s of recycle delay. (a) shows physisorbed CO₂ is only formed at pCO₂= 1000 mbar; (b) analyzes the quantitative carbon of materials and chemisorption at ~ 1 bar, 25 °C within Lewatit® VP OC 1065. The peak at 31 ppm, associated with end group of the material, is clearly observed in (a) while it becomes very weak and does not yield accurate quantitative results due to its relatively low concentration.

Table. S1 Quantified carbon of the ¹³C DPMAS shown in Fig. S1.

Components	Integral (%)	Relative ratio between chemisorption
Ammonium carbamate (I)	43.0	56.5
Carbamate/carbamic acid (II)	12.0	16
Carbamic acid (III)	20.6	27.5
Quaternary carbon in aromatic ring	5.2	-
Aromatic carbon	10.6	-
Aliphatic carbon (C1+C3/C2)	7.8 (5.1/2.7)	-

Calculation of parameter (A) to determine ionic molecular character

Isotropic chemical shift (δ_{iso}), defined as the average of three principal components ($\delta_{iso} = \delta_{11} + \delta_{22} + \delta_{33}/3$), identifies a functional group such as carboxylic carbon atoms. While protonation state has no effect on isotropic chemical shift (δ_{iso}), it significantly impacts a parameter (A), derived from $\delta_{11} + \delta_{33} - \delta_{22}$ in a previous study.¹ It is attributed to the tensor elements δ_{11} and δ_{22} . These elements present opposite signs upon protonation, which results in cancellation in isotropic chemical shift (δ_{iso}), whereas it leads to a higher number in the defined parameter (A). Thus, the parameter (A) is utilized to determine the ionic molecular characters, e.g. $A > 190$ ppm indicating protonated/neutral status as suggested by empirical data,¹ as illustrated in Fig. S2.

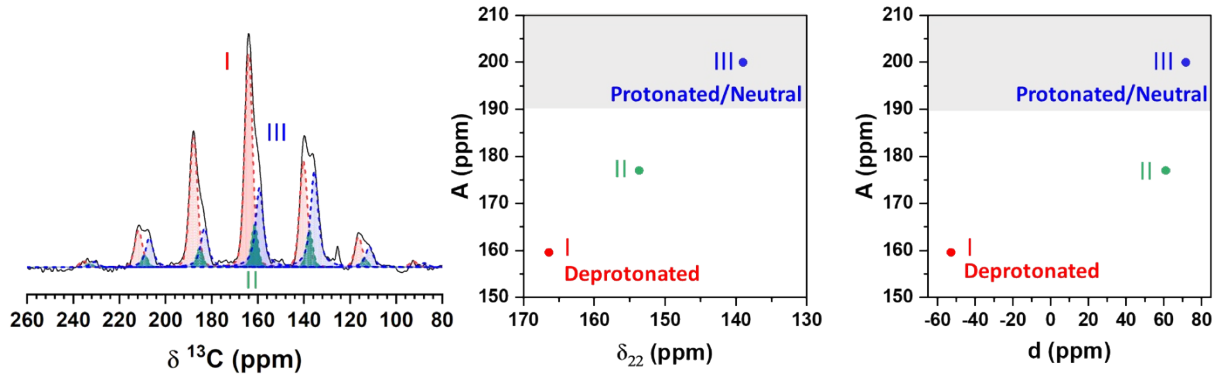


Fig. S2 Low-speed MAS ^{13}C spectra of CO_2 adsorbed Lewatit[®] VP OC 1065 at approximately 1 bar (11.7 T) and the estimated CSA (chemical shift anisotropy) tensor. Asymmetry parameter is $A = \delta_{11} + \delta_{33} - \delta_{22}$, and reduced anisotropy $d = \delta_{33} - \delta_{iso}$.

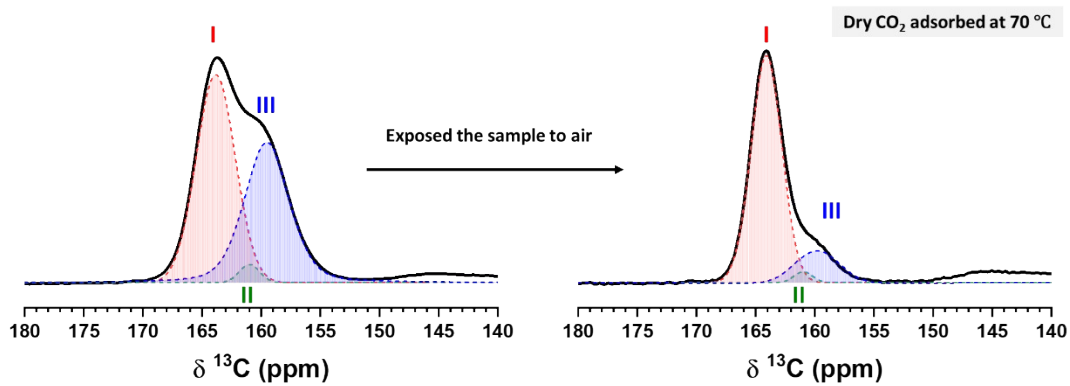


Fig. S3 Stability of the chemisorbed species by exposing the sample to the air. Solid-state NMR of $^{13}\text{CO}_2$ adsorption at ~ 1 bar, 70 °C within Lewatit[®] VP OC 1065 collected at 11.75T (before exposing to the air) and 9.4 T (after exposing to the air).

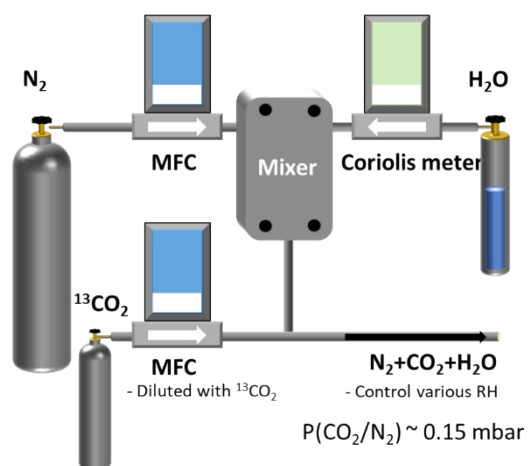


Fig. S4 Schematic of apparatus for preparing co-adsorption (CO_2 , N_2 , H_2O) gas-dosed NMR samples.

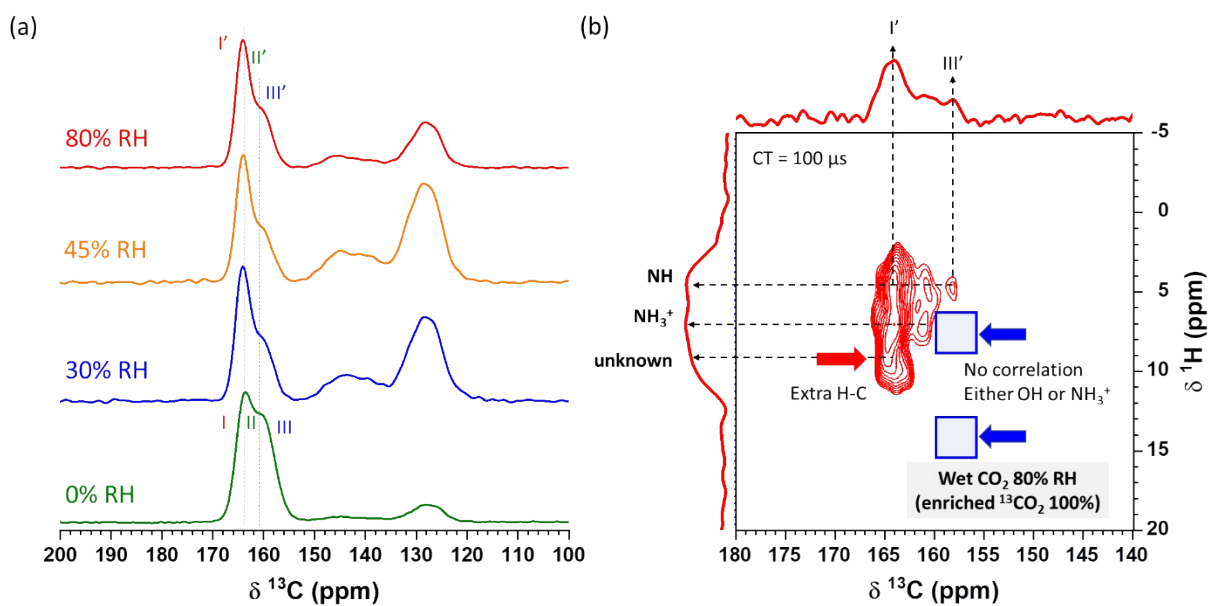


Fig. S5 ^{13}C MAS NMR (9.4 T) spectra dosed with co-adsorption (CO_2 and H_2O) at 1 bar of CO_2 in the presence of water. (a) ^{13}C CPMAS (CT = 2 ms) NMR spectra with variable relative humidity levels (RH0, RH30, RH45, and RH80); (b) ^{13}C - 1H FSLG-HETCOR spectra of co-adsorbed sorbent with RH80 (100 μs of contact time)

Estimation of R_2 to evaluate the pore expansion

The changes in transverse relaxation rate over time indicate a surface-to-volumetric expansion of the pores over time, as illustrated in Fig. 6 and Fig. S6. Carr-Purcell-Meiboom-Gill (CPMG)^{2,3} echo trains yielded these rates and were acquired at intervals of approximately 5 minutes for 3 hours following the introduction of water to the activated sorbents. Inverse Laplace transform (ILT) analysis of the exponential decays of the echo envelopes reveals distinct aqueous domains within the sample: water confined in the pore displays a faster relaxation rate R_2 (shorter T_2) and free water outside the pore manifests a slower R_2 (longer T_2). This assessment is empirically described with in Equation S1

$$R_2 = R_{2b} + \rho \frac{S}{V} + \frac{D(\gamma GT_E)^2}{12} \quad (S\ 1)$$

Here, R_2 is the (measured) pore-confined transverse relaxation rate, R_{2b} is the transverse relaxation rate in the absence of pore confinement, ρ is the surface relaxivity (given by the composition of the walls), S/V is the surface to volume ratio of the pore, D is diffusion coefficient of the fluid, γ is the gyromagnetic ratio of the nucleus, G is external magnetic field gradient, and T_E is experimental echo time.

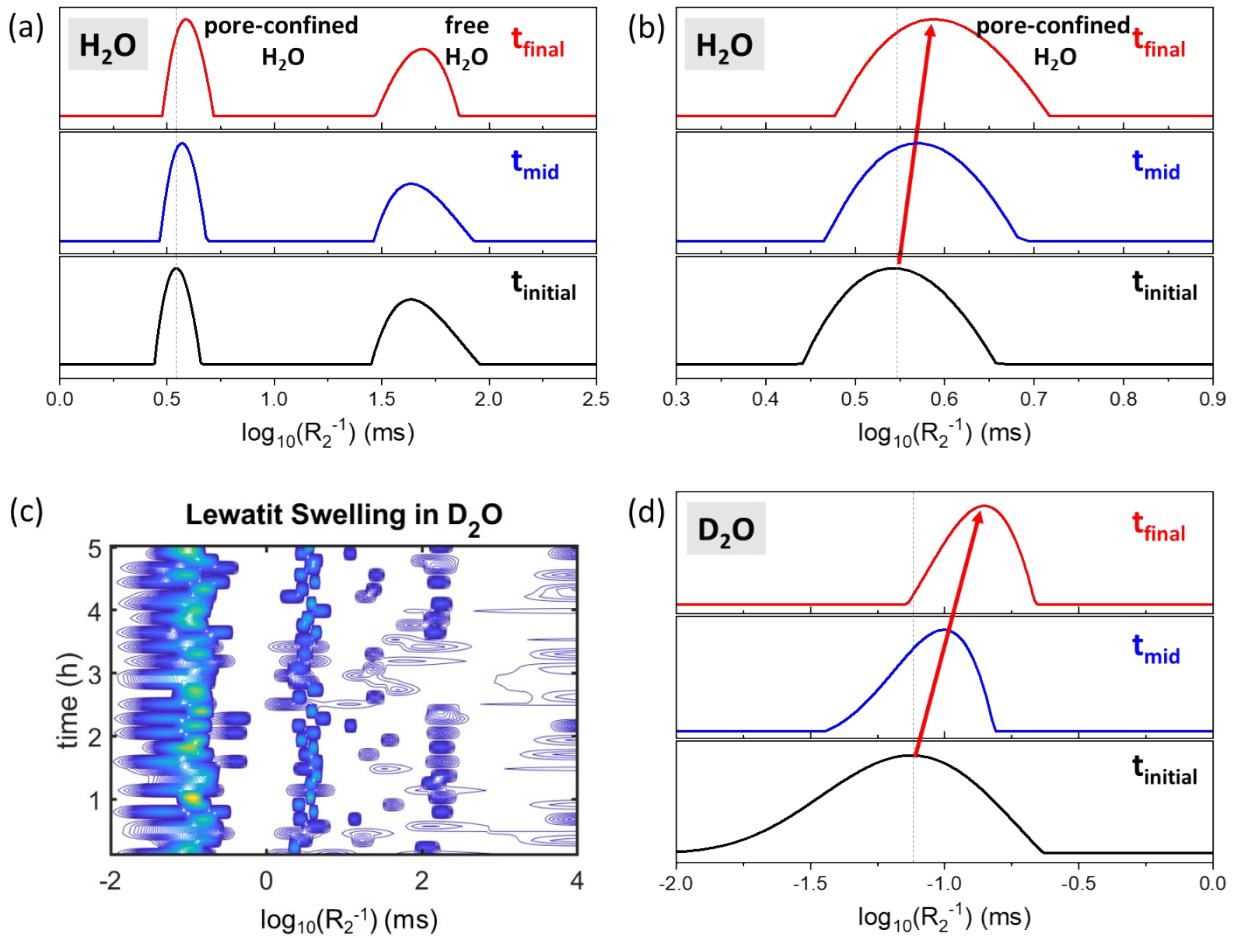


Fig. S6 Changes in transverse relaxation rates ($R_2^{-1} = T_2$) of both H₂O (a, b) and D₂O (c, d) saturated within material, measured at a resonant ¹H frequency of 13.11 MHz over 24 hours. (a) The full range of the R_2 distribution representing pore-confined H₂O and free H₂O; (b) a magnified view of (a), highlighting the R_2 distribution of pore-confined H₂O; (c) measuring R_2 with D₂O over time; (d) range of R_2 showing expanded pore.

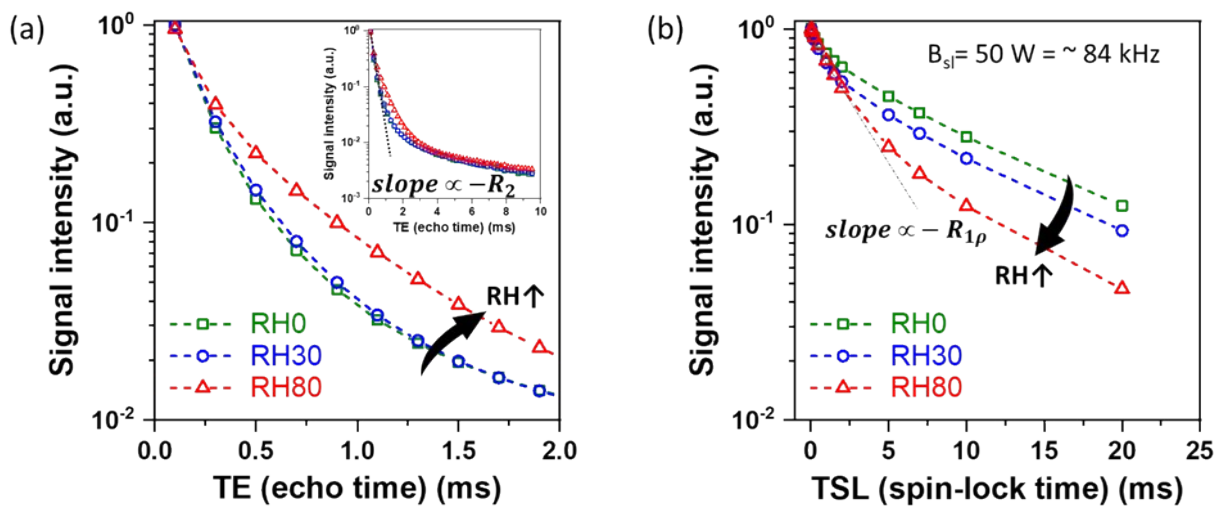


Fig. S7 ^1H NMR relaxation decay curves obtained at 9.4 T of co-adsorbed ($\text{N}_2+\text{CO}_2+\text{H}_2\text{O}$) materials at 25 $^\circ\text{C}$ with RH0, RH30, and RH80 for (a) $T_2 = (1/R_2)$ relaxations; and (b) $T_{1\rho} = (1/R_{1\rho})$ relaxations. At the highest relative humidity, the rate of relaxation at kHz frequencies increases while relaxation rates at MHz frequencies decrease.

References

1. Z. Gu and A. McDermott, *J. Am. Chem. Soc.*, 1993, **115**, 4282–4285.
2. H. Y. Carr and E. M. Purcell, *Phys. Rev.*, 1954, **94**, 630–638.
3. S. Meiboom and D. Gill, *Review of Scientific Instruments*, 1958, **29**, 688–691.