Highly permeable mixed matrix membrane containing CAU-1-NH_2 for H_2 and CO_2 separation

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Electronic Supporting Information:

Experimental details, scanning electron microscope (SEM), powder X-ray diffraction patterns (XRD), thermogravimetric analysis, N_2 adsorption-desorption isotherms, H_2 and CO_2 adsorption isotherms and adsorption kinetics, and H_2 and CO_2 mixture breakthrough curves.

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1. Experimental details

1.1 Synthesis of CAU-1-NH_2 powder

All chemicals and reagents of analytical grade were commercially available and used as received. The typical synthesis procedure of CAU-1-NH_2 is obtained from the reference.[1] A mixture of $AlCl_3•6H_2O$ (2.967 g, 12.3 mmol) and $H_2N–H_2BDC$ (0.746 g, 4.1 mmol) was suspended in methanol (30 ml) and heated at 125 ℃ for 5 h. Then the obtained CAU-1-NH_2 powder was heated at 150 ℃ under vacuum for two days. At last, a yellow microcrystalline product was obtained.

1.2 Preparation of CAU-1-NH_2/PMMA membrane

There are mainly two steps for the preparation of MMMs. The first step is to disperse the filler in the solvent with an ultrasonic bath. The second step is to add polymer. We have prepared 5%, 10%, 15%, 20% and 25% percent based mixed matrix membrane. In all cases, the quality of chloroform remains 15g. Typically, for 15 wt.% concentration, 0.15g CAU-1-NH_2 and 0.85g Poly(methyl methacrylate) PMMA was carefully dissolved in 5g and 10g chloroform, respectively. Then, the two solutions are mixed. After that, the whole mixture is stirred overnight. Before the casting, different intervals of sonication and stirring take place to ensure a well dispersion. Subsequently, the membranes are cast on a flat surface and then left overnight for evaporation of solvent at room temperature. Once dried, the membranes are placed in a vacuum oven for 24 h at 423 K to anneal and remove the remaining solvent.

1.3 Characterizations

The BET surface area was measured on Accelerated Surface Area and Porosimetry System (ASAP 2020M, Micromeritics Company). The TGA was analyzed by Thermogravimetric Thermal Analyzer (Pyris Diamond TG/DTA, Perkin-Elmer Company). The powder X-ray diffraction data were collected from a Bruker D8 Advance X-ray Diffractometer with CuKα radiation (k = 1.5406 Å). Scanning electron microscopy images were obtained from a scanning electron microscope (the Quanta FEG 250, FEI Company). Prior to observation the sample was sputter-coated with a platinum layer to increase their conductivity.

For gas permeation test, the supported CAU-1-NH_2 membrane was sealed in a permeation module with silicone O-rings. The feed gases were fed to the top side of the membrane. All the tests were made in the room temperature and the upstream pressure is 3 bar.

Permeability and selectivity are two key parameters generally used to characterize polymeric membranes.[2] Permeability $\mathbf{P}_A$ is difined as Eq(1), in which V is taken as 30 ml for each permeation test by our soap flow gauge. The symbol S is the virtual permeation area of the membrane (1.6 mm in diameter), while P and t is the permeation pressure (3 bar) and permeation time (recorded in the 30 ml permeation gas), respectively. L is the thickness of the prepared membrane estimated from its cross-section SEM image.

Eq.(1) $$\mathbf{P}_A = (V \times L)/(22.4 \times P \times S \times t)$$

Permeability values are typically reported in Barrer units (1 Barrer = 1 × 10^{-10} cm3 (STP) cm cm^{-2} s^{-1} cm Hg^{-1} = 3.348 ×10^{-16} mol m m^{-2} Pa^{-1} s^{-1}).

The ideal selectivity, S_{AB} (Eq.(2)), is given by the ratio of the two pure gas permeabilities:

Eq. (2) $$S_{AB} = \frac{P_A}{P_B}$$

For permeation of actual A/B mixtures, the mixed separation factor (α_{AB}), is calculated from composition analysis as the ratio of the mole fractions of the components in the permeate stream, y, and the feed stream, x (Eq. (3)).

Eq. (3) $$\alpha_{AB} = \frac{(y_A/y_B)}{(x_A/x_B)}$$

2. Additional table and figures

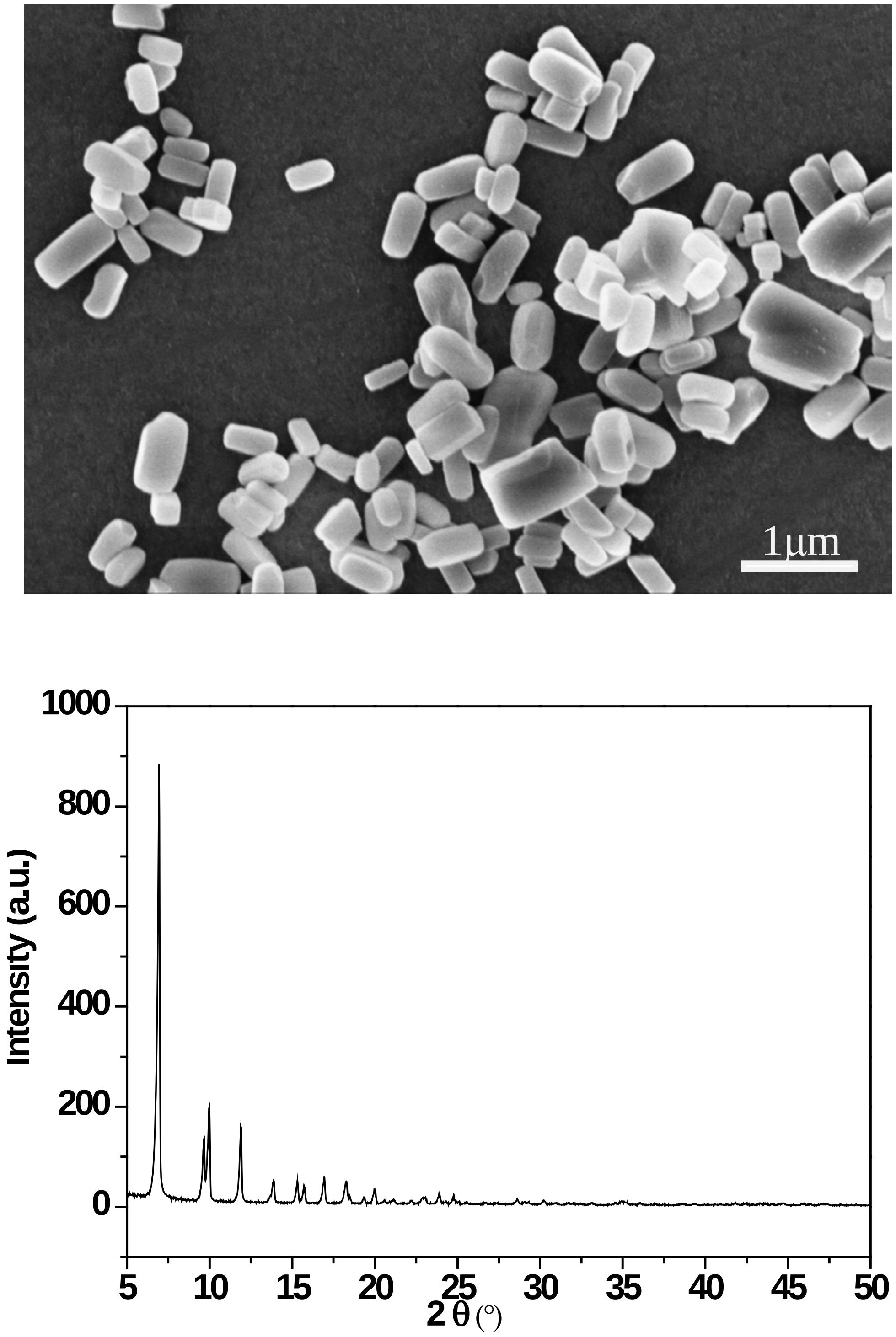


Fig. S1. SEM image (top) and XRD pattern (down) of pure CAU-1-NH_2 powder.

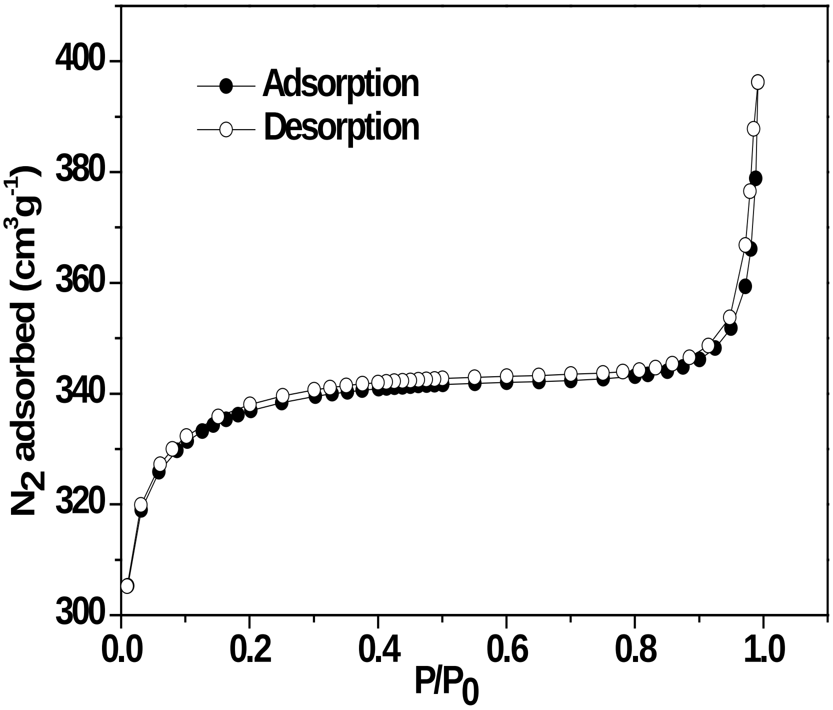


Fig. S2. N_2 adsorption-desorption isotherms of CAU-1-NH_2 powder at 77.3 K.

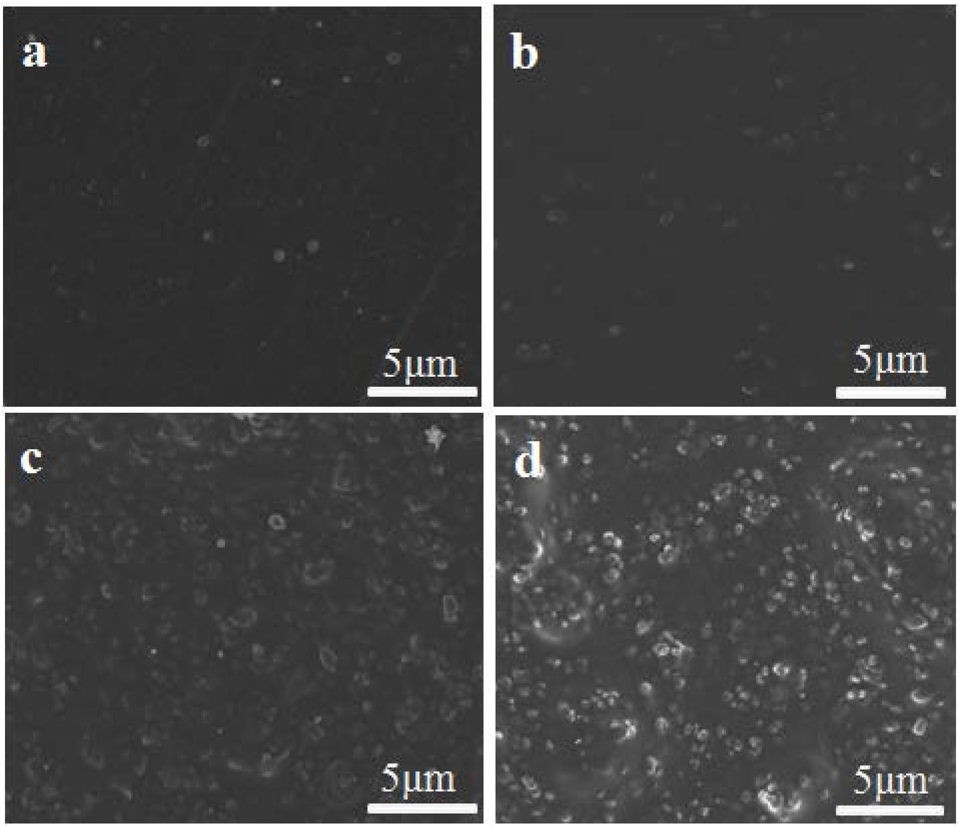


Fig. S3. The surface SEM images of PMMA membrane (a) and CAU-1-NH_2/PMMA with 5 wt% (b), 15 wt% (c) and 25 wt% (d) CAU-1-NH_2 loadings, respectively.

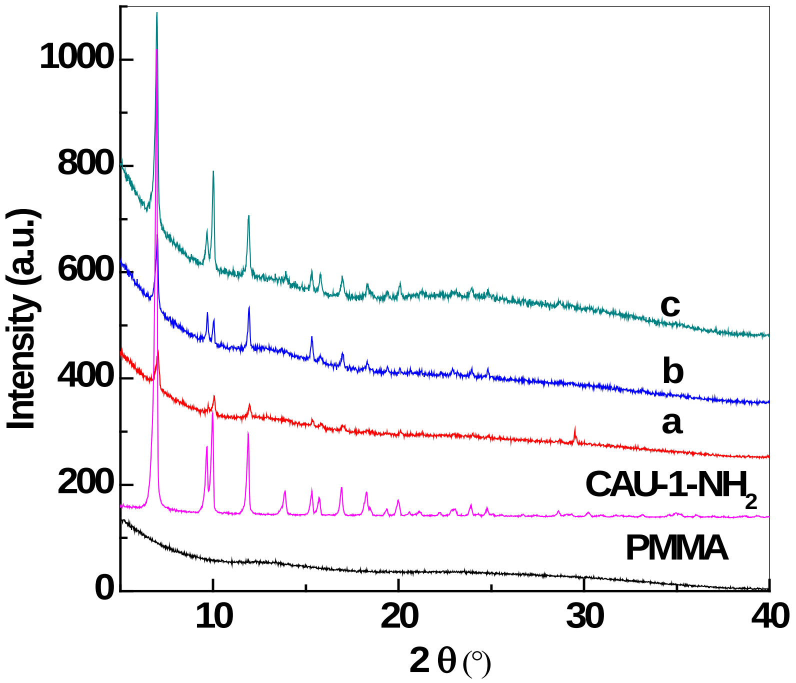


Fig. S4. XRD patterns of CAU-1-NH_2, PMMA and CAU-1-NH_2/PMMA with 5 wt% (a), 15 wt% (b) and 25 wt% (c) CAU-1-NH_2 loadings, respectively.

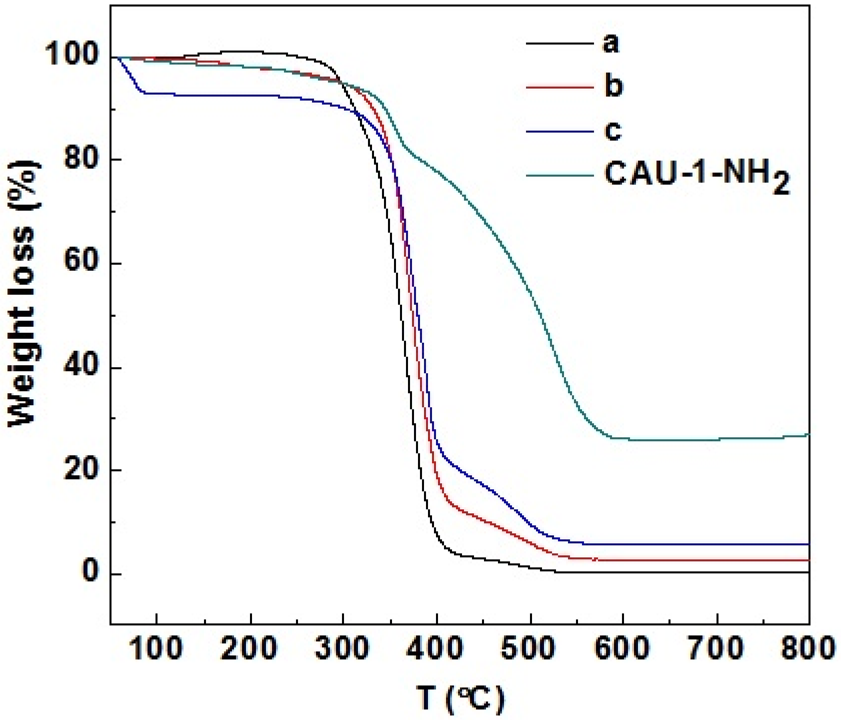
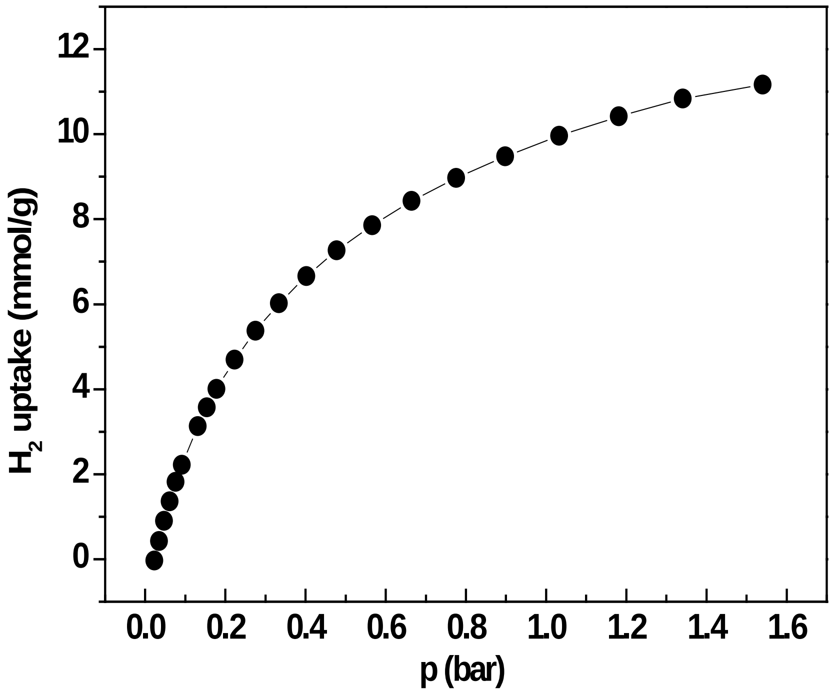


Fig. S5. TGA curves of CAU-1-NH_2 powder and CAU-1-NH_2/PMMA with 5 wt% (a), 15 wt% (b) and 25 wt% (c) CAU-1-NH_2 loadings, respectively.



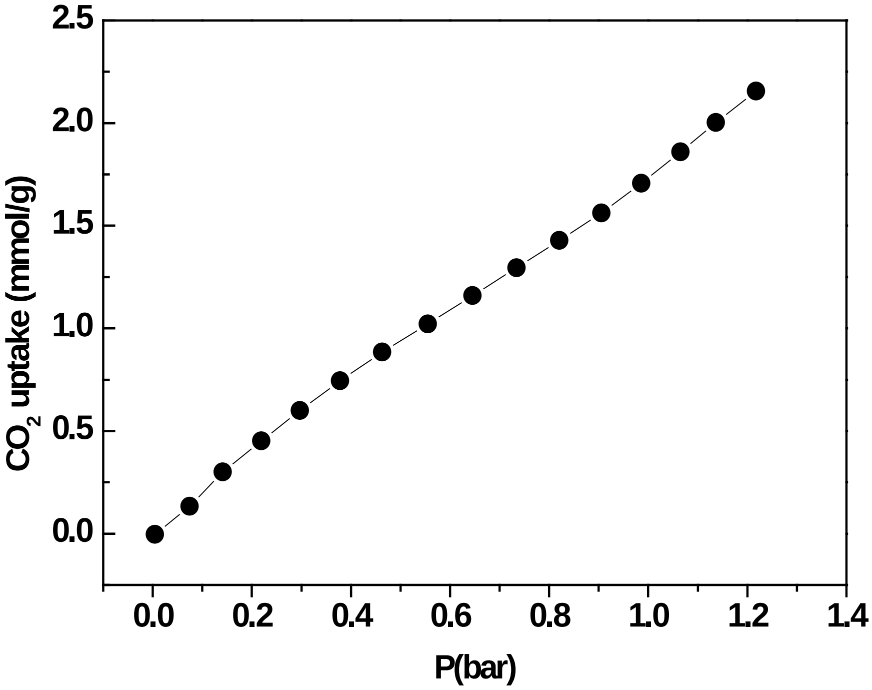
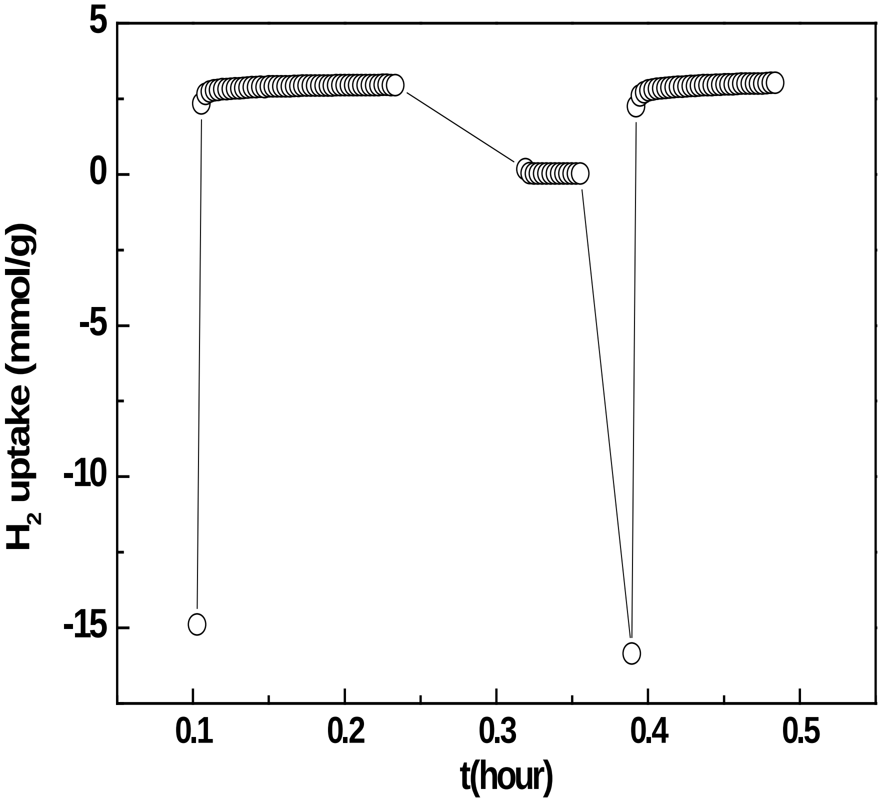


Fig. S6 The adsorption isotherms of H_2 (77 K, top) and CO_2 (303 K, bottom) on CAU-1-NH_2 powders.



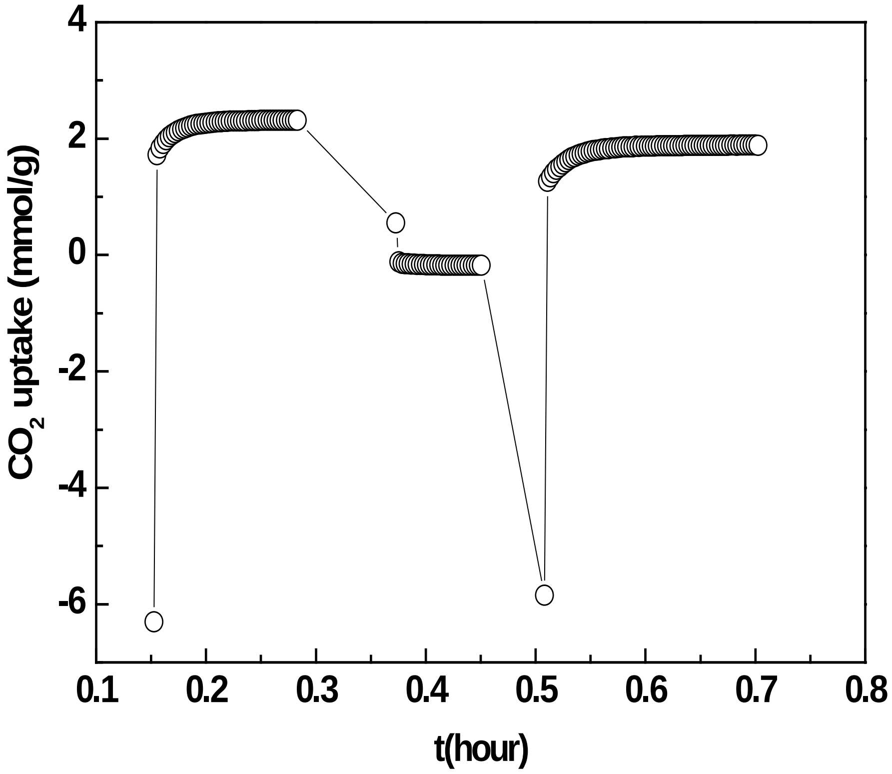


Fig. S7 The adsorption kinetics of H_2 (77 K, top) and CO_2 (303 K, bottom) on CAU-1-NH_2 powders.

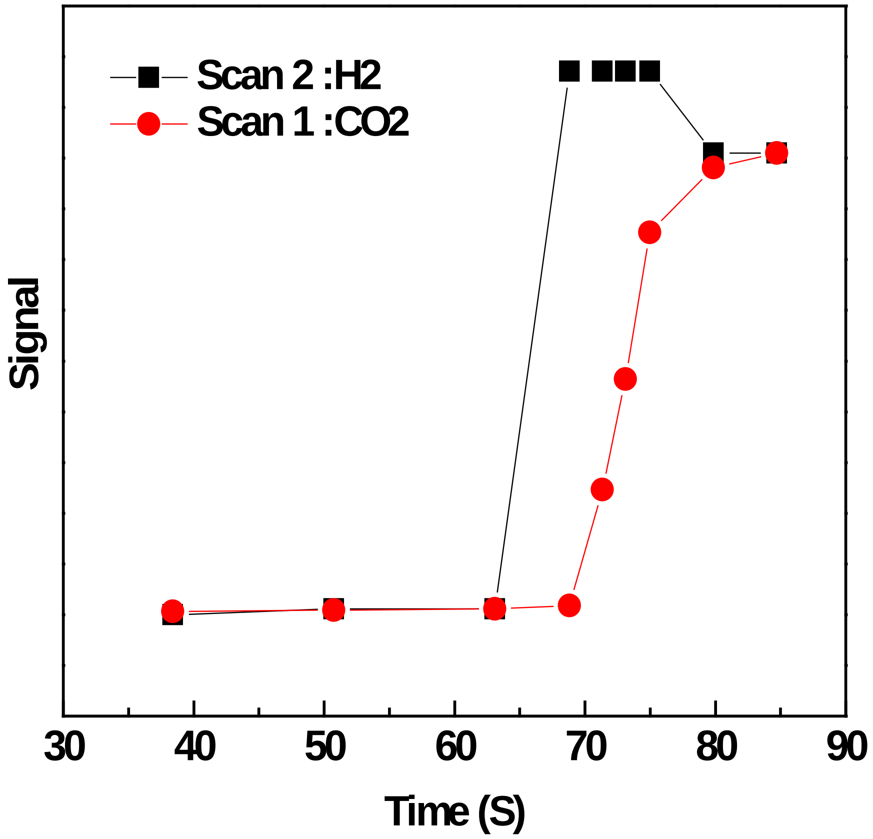


Fig. S8 The breakthrough curves of H_2 and CO_2 mixtures (50:50) on CAU-1-NH_2 powders at 303 K.

Table S1. Comparison of the H_2 and CO_2 permeability and selectivity of different MMMs in this work and literatures. Null means that the thickness is unknown from the references and symbol "–" means that the data are not provided in references. (1 Barrer=7.50062×10^{-18} m^3 (STP) m/m^2 S Pa, and 1GPU=7.5005×10^{-16} m^3 (STP) /m^2 S Pa)

MMMs	Thickness (μm)	Loadings (wt%)	Testing condition	H_2 Permeability (Barrer/GPU)	H_2/CO_2 selectivity	Ref.
ZSM-5/ Matrimid	40	20	25 ℃, 2 bar	22.23 / 0.555×10^4	2.57	3
SAPO-34/ polyethersulfone	-	20	35℃, 2 bar	12.57 / Null	2.45	4
Cu-BPY-HFS/ Matrimid	30	10	25 ℃, 2 bar	16.91 / 0.564×10^4	2.17	5
MOF-5/ Matrimid	50	30	35 ℃, 2 bar	53.8 / 1.076×10^4	2.66	6
ZIF-8/ Matrimid	-	50	35 ℃, 2.6 bar	18.07 / Null	3.8	7
ZIF-7/ Polybenzimidazole	-	50	35 ℃, 3.5 bar	26.2 / Null	14.9	8
CAU-1-NH_2/ PMMA	10	15	25 ℃, 3 bar	1.11× 10^4 /1.11×10^7	13	This work
Liquid crystalline polyester	-	-	35 ℃, 5 bar	0.0545 / Null	100.9	9
Polyaniline	0.8-8.4	-	21℃, 2–2.5 bar	1.753 / 2.191×10^4	23.1	10
PMMA	-	-	25 ℃, -	4.8 / Null	24	11

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