

Supplementary Information for

A new aerogel based CO₂ sorbent developed with a simple so-gel method with supercritical drying

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1 Experimental Section

Sample preparation: 3-(aminopropyl)triethoxysilane (APTES), tetraethoxysilane (TEOS), ethanol (EtOH) and deionized water (W) were used as raw materials. All chemicals were purchased from Sinopharm Chemical Regent Co., Ltd. and used without further purification. To prepare the amine hybrid silica aerogel adsorbent, all of the reactants were mixed at $-5\text{ }^{\circ}\text{C}$ with a molar ratio of TEOS:APTES:EtOH:W=1:5:13.7:11. After 10 min gelation, solvent exchange was performed at room temperature to remove water and residual chemicals in the wet gel (3 cycles, 8h per wash cycle). Methanol, ethanol, isopropanol and acetone were used for solvent exchange to investigate the effects of the solvent on CO_2 adsorption performance. SCD was performed by a Spe-ed SFE system with a 1L vessel (Applied Separations, Inc., Allentown, PA) to dry the wet gels. Wet gels were put into the vessel. The pressure of the vessel was raised to supercritical levels. Ethanol in the wet gels was first replaced by liquid CO_2 at room temperature ($20\text{ }^{\circ}\text{C}$). The temperature of the vessel was then raised to $50\text{ }^{\circ}\text{C}$ for supercritical extraction and maintained at the same temperature for 4h to ensure that the ethanol was completely displaced by CO_2 . During these operations, the pressure of the vessel and the CO_2 flow rate were maintained at 10 MPa and 15 L/min, respectively. The last step was to depressurize the vessel to atmospheric pressure at a CO_2 flow rate of 5 L/min to obtain the amine hybrid silica aerogel (denoted as A-SCD). Depending on the solvent for solvent exchange, the resulting samples are denoted as A-SCD-acetone, A-SCD-methanol, A-SCD-ethanol and A-SCD-isopropanol, respectively.

Sample characterization: Nitrogen adsorption/desorption tests were conducted using a Quantachrome Autosorb-iQ pore structure analyzer. The samples were outgassed under vacuum at $90\text{ }^{\circ}\text{C}$ for 6h before tests. Specific surface areas were calculated using the BET method. Pore-size distributions were calculated using the NLDFT model. Pore volumes were estimated from the adsorbed amount at a relative pressure of $P/P_0 = 0.99$. Zeta potentials of two adsorbents were measured using a Malvern Nano ZS ZEN-3600 Zetasizer at $20\text{ }^{\circ}\text{C}$. To measure the zeta potential, a 10mg sample was dispersed into water by stirring for 10 min. The pH value of the liquid was maintained at the same level (pH = 9.5) by adjusting the particle concentration of the adsorbent. Prior to each zeta potential test, the liquid was homogenized by means of ultrasonic dispersing for 10 min at $20\text{ }^{\circ}\text{C}$. The resulting liquid can be used for a zeta potential test without sediment.

The N₂ adsorption/desorption isotherms and pore-size distributions of A-SCD with different exchange solvent are presented in Fig. S1. The pore structure and zeta potential data of A-SCD with different exchange solvents are summarized in Table S1.

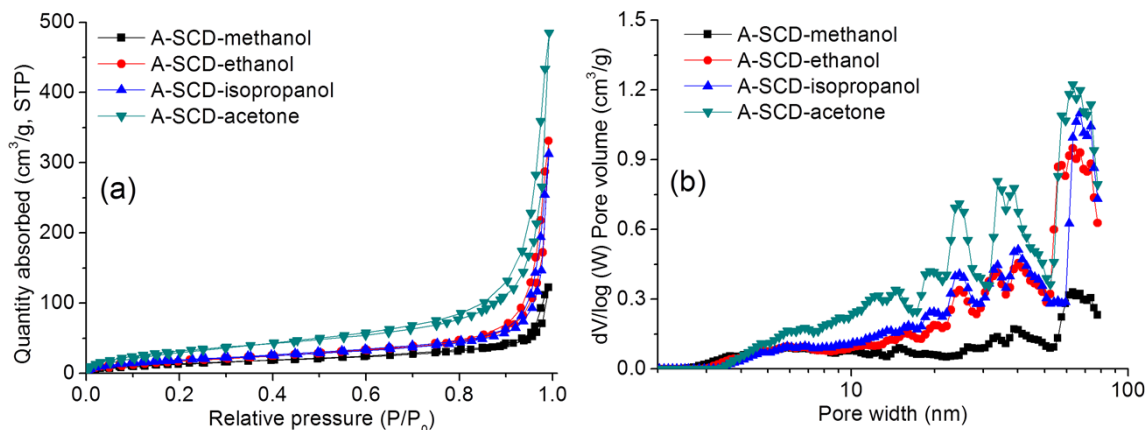


Fig. S1 N₂ adsorption/desorption isotherms (a) and pore-size distributions (b) of A-SCD.

Table S1 Pore structure and zeta potential data of the adsorbents.

Adsorbent	Surface area (m ² /g)	Pore volume (cm ³ /g)	Zeta potential (mV)
A-SCD-methanol	51	0.19	9.7
A-SCD-ethanol	70	0.51	15.2
A-SCD-isopropanol	69	0.48	12.5
A-SCD-acetone	118	0.75	20.4

CO₂ capture test: The setup for the CO₂ capture test at atmospheric pressure is presented in Fig. S2. A fixed bed and a CO₂+N₂ mixture gas with a CO₂ concentration of 1% were used for CO₂ adsorption. Pure N₂ was used for desorption through the temperature swing. The resulting monolithic aerogel adsorbents were ground to particles and mixed with sand (50-70 mesh, Sigma-Aldrich). The mass fraction of adsorbent in the mixture was approximately 4% in order to ensure that there was no pressure drop in the fixed bed. Based on this view, a flow meter was used in the apparatus to detect the pressure drop, as presented in Fig. S2 (part 9). If there was backpressure or leakage in the system, the fixed bed had to be refilled. In consideration of local atmospheric pressure, the gas flow rates for adsorption and desorption were calibrated using an Elster American Meter AL17-1 Wet Test Meter and switched to standard state. The adsorption and desorption

temperatures were controlled by a MTI GSL-1100X tube furnace. The blank or background of the apparatus was measured when there was no adsorbent in the reactor. All of the calculated capacities in this paper have subtracted the background.

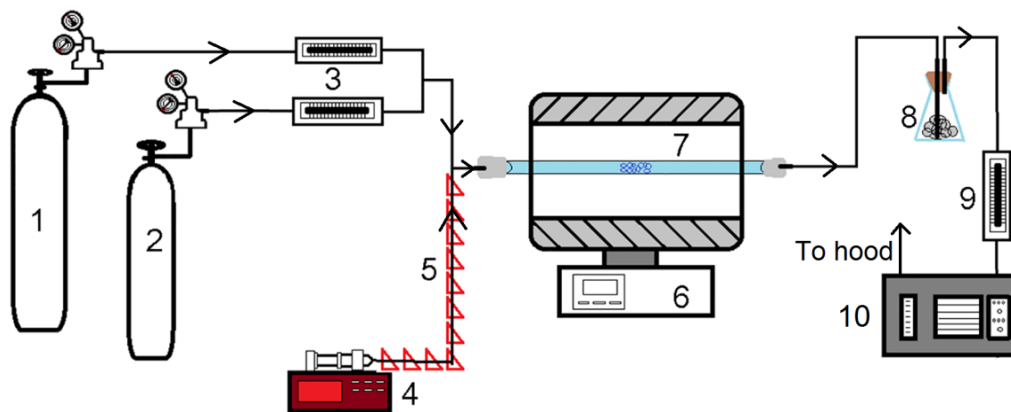


Fig. S2 CO₂ capture setup: (1) N₂ cylinder; (2) N₂+CO₂ mixture gas cylinder; (3) flow meter (FM-1050, Matheson Tri-gas Inc.); (4) syringe pump (NE-300 Just Infusion, New Era Pump Systems); (5) heat tap with a controller (MiniTrol, Glas-Col Inc); (6) tube furnace (MTI GSL-1100X); (7) circular glass tube reactor (9 × 610 mm); (8) water removal unit (silica gel); (9) gas leakage and back pressure checking meter; (10) gas analyzer with data recorder (ZRE Infrared Gas Analyzer, Fuji Electric System Co. Ltd.).

Before the CO₂ adsorption test, the fresh adsorbents were treated by N₂ at 130 °C for 30 min to remove adsorbed moisture and CO₂ from the air. For CO₂ capture, the temperature of the furnace was stabilized to the temperature for CO₂ adsorption. Meanwhile, water vapor (1%) was generated and maintained at a steady state. N₂ flow was then switched to the CO₂+N₂ mixture gas and water vapor for CO₂ adsorption. After finishing CO₂ desorption, the CO₂+N₂ mixture gas was changed to N₂ to purge the pipes of the apparatus until the outlet CO₂ concentration was 0 or very close to 0. The water vapor was cut off, after which the temperature of the furnace was raised to 90 °C with a rate of 20 °C/min and held at that temperature until the outlet CO₂ concentration was 0. For cyclic experiments, the CO₂ adsorption process was repeatedly performed on the desorbed adsorbents using the procedure mentioned above.

Calculation of the CO₂ adsorption capacity: The CO₂ adsorption profiles of the blank and A-SCD-acetone at 25 °C with water vapor is presented in Fig. S3, the gray region represents the totally adsorbed CO₂. The area marked by the red dotted bordered rectangle represents the useful capacity in a practical separation process.

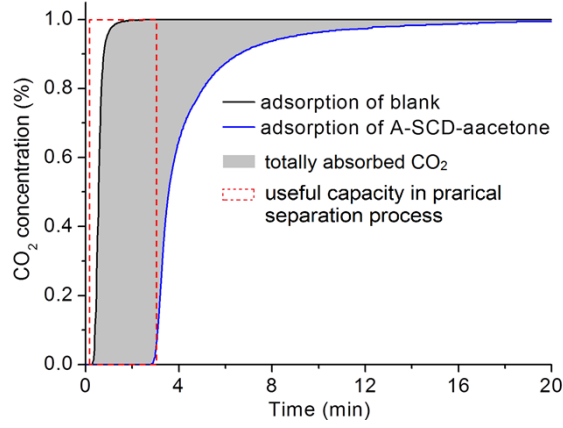


Fig. S3 CO₂ sorption profiles of blank and A-SCD-acetone at 25 °C (adsorption time of 20 min, adsorption gas flow rate of 300 ml/min, weight of sorbent: 0.10 g, 1% moisture).

As presented in Fig. S4, the total CO₂ adsorption capacity can be calculated by subtracting the area below adsorption curve of A-SCD-acetone (A1) from the area below adsorption curve of blank (A2). The calculation methods of the CO₂ capacity of these two areas are same. Fig. S4(a) depicts the schematic diagram for calculating the CO₂ capacity of the area below adsorption curve of A-SCD-acetone. The time (t) can be divided into numbers of Δt (s). During Δt , the CO₂ capacity is described as eq. S1

$$\Delta A_{i,CO_2} (mmol) = \frac{C_i + C_{i+1}}{2 \times 100} \times \Delta V_i \div 22.4 \times 1000 \quad (S1)$$

Where C_i (%) is the CO₂ concentration recorded by gas analyzer at t_i , ΔV (L) is the gas volume flowed through the fixed bed during Δt .

$$\Delta t = t_{i+1} - t_i \quad i=0, 1, 2, 3... \quad (S2)$$

In this research, the data is recorded once per second. Thus, $\Delta t = 1$.

The flow rate v (ml/min) during the test is constant and calibrated to 300 ml/min at standard state, ΔV can be written as

$$\Delta V_i = \frac{\Delta t \times v}{1000 \times 60} \quad (S3)$$

The CO₂ capacity of any Δt can be written as

$$\Delta A_{i,CO_2} (mmol) = \frac{(C_i + C_{i+1}) \times \Delta t \times v}{2 \times 100 \times 60 \times 22.4} = \frac{C_i + C_{i+1}}{896} \quad (S4)$$

The CO₂ capacity of A1 can be described as eq. S5, where m (g) is the weight of the sorbent.

$$Capacity(mm\text{ol} / g) = \frac{\sum_0^i \Delta A_{i,CO_2}}{m} \quad (S5)$$

Similarly, the useful capacity in a practical separation process can be also obtained.

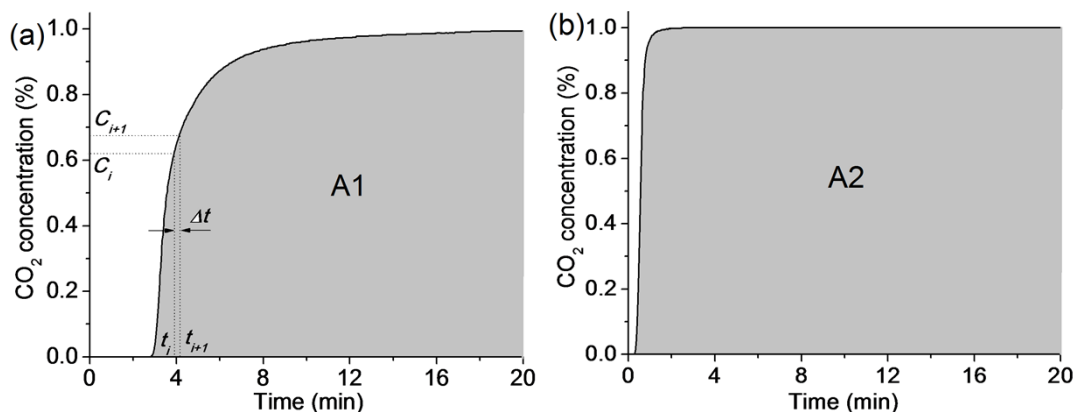


Fig. S4 Schematic diagram for calculating CO₂ capacity.

2 Effect of TEOS/APTES ratio on CO₂ adsorption capacity

Adsorbents with different TEOS:APTES molar ratios of 1:3, 1:4, 1:5, 1:6 and 1:7 were prepared to determine the best APTES/TEOS ratio. The CO₂ adsorption kinetics of A-SCD adsorbents with different APTES contents are presented in Fig. S5.

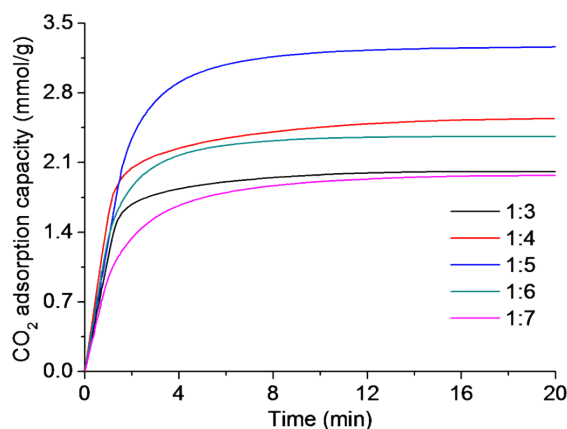


Fig. S5 CO₂ adsorption kinetics of A-SCD with different TEOS:APTES ratios in absence of water at 25 °C (adsorption time of 20 min; adsorption gas flow rate of 300 ml/min; weight of adsorbents: 0.10-0.11 g).

3 Dynamic and static adsorption capacities

The static CO₂ adsorption capacity of A-SCD-acetone at 25 °C was measured using a Quantachrome Autosorb-iQ pore structure analyzer with necessary parts for a CO₂ adsorption test. Correspondingly, the CO₂ adsorption capacity of A-SCD-acetone at 25 °C in the absence of water

was also measured. Fig. S6 presents the results from the two methods, i.e. dynamic and static adsorption capacities of 4.22 and 3.36 mmol/g, respectively. Static CO₂ adsorption capacity is 0.86 mmol/g lower than dynamic CO₂ adsorption capacity. The difference may be explained by observing that the macropores (especially pores >100 nm) are not detectable on the pore structure analyzer, and aerogels have a large number of macropores [S1-S3].

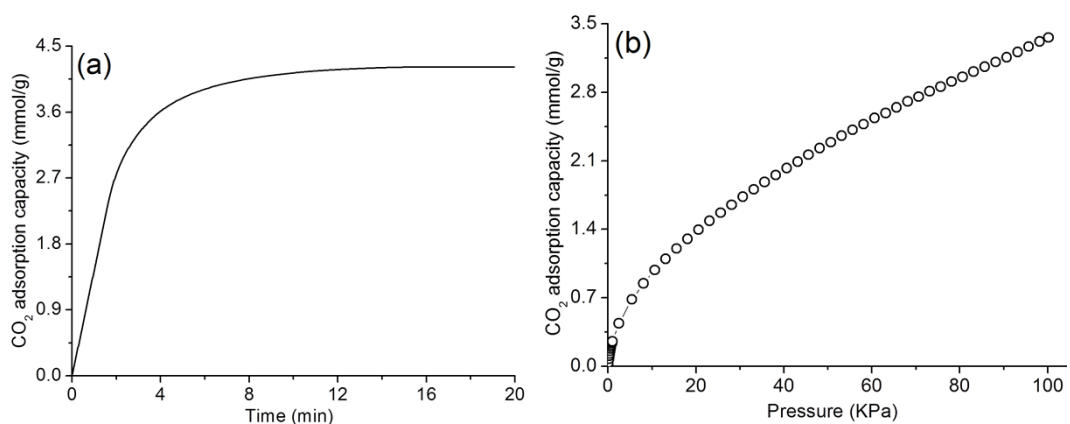


Fig. S6 Dynamic adsorption capacity and static adsorption capacity of A-SCD-acetone in absence of moisture at 25 °C: (a) dynamic adsorption capacity (adsorption time of 20 min; adsorption gas flow rate of 300 ml/min; weight of adsorbents: 0.10 g); (b) static adsorption capacity.

4 CO₂ adsorption in mixture gas with different CO₂ concentration

The CO₂ adsorption kinetics in 1% and 10% CO₂ flow are compared in Fig. S7. As expected higher CO₂ concentration leads to higher CO₂ adsorption capacity and adsorption rate.

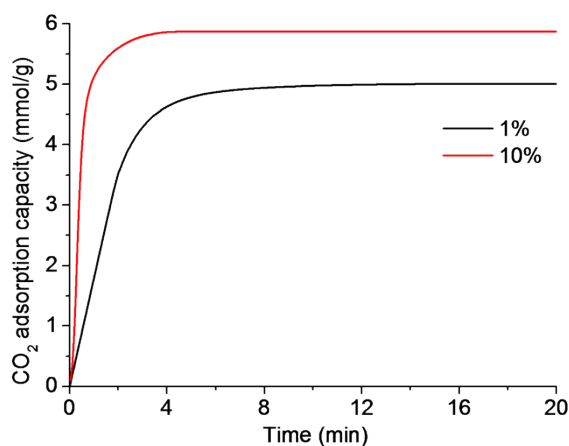


Fig. S7 CO₂ adsorption kinetics of A-SCD-acetone in mixture gas with 1% and 10% CO₂ (adsorption time of 20 min; adsorption gas flow rate of 300 ml/min; weight of adsorbents: 0.10 g; 1% or 10% moisture with 1% or 10% CO₂ mixture gas).

References

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