

Electronic Supplementary Information

Highly efficient and reversible CO₂ adsorption by amine-grafted platelet SBA-15 with expanded pore diameter and short mesochannels

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Experimental Section

Materials

P123, tetraethyl orthosilicate (TEOS, 98%), APTMS (99%), APAETMS (97%), APAEAETMS (97%) and anhydrous toluene were purchased from Sigma-Aldrich. ZrOCl₂•8H₂O and TMB were obtained from Acros. CO₂ (99.999%) and N₂ (99.99%) were purchased from Praxair. Anhydrous toluene was redistilled prior to use. Other chemicals were used without further purification.

Preparation of the supports and the sorbent

In a typical synthesis of the platelet SBA-15, ZrOCl₂•8H₂O (0.32 g) and P123 (2.00 g) were dissolved in 2.0 M aqueous HCl (80 mL). Then TEOS (4.20 g) was added into this solution to pre-hydrolyze for 30 min with stirring at 35 °C. After that, TMB (1.00 g) was added and the mixture was stirred at 35 °C for another 20 h. Then the mixture was sealed into the reaction kettle to undergo hydrothermal treatment at 90 °C for 48 h under static conditions.

Finally, the product was filtered, thoroughly washed, dried overnight at 50 °C and then calcined at 550 °C for 8 h.

Traditional fiber-like SBA-15 was synthesized as follows. In brief, a mixture of TEOS (4.20 g) and P123 (2.00 g) dissolved in 2.0 M HCl (80 mL) was stirred at 35 °C for 20 h. The rest of the synthesis procedure was the same with the preparation of SBA-15-p. The obtained sample was named SBA-15-f.

The grafting of APTMS on SBA-15-p or SBA-15-f surfaces was achieved by refluxing SBA-15-p (1.0 g) or SBA-15-f (1.0 g) with the mixture of anhydrous toluene (100 mL) and APTMS (10 mL). The mixture was stirred and refluxed at 80 °C for 24 h with an appropriate stirring under a nitrogen atmosphere. The resulting product was washed repeatedly with anhydrous toluene and then dried under vacuum at 60 °C overnight. The immobilization method of APAETMS and APAEAETMS on the SBA-15-f or SBA-15-p was the same as described above. The obtained samples were named mono-SBA-15-p, di-SBA-15-p and tri-SBA-15-p, or mono-SBA-15-f, di-SBA-15-f and tri-SBA-15-f, respectively.

Characterization of the sorbent and its supports

The morphology of the samples was characterized by transmission electron microscope (TEM) and scanning electron microscope (SEM) techniques. The TEM images were obtained with a 2100 JEOL operating at 200 kV, while the SEM images were obtained using a Quanta 200 instrument working at 20kV equipped with an OXFORD INCA 250 energy-dispersive spectrometer (EDS). Nitrogen adsorption-desorption isotherms were measured at -196 °C using an ASAP 2020 Micromeritics Analyzer. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449C Thermogravimetric Analyzer and the samples were heated from 25 °C to 850 °C at a temperature ramp of 5 °C min⁻¹ under air flow. X-ray diffraction (XRD) patterns were recorded by a Bruker D8-ADVANCE X-ray Diffractometer. The ATR-IR spectra were recorded using a Jasco FT/IR-4100 spectrometer. ¹³C CP MAS NMR was obtained by Burker AVANCE III NMR spectroscopy.

Determination of the grafted amine loadings of samples

The amine loading amounts of amine-grafted sorbents were determined by the weight loss occurred at high temperature, which can be measured by TGA. With mono-SBA-15-p being an example, the detail of determination of the grafted amine loading of samples is

provided below. Considering the density and geometric distribution of silanols on the sorbent support, APTMS grafted more likely with 2 surface silanols than 3 surface silanols when performing the silanization reaction.¹The weight loss of the samples was contributed to the complete removal of 3-aminopropyl group and one methoxyl group. Thus we can calculate amine loading amounts of the sorbents based on the weight loss.

CO₂ adsorption and desorption isotherms

Adsorption and desorption isotherms of pure CO₂ were determined by an ASAP 2020 Micromeritics Analyzer in the pressure range from 0.01 to 1.0 bar. An adsorbent weight of *ca.* 150 mg was loaded into the sample cell, and constant temperature circulating water was used to keep the sample temperature at the desired values.

CO₂ breakthrough curves on mono-SBA-15-p

CO₂ breakthrough curves were determined on a fixed-bed flow sorption system equipped with a thermal conductivity detector. The sample cell was loaded with *ca.* 500 mg of adsorbent. Then 10% CO₂ balanced with N₂ stream at a total flow rate of 20 mL/min was introduced and passed through the adsorbent bed until adsorption saturation was reached. Alternatively, the purge gas (N₂) was bubbled in a water-containing saturator maintained at ambient temperature to investigate the influence of moisture on CO₂ adsorption.

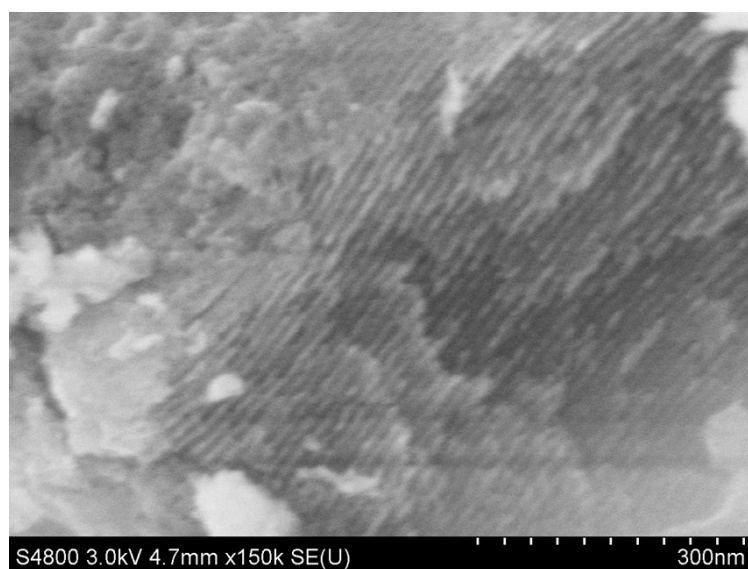


Fig. S1 The high-SEM image of SBA-15-p sample.

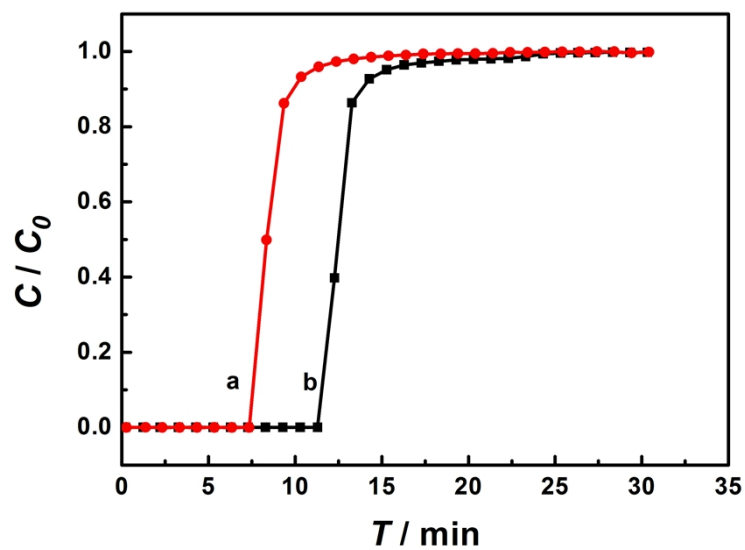


Fig. S2 Breakthrough curves of mono-SBA-15-p: (a) dry CO_2 , (b) wet CO_2 determined under the conditions: adsorption at 25 °C, gas flow rate of 20 cm^3/min , and inlet CO_2 concentration of 10 vol%.

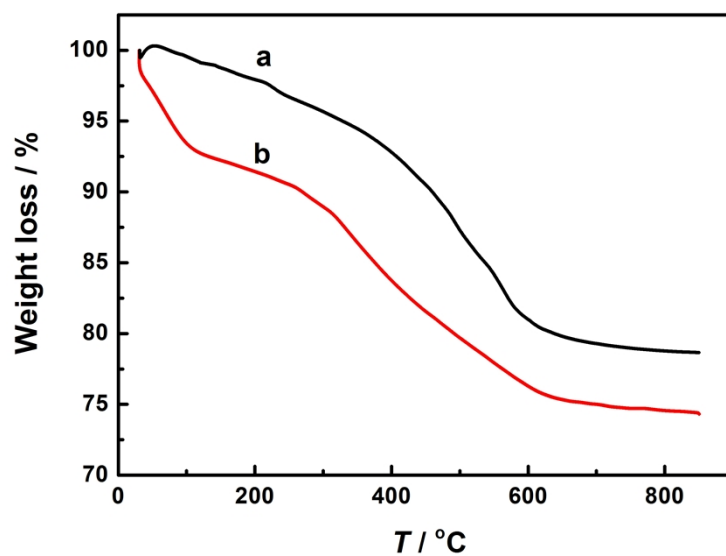


Fig. S3 TGA thermograms of mono-SBA-15-p in an air atmosphere : (a) before CO_2 uptake, (b) after CO_2 uptake.

Table S1 The Isotherm Tabular Report of raw data in the Analyzer for mono-SBA-15-p.

Absolute Pressure (mmHg)	Quantity Adsorbed (mmol/g)	Elapsed Time (h:min)
0.4	0.69	06:27
1.4	0.93	38:45
4.0	1.01	46:12
10.0	1.10	54:59
19.8	1.17	60:51
38.7	1.23	64:56
83.2	1.32	67:55
116.1	1.34	69:13
201.2	1.40	70:15
280.0	1.44	70:56
392.3	1.49	71:29
545.8	1.53	71:56
756.5	1.59	72:19

Table S2 The Isotherm Tabular Report of raw data in the Analyzer for mono-SBA-15-f.

Absolute Pressure (mmHg)	Quantity Adsorbed (mmol/g)	Elapsed Time (h:min)
0.2	0.13	02:08
0.5	0.19	03:53
0.7	0.21	05:38
1.3	0.25	08:27
2.7	0.29	11:49
3.9	0.31	14:18
7.9	0.35	15:38
10.3	0.37	16:38
19.8	0.42	17:42
37.8	0.48	18:37
72.6	0.55	19:21
102.5	0.59	19:47
200.9	0.69	20:12
280.2	0.75	20:28
391.5	0.82	20:42
545.7	0.90	20:55
760.2	0.99	21:07

Table S3 Comparison of Amine Sorbents as CO₂ Traps at 1 bar.

Material ^[a]	Temperature (° C)	Capacity (mmol CO ₂ g ⁻¹ sorbent)	mmol CO ₂ /mmol N	Reference
mono-SBA-15-p	25	1.58	0.67	this work
di-SBA-15-p	25	2.01	0.52	this work
tri-SBA-15-p	25	2.67	0.45	this work
[Li(EA)][Tf ₂ N]	40	1.55	0.54	Wang ²
[P ₆₆₆₁₄][p-AA]	30	1.48	0.94	Wang ³
SBA-HA	25	3.11	0.44	Jones ⁴
MC400/10PEI%83	75	4.45	0.23	Jones ⁵

^[a] [Li(EA)][Tf₂N]: monoethanolamine-coordinate lithium bis(trifluoromethylsulfonyl)imide; [P₆₆₆₁₄][p-AA]: trihexyl(tetradecyl)phosphonium 4-amino-3-methylbenzoate; SBA-HA: a covalently tethered hyperbranched aminosilica (HAS) material; MC400/10PEI%83: oligomeric amine (polyethylenimine, PEI) functionalized mesoporous silica capsules, where 400 and 10 represent the diameter and the shell thickness of the mesoporous capsules in nanometres, respectively, and the weight percentage of amine in the sorbent is 83%.

Reference

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