

## Supplemental Information

### CO<sub>2</sub> capture on easily regenerable hybrid adsorbents based on polyamines and mesocellular silica foam. Effect of pore volume of the support and polyamine molecular weight.

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#### 1. Figures and Tables

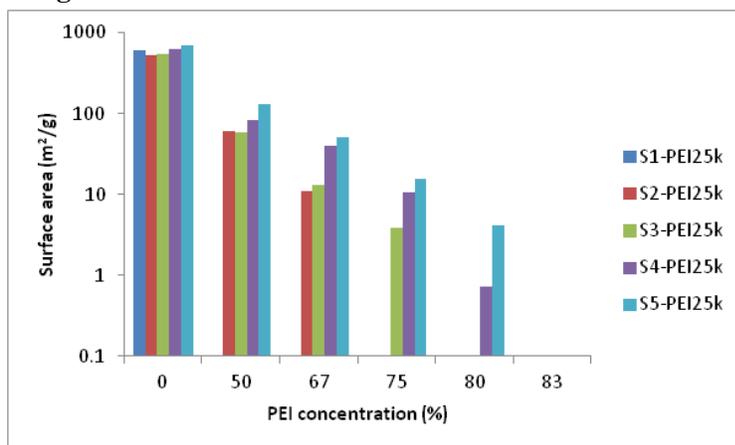


Figure S1: Surface area of adsorbents based on MCFs as a function of PEI25k loading in the adsorbent.

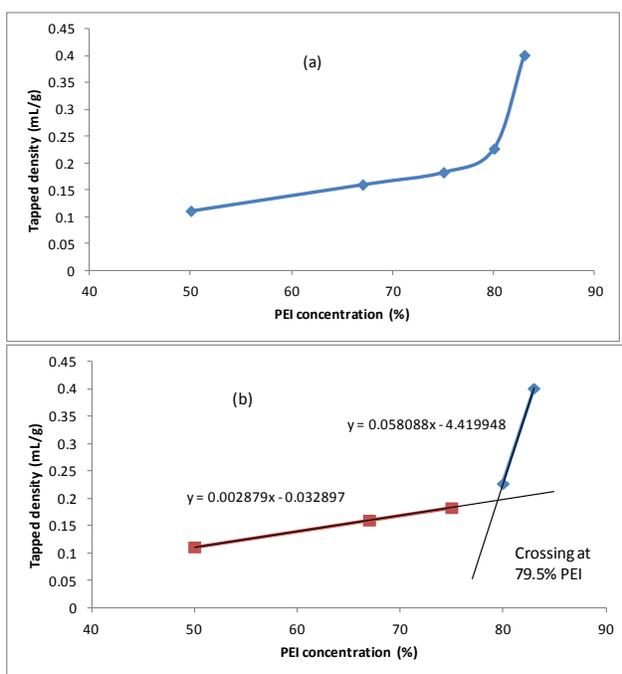


Figure S2. Tapped density of S5-PEI25k as a function of PEI concentration.

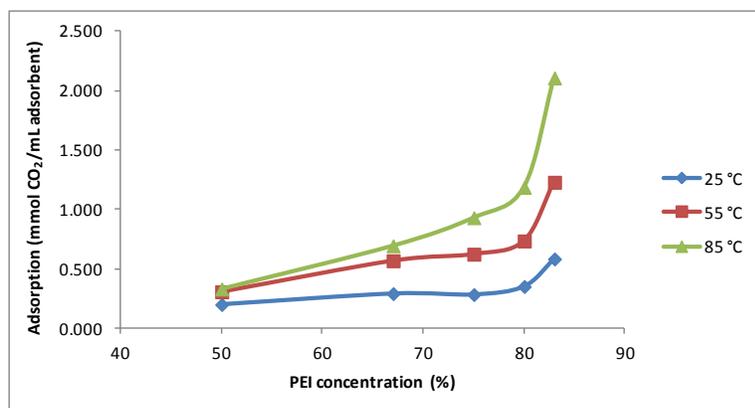


Figure S3. CO<sub>2</sub> adsorption in mmol/mL adsorbent as a function of PEI concentration in S5-PEI25k.

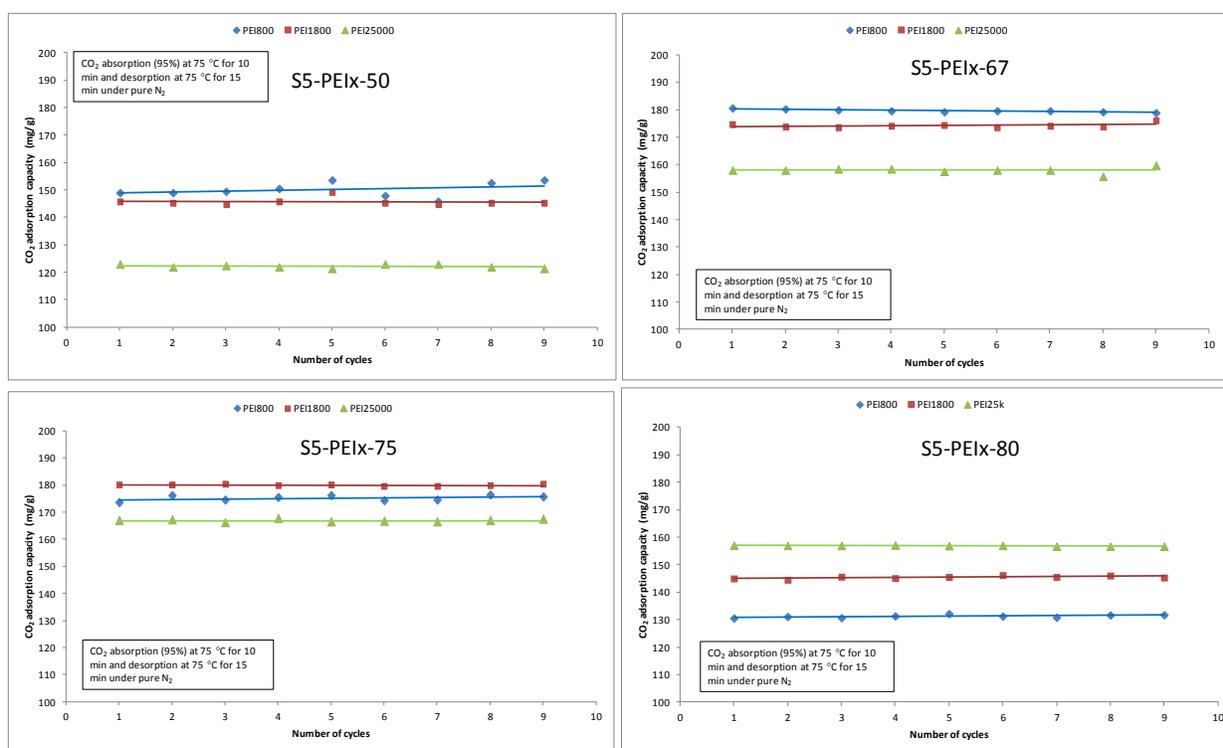


Figure S4. Adsorption capacity in short adsorption/desorption cycles at 75 °C as a function of PEI M<sub>w</sub> and concentration. 10 min adsorption under 95% CO<sub>2</sub>, 15 min desorption under N<sub>2</sub>, 9 cycles.

Table S1. CO<sub>2</sub> adsorption in mmol/mL adsorbent as a function of PEI concentration in S5-PEI25k

	25 °C	55 °C	85 °C
<b>S5-PEI25k-50</b>	0.198	0.306	0.329
<b>S5-PEI25k-67</b>	0.290	0.567	0.693
<b>S5-PEI25k-75</b>	0.282	0.622	0.930
<b>S5-PEI25k-80</b>	0.350	0.733	1.185
<b>S5-PEI25k-83</b>	0.582	1.228	2.107

Table S2. CO<sub>2</sub> adsorption on S5-PEI in mmol CO<sub>2</sub>/g PEI as a function of the molecular weight of PEI and PEI loading (from 50% to 83%)

	25°C	55°C	85°C
<b>S5-PEI800-50</b>	5.43	7.01	8.16
<b>S5-PEI800-67</b>	4.12	5.84	7.61
<b>S5-PEI800-75</b>	4.12	5.78	7.96
<b>S5-PEI800-80</b>	3.68	5.26	7.43
<b>S5-PEI800-83</b>	3.18	4.63	6.81
<b>S5-PEI1800-50</b>	4.52	6.62	6.79
<b>S5-PEI1800-67</b>	3.41	5.50	6.63
<b>S5-PEI1800-75</b>	2.82	5.03	6.88
<b>S5-PEI1800-80</b>	2.55	4.38	6.67
<b>S5-PEI1800-83</b>	2.29	3.80	6.28
<b>S5-PEI25k-50</b>	3.56	5.50	5.92
<b>S5-PEI25k-67</b>	2.58	5.23	6.55
<b>S5-PEI25k-75</b>	2.05	4.53	6.78
<b>S5-PEI25k-80</b>	1.92	4.04	6.53
<b>S5-PEI25k-83</b>	1.75	3.69	6.33

Table S3. CO<sub>2</sub> adsorption on S5-PEI in mg CO<sub>2</sub>/g PEI as a function of the molecular weight of PEI and PEI loading (from 50% to 83%)

	25°C	55°C	85°C
<b>S5-PEI800-50</b>	238.7	308.6	359.1
<b>S5-PEI800-67</b>	181.4	257.1	335.0
<b>S5-PEI800-75</b>	181.1	254.3	350.1
<b>S5-PEI800-80</b>	162.1	231.6	327.1
<b>S5-PEI800-83</b>	139.8	203.7	299.4
<b>S5-PEI1800-50</b>	199.1	291.3	298.6
<b>S5-PEI1800-67</b>	150.0	242.0	291.6
<b>S5-PEI1800-75</b>	124.1	221.1	302.5
<b>S5-PEI1800-80</b>	112.0	192.9	293.4
<b>S5-PEI1800-83</b>	100.6	167.0	276.3
<b>S5-PEI25k-50</b>	156.8	242.1	260.7
<b>S5-PEI25k-67</b>	113.6	230.1	288.3
<b>S5-PEI25k-75</b>	90.3	199.4	298.2
<b>S5-PEI25k-80</b>	84.6	177.9	287.1
<b>S5-PEI25k-83</b>	77.1	162.2	278.6

Table S4. Comparison of CO<sub>2</sub> adsorption capacities with PEI-impregnated silica supports under dry condition

Support	M <sub>w</sub> of PEI	PEI loading (%)	T (°C)	p <sub>CO2</sub> (atm)	Capacity (mg/g)	Reference
Fumed silica	800	50	70	1	147	[1]
MCM41	800	50	75	1	112	[2]
MCM48	800	50	75	1	119	[3]
SBA15	800	50	75	1	127	[3]
SBA16	800	50	75	1	129	[3]
KIT-6	800 <sup>a</sup>	50	75	1	135	[3]
PE-SBA15	800	50	45	1	138	[4]
Silica Monolith	800	45	75	1	132	[5]
		55	75	1	160	[5]
MCF/x	1300	50	75	0.5	105	[6]
S5	800	50	85	1	130	This work
MCF	423	80	75	1	264	[7]
S5	800	80	85	1	267	This work

<sup>a</sup> Linear PEI

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## 2. Preparation of the MCF supports

### 2.1. Preparation of S-[NH<sub>4</sub>F]-0 to S-[NH<sub>4</sub>F]-2.57

In the preparation of the S-[NH<sub>4</sub>F]-0 to S-[NH<sub>4</sub>F]-2.57 series, typically, 6.05 g P123 was added to 94 mL of DI water and 6 mL of glacial acetic acid. This mixture was kept under stirring at 40 °C for 18 h to obtain a homogenous solution. Subsequently, 10.5 mL of 1,3,5-trimethylbenzene (TMB), the swelling agent, was added and the solution stirred for an additional 2 h. After that, according to the [NH<sub>4</sub>F]/[Si] ratio, a corresponding amount of NH<sub>4</sub>F was added. Within a minute, a solution of 9 mL sodium silicate and 60 mL DI water was slowly poured into the prepared solution. In this series of experiments, the more NH<sub>4</sub>F was added, the faster the precipitate formed. For example, the support prepared without NH<sub>4</sub>F took up to 5 min to form a precipitate, while the one with the largest amount of NH<sub>4</sub>F formed a precipitate within 5 s. The combined mixture was vigorously stirred for 10 min before letting it sit under static conditions at 40 °C for 24 h. The temperature was increased to 70 °C and the solution aged for another 24 h. The resulting white suspension was filtered with a Buchner funnel and washed copiously with DI

water. Any organic components present were removed by calcination at 560 °C for 6 h with a temperature ramp of 5 °C/min from room temperature.

## 2.2. Preparation of S-1C/min to S-10C/min

Solution 1: 24 g P123 was added to 375 mL of DI water. This mixture was kept under stirring at 40 °C for 18 h resulting in a slightly cloudy solution. 2.60g NH<sub>4</sub>F and 23 mL glacier acetic acid were then added to the above solution 1 which was stirred for another 30 min.

Solution 2: 36 mL of sodium silicate was dissolved in 250 mL DI water, heated to 40 °C.

Solution 2 was poured slowly into Solution 1. The mixture was stirred vigorously for 10 min at 500r/min before letting it sit under static condition for 24 hrs.

The temperature was increased to 70 °C and the solution aged for another 24 h.

The resulting white suspension was filtered on a Buchner funnel and washed copiously with 4 L DI water. The obtained white solid was put into a furnace for calcinations. The temperature rate increase was varied from 1° C/min up to 10 °C/min in the following temperature program of 25 °C to 120 °C (1 °C/min), 120 °C (2h), 120 °C to 560 °C (x °C/min), 560 °C (6hr) where x represented the heating rate. The supports were named S-xC/min where x represented the heating rate from 1 to 10 °C.

## 2.3. Preparation of S-noTMB to S-TMB-eq.24h

Solution 1: 24 g P123 was added to 375 mL of DI water followed by 23 mL of glacial acetic acid. This mixture was kept under stirring at 40 °C for 18 h to obtain a homogenous solution. The pore swelling agent, 42 mL of 1,3,5-trimethylbenzene (TMB), was added and the solution which turned to cloudy white the solution stirred for an additional 0 to 24h. 2.52g NH<sub>4</sub>F was then added to the solution.

Solution 2: 36 mL of sodium silicate was dissolved in 250 mL DI water, heated to 40 °C.

Within 1 min of the NH<sub>4</sub>F addition to solution 1, Solution 2 was slowly poured into solution 1.

The combine reaction mixture was vigorously stirred for 10 min before letting it sit under static conditions at 40 °C for 24 h.

The temperature was increased to 70 °C and the solution aged for another 24 h.

The resulting white suspension was filtered on a Buchner funnel and washed copiously with 4 L DI water. The obtained white solid was put into a furnace for calcinations following the temperature program of 25 °C to 120 °C (5 °C/min), 120 °C (2h), 120 °C to 560 °C (5 °C/min), 560 °C (6hr)

The supports were denominated as S-TMB-eq.xh where x represented the time the solution was left under equilibration after addition of TMB. The support S-noTMB in which no TMB was used was the same as S-5C/min (preparation described above).

## 2.4. Preparation of S1-S5

### S1

Solution 1: 24 g P123 was added to 375 mL of DI water. This mixture was kept under stirring at 40 °C. 23 mL glacial acetic acid and 1.26g NH<sub>4</sub>F were then added to the solution under stirring.

Solution 2: 36 mL of sodium silicate was dissolved in 250 mL of DI water and heated to 40 °C.

Solution 2 was poured in Solution 1 under vigorous stirring (500r/min). After 10 min stirring the mixture was left under static conditions at 40 °C for 24 hrs.

The temperature was increased to 70 °C and the solution aged for another 24 h. The resulting white suspension was filtered on a Buchner funnel and washed copiously with 4 L DI water. The obtained white solid was put into a furnace for calcinations following the temperature program of 25 °C to 120 °C (5 °C/min), 120 °C (2h), 120 °C to 560 °C (5 °C/min), 560 °C (6hr).

### **S2 (same support as S-2C/min)**

Solution 1: 24 g P123 was added to 375 mL of DI water. This mixture was kept under stirring at 40 °C for 18 h resulting in a slightly cloudy solution. 2.60g NH<sub>4</sub>F and 23 mL glacial acetic acid were then added to the above solution 1 which was stirred for another 30 min.

Solution 2: 36 mL of sodium silicate was dissolved in 250 mL DI water, heated to 40 °C.

Solution 2 was poured slowly into Solution 1. The mixture was stirred vigorously for 10 min at 500r/min before letting it sit under static condition for 24 hrs.

The temperature was increased to 70 °C and the solution aged for another 24 h.

The resulting white suspension was filtered on a Buchner funnel and washed copiously with 4 L DI water. The obtained white solid was put into a furnace for calcinations following the temperature program of 25 °C to 120 °C (1 °C/min), 120 °C (2h), 120 °C to 560 °C (2 °C/min), 560 °C (6hr).

### **S3 (same preparation as S-5C/min)**

Same procedure as for S2 except for the calcinations step which followed the temperature program: 25 °C to 120 °C (5 °C/min), 120 °C (2h), 120 °C to 560 °C (5 °C/min), 560 °C (6hr).

### **S4 (same preparation as S-TMB-eq. 0h)**

Solution 1: 24 g P123 was added to 375 mL of DI water followed by 23 mL of glacial acetic acid. This mixture was kept under stirring at 40 °C for 18 h to obtain a homogenous solution. The pore swelling agent, 42 mL of 1,3,5-trimethylbenzene (TMB), was added and the solution turned to cloudy white. 2.52g NH<sub>4</sub>F was then added shortly after (within 5 min).

Solution 2: 36 mL of sodium silicate was dissolved in 250 mL DI water, heated to 40 °C.

Within 1 min of the NH<sub>4</sub>F addition to solution 1, Solution 2 was slowly poured into solution 1.

The combine reaction mixture was vigorously stirred for 10 min before letting it sit under static conditions at 40 °C for 24 h.

The temperature was increased to 70 °C and the solution aged for another 24 h.

The resulting white suspension was filtered on a Buchner funnel and washed copiously with 4 L DI water. The obtained white solid was put into a furnace for calcinations following the temperature program of 25 °C to 120 °C (5 °C/min), 120 °C (2h), 120 °C to 560 °C (5 °C/min), 560 °C (6hr)

### **S5 (same preparation as S-TMB-eq.2h)**

24.2 g P123 was added to 375 mL of DI water and 23 mL of glacial acetic acid. This mixture was kept under stirring at 40 °C for 18 h to obtain a homogenous solution. The pore swelling agent, 42 mL of 1,3,5-trimethylbenzene (TMB) was added and the solution stirred for an additional 2 h. After that, 2.52 g of ammonium fluoride was added. Within a minute, a solution of 36 mL sodium silicate and 250 mL DI water was slowly poured into the prepared solution. The combine reaction mixture was vigorously stirred for 10 min before letting it sit under static conditions at 40 °C for 24 h. The temperature was increased to 70 °C and the solution aged for another 24 h. The resulting white suspension was filtered on a Buchner

funnel and washed copiously with DI water. Any organic components present were removed by calcination at 560 °C for 6 h with a temperature ramp of 2 °C min from room temperature to 120 °C followed by two hours at 120 °C and heating to 560 °C at a rate of 5 °C/min to afford a light and fluffy white solid.

The amount of S5 solid obtained was 12.0 g, corresponding to a yield of 90.5%.

[36 mL \* 1.39 g/mL \* 26.5% are SiO<sub>2</sub> = 13.26 g; yield = 12/13.26 \* 100% = 90.5%]