Supporting Information

Efficient CO_2 Sorbents based on Silica Foam with Ultra-large Mesopores

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Table S1. Structural features for the mesoporous supports and the sorbents.

Sample ID	BET surface area / m^2g^{-1}	Pore size [a] / nm	Pore volume [b] / cm^3g^{-1}
MCM-41	1030	2.6	0.67
MCM-41PEI423%50	7.68	19.2	0.027
MCM-41PEI423%75[c]	1.80	11.4	N/A
MCM-41PEI423%80[c]	0.54	5.6	N/A
SBA-15	828	5.6	0.89
SBA-15PEI423%50	5.46	15.3	0.025
SBA-15PEI423%75	2.38	7.2	0.023
SBA-15PEI423%80 [c]	0.33	7.8	N/A
Foam	446	13.9	1.46
F- PEI423%50	128	33.3	1.10
F- PEI423%75	32.2	29.8	0.24
F- PEI423%80	5.2	18.5	0.001

[a] The pore size of the foam and the foam-supported PEI sorbents were calculated using the simplified Broekhoff-de Boer method, while that of MCM-41, SBA-15 and their sorbents were estimated by the Barrett–Joyner–Halenda model using the adsorption branch. [b] The total pore volume was estimated from the amount of N_2 adsorbed at $P/P^0 = 0.99$. [c] The pore volume is below the detection limit.

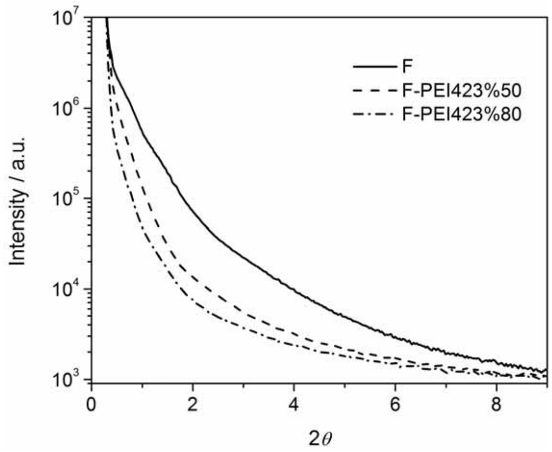

Fig. S1 XRD patterns of the as-synthesized silica foam and the adsorbents with different PEI loadings.

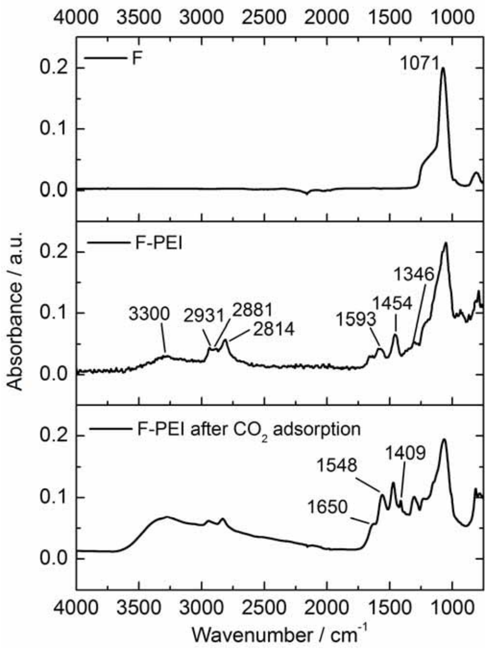

Fig. S2 ATR/FTIR spectra of the foam support and the PEI-impregnated sorbent before and after CO_2 capture.

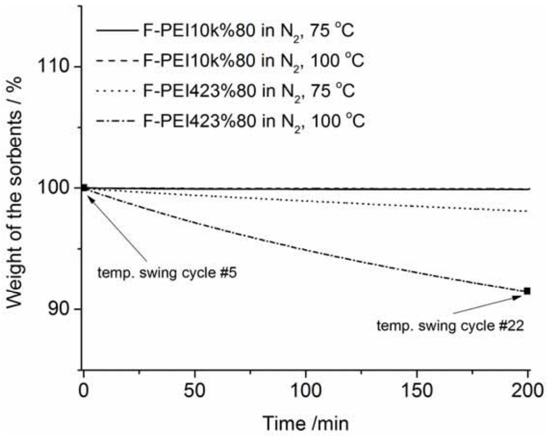

Fig. S3 Weight-loss of the foam-supported PEI sorbents under N_2 at different temperatures for 200 min and the weight change of F-PEI423%80 from the temperature swing cycle #5 to # 22 (the weight of F-PEI423%80 at temperature swing cycle # 22 is normalized based on that at cycle # 5).

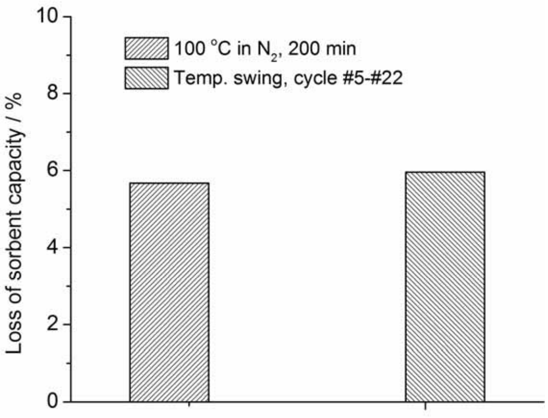

Fig. S4 Comparison of deactivation of F-PEI423%80 after keeping the sorbent under N_2 at 100 °C for 200 min and that from the temperature swing cycle # 5 to #22.

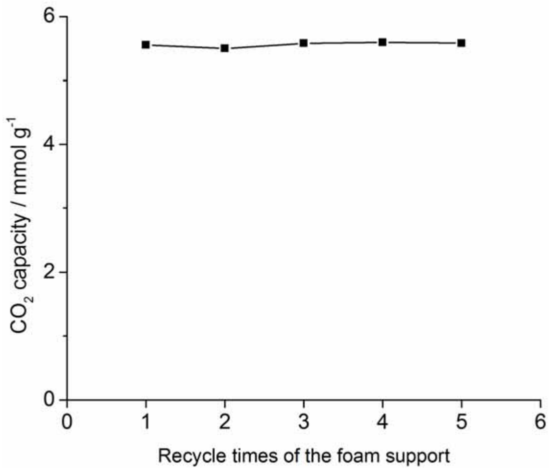

Fig. S5 CO_2 capacity of F-PEI423%80 using the recycled foams. The capacities were measured under dry 80% CO_2 at 75 °C for 60 min.

Relationship between the structure of bulk mesoporous supports and sorbent performance

Theoretically, the adsorption rate is proportional to the active adsorption sites of the sorbent, *i.e.*

$$\frac{dn}{dt}=m\left[\int F_p dr dA_p^{'}+\int F_{ex} dr dA_{ex}^{'}\right]/(1+\rho_{amine}V_{amine}) \tag{S1}$$

where n is the adsorption capacity, $A_p{}'$ and $A_{ex}{}'$ are the surface area of the stagnant diffusion layer in the pores and on the external surfaces, respectively, accessible by CO_2, and m is a constant. The terms F_p and F_{ex} correspond to the CO_2 concentrations in the amine stagnant diffusion layer inside and outside the pores, respectively, and V_{amine} is the volume of the amine loaded.

For bulk mesoporous supports with moderate amine loadings, we assume that most of the impregnated amine resides in the mesopores. In general, supported amine sorbents exhibit two-stage adsorption kinetics and the working capacity mainly depends on the linear adsorption increase in the first stage over an adsorption time period t. Therefore,

$$n\approx mt\int F_p dr dA_p^{'}/(1+\rho_{amine}V_{amine}) \tag{S2}$$

For simplicity, the mesopores are assumed to be cylinders (with pore radius = R and length = L_p) and uniformly coated with the amine. Thus, the interfacial surface area of the stagnant diffusion film in contact with CO_2, $A_p{}'$, is

$$A_p^{'}\approx 2\pi^{0.5}L_p^{\ 0.5}(V_{p,e}-V_{amine})^{0.5} \tag{S3}$$

where $V_{p,e}$ is the effective pore volume of the support, i.e. the maxium space that can be actually taken by the amine and accessible to CO_2. It should be pointed out that $V_{p,e}$ is not directly related to V_p (the total pore volume of the support). For example, an increase of V_p does not always correspond to a higher $V_{p,e}$ if the pores are either unfillable or blocked by the amine.

Following the first-order reaction of CO_2 with the amine, the CO_2 flux diffused in a stagnant film[1] is

$$\frac{\delta\int F_p dr}{C_{CO_2}D}=\frac{\phi}{\sinh\phi}\left[\cosh\phi-\frac{1}{\cosh\phi+(V_{amine}/A_p^{'}\delta)\phi\sinh\phi}\right] \tag{S4}$$

and $$\phi=\delta\sqrt{k/D} \tag{S5}$$

where C_{CO_2} is the concentration of CO_2 in the stream, k is the reaction constant of CO_2 with the amine,and D is the diffusion coefficient of CO_2 in the stagnant layer.

By substituting Eqn. (S3), (S4) and (S5) into Eqn. (S2) we obtain

$$\begin{aligned}
&n\approx 2\pi^{0.5}L_p^{\ 0.5}(V_{p,e}-V_{amine})^{0.5}mtC_{CO_2}\frac{\sqrt{kD}}{\sinh\phi}\\
&\left[\cosh\phi-\frac{1}{\cosh\phi+\dfrac{V_{amine}}{2\pi^{0.5}L_p^{\ 0.5}(V_{p,e}-V_{amine})^{0.5}\delta}\phi\sinh\phi}\right]\\
&/(1+\rho_{amine}V_{amine})
\end{aligned} \tag{S6}$$

1. R. B. Bird, W. E. Stewart and E. N. Lightfoot, in *Transport Phenomena*, John Wiley & Sons, New York, 2001, p. 557.