

Amine-impregnated silica monolith with a hierarchical pore structure: enhancement of CO₂ capture capacity†

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A polyethylenimine-impregnated hierarchical silica monolith exhibited significantly higher CO₂ capturing capacity than other silica-supported amine sorbents, and produced a reversible and durable sorption performance.

The increase of CO₂ emissions into the earth's atmosphere has raised serious concerns about global warming.^{1–2} Currently, large-scale separation of CO₂ produced in fossil fuel combustion is handled *via* liquid amine-based sorption processes in which amine species in various capturing sorbents react with CO₂ to form a carbamate complex. Recently, several silica materials incorporating a CO₂ capturing agent have emerged as dry sorbents for CO₂. Silica support alone has negligible CO₂ capture capacity (less than 10 mg CO₂/g-sorbent), but dispersion, immobilization, and confinement of the amine functional groups inside the porous silica support can result in a stable, mass transfer efficient, less toxic and less corrosive material than the corresponding liquid amines. These sorbents can be prepared either by grafting with diverse amine species^{3–11} or impregnation with polyethylenimine (PEI), tetraethylenepentamine (TEPA) or diethanolamine (DEA) dissolved in an organic solvent,^{12–16} in which amine-functionalities are well dispersed inside the pores of support materials. We recently carried out a systematic comparison of various mesoporous silica support materials for PEI-impregnation,¹⁵ and it was established that KIT-6, possessing 3-D mesopores with large pore volume, is more effective than MCM-41, MCM-48 or SBA-15 for CO₂ capture.

In this work, we report on the utilization of monolithic silica exhibiting a hierarchical pore structure as a support for amine impregnation. Silica monolith materials exhibiting a multimodal hierarchical pore structure can offer the benefits of each pore size regime combined in a single structure; the micro- or mesopores possess size- or shape-selectivity and high surface area, whilst the macropores would provide easier access to the active sites and reduce the pressure drop over the material.^{17,18} Overall, a significantly larger pore volume will be available for increased PEI or TEPA loading in good dispersion, coupled with enhanced mass transfer of CO₂ to the sorption sites, than with simple mesoporous silica support materials. To the

best of our knowledge, this is the first report of a silica monolith—which is better known as a chromatographic stationary phase^{19,20} or an enzyme support material²¹—being adopted for this purpose.

The silica monolith was prepared based upon the method of Smått *et al.*²² using tetraethoxysilane (TEOS), polyethylene glycol (PEG) dissolved in an aqueous nitric acid solution, and cetyltrimethylammonium bromide (CTAB) at a gel composition of TEOS:HNO₃:H₂O:PEG:CTAB = 1.00:0.25:14.69:0.54:0.0899. PEG has been used together with CTAB to control the particle aggregation and internal structure, respectively. PEI or TEPA was introduced into the silica monolith pieces by wet impregnation procedures as reported by Xu *et al.*¹² and Yue *et al.*¹³ (samples designated as *x*PEI or *x*TEPA/monolith, *x* being the quantity of PEI or TEPA introduced in weight percentage). A TGA unit connected to a flow panel and a mass spectrometer was used for CO₂ sorption measurement (see Fig. S1 for temperature steps programmed†). The TGA balance can measure accurately up to 1 μg. Ultra high purity N₂ was used as a purge gas. The sorption run was carried out using high purity CO₂ (99.999%) gas and 5% CO₂ (N₂ as balance gas). A feed flow rate of 30 mL min⁻¹ was controlled with a MFC to the sample chamber.

A typical type IV N₂ adsorption isotherm with pronounced capillary condensations reflecting internal mesopores (structural mesoporosity) and inter-particle voids between the primary particles (textural mesoporosity) was obtained for the calcined silica monolith (Fig. S2, A(a)†). The pore size distribution curve by N₂ adsorption showed a sharp peak centered at 3 nm with high uniformity (Fig. S2 B†), and two peaks centered at 17 and 120 nm corresponding to the textural mesopores and macropores, respectively, were detected by Hg porosimetry (Fig. S3†). The total pore volume measured by Hg porosimetry was *ca.* 3.2 cm³ g⁻¹ with a BET surface area of 950 m² g⁻¹. The interconnected open network of the silica monolith is clearly shown in SEM and TEM micrographs (Fig. S4†). After amine was introduced, the adsorption branch of the N₂ isotherm shifted to a lower pressure range. The BET surface area and pore volume of the PEI/monolith decreased as the PEI loading amount increased, confirming that PEI was successfully introduced into the channels of the support¹² (Fig. S2 and Table S1†).

A CO₂ sorption test for the amine-impregnated monolith was conducted at 75 °C, which corresponds to the optimum conditions reported earlier.^{12,15} For these amine-impregnated systems, a comparatively high temperature was needed for efficient carbon dioxide sorption in order to overcome the viscosity of the amine-based chemical agents. As the temperature

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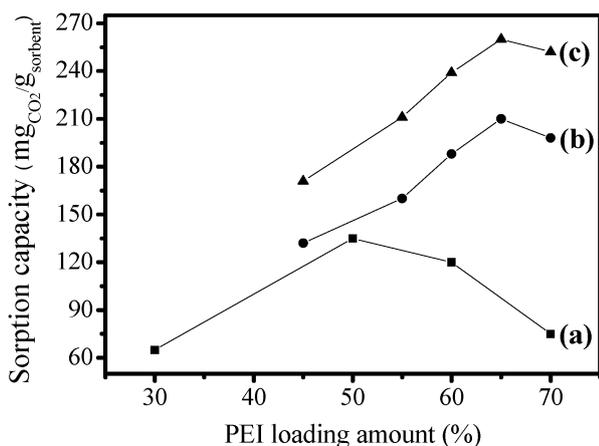


Fig. 1 Comparison of CO₂ sorption capacities with amine loading levels at 75 °C: (a) PEI/KIT-6,¹⁵ (b) PEI/monolith, and (c) TEPA/monolith.

is increased, these amine groups in PEI or TEPA become flexible and more CO₂-affinity sites are exposed to the CO₂. The sorption performance obtained was then compared against that of KIT-6, which was the best support material for amine-impregnation among the mesoporous silicas tested.¹⁵ As shown in Fig. 1, using 50PEI/KIT-6, 135 mg CO₂/g-sorbent was measured and the CO₂ sorption capacity decreased as the PEI loading was further increased to 60 wt%. The PEI/monolith (and TEPA/monolith) system, on the other hand, exhibited maximum CO₂ sorption capacities of 210 and 260 mg CO₂/g-sorbent at 65 wt% PEI (and TEPA) loadings. These are the highest amounts of captured CO₂ reported thus far among the amine-impregnated systems, clearly demonstrating the remarkable properties of the silica monolith as a support material for amine species. In addition, sorption level reached *ca.* 95% of the total CO₂ capturing capacity (200 mg CO₂/g-sorbent) in just 15 min, and CO₂ could be desorbed reversibly at a moderate temperature of 75 °C by simple N₂ flushing, lower than the typical temperature for solid amine sorbents which is usually from 100–140 °C.²³ The desorption rate of the PEI/monolith was also faster compared to the result for PEI/MCM-41.¹² These outstanding performances of the silica monolith can be attributed to the high pore volume that can accommodate a significantly larger amount of PEI (and TEPA), and the textural mesoporosity and macroporosity which facilitate efficient transportation of CO₂ to the sorption sites located inside the pores. The higher N concentration and less viscous nature of TEPA than PEI rendered it more readily activated with increasing temperature, and produced a higher sorption capacity. The decreases in the CO₂ capturing efficiency of 70PEI/monolith and 70TEPA/monolith indicate that too much introduced PEI (and TEPA) leads to poor dispersion of PEI (or TEPA) as pointed out earlier.¹⁵ This is evidenced by the gel-like morphology of the 75PEI/monolith (and 75TEPA/monolith) compared with other samples showing a dry surface after amine-impregnation at lower loadings.¹⁶ As shown in Table 1, at 60, 75, and 90 °C, CO₂ sorption capacities of 171, 210, and 202 mg CO₂/g-sorbent were measured over the 65PEI/monolith, while comparatively higher CO₂ sorption

Table 1 CO₂ sorption capacities of amine-impregnated silica monolith

Samples	Sorption capacity (mg CO ₂ /g-sorbent)		Temperature (°C)
	99.999% CO ₂	5% CO ₂	
45PEI/monolith	132	98	75
55PEI/monolith	160	114	75
60PEI/monolith	188	130	75
65PEI/monolith	171	—	60
	210	165	75
	202	—	90
70PEI/monolith	198	144	75
45TEPA/monolith	171	—	75
55TEPA/monolith	211	—	75
60TEPA/monolith	239	—	75
65TEPA/monolith	225	—	60
	260	—	75
	206	—	90
70TEPA/monolith	252	—	75

capacities of 225, 260, and 206 mg CO₂/g-sorbent were achieved with the TEPA/monolith.

As shown in Fig. 2, the 65PEI/monolith demonstrated very reversible and stable CO₂ sorption–desorption performance during 5 repeated runs. The TEPA/monolith, on the other hand, showed a steady decrease in sorption capacity during a 5 run sorption–desorption cycle at 75 °C, most likely due to TEPA leaching.¹¹ We subsequently repeated the run at 65 °C

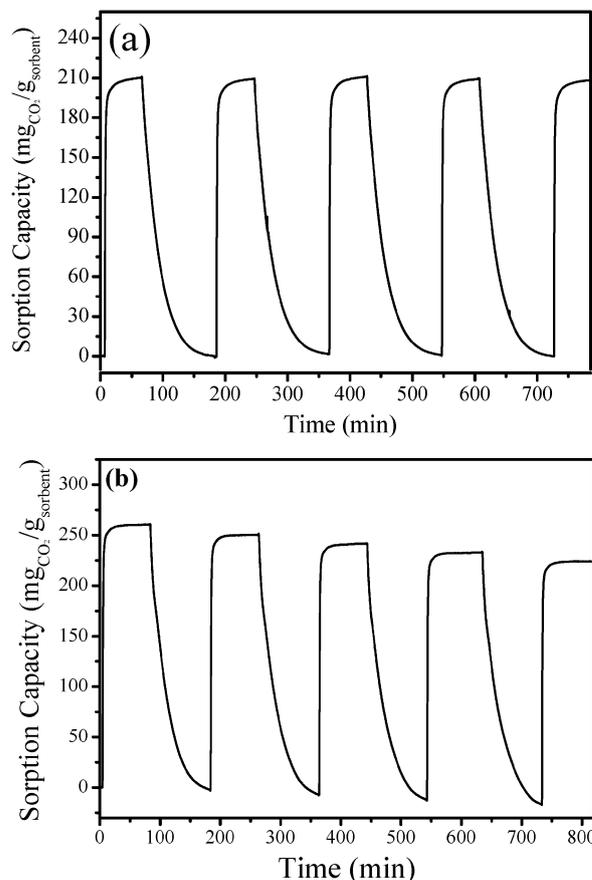


Fig. 2 Recycle runs of CO₂ sorption–desorption on (a) 65PEI/monolith and (b) 65TEPA/monolith at 75 °C.

for the latter, but the leaching problem persisted and the CO₂ desorption rate became unacceptably slow (Fig. S5†).

For practical implementation, a sorbent should also display a good sorption capacity under diluted CO₂ conditions. Hence we measured the CO₂ sorption capacities of the PEI/monolith (not the TEPA/monolith because of the weak stability) using 5% CO₂(balance N₂) at different temperatures. As shown in Table 1, 165 mg CO₂/g-sorbent was measured for the 65PEI/monolith at 75 °C, which is still higher than the best result obtained over PEI/KIT-6 using high purity CO₂. Amine-supported sorbents also function efficiently in the presence of moisture.^{24,25} Theoretically, 2 mol of amine species can react with 1 mol CO₂ in dry conditions, whereas the reaction stoichiometry changes to 1:1 in the presence of water (2R-NH₂ + CO₂ → R-NH₃⁺ + R-NHCOO⁻, R-NH₂ + CO₂ + H₂O → R-NH₃⁺ + HCO₃⁻).²³ We confirmed the positive moisture effect in our system using the 65PEI/monolith, and the CO₂ sorption capacity in humid conditions was ca. 24% higher than that under the dry conditions (Fig. S6†).

In summary, monolith silica with a hierarchical pore structure was prepared, and tested as a CO₂ capturing sorbent after amine impregnation for the first time. The hybrid material demonstrated the highest CO₂ capturing capacity reported to date under the given conditions, surpassing similar amine-supported systems by large margins. In particular, the PEI/monolith exhibited very reversible and durable CO₂ capturing performance, and also shows excellent performances in both diluted and moisture-containing CO₂ conditions. PEI/monolith will be a very promising CO₂ sorbent in the future.

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