Mesoporous silica supported polyethyleneimine for CO$_2$ capture from air

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Abstract

CO$_2$ capture technologies as combined with utilization and/or storage technologies to effect a reduction in atmospheric CO$_2$ concentration, are considered essential to the realization of the Paris Agreement ambition to limit global warming to well below 2 °C by year 2100. Reductions in the volume of CO$_2$ emissions from large fixed point-source emitters such as fossil fuelled power generators are sought for this purpose. However, progress towards this goal remains slow, in part due to the absence of appropriate market drivers, reluctance to invest in a declining market, and an apparent view that the substitution of coal with gas will provide a sufficient sector “contribution”. The direct capture of CO$_2$ from air provides an alternative approach to help restore the Earth’s natural climate cycles over the longer term, and also provides a means by which the similarly large volume of dispersed mobile CO$_2$ emissions can be addressed.

The capture of CO$_2$ from very dilute gas streams such as air presents a greater technical challenge, but is technically feasible. Importantly, this approach can be implemented free of the potential conflict of interest of emitters, and lends itself to co-location with storage and/or utilization sites so as to minimize transportation costs and, potentially, achieve better economies of scale. Polyethyleneimine (PEI) loaded mesoporous silica type composite sorbents are of interest for this application given their known ability to provide selective CO$_2$ capacity at low CO$_2$ partial pressures such as in air (~400 ppm); for example, they have been previously considered for the management of closed cabin atmospheres.

The present study considers the fitness for purpose of a range of PEI loaded mesoporous silica composites as adsorbents for CO$_2$ capture from air. The composites include those separately prepared with SBA-15 and siliceous meso-cellular foam (MCF) type mesoporous silicas, and loaded with PEI via wet infiltration. Composites were separately prepared with both linear and branched PEI to facilitate study of the relative potential of these two amine types for the application. It was thought that the branched PEI would better scavenge CO$_2$ from the dilute gas stream than linear PEI, given the greater affinity of primary amines for CO$_2$ than secondary amines. Composites were prepared with different PEI loadings (20 – 80 % mesopore volume equivalents) to facilitate study of the effect of PEI loading on the application potential of these sorbent types. Although increase in PEI loading translates to greater theoretical CO$_2$ capacity, it also brings about a greater barrier to the diffusion of CO$_2$ to an increasing fraction of the PEI, such that different loadings would likely be preferred for optimal performance under different process conditions.

Although not necessarily representative of the sorption process dynamics envisaged for the process technology, static fixed-volume CO$_2$ dosing (30, 50 & 75 °C) studies were undertaken to estimate the sorbents’ pressure dependent capacities for CO$_2$ (0 – 1 atm) and provide for their “quick” broad
range screening. The equilibration tolerances employed at first proved to be inadequate for highly accurate assessments, as evidenced by the observation of hysteresis in the isotherms obtained. Tighter equilibration criteria were subsequently identified that minimized this hysteresis, but these could not be broadly employed because of the long time necessary for their completion. It was found useful to plot the capacity data against a log pressure scale to facilitate simultaneous consideration of their potential for different applications (refer Figure 1). SBA-15 based linear PEI composites (20, 40, 60 & 80% loadings) exhibited a greater affinity for CO$_2$ at the lower temperatures, with the 60 % loading being favored; the analogous MCF based composite exhibited slightly greater capacity at 30 °C, but less at 50 °C. The branched PEI analogs exhibited much greater capacities over the temperatures studied, consistent with the greater affinity for CO$_2$ of primary over secondary amines. For the MCF based branched PEI composites series (60, 70, 75 & 80 % loadings), the 60 % loading composite was found to exhibit the largest CO$_2$ capacity at 30 °C; the 70 % loaded composite exhibited greatest capacity at 50 °C, but lower than at 30 °C. The SBA-15 composite with 60 % branched PEI loading exhibited the greatest capacity overall at 30 °C with 0.404 mmol/g, consistent with the higher surface area of the base support material. It is noted that additional time was required to realize the greater theoretical capacity of MCF supported materials given its larger mesopore volume per unit mass.

Separately, thermogravimetric analyses (TGA) of the CO$_2$ uptake of these sorbents from simulated air (400 ppm CO$_2$ in Ar) was conducted. This followed preliminary degassing in an Ar purge at 110 °C. This technique better indicates the dynamic potential of the sorbents under realistic separation process conditions. The 4-hour sorption period initially applied revealed that the sorbents did indeed possess larger capacities than suggested by the initial dosing experiments. Nevertheless, again the capacity exhibited by each composite appeared far from equilibrated. Longer equilibration times (21 h) and faster gas flows are now being employed to better characterize the sorption potential of the materials closer to their equilibrium capacities. Early results have revealed sorbents to indeed exhibit larger CO$_2$ capacities (see Figure 2). Furthermore these results (Figure 2) suggest that distinct stages of adsorption occur, and that these vary with PEI loading and process temperature. This is thought to result from PEI sorption sites with differing degrees of accessibility (e.g. surface level and sub-surface level sites).

**Figure 1**: CO$_2$ isotherms (30 °C) obtained for select linear (l) and branched (b) PEI loaded MCF (M), and SBA-15 (S), type composites as obtained via static fixed-volume CO$_2$ dosing analysis.

**Figure 2**: CO$_2$ sorption (20 °C) by branched PEI loaded MCF composites (60, 70 & 80 % MCF mesopore volume equivalent PEI loadings) during exposure to simulated air (400 ppm CO$_2$ / Ar) via in-situ TGA (35, 35 & 70 ml/min respectively).