3-Dimensional Silica as a Test Case for High Amine Efficiency Solid Adsorbents

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In this work, a novel amine-silica adsorbent system utilizing multi-porous channels for amine loading and carbon dioxide diffusion will be presented. This system allows for amines to be impregnated onto the solid platform without significant blocking of available diffusion channels, something currently impossible on the solid-amine systems available to date. Amine loading into large pores was obtained by the introduction of Polyethylenimine (PEI, Mw ~800 g/mole), with the goal of allowing for diffusion of gases to the loaded amine sites due to diffusion of gas through the untouched small pore channels. The 3dd-PEI species acts as a test of our hypothesized solution to the amine content-carbon diffusion problem, while 3dd-TEPA acts as a control test where size selection does not allow for preferential pore loading. The amine-silica support was tested for its ability to capture carbon dioxide in order to lessen the severity of global climate change, one of the premier threats facing the world today[1]. Recent works have shown that the pore geometry of the underlying solid adsorbent, as well as how amine interacts with these pore spaces, can play a significant role in capture performance; in some cases ignoring these interactions have yielded materials that significantly underperform expectations [2–4]. Specifically, it has been shown that the interaction between pore geometry and aminopolymer groups can set limits on the obtained amine efficiency, gas diffusion rate, and capture capacity for adsorbent systems [2]. This is caused by inefficient utilization of the available pore space, since the amount of amine loaded into a pore will necessarily degrade the ability for carbon dioxide to diffuse through that same pore, an issue that was previously ignored due to the high capacities possible on a small number of adsorbent species.

In order to overcome these challenges increasingly complicated pore systems are now being researched as a part of amine-loaded adsorbent systems. Previous work has shown that systems where the pore channel used for carbon dioxide diffusion is also the pore channel where amine is added to the support will necessarily lead to degraded capture performance at high amine contents. As a solution to this issue, this work investigates a porous silica species with two significantly different but interconnected pore systems. The sorbent chosen for this work is 3-Dimensional Disordered Silica, also known as 3dd silica. 3dd silica is composed of agglomerated microporous spheres of zeolite Beta, providing significant surface areas and high porosity. This material was chosen because of the availability of both microporous channels (diameter of < 10 Å) in the spheres, and mesoporous channels (diameters from 12 – 80 Å) between spheres. Since these inter-sphere mesopores are available both by diffusion along these mesopore channel paths and through the microporous spheres themselves the material contains diffusion paths along all 3 axes. And, since the large channels are accessible through the microporous spheres, it should be possible to load large aminopolymer species in these inter-sphere channels without degrading CO_2 diffusion, something that has been impossible to date on any other porous amine loaded support.

In this work, the 3dd-silica species were loaded with a large (Polyethylenimine, PEI, MW~800 g/mole) and a small (tetraethylenepentamine, TEPA, MW~180 g/mole) amine group, in order to test the efficacy of utilizing size selection to preferentially load the available pore channels. Amine loading occurred through wetness impregnation followed by volatilization of solvent, forcing the amine groups into the pore channels. Once loaded with various amine contents, the material was tested for carbon capture performance, including determination of amine efficiency and percentage of equilibrium capacity. Carbon dioxide capture trials as well as amine content data were obtained via thermogravimetry carried out in CO_2 (TA Q500 TGA in the temperature range 298 K ≤ T≤ 1000 K on N_2-degassed samples. The capture capacity for CO_2, the amine efficiency, and the percentage of equilibrium capacity achieved was then calculated from the TGA-data. The amine content was approximated using thermal decomposition curves, by heating the sample to 800 °C and observing the change in weight in the temperature bounds observed for decomposition of PEI or TEPA, respectively.

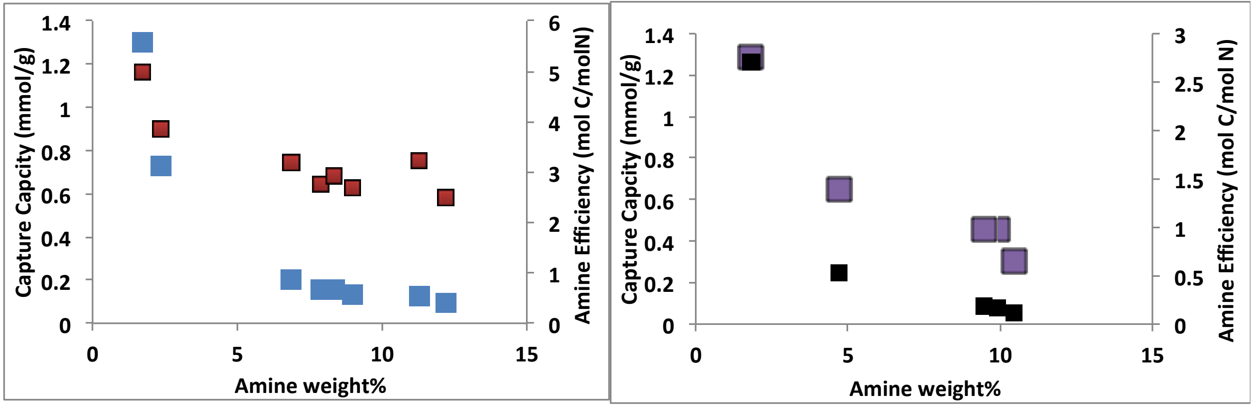

Figure 1: Capture capacity (red for PEI, purple for TEPA) and amine efficiency (blue for PEI, black for TEPA) data for 3dd-PEI (left) and 3dd-TEPA (right). This shows that 3dd-PEI does not undergo significantly degraded capacity or efficiency at high amine content, while 3dd-TEPA becomes ineffective for carbon capture at these loadings.

Capacity data are shown in Fig. 1 for the PEI and TEPA samples. The capture capacity of 3dd-PEI is seen plateauing at increasing amine content, supporting our hypothesis that high amine content will not block the diffusion of gases. At the same time, 3dd-TEPA is seen to decrease in capacity with increasing amine content, suggesting that the pore space is blocked in this system. The amine efficiency data further demonstrate the efficacy of using large polymer groups to preferentially fill in the large channels of the zeolite beta spheres. For 3dd-PEI, we observe that the amine efficiency plateaus at this maximum value, while for 3dd-TEPA the amine efficiency drops to below 0.1 moles CO_2/mole N. This result is attributed to different pore filling mechanisms when large aminopolymer (PEI) is loaded as opposed to small amine (TEPA) into the multi-porous 3dd silica substrate.

These results-demonstrate that in the use of large amines can lead to retained amine efficiencies and high carbon dioxide capacities on 3dd silica, while the small amine group leads to significantly degraded amine efficiencies and capture capacities. These data further prove our hypothesis as to the mechanism underlying decreased capacities on porous samples loaded with amines. This work acts as a platform from which the optimization of solid loaded amine systems can begin, utilizing the understanding of these less complex pore systems to engineering high capacity, high efficiency adsorbent technologies.

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Works Cited

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