

Templated polymeric materials as adsorbents for the post-combustion capture of CO₂

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Abstract

Increasing awareness of the influence of greenhouse gases on global climate change has led to recent efforts to develop strategies for the reduction of carbon dioxide (CO₂) emissions. The strategy that is receiving the most attention involves the capture of CO₂ from large point sources (such as fossil fuel-fired power plants) and long-term storage underground or in the ocean. Aqueous solutions of amines have long been used by industry as absorbents for acid gas (CO₂, H₂S) removal. However, they have a number of shortcomings for treating flue gases. As an alternative, adsorption is considered to be a promising technologies for capturing CO₂ from flue gases, with the potential to overcome the problems associated with liquid amines. Chemical adsorbents, containing basic nitrogen functional groups, have been demonstrated to be the most effective for post-combustion capture. Nanocasting, a technique by which a removable inorganic template is used to generate porous polymers with high surface area, without high temperature activation has been used to generate adsorbents whilst preserving the most basic nitrogen for adsorption. Nitrogen incorporated into the polymer matrix results in greater stability of the adsorbents in terms of volatile and thermal loss of nitrogen. Textural properties and CO₂ adsorption performance of these novel adsorbents will be discussed

Keywords

Adsorption, Co2 capture, Gas clean-up

INTRODUCTION

Increasing awareness of the influence of greenhouse gases on global climate change has led to recent efforts to develop strategies for the reduction of carbon dioxide (CO₂) emissions. In 2000, the burning of coal generated 37.8% of all CO₂ arising from fossil fuels (IEA 2002) and as a result the strategy that is receiving the most attention involves the capture of CO₂ from large point sources (such as fossil fuel-fired power plants). The greenhouse gas can then be stored underground or in the ocean over the long term. To achieve this economically CO₂ must be in a relatively pure high pressure form, requiring the capture and compression of the CO₂ emitted by the power plant.

The CO₂ capture step is projected to account for the majority (ca. 75%) of the expense for the carbon capture and subsequent storage process. Aqueous solutions of amines, for example monoethanolamine, have long been used by industry as absorbents for acid gas (CO₂, H₂S) removal, and in fact provide a large percentage of the natural gas sweetening operations (Chapel *et al.*, 2001). However, regarding their application to flue gases, these technologies need significant modification and this ultimately leads to high capital and running costs (Herzog *et al.*, 1993).

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Therefore, the development of alternative low cost technologies is crucial in the long term to provide a more cost and environmentally effective route CO₂ capture and storage on a global scale.

Adsorption is considered to be one of the more promising technologies for the efficient capture of CO₂ from flue gases. Activated carbons are well known as adsorbents of gases and vapours (Bansal et al 1988). Some of the most successful adsorbents for CO₂ have been developed via the alteration of the surface chemistry of porous substrates by impregnation with amine polymers, for example polyethylenimine (Xu *et al.*, 2003, Arenillas *et al.*, 2005). Another method is the modification of the surface chemistry of the carbon matrix by the incorporation of heteroatoms such as nitrogen to enhance the specific adsorbate-adsorbent interaction. Nitrogen incorporation has previously been demonstrated to enhance the adsorptive properties of activated carbons for hydrogen sulphide, SO_x, NO_x and acetaldehyde (Adib *et al.*, 2000) and recently CO₂ (Arenillas *et al.*, 2005, Drage *et al.*, 2007). However, the complexity of the carbon structure prevents the conventional activation techniques from generating carbon materials with a strictly controlled pore structure. Activation also involves heating of the precursor material to high temperatures (~900 °C), destroying original functionality, with the most potent functional groups for the adsorption of CO₂, such as amine groups, lost or converted to pyridinic groups (Arenillas *et al.*, 2005, Drage *et al.*, 2007).

Nanocasting or templating is a route by which high surface area adsorbents can be generated without the requirement for thermal treatment or activation. In nanocasting an inorganic diluent such as a silica is used to shape the in-growing polymer. On dissolution of the inorganic template the polymer remains as a mirror image, inheriting the porosity of the template. This paper describes recent studies using this novel templating or nanocasting technique for the generation of porous nitrogen containing polymers without high temperature activation for CO₂ capture.

EXPERIMENTAL

All reagents and solvents were supplied by Sigma-Aldrich, UK, were reagent grade and used without further purification. Porous melamine-formaldehyde (MF) resins were synthesized in the presence of 7 nm and 14 nm fumed silica as a templating / pore creating agent. Melamine (20g) was added slowly over 4 hours to a mixture of formaldehyde in water (180 ml 37 wt.% solution) with 5 - 10 wt.% methanol at 80 °C to form hexamethylmelamine. The solution was adjusted to pH 7-8 by adding K₂CO₃. Condensation reaction was initiated by raising the reaction temperature to 95 °C and adjusting the solution to pH 5-6 by the addition of HCl. The reacting mixture was stirred for a further 2 hours before cooling to room temperature and adding 4 ml of 48% H₂SO₄. At this point varying amounts (20 - 30g) of fumed silica were added and thoroughly mixed into the solution. The mixture was cured at 50 °C for 1 hour and left at room temperature for 24 hours until completely solid. Powdered samples were neutralized with a 5% solution of NH₃, before removal of the silica template from the MF resin by dissolution in alkaline NaOH solution. The adsorbents were washed and dried at 120 °C for 1 hour prior to characterization.

The organic carbon, hydrogen and nitrogen content of the MF derived active carbon adsorbents were determined using a Thermo 1112 Series Flash EA. Oxygen content was determined by difference. Textural characterisation was carried out using a ASAP 2010 with N₂ adsorption isotherms measured at -196 °C.

Assessment of the CO₂ adsorption and desorption potential was determined using a TA Q500, thermogravimetric analyser (TGA). Temperature-programmed analysis was used to evaluate the influence of temperature upon the CO₂ adsorption capacity of the adsorbents. Temperature resolved CO₂ adsorption capacity was determined as follows: 10 mg of adsorbent was placed in an alumina crucible and heated to 100 °C in N₂ atmosphere at a flow rate of 20 ml min⁻¹ and held isothermally for 30 minutes to remove any remaining moisture. The temperature was decreased to 25 °C and the gas switched to CO₂ with a flow rate of 20 ml min⁻¹. The sample was held isothermally at 25 °C for 2 hours, and the weight increase measured used to derive the CO₂ adsorption capacity of the materials at room temperature. The temperature was then increased gradually at a rate of 0.25 °C min⁻¹, the slow heating rate allowing for equilibrium adsorption capacity to be attained, up to 100 °C, with the weight change of the adsorbent monitored to measure the adsorption capacity of the materials. After which the gas was switched to nitrogen whilst the temperature was maintained at 100 °C in order to study the desorption capacity of the adsorbents.

RESULTS AND DISCUSSION

The nanocasting technique has been applied successfully to generate a range of CO₂ adsorbents with no, or mild thermal treatment. Techniques for the dissolution of the silica template have been developed which do not alter the chemistry of the amine polymer. Nitrogen adsorption isotherms for a range of adsorbents are presented in Figure 1. A range of surface areas have been generated by variation in the properties and amount of the silica template, cure conditions and degree of thermal alteration. This has demonstrated the techniques ability to generate high surface area materials from MF resin, which has previously been demonstrated to be difficult using chemical activation techniques (Drage *et al.*, 2007).

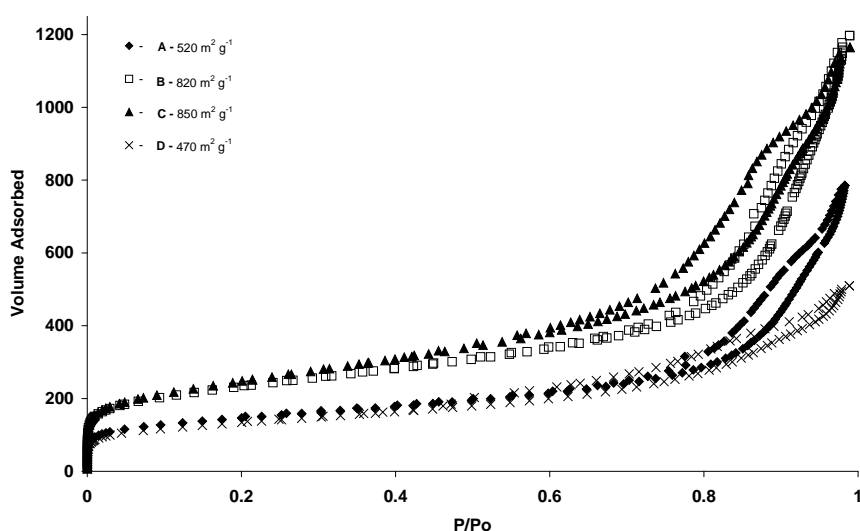


FIGURE 1. N₂ adsorption isotherms at -196 °C for a series of templated melamine-formaldehyde resin adsorbents.

Temperature resolved adsorption capacities were determined by TGA analysis. Figure 2 presents the adsorption capacities of two MF resin adsorbents. Adsorption capacity is highest in both cases

at 25 °C and decreases gradually with increasing temperature. The capacity and decrease in adsorption of CO₂ at elevated temperature is superior to the performance of a standard commercial activated carbon. The decrease in capacity with temperature differs from the performance of polyethylenimine based adsorbents that remain constant up to approximately 90 °C (Drage *et al.*, 2007). The difference chemistry of the nitrogen of the MF resin and PEI based adsorbents is proposed to account for this difference in performance. The mixture of primary, secondary and tertiary aliphatic amines are more basic (having a pK_a of approximately 10) than the amide and triazine ring nitrogen (pK_a approaching zero) of the MF resin. From this it is clear that although the technique is effective in producing high surface area materials, exploration of different polymer types is required to generate adsorbents containing sufficiently basic nitrogen. Research is underway to explore different polymer classes to optimize adsorption capacities.

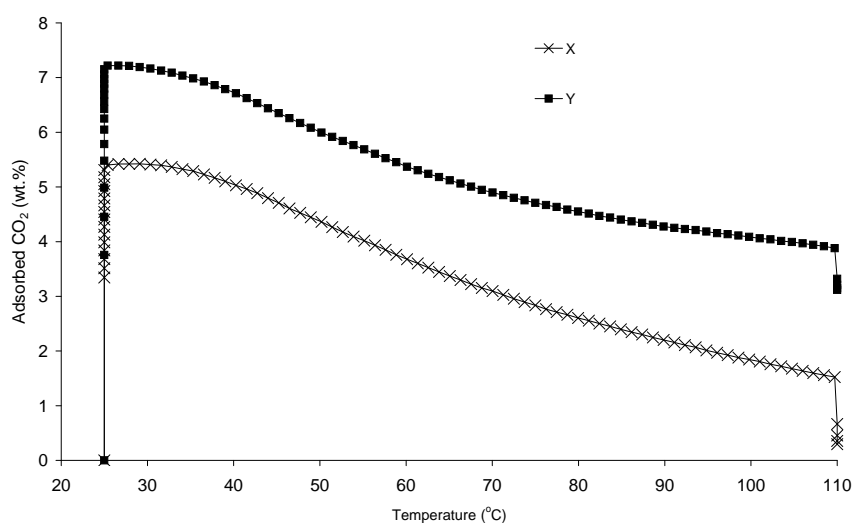


FIGURE 2. CO₂ adsorption capacity of two templated melamine-formaldehyde resin adsorbents from 25 - 100 °C, heated at 0.25 °C min⁻¹.

CONCLUSIONS

A range of novel highly porous adsorbents for CO₂ have been generated by the templated synthesis of MF resin, using silica as an inorganic template material. While the technique has been demonstrated to be effective at generating porous polymeric materials, research is on-going into materials containing the basic nitrogen optimal for CO₂ adsorption.

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