Developing strategies for the regeneration of polyethylenimine based CO_2 adsorbents

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Abstract

Adsorption is considered to be one of the more promising technologies for capturing CO_2 from flue gases. The efficient adsorption of CO_2 at low partial pressures, associated with post-combustion capture, require chemical type adsorbents containing basic amine functional groups. It has been demonstrated that amine polymers, for example polyethylenimine (PEI), immobilised on various porous substrates, silica, zeolites and fly ash, are effective adsorbents for CO_2. When considering the use of adsorption for large scale CO_2 capture, the ease of regeneration and the lifetime of the adsorbents are critical factors in determining their efficiency, cost and therefore feasibility for use. In this paper two approaches, thermal swing adsorption (TSA) cycles over a range of temperatures and time in an atmosphere of CO_2 and thermally assisted pressure swing desorption, are explored for the regeneration of the PEI based adsorbents. The reactions occurring during the TSA regeneration of PEI based adsorbents in an atmosphere of CO_2, especially the formation of a thermostable complex between PEI and CO_2 above 130 °C are described. Identification of the complex by FTIR, XPS and ^{13}C NMR and its attempted regeneration will be described. Overall, the results from this research have implications for the selection of regeneration strategies of all amine based CO_2 adsorbents.

Keywords
Adsorption, CO_2 capture, Gas clean-up

INTRODUCTION

It is generally accepted that this increase is at least part responsible for global warming. Consequently, CO_2 capture from large point sources has recently received attention as a potential means of mitigating fossil fuel CO_2 emissions, with adsorption considered to be one of the most promising technologies. The success of such an approach is however dependent on the development of an adsorbent that, at flue gas temperatures, has both a high CO_2 selectivity and adsorption capacity and whilst under regeneration is stable, does not incur a significant energy penalty and therefore economic cost.

Some of the most successful adsorbents for the capture of CO_2 at close to atmospheric pressure have been developed via the alteration of the surface chemistry of porous substrates by impregnation with amine polymers (Birbara *et al*., 1999, Filburn *et al*., 2002 Leal *et al*., 1995). Polyethylenimine (PEI) impregnated onto various substrates, low cost fly ash derived carbons (Arenillas *et al*., 2005) and MCM-41 (Xu *et al*., 2003) has produced highly effective CO_2 adsorbents.

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The ease of regeneration and the lifetime of adsorbents are critical factors in determining their efficiency and therefore feasibility for use as CO_2 capture technologies. Previously two approaches, thermal swing (TSA) and pressure swing (PSA) regeneration have been described for PEI based adsorbents (Drage *et al.*, 2006). This paper describes the reactions occurring during the TSA regeneration of PEI based adsorbents in an atmosphere of CO_2, especially the formation of a thermostable complex between PEI and CO_2 above 130 °C during TSA cycles. Analysis of the complex by FTIR and ^{13}C NMR and its attempted regeneration will be described. Overall, an understanding of this reaction will be crucial for the selection of regeneration cycles and the lifetime of amine based adsorbents.

EXPERIMENTAL

A proprietary inorganic support was used for the preparation of the adsorbent in this study. The inorganic support had a BET surface area of approximately 250 m^2 g^{-1}, pore volumes of 1.7 cc g^{-1} and a mean pore diameter of approximately 20 nm. PEI, branched 1800 molecular mass form was supplied by Sigma-Aldrich, UK. The adsorbent was synthesised by the impregnation of a mesoporous inorganic supports with PEI. PEI was incorporated into the support by a wet impregnation method (Xu *et al.*, 2003) and has been described elsewhere (Drage *et al.*, 2006).

The stability of PEI in air, nitrogen and CO_2 over a temperature range of 25 - 200 °C was determined using a Perkin Elmer, Pyris 1, thermogravimetric analyser (TGA). Approximately 10 mg of adsorbent was placed in an alumina crucible and heated to 100 °C in a N_2 atmosphere at a flow rate of 20 ml min^{-1} and held isothermally for 30 minutes to remove any moisture. The temperature was decreased to 25 °C and the gas switched to either nitrogen, air or CO_2 with a flow rate of 20 ml min^{-1}, these conditions were maintained for 2 hours. The temperature was then increased gradually at a rate of 0.25 °C min^{-1}, the slow heating rate allowing equilibrium to be attained, up to 200 °C, with the weight change of the adsorbent monitored throughout.

High temperature adsorbent regeneration was performed by TGA. Following drying (100 °C in nitrogen for 30 minutes), the adsorption capacity was determined isothermally at 75 °C in a stream of CO_2 (20ml min^{-1}). Regeneration was undertaken by heating the adsorbent to 240 - 250 °C, at 15 °C min^{-1} for various periods of time from 1 min to 1 hour in nitrogen. This was followed by further determination of the CO_2 adsorption capacity after cooling the furnace to 75 °C at 15 °C min^{-1}.

The organic carbon, hydrogen and nitrogen content of the adsorbents were determined with a Thermo 1112 Series Flash EA. Sample mass was corrected to the organic content of the adsorbent determined by loss on ignition analysis conducted using TGA. Solid state ^{13}C NMR spectra were obtained using a Bruker DSX200 instrument equipped with double-bearing probes for cross polarization (CP) and magic angle spinning (MAS). The resonance frequency for ^{13}C was 50 MHz, the sample was spun at the magic angle with a speed of 6.0 kHz. Typically ten thousand scans were accumulated with high power ^1H decoupling for the CP experiments. For CP, the contact time was 3.0 ms and the relaxation delay was 1.5 s.

RESULTS AND DISCUSSION

The thermal stability of the supported polytheylenimine in nitrogen, air and CO_2 up to 200 °C is presented in Figure 1. In an atmosphere of air and nitrogen the mass of adsorbent decreases between 95 and 125 °C, most likely as a result of moisture loss, either adsorbed or tightly bound in the inorganic support. It is also possible that slow volatilisation of PEI may also be occurring at these temperatures. Above 135 °C a more rapid decrease in mass occurs, especially in the presence of air where the weight decrease is as a result of volatilization and / or thermal degradation. In the presence of CO_2 there is a significant increase in mass as a result of adsorption of carbon dioxide which is constant up to approximately 85 °C, above this temperature CO_2 adsorption becomes less favourable and adsorption capacity decreases to a minima at 135 °C. Whilst it would be expected that the adsorbent would undergo a further weight loss as seen in N_2 and air above 135 °C, an increase in weight is observed. This indicates that a further reaction is taking place between the amine and CO_2 resulting in the formation of a thermostable complex. The composition of this complex, which is further evident from a colour change in the adsorbent, will be explored further by post-test analysis.

The formation of the thermostable complex is crucial for the regeneration of the adsorbents. Regeneration temperatures above 145 °C recovering approximately 90% of the original adsorption capacity, as predicted from thermal stability analysis (Figure 1). However, adsorption capacity decreases significantly from the first to the second regeneration cycle, leading to a 10 % loss in capacity between the two cycles at 180 °C as a result of formation of the thermostable complex. This destructive effect of the thermostable complex on adsorption capacity can be further illustrated by simulating a greater number of regeneration cycles, with sixty simulated regeneration cycles at 130 - 140 °C resulting in a decrease of approximately 30 wt.% in adsorption capacity (Drage *et al.*, 2006).

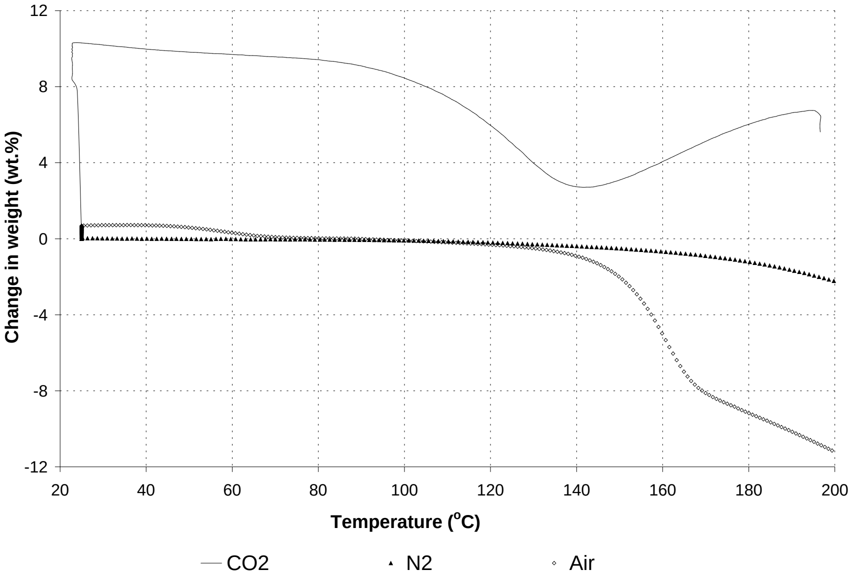

FIGURE 1. TGA profile for the behaviour of the PEI based adsorbent in N_2, CO_2 and air, whilst slowly heated from 25 - 200 °C at 0.25 °C min^{-1}.

Post test analysis has been performed to determine the composition of the thermostable complex. The adsorbent was reacted for 16 hours in CO_2 at 140 °C to generate a material almost completely composed of the thermostable complex. As the resultant complex was insoluble in organic solvents, analysis was required in the solid state.

Elemental analysis of the adsorbent prior to contact with CO_2 resulted in the expected composition for PEI (Table 1). The ratio of carbon and oxygen to nitrogen increases for the equilibrium and thermostable adsorbed CO_2 cases. The increase in oxygen for both cases, is double that of the increase in carbon, consistent with the adsorption of CO_2. The increase in carbon and oxygen for the equilibrium case is as expected for the adsorption of 10 wt.% CO_2. The relative proportion of carbon and oxygen is slightly less for the thermostable complex than for the equilibrium case. However, this is as expected due to the decreased adsorption capacity observed for the thermostable complex. The results of the elemental analysis indicate that the whole of the carbon dioxide molecule, is still included in the thermostable complex.

Adsorbent	**N**	**C**	**H**	**O**
40% PEI	1.00	1.97	5.64	0.00
40% PEI, adsorbed CO_2 (m)	1.00	2.25	4.84	0.52
40% PEI, adsorbed CO_2 (t)	1.00	2.25	5.50	0.50
40% PEI thermostable complex	1.00	2.22	4.88	0.38

TABLE 1. Relative ratio of CHNO relative to nitrogen for thePEI based adsorbent, under equilibrium conditions measured (m) and theoretical (t) and the thermostable complex.

Analysis of the complex by NMR and FTIR confirms the CO_2 is still completely bound into the adsorbent. ^{13}C NMR spectra confirm that alteration of the aliphatic structure of PEI has occurred when comparing the thermostable complex to the equilibrium adsorbed case. However, the spectra do not reveal any significant differences capable of explaining the bonding of the thermostable complex. DRIFT analysis spectra differ between the equilibrium and thermostable complex, especially between 1300 - 1600 cm^{-1}, corresponding to carbon-nitrogen and carbon-hydrogen bonding. Bands in the region of 1600 - 1700 cm^{-1} differ significantly and possibly indicate the presence of amide type bonding. Full assignment and interpretation of the spectra is on-going.

CONCLUSIONS

Study of the equilibrium performance in an atmosphere of CO_2 of the PEI-based adsorbent with temperature revealed the formation of a thermostable complex above 135 °C. As a result thermal regeneration of the chemical adsorbent is seen to be a trade off between efficient regeneration and degradation of the adsorbent by the irreversible complex formation. The exact nature of the complex is yet to be ascertained and full interpretation of the analysis of the solid is underway. The thermostable complex is partially regenerable at high temperature in N_2, however regeneration required heating to a temperature at which degradation and / or melting and pooling of the adsorbent occurs.

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