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Efficient and Rapid Screening of Novel Adsorbents for Carbon Capture in the UK IGSCC Project

E. Mangano[a], S. Brandani[a,*], M. C. Ferrari[a], H. Ahn[a], D. Friedrich[a], M. L. Lozinska[b], P. A. Wright[b], J. Kahr[b], R. Morris[b], M. Croad[c], N. McKeown[c], H. Shamsipour[d], P. Budd[d].

[a]The University of Edinburgh, SCCS, School of Engineering, Mayfield Road, Edinburgh EH9 3JL, United Kingdom
[b]University of St. Andrews, School of Chemistry, North Haugh, St. Andrews KY16 9ST, United Kingdom
[c]Cardiff University , School of Chemistry, Park Place, Cardiff CF10 3AT, United Kingdom
[d]The University of Manchester, School of Chemistry, Oxford Road, Manchester M13 9PL, United Kingodom

Abstract

Here we present the results of the rapid screening of novel adsorbents for CO_2 capture. The materials were synthesized as part of the Innovative Gas Separations for Carbon Capture (IGSCC) project, a UK wide consortium which involves the University of Edinburgh in collaboration with the University of St. Andrews, Cardiff University, Imperial College London, the University of Manchester and University College London. For the first time a wide range of materials relevant for carbon capture are investigated with regard to the CO_2 capacity at the same conditions and using the same technique. More than 120 samples, belonging to different classes of adsorbents, were investigated: MOFs, zeolites, PIMs, carbons and silicas. The conditions chosen are the ones of interest for post-combustion applications: 0.1 bar and 35 ºC. All the samples were tested using the Zero Length Column (ZLC) method. Relative to other technique, the ZLC presents the advantage of requiring a very small amount of sample (< 15 mg) allowing to obtain rapidly kinetic and equilibrium properties of the novel materials.
For each class of materials one typical sample will be shown and compared to typical commercial materials as benchmarks.

Keywords: Carbon capture; zeolites; MOF; PIM; activated carbon; ZLC.

* Corresponding author. Tel.: +44 (0)131-651-9030; fax: +44 (0)131-650-6551.
E-mail address: s.brandani@ed.ac.uk.

1. Introduction

The concentration of carbon dioxide in the atmosphere has registered an unprecedented increase in the last decades [1], and there is strong evidence that most of the global warming of the past 50 years is attributable to human activities [2, 3]. CO_2 is the most important anthropogenic greenhouse gas (GHG), with a value of 77% of the total anthropogenic emissions and the combustion of fossil fuels is responsible for the greatest part of the CO_2 emitted from anthropogenic sources. In order to achieve a worldwide reduction in CO_2 emitted by 50% by 2050 it has been estimated that a reduction of the direct emissions from industry of 21% compared to the actual levels [4-6] is needed. Among all the possible mitigation strategies, post-combustion CO_2 capture presents the main advantage that it can be retrofitted to existing power plants with no further modifications, so it is very likely to be the capture method adopted for most of the existing plants. With this regard separation of CO_2 using either membranes or porous adsorbents is one of the capture options being investigated since they have the potential to satisfy the environmental and energetic constraints.

The flue gas from a power plant is released generally at atmospheric pressure and the CO_2 contents vary depending on the fossil fuel used for the combustion: from 3-4 % for a natural gas combined cycle, to 11-13 % and 12-15 % for an oil or coal fired power plant, respectively [2]. Several reviews [7-9] have appeared recently summarising the studies reported on different classes of adsorbents which may have the characteristics of possible candidates for a post combustion PSA or TSA process, but very often the data reported on the performance of the adsorbents refer to conditions that are far from the real point of interest for a flue gas stream.

Here we present for the first time a direct and systematic comparison of the adsorption performance of several materials belonging to the most promising classes of adsorbents. This was possible by testing the samples using the same experimental technique and at the same conditions. With this regard the Zero Length Column (ZLC) revealed to be an essential tool for the rapid ranking of prototype adsorbents, allowing the characterisation of the equilibrium and kinetic properties of more than 120 different samples. The experimental conditions were chosen in order to be representative of the real conditions of a typical flue gas stream from a power plant: 0.1 bar of CO_2 and 35 °C.

The novel adsorbent materials were synthesised as part of the "Innovative Gas Separations for Carbon Capture" (IGSCC) project, a UK-wide research consortium aiming to develop novel separations based on absorption, adsorption and membrane processes which are needed to reduce the energy consumption and cost of carbon capture. The consortium is led by the University of Edinburgh (UoE) and involves the collaboration with the University of St. Andrews (StA), Cardiff University (CU), Imperial College London (ICL), the University of Manchester (UoM), and University College London (UCL). As a result of the different expertise contributed by the members of the consortium, several classes of materials were investigated: several types of Zeolites, MOFs and Mesoporous Silicas (StA); Carbons (UoM, CU, and UCL); and Oxides with surface functional groups (UCL).

Nomenclature	
c	gas phase concentration, mol/m^3
c_0	initial gas phase concentration, mol/m^3
t	time, s
q	adsorbed phase concentration, mol/kg

F	purge volumetric flowrate, m^3/s
M	mass of the sample, kg

2. Experimental method

The CO_2 adsorption capacity at 0.1 bar CO_2 and 35 ºC for all the samples was estimated using the Zero Length Column (ZLC) method. The technique was first introduced by Eic and Ruthven for the measurements of intracrystalline diffusion in zeolites [10] and it was then extended to measurements under equilibrium conditions [11, 12]. The technique is based on following the desorption curve of a very small amount of adsorbent sample previously equilibrated with a known concentration of adsorbate. The column consists in a 1/8" Swagelok union in which the sample is housed in monolayers between two sinter discs. The small size of the column offers, relative to other methods, the key advantage of requiring a very small amount of sample (10-15 mg) which is essential when prototype materials have to be tested.

The small size of the column and the small amount of sample used allow to neglect the external heat and mass transfer resistances as well as the effect of axial dispersion. All this greatly simplifies the interpretation of the data and allows the rapid ranking of the CO_2 capacity of novel prototype materials.

To control the system temperature, the ZLC is inside an oven. Drying columns are used for each gas line entering the system ensuring that the experiments are carried out in dry conditions.

The experiment consists in first equilibrating the sample with a mixture of 10% of CO_2 (sorbate) in He (carrier) at a constant flowrate. When equilibrium between the gas phase and the adsorbed phase is reached, the desorption starts by switching the inlet flow to pure He (purge) and the outlet gas phase concentration from the column is monitored. An on-line quadrupole mass spectrometer (Ametek Benchtop) is connected to the ZLC to monitor the outlet gas concentration.

The system can be operated under equilibrium or kinetic control by simply changing the purge flowrate: high flowrate (0-50ml/min) and low flowrate (0-3 ml/min) mass flow controllers are provided for the feed and purge line. Equilibrium and kinetic properties can be then investigated in the same series of experiments, simply using both sets of mass flow controllers.

Before each experiment the samples were regenerated overnight under flow of pure He. During the regeneration the temperature is slowly increased from room temperature to a temperature which allows complete dehydration with no damage for the sample.

The CO_2 capacities is evaluated from the integration of the desorption curves [12, 13].

3. Materials

Thanks to expertise of the partners of the IGSCC consortium different classes of adsorbents were investigated:

- MOFs, synthesised at the University of St. Andrews
- Zeolites and Silicas, synthesised at the University of St. Andrews
- Carbon based materials, synthesised at the University of Manchester and University College London
- PIMs, synthesised at the University of Manchester and Cardiff University.

The performances of the samples were compared with the ones of two commercial adsorbents as benchmark materials, zeolite 13X and silicalite HiSiv3000 from UOP. The benchmark materials were also tested on the same system and at the same conditions to allow a direct comparison.

4. Results

Due to the large number of sample tested, for each class of materials one representative sample will be discussed. A way to compare easily the adsorption capacity of different adsorbents at the same conditions is to normalize the ZLC desorption curves by the mass of sample used in the experiment: the area under the curve is directly proportional to the amount adsorbed. The ZLC response for each sample will be then compared to the benchmark by plotting the curves as c/c_0 vs. Ft/M in which F is the purge flowrate, t the time, M is the mass of the sample and c/c_0 is the concentration in the gas phase normalized by the initial concentration c_0.

4.1. MOFs

MOFs are a relatively new class of adsorbents which have been widely investigated in the past few years. Their structure consists in organic-inorganic hybrid networks formed by metal ligand bonds [9]. One of their main attractive features is the possibility to modify their structures and functional properties by changing the building blocks used in their construction.

It is then possible to finely control pore dimension, shape of the channels, and chemical potential of the surface, giving in the end the possibility to built the adsorbent with the desired adsorption properties [14]. Thanks to their high surface area and large pore volume MOFs show generally higher CO_2 capacity at high pressure compared to zeolites [15]. Despite to their relatively low capacity at low partial pressure, their high thermal stability and the fully reversible CO_2 adsorption make them very promising materials for pressure-swing processes [15, 16].

With regard to low pressure applications Mg-CPO-27 has showed to be a very promising material, exhibiting good adsorption capacity at low pressure [17]. In order to enhance the performance of the materials at the University of St. Andrews several Mg- and Ni-CPO-27 were developed by inducing post-synthesis treatments to increase the porosity and the metal-site content.
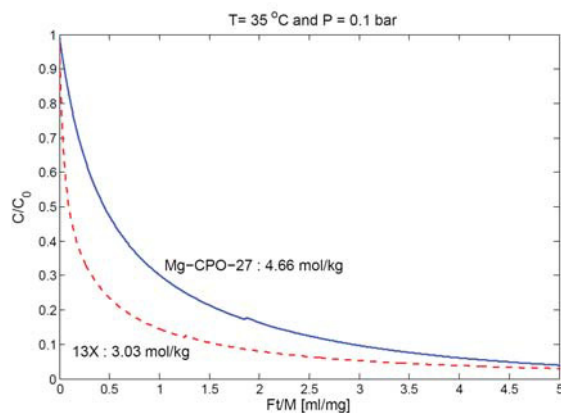

Fig. 1. ZLC curves for Mg-CPO-27 and zeolite 13X at 0.1 bar and 35 ºC.

Fig. 1 shows the ZLC desorption curve for a non-modified sample of Mg-CPO-27 compared with zeolite 13X. The sample was synthesised following the procedure as described in literature [18, 19]and no post-synthesis treatments were induced. From the plot of fig. 1 it can be easily seen that the area under the ZLC curve relative to the MOF sample is higher than the one relative to 13X, indicating a higher value pf the CO_2 capacity. The value of CO_2 uptake obtained for the sample is 4.66 mol/kg which is consistent with what reported in literature [20, 21], while the one relative to 13X is 3.03 mol/kg.

4.2. Zeolites

Zeolites have been widely investigated in the last decades as adsorbents for carbon capture applications[8]. They are generally characterised by a relatively high CO_2 capacity at low pressure which makes them very promising candidates for CO_2 separation from atmosphere and flue gas. Several studies have indicated zeolite 13X as one of the best adsorbents for post combustion applications, for this reason is very often used as a benchmark material for the comparison with other candidates for CO_2 separation processes [22, 23]. The adsorption performance of zeolites can be greatly enhanced by creating internal space to host the CO_2 and improving the electrostatic interactions between the adsorbent and CO_2 by the insertion of extra-framework cations. With this regard several types of zeolite samples, mainly Chabazite and Rho, were synthesised at the University of St. Andrews with different extra framework cations and different ion content, trying to optimise the CO_2 performances.

Fig. 2 shows the ZLC curve of a sample of Na-Y zeolite which is used as starting materials for the synthesis of Chabazites [24, 25]. Visibly the capacity of the Na-Y is slightly lower than 13X with a value of 2.25 mol/kg: the optimization of the synthesis of Chabazites should results in samples with higher capacity than Na-Y.
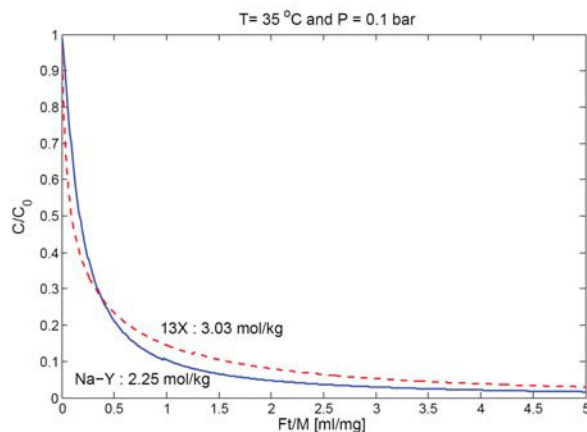

Fig. 2. ZLC curves for Na-Y and 13X zeolites at 0.1 bar and 35 ºC.

4.3. Carbons

Carbon-based adsorbent have been investigated and used for a wide range of gas separation, this, together with the relatively low cost of the synthesis has increased the interest in possible applications of this class of adsorbents for CO_2 separation processes. They are generally characterised by lower values of

CO_2 adsorption capacity compared to zeolites at low CO_2 partial pressure but higher in the high pressure region [26]. On the other hand their characteristic low heat of adsorption represents a key feature for any application at low energy requirement [27]. In the attempt of increasing their adsorption properties, at the University of Manchester several carbon based adsorbents were synthesized by modifying a commercial BPL carbon introducing amine functional groups. Adding basic chemical groups has simultaneously the advantage of an increase of the CO_2 affinity and the disadvantage of likely decrease of the available surface area for adsorption [27]. Fig. 3 shows the ZLC desorption curve of the non-modified BPL carbon sample. Due to the relatively low CO_2 capacity, HiSiv3000 was chosen as reference material. It can be noted that the area under the two curves does not differ much: the values of the capacity obtained are 0.35 and 0.38 mol/kg, for BPL carbon and HiSiv3000, respectively.
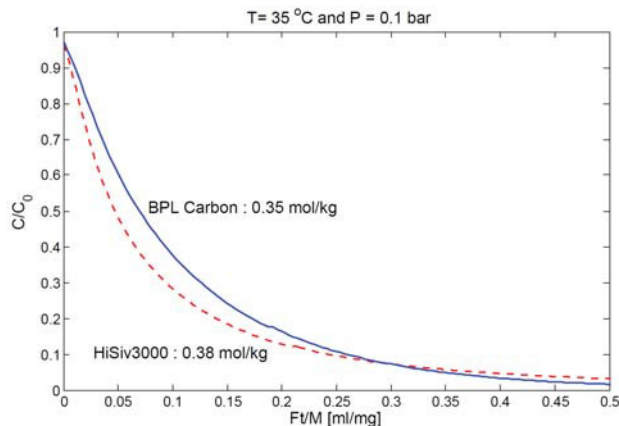

Fig. 3. ZLC curves for BPL carbon and silicalite HiSiv3000 at 0.1 bar and 35 ºC.

4.4. PIMs

PIMs (Polymers of Intrinsic Microporosity) are a new class of polymers recently invented by Prof. Budd (University of Manchester), Prof. McKeown (Cardiff University) and collaborators.

In 2004 Budd et al. [28] presented for the first time this new class of non-network polymers which acted like microporous materials with no need of a network of covalent bonds. Their microporosity arises from the presence of a "site of contortion" which hinders the rotation of the chains around it and, hence, prohibits any efficient space packing in the solid state: the resulting micropores dimensions in the range of 0.4 – 0.8 nm. It is intrinsic because it comes exclusively from the molecular structure and it is totally independent from any thermal or processing history of the material.

These polymers have very good potential to make gas separation membranes for different applications [29]. For the first time we tried to characterize with regard to the CO_2 capacity several types of PIMs synthesised with different methods and modified with to increase porosity and affinity to CO_2. The results obtained are similar to those of carbons and the unmodified PIM-1 showed a very low uptake (0.14 mol/kg). It should be pointed out that these materials will be used to make membranes so the capacity combined with the excellent transport properties of these polymers will play a more important role.

5. Conclusions

For the first time, a wide range of materials belonging to the most promising classes for carbon capture were systematically tested and compared at the same conditions and using the same technique. This allows for a direct comparison between the samples. With this regard the Zero Length Column (ZLC) revealed to be an essential tool for the rapid ranking of prototype adsorbents, allowing the characterisation of the adsorption properties of more than 120 different samples. This was possible thanks to the very small amount of sample required which make the technique ideal for the testing of prototypes.

The experimental conditions were chosen in order to be representative of a typical real flue gas stream from a power plant: 0.1 bar of CO_2 and 35 °C. Fig. 4 compares the CO_2 adsorption capacity for the samples tested, showing the best samples in each category. The MOF and zeolite samples resulted to be the best adsorbents with capacity close to and even higher than the current commercial standard 13X.

Furthermore for the first time a systematic characterisation of a novel class of polymers, PIMs, was performed. The information acquired will give directions to the future development of membranes for CO_2 separations.
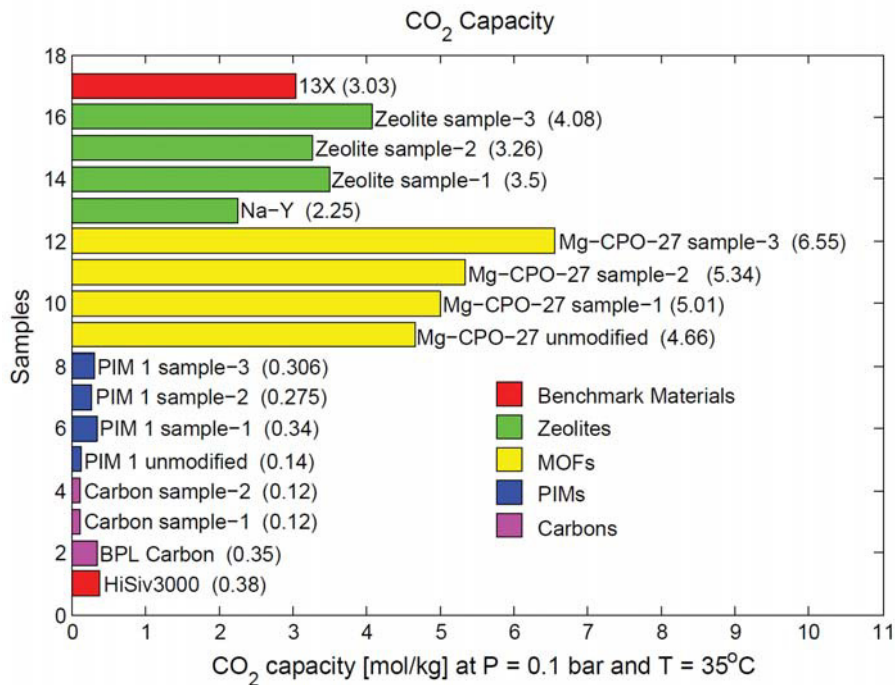

Fig. 4. CO_2 adsorption capacity at 0.1 bar and 35 ºC for representative samples.

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