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CO₂ capture by adsorption with nitrogen enriched carbons

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Abstract

The success of CO₂ capture with solid sorbents is dependent on the development of a low cost sorbent with high CO₂ selectivity and adsorption capacity. Immobilised amines are expected to offer the benefits of liquid amines in the typical absorption process, with the added advantages that solids are easy to handle and that they do not give rise to corrosion problems. In this work, different alkylamines were evaluated as a potential source of basic sites for CO₂ capture, and a commercial activated carbon was used as a preliminary support in order to study the effect of the impregnation. The amine coating increased the basicity and nitrogen content of the carbon. However, it drastically reduced the microporous volume of the activated carbon, which is chiefly responsible for CO₂ physisorption, thus decreasing the capacity of raw carbon at room temperature.

Keywords: CO₂ capture, sorption, amine impregnation

1. Introduction

According to IPCC's Third Assessment Report [1], there is fresh and stronger evidence that most of the warming of the earth's atmosphere observed over the past 50 years is attributable to human activities and that is expected to continue throughout the present century. The greenhouse gas with the largest impact on climate change as a result of human activity is carbon dioxide, CO₂, with 39 % of total emissions released from electricity generation, 23 % from transport and 22 % from industry [2].

The technological options for cutting CO₂ emissions to the atmosphere are: (i) to reduce energy consumption by increasing efficiency, (ii) to switch to less carbon intensive fuels, (iii) to increase the use of renewable energy sources or nuclear energy, (iv) to capture CO₂ by enhancing the biological absorption capacity of forests and soils, and (v) to capture and store CO₂ chemically or physically.

Among these major options that are aimed at reducing anthropogenic CO₂ emissions, the capture and storage pathway offers several advantages. It provides the time needed for the renewable energies to bring costs down and to pave the way for necessary technology advances, while enabling cleaner use of fossil carbon sources to be made during the transition period.

The capture process routes of post-combustion (i.e., CO₂ capture from flue gases), pre-combustion (i.e., CO₂ capture after the gasification process and before the combustion step) and denitrogenation (i.e., oxyfuel, using O₂ instead of air as a comburent gas), can be readily followed by using existing separation processes and energy conversion processes. The technological challenge is in the scale-up, its application to power generation and the integration of all these processes. There is also scope for the use of novel capture technologies, which are currently under investigation and show considerable promise as regards improvement of performance and cost reduction in the medium to long term.

CO₂ is already separated from industrial gas streams to meet process demands, as in the case of natural gas sweetening and ammonia production. Chemical absorption with amines is used for over 95 % of all gas sweetening in the United States, while other methods such as carbonate processes, solid bed adsorbents and physical absorption account for the remaining 5 %. To date, CO₂ capture has been applied only to pilot-scale power plants, but not yet to large-scale plants. This ready-to-use technology

presents a series of drawbacks when applied to post-combustion capture due to the large volume of flue gases: it is space-, cost-, and energy-intensive [3, 4]. Thus, the goal in reducing CO₂ emissions on an industrial scale is the development of a low cost means of capturing CO₂. Adsorption is considered as one of the potential options. However the success of this approach is dependent on the development of a low cost adsorbent with a high CO₂ selectivity and adsorption capacity, even at moderate temperatures. There are several works in the bibliography on modified adsorbents that enhance CO₂-solid interaction by nitrogen enrichment [5-9], or by immobilising amines on different supports [10-17].

CO₂ and immobilised amines are expected to show similar reactions to liquid amines in the typical absorption process [18], with the added advantages that solids are easy to handle and that they do not give rise to the corrosion problems caused by the circulation of very basic solutions [19].

In this work, three amines were evaluated as a potential source of basic sites for CO₂ capture. A commercial mesoporous carbon was used as a preliminary support in order to optimise the impregnation method and to study the behaviour of the immobilised amines at different temperatures and under various cycles of capture and regeneration. The aim of this work was to evaluate the influence of the modification of the chemical surface properties of the sorbents on their capture capacity and its variation with temperature. The potential regeneration of the sorbents and their suitability for application in cyclic processes were also evaluated.

2. Experimental

The carbon materials obtained were characterized in terms of texture, elemental composition, surface chemistry, thermal stability and CO₂ capture performance.

2.1. Preparation of the sorbents

Commercial activated carbon Norit CGP Super, referred to as N, was selected as the raw material for this study. This powdered activated carbon is manufactured by the chemical activation of wood using the phosphoric acid process. Textural characterization of N showed a mesoporous volume of $0.648 \text{ cm}^3 \text{ g}^{-1}$ calculated by the density functional theory (DFT) method [20] from the N_2 adsorption isotherm at -196°C , and a micropore volume of $0.204 \text{ cm}^3 \text{ g}^{-1}$ calculated by the Dubinin-Radushkevich (DR) method [21] from the CO_2 adsorption isotherm at 0°C .

A series of sorbents were obtained by filling N with different amine compounds: diethylenetriamine, pentaethylenhexamine, and polyethylenimine, which will be referred to as DETA, PEHA, and PEI, respectively. Some of the main physico-chemical characteristics of these substances are presented in Table 1. The amines were incorporated through a wet impregnation method adapted from Xu et al. [22], which entailed dissolving the desired amount of amine in 20 cm^3 of methanol by mechanically stirring the mixture for 15 min. The solution was then poured over 2 g of activated carbon previously dried at 100°C overnight and allowed to mix in a rotary evaporator for 30 min at room temperature. Subsequently, the resulting slurry was kept at 60°C and 300 mbar under reflux for 30 min, after which the methanol was eliminated by maintaining the conditions without reflux for a further 30 min. To complete the drying step, the pressure was reduced to 150 mbar, and maintained for 2 h. The initial amount of amine to be used was decided on the basis of the mesoporous volume of the support and the amine density. The sorbents were denoted as NX, where X represents the amine loaded.

2.2. Chemical characterization

The prepared sorbents were subjected to proximate and ultimate analysis to quantify the degree of impregnation achieved from the increase in volatile matter and nitrogen content. In order to study the influence of impregnation on the acid-base properties of the carbon surfaces, the point of zero charge (pH_{PZC}) was estimated by a mass titration method adapted from Noh and Schwarz [23]. Finally, to elucidate the nature of the surface functionalities, diffuse reflectance infrared Fourier transform (DRIFT) spectra of the samples were obtained without sample dilution in a Nicolet Magna-IR 560 spectrometer at 128 scans and a resolution of 4 cm^{-1} .

2.3. Textural characterization

The textural characterization of the prepared sorbents was carried out by measuring He density in a Gas Pycnometer AccuPyc 1330, and N_2 and CO_2 adsorption isotherms in a TriStar from Micromeritics at $-196\text{ }^\circ\text{C}$ and $0\text{ }^\circ\text{C}$, respectively. Prior to the measurements the samples were outgassed at room temperature under vacuum for 24 h. The apparent surface area was evaluated from the N_2 adsorption isotherm by the BET equation in the linear form proposed by Parra et al. [24].

2.4. Thermogravimetric study

The thermal stability was evaluated in a thermogravimetric analyser Setaram TGA 92 coupled to a Nicolet Nexus FTIR spectrometer through a TGA interface. The gas line was heated to avoid condensation and secondary reactions of the evolved gases.

2.5. CO_2 sorption measurements

The CO_2 adsorption and desorption performance of the sorbents was evaluated in a Setaram TGA 92 thermogravimetric analyser.

2.5.1. Non- isothermal tests

Temperature programmed adsorption tests (TPA) were carried out to evaluate the influence of temperature upon the CO_2 capture capacity of the sorbents. This entailed

degasifying the sample under vacuum for 30 min, recovering the pressure by means of an inert gas (Ar) and then changing to CO₂ at a flow rate of 50 cm³ min⁻¹ for 1 h. The mass increase was interpreted as the CO₂ adsorption capacity of the sample at room temperature. Subsequently, the temperature was increased at a rate of 0.5 °C min⁻¹ to 100 °C and this temperature was maintained for 1 h. The mass change during heating was recorded to study the effect of temperature on the CO₂ capture performance of the sorbents.

2.5.2. Isothermal tests

Isothermal CO₂ capture tests at 25 °C were carried out to evaluate the suitability of the samples for cyclic operation. These tests consisted of 3 vacuum swing adsorption (VSA) cycles, each cycle entailing a 30 min CO₂ capture step followed by regeneration under vacuum for 30 min, and normal pressure recovery with an inert gas. The mass increase during the capture step was interpreted as the CO₂ adsorption capacity of the samples.

3. Results and discussion

3.1. Characterization

The amines under evaluation were subjected to pyrolysis in 50 cm³ min⁻¹ of Ar at a heating rate of 15 °C min⁻¹ to study their thermal stability. When the amines are free, in liquid form, the loss of mass takes place abruptly at different temperatures: DETA starts to decompose at 100 °C, PEHA at 230 °C and PEI at 270 °C, as shown in Figure 1. The sequence of increasing thermal stability is in accordance with the molecular weight of the amines. To evaluate the interaction between the amine coating and the carbon support, the sorbents were also pyrolysed and their thermal stability was studied. The mass loss profiles of the impregnated carbons are similar, taking place gradually from

100 to 400 °C, as can be seen in Figure 2. This may be due to two contrary effects: on the one hand the stabilising effect of the carbon due to the interaction forces between the solid and the liquid film and, on the other hand, the greater dispersion of the amine film on the high surface of the carbon, which will promote decomposition at lower temperatures. The mass loss for the impregnated samples could be mainly assigned to desorption and/or decomposition of the amine polymer. Desorption of the polymer would imply that it is not chemically linked to the carbon support. Gas analysis allowed identification of the main species evolving during the experiments.

In the TPD analyses, the only gases evolved from N were H₂O, CO₂ and CO, as was to be expected for an unmodified activated carbon. However, NH₃ and CH₄ were also evolved from the impregnated carbons due to the decomposition of the amine coating, thus demonstrating the success of the impregnation approach. It should be noted that no methanol was detected, i.e. the solvent was completely removed during the drying stage. Although amine was expected to desorb during the first stages of the TPD test, gas analysis by FTIR did not show any significant intensity that could be undoubtedly assigned to amine polymer IR absorption bands. Nevertheless, it should be pointed out here that most of the amine characteristic bands appear in the range of the hydrocarbons and ammonia. Therefore, the amine loading of the prepared sorbents can be quantified from the proximate analysis, shown in Table 2, by subtracting the volatile matter of the raw carbon from the corresponding value of the impregnated samples. Table 2 also shows that the nitrogen content was successfully increased from a negligible amount up to 14 % through impregnation. The nitrogen content of the final sorbents depends not only on the amount of amine incorporated into the carbon but also on the nature of the amine, as can be seen from N-DETA which has the lowest loading but the highest nitrogen content.

The effect of the impregnation on the chemical properties of the carbon surface was studied by measuring the pH_{PZC} of the samples. From the values of pH_{PZC} (Table 2), it can be seen that the surface of the carbon changed from acidic (pH_{PZC} of 3.9), in accordance with the manufacturing process of the carbon, to basic (pH_{PZC} of around 9) after impregnation with the strongly basic amines. The nature of the acidic surface groups of N was elucidated by the DRIFT spectrum (Figure 3). The presence of carboxyl-carbonates groups might explain both the peak circa 1600 cm^{-1} and the broad band between 1000 and 1500 cm^{-1} [25]. The broad band around 3400 cm^{-1} is clearly related to hydroxyl groups, and the smaller bands ca. 1700 and 3060 cm^{-1} could easily be due to carboxylic acids [25]. The DRIFT spectra of the impregnated samples (Figure 3) present a sharp peak at 1677 cm^{-1} and smaller bands around 1400 cm^{-1} due to the amino groups, and bands around 2950 cm^{-1} associated to the aliphatic chains of the amines incorporated onto the carbon. Thus, the amines were immobilised on the carbon surface without suffering any radical change in their nature.

The influence of the impregnation on the textural characteristics of the carbon was evaluated through the analysis of the N_2 and CO_2 adsorption isotherms. From the N_2 isotherms of the samples, shown in Figure 4, and also from their BET values (Table 2), it can be seen that the impregnation produces a drastic decrease in the surface area due to the blockage of the pores, as previously observed by other authors [8, 10]. Figure 5 shows the CO_2 adsorption isotherms of the samples. It has been previously reported that the shape of CO_2 adsorption isotherms at $0\text{ }^\circ\text{C}$ is related to the mechanism of adsorption. N presents a near rectilinear isotherm, which is a result of a mechanism of surface coverage, associated to pore sizes greater than two molecular dimensions of CO_2 [26]. The modified sorbents present curved isotherms. In carbon adsorbents this shape is associated to a micropore filling mechanism that occurs in narrow micropores of

unimolecular size [26]. However, in the case of the impregnated samples, the pronounced elbows could also be explained by the contribution of chemisorption. It should be noted that, although only the adsorption branch is shown, some hysteresis at low pressure was found; the lag between the adsorption and desorption isotherms being greater for the impregnated samples. This can also be explained by irreversible adsorption due to the contribution of CO₂ chemisorption, which could be beneficial to the application of the sorbents in CO₂ capture, as long as it enhances capture without hindering regeneration.

3.2. CO₂ capture performance

Sorbent performance in the capture of CO₂ was monitored by the mass increase of the samples when exposed to CO₂, and the capture capacity expressed as weight percentage of the fresh sorbent. The temperature-programmed CO₂ capture tests of the studied sorbents are presented in Figure 6. In all cases, the highest capacity occurs at room temperature, the increase in temperature acting to the detriment of capture. This was to be expected due to the exothermic character of physisorption, which is the only mechanism available for CO₂ capture in the case of raw N, and also to the contribution of the exothermic CO₂ sorption reaction in the case of the impregnated samples. Instead of the common downward trend, the impregnated carbons present a softer slope with temperature than raw N, due to the stronger interactions between the acidic gaseous CO₂ and the basic amine groups present on the impregnated carbon surface. This effect is more acute in the case of N-DETA, which has the highest nitrogen content.

The fact that the raw carbon presents the highest CO₂ capture capacity at room temperature is due to the higher contribution of physisorption, which is limited in the case of the modified sorbents due to the pores being blocked by the amine film. Some authors [10, 22] have reported improvement in the capture performance of raw supports

through impregnation with PEI at room temperature. For instance, in the work of Xu *et al.* [22] PEI-modified mesoporous molecular sieve of MCM-41 type presented CO₂ adsorption capacities of 32.9 mg CO₂ / g adsorbent (3.29 wt %) at 25 °C and 11.2 wt% at 75 °C, higher than that obtained for pure PEI of 11 wt. %. However, in such cases the supports themselves presented low capacities (i.e., 2.73 wt% for MCM-41 at 25 °C and 0.86 wt% at 75 °C), thus showing a synergetic effect of the support on the adsorption of CO₂ by PEI. These low capacities of the supports can be mainly ascribed to their poor textural properties or, as in the case of MCM-41, to weak interactions between the support and CO₂, particularly at relatively high temperatures. This is in accordance with the previous findings from our group [27-29] when impregnating different supports, such as activated alumina and low cost activated carbons obtained from sewage sludge and olive stones. The alumina and the sludge carbon were mesoporous materials with relatively low surface areas that presented low capture capacities (3 and 1 wt%, respectively) in their unimpregnated form, but after impregnation with alkylamines these capacities doubled. However, the microporous carbon obtained from olive stones presented relatively high capacities in its unmodified form (9 wt%) due to its high surface area, and impregnation showed no important improvement in capture performance. Other authors [8] have also reported negative effects on capture capacities of activated anthracites impregnated with PEI at room temperature. Activated carbons are good adsorbents on their own, presenting acceptable CO₂ capacities without modification, due to their high surface areas and adequate pore size distribution for gas separation. Maroto-Valer *et al.* [8] reported that only pores smaller than 1 nm are effective for CO₂ capture at atmospheric pressure. Impregnation does not seem to be the best approach for improving the capture performance of activated carbons at room temperature because the coating blocks the microporous texture, which is the factor

chiefly responsible for the physisorption of CO₂. The objective should be to enhance chemisorption by modifying the carbon surface without cancelling physisorption.

Although high CO₂ capture capacities are essential for the application of the sorbents, regeneration is also a crucial stage. There are two main possibilities for CO₂ capture with solid sorbents: Temperature Swing Adsorption (TSA) and Pressure Swing Adsorption (PSA). Considering the sensitivity of the surface amino groups to temperature, the PSA operation would seem to be more suitable for the impregnated sorbents. Although PSA technology for removal of trace amounts of CO₂ in air purification processes is well developed, it appears inappropriate for the recovery of CO₂ from streams which contain >3% CO₂ [30]. Thus, in the case of post-combustion capture, it would not be economical to compress the enormous volume of flue gases. Capture should take place at normal pressure and the regeneration of the sorbents at reduced pressure, which results in a concentrated CO₂ stream ready for compression and transport. Vacuum Swing Adsorption (VSA) with solid amine sorbents is already used in space life support applications for removing CO₂ from the environment by making use of the space vacuum to regenerate the sorbent [12]. Moreover, VSA where the product CO₂ is recovered at sub-ambient pressure is seen to be more prospective for CO₂ capture from flue gases [31].

From the VSA cycles of the samples, presented in Figure 7, it can be seen that, while N reaches the plateau of maximum capture capacity in 20 minutes, the impregnated samples present a continual upward tendency for the 30 minutes of the capture step and attain no equilibrium capacity. Therefore impregnation slows down the kinetics of the capture process, due to the diffusion of gaseous CO₂ through the amine film. It is also noticeable from the figure that there is a slight upward tendency in the base line of the impregnated samples, indicating that the regeneration is not fully complete. Actually,

the CO₂ capture capacities of cycles 2 and 3 are slightly smaller than that of fresh sorbents, as can be seen from Table 3. This is due to the contribution of chemisorption which hinders regeneration.

Most of the works on CO₂ recovery applying VSA use adsorbents of physisorption type (i.e. zeolites). For instance, *Chaffee et al.* [32] reported the results based on the use of zeolite 13X on a pilot scale VSA apparatus to study the capture of CO₂ from CO₂ / N₂ gas streams and performing cycles of 6 and 9-steps. A purity of over 90 % together with 60-70 % recoveries were achieved for a 9-step cycle. Thus, absolute power requirement and energy penalty are substantially smaller than previously reported for PSA capture of CO₂ [33].

Conclusions

Although impregnation with amines is already used in commercial sorbent synthesis for CO₂ separation, its application to activated carbons reduces drastically their microporous volume, which is the factor mainly responsible for CO₂ physisorption, thereby decreasing their capture capacity at room temperature. However, at medium temperatures (70-90 °C), the contribution of chemisorption associated to the incorporated amino groups may improve the performance of the carbon.

The vacuum swing operation for CO₂ flue gas recovery yields a concentrated CO₂ stream without dilution. VSA applied to the prepared impregnated carbons do not achieve complete regeneration because of the chemisorption character of these adsorbents. However, when physisorption type adsorbents (i.e., zeolites) are used, VSA seems to be an adequate operation mode for CO₂ capture.

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Table 1 Physico-chemical properties of the amines used

Amine	Molecular Formula	Molecular Weight	N content (% wt)	Density (g cm ⁻³)	pH
Diethylenetriamine (DETA)	C ₄ H ₁₃ N ₃	103	41	0.95	14.8
Pentaethylenhexamine (PEHA)	C ₁₀ H ₂₈ N ₆	232	36	1.00	13.6
Polyethylenimine (PEI)	H(NHCH ₂ CH ₂) _n NH ₂	423 ^a	35 ^b	1.07	13.8

^a Number Average Molecular Weight (M_n)

^b Based on M_n and an average n of 9.43 calculated from M_n.

Table 2 Chemical and textural characterization of the carbon sorbents studied

Sample	Proximate analysis (% db)			Ultimate analysis (% daf)				pH _{PZC}	He density (g cm ⁻³)	S _{BET} (m ² g ⁻¹)
	VM	Ash	FC ^a	C	H	N	O ^a			
N	11.2	4.4	84.4	87.7	2.4	0.2	9.7	3.9	1.64	1762
N-DETA	37.8	2.6	59.6	76.7	4.9	14.1	4.3	9.3	1.35	157
N-PEHA	41.3	3.2	55.5	74.9	4.9	11.7	8.5	9.0	1.29	170
N-PEI	40.4	2.6	57.0	75.6	5.6	13.2	5.6	9.3	1.32	90

^a Calculated by difference.

Table 3 CO₂ capture capacity of the carbon sorbents studied

Sample	Amine used (wt %)	Amine content ^a (wt %)	CO ₂ capture capacity at 25 °C		
			1 st cycle	2 ^{sd} cycle	3 rd cycle
N	-	-	7.3	7.1	6.9
N-DETA	39	27	4.0	3.5	3.4
N-PEHA	40	31	4.8	4.0	3.5
N-PEI	43	30	4.9	4.2	4.0

^a Calculated from the proximate analysis (daf).

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Figure 7. VSA cyclic operation of the studied sorbents at 25 °C.

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Figure 1. Thermal stability of the amines used.

Figure 2. Thermal stability of the sorbents studied.

Figure 3. DRIFT spectra of the samples studied.

Figure 4. N_2 adsorption isotherms at $-196\text{ }^\circ\text{C}$ for the series of samples studied.

Figure 5. CO₂ adsorption isotherms at 0 °C for the series of samples studied.

Figure 6. Evolution of the CO₂ uptake during temperature-programmed CO₂ capture tests for the studied samples -heating rate of 0.5 °C min⁻¹ between 25 and 100 °C under 50 cm³ min⁻¹ of CO₂-.

Figure 7. VSA cyclic operation of the studied sorbents at 25 °C.