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Doped phenol-formaldehyde resins as precursors for precombustion CO_2 capture adsorbents

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Abstract

The use of solid sorbents for precombustion CO_2 capture, which implies the removal of CO_2 from the shifted-syngas prior to electricity generation, has acquired increasing interest in recent years. As an alternative method for precombustion CO_2 capture, adsorption can be considered a promising technology, offering potential energy savings compared to absorbent systems. Solid sorbents are currently used in pressure swing adsorption (PSA) systems for the purification of hydrogen in petrochemical industries. In the present work, phenol formaldehyde resin-based adsorbents have been prepared to be applied in precombustión CO_2 capture applications. The produced carbons showed superior performance when compared to commercial CO_2 adsorbents and a great selectivity towards CO_2.

1. Introduction

Commercial methods to capture CO_2 have long been used in the chemical and petrochemical industries. These methods, applied to the removal of H_2S and CO_2 from gaseous streams, are mostly based on chemical absorption with aqueous solutions of alkanolamines (MEA, DEA, MDEA), in the case of combustion flue gases, or physical absorption with solvents (Rectisol®, Selexol®), in the case of high CO_2 partial pressures. However, these processes present several drawbacks such as high energy consumption, degradation, short life and high solvent cost [1]. Alternative methods have been proposed for CO_2 capture but, currently, advanced research is focused on membranes and adsorption with solid sorbents [2,3]. Adsorption is considered a promising technology for CO_2 capture applications since adsorbents present high adsorption capacity, great selectivity, good mechanical properties and they remain stable over repeated adsorption-desorption cycles [4,5]. Activated carbons are suitable candidates for CO_2 capture,

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their adsorption performance being dependent on the pore structure and the properties of the surface chemistry [6]. Although capture capacities of activated carbons are, in general, lower than those of zeolites and molecular sieves under low pressure and ambient conditions, they present a series of advantages as CO_2 adsorbents such as larger capacities at higher pressures, ease of regeneration, potential low-cost and less sensitiveness to moisture. Phenolic-resin-based activated carbons offer further advantages in that they can be produced in a wide variety of physical forms (including granular or extruded, fibres, monolithic structures), allow close control of porosity, present a very low level of impurities and good physical strength [7,8].

In this work, phenol formaldehyde resins were synthesised with and without the addition of organic additives. These resins were carbonised and activated with CO_2 to produce phenolic-resin-based activated carbons. Samples were chemically and texturally characterised and their CO_2 capture performance evaluated under pure CO_2 flow (adsorption isotherms) and CO_2/H_2 mixtures (breakthrough curves).

2. Experimental

2.1. Synthesis of materials

In this work, phenol formaldehyde resin (PF) samples have been prepared following different synthesis pathways. During the synthesis, phenol and formaldehyde were mixed and heated in the presence of a catalyst. In some cases, an organic additive, ethylene glycol (EG) or polyethylene glycol (PEG), was also added. The following samples were produced: samples NA and CLA were synthesised without additive using NH_4OH and HCl, respectively, as catalyst; samples E1A and PE10 were prepared adding EG (1 wt.%) and PEG (10 wt.%), respectively, during the acid-catalysed synthesis route. Afterwards, the resins were cured in a rotary evaporator by heating under vacuum [9-12].

2.2. Carbonisation and activation with CO_2

The cured resins were then carbonised and activated with CO_2 to develop microporosity in the samples. Carbonisation was performed in a horizontal furnace up to 800ºC under a stream of 50 mL min^{-1} of N_2. Activation with CO_2 was conducted in a vertical furnace, in a flow rate of 10 mL min^{-1} of CO_2 at 900ºC. Activated carbons with various degrees of burn-off were prepared.

2.3. Characterisation

The obtained carbons were characterised in terms of texture and chemical composition. For the textural characterisation, the micropore volume, W_0 [13], the average micropore width, L_0 [14], and the BET surface area, S_{BET} (m^2g^{-1}), were determined from the N_2 and CO_2 adsorption isotherms at 77 and 273 K, respectively.
Chemical characterisation involved proximate and ultimate analyses and evaluation of the point of zero charge (pH_{PZC}).

2.4. CO_2 capture capacity

The capture performance of the adsorbents was determined under pure CO_2 and CO_2/H_2 mixtures, to evaluate the equilibrium capacities and the maximum working capacities of the samples, respectively. CO_2 capture tests at 25ºC and atmospheric pressure were conducted in a thermogravimetric analyser by recording the mass uptake of the samples when exposed to pure CO_2 atmosphere. High pressure CO_2 and H_2 adsorption isotherms were evaluated in a magnetic suspension balance at 25ºC and pressures up to 30 (CO_2) and 40 bar (H_2). The maximum CO_2 uptakes of the samples at high pressures and their selectivity towards CO_2 were assessed.
The CO_2 capture performance of the adsorbents in a binary mixture of CO_2 and H_2 was also evaluated by obtaining the breakthrough curves of the samples in a purpose-built bench-scale system. The maximum working capacities were evaluated after seven consecutive adsorption-desorption cycles that involved an adsorption step at 15 bar and room temperature, followed by complete regeneration of the adsorbent at atmospheric pressure and 80 ºC.

3. Results and discussion

3.1. Chemical analysis

Ultimate analysis and pH_{PZC} of the prepared carbons are included in Table 1. The main element in the samples composition is carbon (~97 wt.%). The obtained carbons show basic character (pH > 7), due to the devolatilisation of oxygenated compounds during carbonisation. Basicity also increased after activation with CO_2, because part of the oxygen that was incorporated to the surface of the char during the activation step is in the form of basic oxygen groups (i.e., pyrone) [12,15].

Table 1 Chemical characterisation of the prepared adsorbents

Sample	Ultimate Analysis (wt.%, daf)				pH_{PZC}
	C	H	N	O*	
NA	97.3	0.3	0.9	1.5	8.8
CLA	97.4	0.1	–	2.5	9.4
E1A	97.2	0.1	–	2.7	8.8
PE10	95.7	0.1	–	4.2	7.5

O*: calculated by difference

3.2. Textural characterisation

Table 2 summarises the textural parameters calculated from the N_2 and CO_2 adsorption isotherms at 77 and 273 K, respectively, and the helium density of the PF carbons.
Helium density in PF samples is around 2 g cm^{-3}. Activation with CO_2 resulted in a significant textural development. The prepared carbons are mainly microporous. BET surface areas (S_{BET}) and total micropore volumes ($W_{0\,N2}$) are similar for the activated samples, but lower for the carbonised sample PE10. Analysing the narrow microporosity in the PF carbons, here assessed by the CO_2 adsorption isotherms, differences between the activated samples can be observed. E1A shows the highest narrow micropore volume ($W_{0\,CO2}$) (0.33 cm^3 g^{-1}), most probably as a consequence of the addition of EG during the synthesis. Regarding the average narrow micropore widths ($L_{0\,CO2}$), the activated samples present average values around 0.7 nm while sample PE10 exhibits the smallest average narrow micropore width.

Table 2 Textural parameters calculated from the N_2 and CO_2 adsorption isotherms of PF carbons

| Sample	d_{He} (g cm^{-3})	N_2 adsorption at 77 K		CO_2 adsorption at 273 K	
		S_{BET} (m^2 g^{-1})	$W_{0\,N2}$ (cm^3 g^{-1})	$W_{0\,CO2}$ (cm^3 g^{-1})	$L_{0\,CO2}$ (nm)
NA	2.08	1211	0.45	0.26	0.70
CLA	2.11	1381	0.51	0.29	0.74
E1A	1.96	1369	0.51	0.33	0.73
PE10	1.92	472	0.25	0.23	0.58

Since the molecular size of CO_2 is 0.209 nm, only pores less than 1.0 nm are effective towards CO_2 capture at atmospheric pressure. Thus, the textural characterisation suggests that the produced carbons present suitable porous structure to be applied as CO_2 adsorbents.

3.3. CO_2 capture capacity

Figure 1 shows the CO_2 uptake for each sample at 298 K and atmospheric (1 bar) and high pressure (30 bar). CO_2 capture capacities are expressed in mmol of CO_2 per gram of adsorbent (mmol g^{-1}).These values correspond to the equilibrium CO_2 uptakes under the tested conditions. Figure 1 shows the
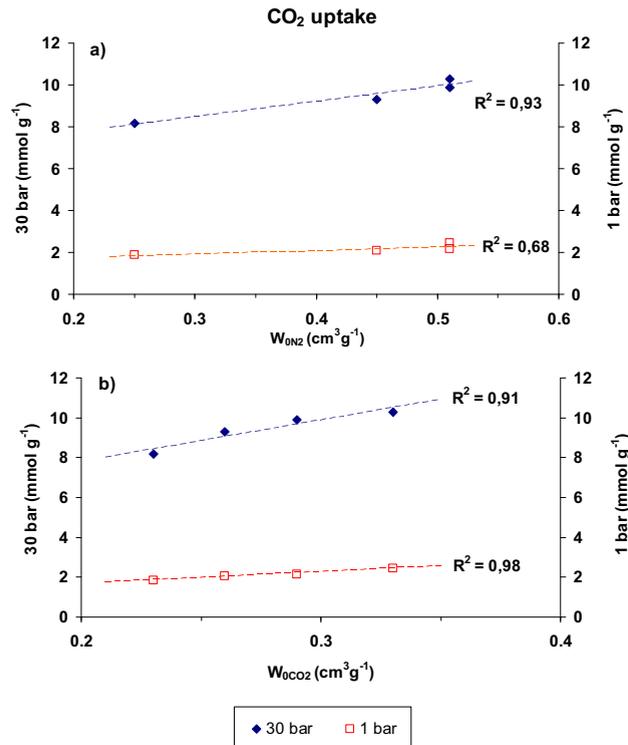
correlation between the CO_2 uptakes and the total micropore ($W_{0\,N2}$) and narrow micropore ($W_{0\,CO2}$) volumes.

The maximum CO_2 uptake at atmospheric pressure was achieved by sample E1A, 2.46 mmol g^{-1}, closely followed by samples CLA and NA that reached 2.16 and 2.07 mmolg^{-1}, respectively (see Figure 1). These values are comparable or slightly superior to those assessed on commercial activated carbons [4,16-18].
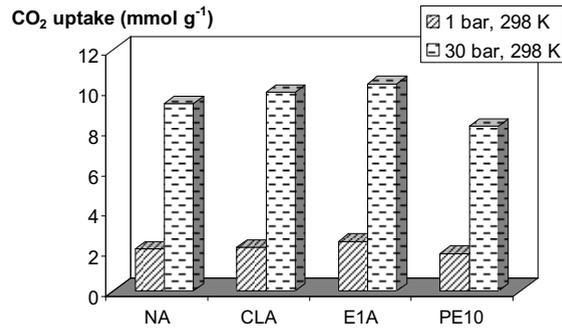
Figure 1. CO_2 uptakes (mmolg^{-1}) at 298 K, and 1 and 30 bar, respectively.

At 30 bar, the maximum CO_2 uptake corresponded to E1A that reached 10.30 mmolg^{-1}, followed by CLA, 9.89 mmolg^{-1}. High-pressure CO_2 capture capacities are greater than those of commercial CO_2 adsorbent materials like zeolite 13X (7.4 mmol g^{-1} at 32 bar and 298 K [19]) or BPL carbon (8.4 mmol g^{-1} at 55 bar and 298 K [20]).

Figure 2. Correlation between the CO_2 uptakes at 1 and 30 bar, and $W_{0\,N2}$ (a) and $W_{0\,CO2}$ (b).

On the other hand, the carbonised sample, PE10, presented the lowest CO_2 uptakes: 1.86 and 8.18 mmolg^{-1} at 1 and 30 bar, respectively.

Relating the results of these tests to the textural characteristics of the adsorbents (see Figure 2) it can be observed that there is a good correlation between CO_2 uptake and narrow micropore volume ($W_{0\ CO2}$). In the particular case of CO_2 adsorption at atmospheric pressure, the higher $W_{0\ CO2}$, the greater the CO_2 uptake (Figure 2b). At high pressure there is also a good correlation between the CO_2 uptake and the total micropore volume ($W_{0\ N2}$) that, on the other hand, does not exist at atmospheric pressure (see R^2 in Figure 2a). At atmospheric pressure the presence of narrow microporosity plays a key role on the CO_2 adsorption performance. However, at higher pressures, CO_2 is also adsorbed on the super-microporosity range (pore sizes between 0.7 and 2 nm). In addition, these correlations show that it is possible to assess the maximum CO_2 adsorption capacity of an adsorbent from its textural characterisation [17].

It is worth to draw attention on sample PE10 that shows a CO_2 uptake at atmospheric pressure comparable to the activated resins. This may be due to the organic additive (PEG) that enhances narrow microporosity development.

The CO_2 capture performance of sample E1A in a ternary mixture containing 20-40 vol.% of CO_2 and 50-70 vol% H_2 (N_2 balance), was also evaluated. The values of CO_2 adsorption capacities shown in Table 3, were obtained from the average capacity of seven consecutive breakthrough curves.

Table 3 CO_2 capture capacities of E1A at ambient temperature and 15 bar in $CO_2/H_2/N_2$ mixtures

Cases	P (bar)	T (K)	CO_2 (vol%)	H_2 (vol%)	CO_2 capture capacity (mmol CO_2 g^{-1})
1	15	298	20	70	4.57
2	15	298	40	50	6.14

CO_2 adsorption capacity is reduced when the partial pressure of CO_2 is diminished, as expected for conventional adsorption processes. According to the high pressure CO_2 adsorption isotherms, the maximum CO_2 uptake of E1A was 4.77 mmol g^{-1} at 3 bar and 6.45 mmol g^{-1} at 6 bar. Cases 1 and 2 correspond to CO_2 partial pressures in the feed stream of 3 and 6 bar, respectively. Thus, the CO_2 capture capacities assessed during these experiments are close to those of the equilibrium, showing the great selectivity of the carbon towards CO_2.

4. Conclusions

Addition of organic additives, ethylene or polyethylene glycol, during the synthesis of phenol-formaldehyde resins enhanced the textural characteristics of the prepared activated carbons. The CO_2 capture performance of the phenol-formaldehyde resin-based carbons showed promising results at atmospheric and high pressures, when compared to commercial CO_2 adsorbents. In addition, it has been demonstrated that CO_2 adsorption relies on both the width and volume of micropores. The sample produced with addition of ethylene glycol, E1A, reached the greatest CO_2 uptakes (2.46 mmol g^{-1} at atmospheric pressure and 10.30 mmol g^{-1} at 30 bar). Great selectivity of the carbons to separate CO_2 from CO_2/H_2 mixtures was observed.

From the results presented here it can be concluded that phenol-formaldehyde resin carbons show promising characteristics to be applied in precombustion CO_2 capture processes. Further research is currently being undertaken in our research group to tailor and improve the characteristic of these resin adsorbents, without increasing the cost of the production process.

5. Acknowledgements

6. References

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