

Is N-doping in porous carbons beneficial for CO₂
storage? Experimental demonstration of the relative
effects of pore size and N-doping

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Abstract

The relative influence of nitrogen doping and pore size of highly microporous carbon materials, with virtually identical porosity, on CO₂ uptake capacity at low pressure (≤ 1 bar) is presented in this report. The carbon materials are prepared via a range of synthesis methods, including activation of a variety of carbon precursors (biomass, polypyrrole or carbon nanotube superstructures) and carbonisation of an organic salt (Potassium hydrogen phthalate), which generated a series of carbons with closely matched porosity but which are either N-free or N-doped. The carbons have total surface area of 920 ± 60 m²/g, micropore surface area of 860 ± 40 m²/g, values that are $\pm 5\%$ of each other and within the repeatability range (or experimental error) of the porosity measurements. The carbons have identical micropore volume of $0.39 - 0.40$ cm³/g, and similar overall pore size and apparent pore size distribution. The similar porosity allowed a simple and straightforward analysis of the influence of N-doping on CO₂ uptake without any ambiguities associated with changes in surface area and pore volume. Contrary to many previous reports wherein both N-doping and porosity varied, we show that the presence of N has no beneficial effect on the adsorption of CO₂. Rather, we show that the low pressure adsorption of CO₂ on carbons is critically sensitive to the pore size, in particular to minute changes in micropore size distribution within the pore size range $5 - 10$ Å. The pore size also exerts greater influence on both the isosteric heat of CO₂ adsorption and the selectivity for CO₂ over N₂.

Introduction

The carbon dioxide that is generated during the burning of fossil fuels to produce energy is currently considered as being a major contributor to causing effects that lead to global warming.^{1,2} Given the continuing global dependence on fossil fuels as energy source, there are on-going efforts to either find alternative energy sources or find ways to cut down the level of CO₂ emissions. To facilitate the latter, there are a wide range of intensive research efforts aimed at finding materials that can efficiently capture and store the CO₂ emitted from anthropogenic sources and in particular from post-combustion fossil fuel burns. A wide range of solid-state materials, and in particular those that possess porosity, are currently under investigation for the capture, storage and sequestration of CO₂.³⁻¹⁶ Porous carbon-based materials are increasingly showing promise as CO₂ storage materials and are attractive due to their ready availability, robustness (chemical, mechanical and thermal), low cost and amenability to tailoring of their porosity.^{11,12,14-34}

The introduction of basic nitrogen functionalities into the framework of porous carbons has been used as a means to mimic the amine scrubbing process and for enhancing the uptake of CO₂. Porous carbons containing N atoms can be prepared by three methods: i) the carbonisation of N-containing precursors such as acetonitrile³⁵ and melamine,^{36,37} ii) co-carbonisation of mixtures of N-containing organic compounds with N-free materials³⁸⁻⁴⁰ and iii) heat-treatment of porous carbons with N-containing gases such as ammonia.^{41,42} Whilst N-doping is claimed to improve the CO₂ uptake and heats of adsorption,^{16,29,43,44} this is often accompanied by some changes (usually reduction) in the porosity of the doped carbon material.⁴⁵ Recently, there have been some detailed studies aimed at ascertaining the effect of N-doping on the CO₂ uptake of carbons, but the conclusions have been varied.⁴⁶⁻⁴⁸ Sevilla *et al* observed analogous CO₂ capture capacity for undoped and N-doped activated carbons and concluded that the nitrogen functionalities present in N-doped carbons do not influence CO₂ adsorption.⁴⁶ Similarly, Titirici *et al* performed molecular simulation studies and concluded that N-doping offered no significant improvement in the CO₂

uptake especially for carbons with slit-shaped pores.⁴⁷ These two studies are at odds with that of Xing *et al*, who on the other hand investigated a series of N-doped activated carbons and concluded that CO₂ storage capacity was independent of the specific surface area and micropore volume of the activated carbons, but closely related to the N content of the carbons with higher content favouring CO₂ uptake.⁴⁸

However, notwithstanding the apparently conflicting conclusions available in the literature regarding the effect of N, previous studies were performed on carbon materials where *both* the N content (presence or absence) and pore size were varied.⁴⁶⁻⁴⁸ Given the well-established critical role played by pore size in determining CO₂ uptake, the only way to eliminate any ambiguities about the effect of N-doping is to experimentally determine how the presence of N affects CO₂ uptake in carbons with similar porosity and crucially with *identical* or at the very least very closely matched pore size. Such a study is essential given that N-doping is claimed to be beneficial for CO₂ storage in porous carbons while pore size is known to significantly affect the CO₂ uptake of porous materials, carbons included. As far as we know, there have been no studies that probe the effect of N-doping in a set of carbon materials with *identical or closely matched pore size*. The absence of such studies may be explained by the fact that it is not trivial to prepare functionally different (i.e., with or without N) carbon materials that nevertheless possess similar levels of porosity and in particular identical pore size. A true and direct experimental probe of the effects of N-doping in porous carbons on CO₂ uptake requires that the pore size remain unchanged. It is expected that such a study will remove any ambiguities and clearly demonstrate the effect of N-doping. In an attempt to clarify the relative effects of pore size and N-doping, we have used a range of synthesis routes to prepare a series of N-free and N-doped porous carbons with comparable porosity and similar pore size. This enabled a simple and direct demonstration, with no ambiguity, of how the presence or absence of N affects CO₂ uptake.

Experimental Section

Material synthesis: To generate N-free and N-doped carbons with similar porosity and in particular identical or closely matched pore size, we relied on a variety of synthesis regimes.

N-free samples: N-free samples were prepared via activation of biomass-derived biochar or thermal treatment of an organic salt.

Sample SD2600: Wood (Eucalyptus) sawdust was used as starting material. The biochar was prepared by heating an aqueous suspension of sawdust (320 g/l) in a stainless steel autoclave at 250 °C for 2 h. The resulting solid biochar product (so-called hydrochar) was recovered by filtration and washed thoroughly with distilled water and then dried at 120 °C for 4 h. For activation, the hydrochar was thoroughly mixed with KOH at KOH/hydrochar weight ratio of 2 in an agate mortar. The KOH/hydrochar mixture, in an alumina boat, was heated (at heating ramp rate of 3 °C/min under a flow of nitrogen gas flow in a horizontal furnace) to 600 °C for 1 h. The resulting activated carbon was thoroughly washed with HCl to remove any inorganic salts, and then with distilled water until neutral pH, and dried in an oven at 120 °C for 3 h.

Sample CKHP700-1: The starting material, potassium hydrogen phthalate (KHP), was placed in a horizontal furnace (2 g in an alumina boat) and heated (at ramp rate of 10 °C/min) under nitrogen flow to 700 °C and held for 1 h. After cooling under a flow of nitrogen, the obtained carbon product was washed with distilled water until neutral pH and dried at 120 °C for 3 h.

N-doped samples: Nitrogen atoms were introduced into activated carbon frameworks via two methods, namely, (i) activation of an n-doped carbon sample at 600 °C and KOH/carbon ratio of 2 (sample designated as *n*CN2600) and by activation of polypyrrole at 600 °C and KOH/carbon ratio of 2 (sample designated as Py2600).

Sample *n*CN2600: A sample of carbon nanotube (CNT) superstructures prepared as previously described was used as starting material.⁴⁹ For N-doping, an ethanol washed CNT sample was thoroughly mixed with ammonium carbonate (NH₄CO₃) at a NH₄CO₃/carbon mass ratio of 5. The

mixture was transferred into an autoclave and heated at 200 °C for 10 h. The resulting N-doped CNT sample was washed with deionised water and air dried. For activation, the N-doped CNT sample was thoroughly mixing with KOH in an agate mortar at a KOH/carbon weight ratio of 2. The KOH/carbon mixture was then heat treated, at a heating ramp rate of 3 °C/min, in a horizontal furnace under a flow of nitrogen gas to 600 °C and held for 1 h. The activated sample was then thoroughly washed several times with HCl to remove any inorganic salts, and then with distilled water until neutral pH was achieved. Finally, the carbon was dried in an oven at 120 °C for 3 h.

Sample Py2600: The starting material, polypyrrole (PPY) was prepared by adding 3 g of distilled (under nitrogen) pyrrole to a 200 ml solution of 0.5 M FeCl₃, which was then magnetically stirred for 2 h. The resulting PPY product was separated by filtration and washed with distilled water and dried. The PPY was then activated with KOH at a KOH/PPY ratio of 2 and activation temperature of 600 °C as described above.

Material characterization: Nitrogen sorption isotherms and textural properties of the carbons were determined at -196 °C using nitrogen in a conventional volumetric technique by a Micromeritics ASAP 2020 sorptometer. Before analysis, the samples were evacuated for 12 h at 300 °C under vacuum. The surface area was calculated using the BET method based on adsorption data in the relative pressure (P/P₀) range 0.02 to 0.22 and total pore volume was determined from the amount of the nitrogen adsorbed at P/P₀ = 0.99. Micropore surface area and micropore volume were obtained via *t*-plot analysis. The pore size distribution (PSD) was determined using a Non Local Density Functional Theory (NLDFT) model using nitrogen adsorption data. X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos AXIS ULTRA with a monochromated Al K α X-ray source (1486.6 eV) operated at 10 mA emission current and 12 kV anode potential. The analysis chamber pressure was better than 10⁻⁹ Torr. FAT (fixed analyser transmission) mode was used, with pass energies of 160 eV (or 80 eV) for survey scans and 40 eV for high resolution scans. The magnetic immersion lens system allows the area of analysis to be

defined by apertures, a 'slot' aperture of 300 x 700 μm for wide/survey scans and a 110 μm aperture for high resolution scans. The take-off angle for the photoelectron analyser was 90 degrees and acceptance angle of 30 degrees (in magnetic lens modes). Data analysis was carried out using CASAXPS software with Kratos sensitivity factors to determine atomic % values from the peak areas. Charge correction was applied to the data at the processing stage.

CO₂ uptake measurements: CO₂ uptake measurements were performed using a Hiden intelligent gravimetric analyzer (IGA-003). Prior to analysis, the carbon samples were outgassed overnight under vacuum at 250 °C. Then the CO₂ uptake isotherms were obtained at 25 °C in the pressure range 0 – 20 bar.

Results and discussion

Amount and nature of nitrogen in N-doped carbons

We first comment on the amount and nature of N on the two N-doped carbons, *n*CN2600 and Py2600. The N content of the N-doped carbon is given in Table 1; the *n*CN2600 sample prepared by the activation of N-containing CNT superstructures has a lower nitrogen content of 5.9 wt% compared to 12.4 wt% for sample Py2600, which was obtained by activating polypyrrole. The samples therefore represent carbons with a moderate (*n*CN2600) and high (Py2600) N content.^{16,29,43-48} The nature of the nitrogen species on the surface of the N-doped activated samples was investigated by X-Ray Photoelectron Spectroscopy (XPS). The XPS spectra of the N 1s core level of samples *n*CN2600 and Py2600 are shown in Figure 1. The spectra show a N 1s signal which is split into two peaks, centred at 398.7 and 400.1 eV., corresponding to 'pyridinic' (pyridine-like) and pyrrolic (pyrrole-like)/pyridonic-N nitrogen environment.^{29,43} The pyrrolic and pyridonic environments are not easily distinguishable with XPS. However, given the exposure of both samples to relatively high temperature (600 °C) during activation, it is unlikely that pyrrolic sites will exist, which means that the majority of the N in both samples is in the form of pyridonic

groups along with a smaller proportion of pyridinic moieties. The present N-doped carbons are therefore, in terms of the N moieties they possess, similar to previously reported samples that have been investigated for CO₂ capture.^{16,29,43-51}

Table 1. Textural properties and CO₂ uptake of N-doped and N-free carbons.

Sample	Nitrogen content (%)	Surface area (m ² /g) ^a	Pore volume (cm ³ /g) ^b	Pore size (Å) ^c	CO ₂ uptake ^d (mmol/g) and uptake density ^e (μmol/m ²) ^f	
					0.15 bar	1.0 bar
<i>n</i> CN2600	5.9	979 (880)	0.54 (0.39)	6.8/8.5/12.5	1.0 (1.02)	2.8 (2.9)
Py2600	12.4	976 (906)	0.47 (0.40)	6.8/8.5/12	1.3 (1.31)	3.4 (3.5)
CKHP700-1	-	932 (900)	0.44 (0.39)	6.8/8.5/12	1.6 (1.71)	4.2 (4.5)
SD2600	-	866 (823)	0.46 (0.39)	6.8/8.5/12	1.3 (1.50)	4.3 (5.0)

The values in the parenthesis refer to: ^amicropore surface area and ^bmicropore volume. ^cpore size distribution maxima obtained from NLDFT analysis. ^dCO₂ uptake at 25 °C and 0.15 bar or 1.0 bar. The values in the parenthesis refer to CO₂ uptake density ((μmol/m²)).

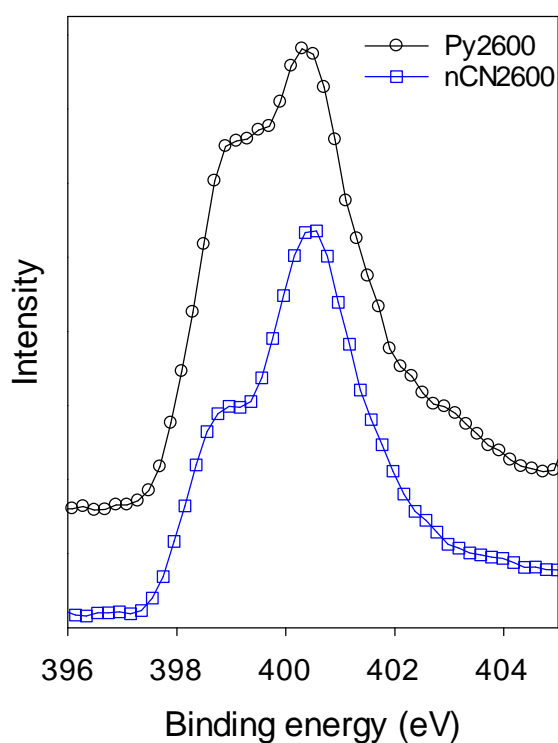


Figure 1. XPS spectra showing N 1s peaks for N-doped carbon samples Py2600 and *n*CN2600.

Textural properties

In the synthesis of the carbon samples, we aimed to generate materials with or without N but with similar porosity and as much as possible, identical pore size and pore size distribution. Figure 2A shows the nitrogen sorption isotherms of all four samples. All the carbons exhibit a type I isotherm, typical of highly microporous materials, in which virtually all of the nitrogen sorption occurs at relative pressure (P/P_0) below 0.01. Clearly, the carbons are not only highly microporous but also exhibit very similar types of isotherms both in terms of the shape and the amount of nitrogen adsorbed. All isotherms show a sharp adsorption ‘knee’, which occurs at similar P/P_0 , followed by an adsorption plateau. The textural properties of the four carbons, summarised in Table 1, reveal that both the surface area and pore volume are within a narrow range. The total surface area of all four samples is very similar being $920 \pm 60 \text{ m}^2/\text{g}$, while the micropore surface area range is even narrower at $860 \pm 40 \text{ m}^2/\text{g}$. Thus the total surface area and micropore surface area values are within $\pm 5\%$ of each other. Such variability is within the repeatability range (or experimental error) of the BET measurements, which means that the surface area of all four samples can be considered as being similar allowing for the experimental error or extent of repeatability. Furthermore the total pore volume of samples Py2600, CKHP700-1 and SD2600 is virtually identical (ca. $0.45 \text{ cm}^3/\text{g}$ and within $\pm 3\%$ of each other), while that of sample *n*CN2600 is slightly higher at $0.54 \text{ cm}^3/\text{g}$. However, more importantly, the micropore volume of all four samples is virtually identical at $0.39 - 0.40 \text{ cm}^3/\text{g}$. This similarity in micropore volume is noteworthy and germane for the present study since the micropore volume is far more important than total pore volume in determining CO_2 uptake at low pressure and ambient temperature.^{12-24,29-34,46,47,49,52-56}

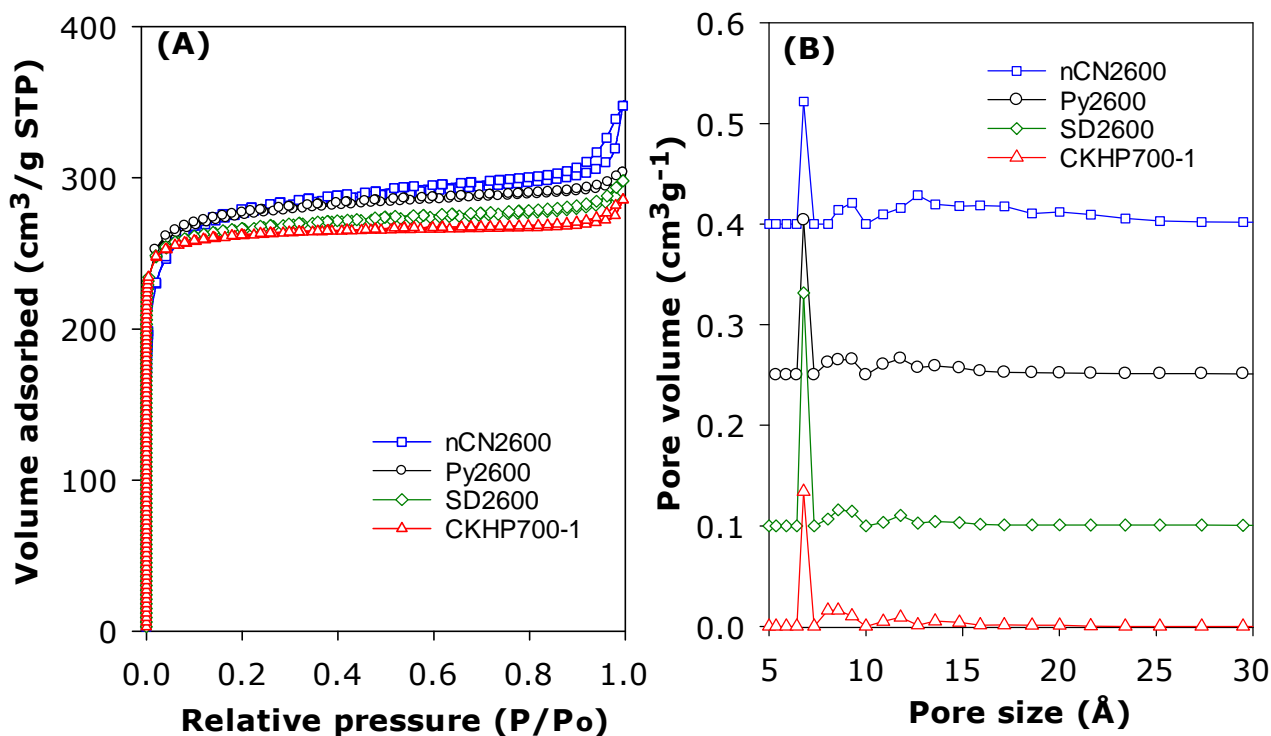


Figure 2. (A) Nitrogen sorption isotherms and (B) corresponding pore size distribution curves of a variety of porous carbons. See experimental section for sample designation.

The four synthesis regimes utilized, therefore, were able to yield porous carbon materials with closely matched porosity in terms of surface area and pore volume. However, it is also necessary that the pore size of the four materials be very closely matched to remove any ambiguities associated with large variations.^{12-24,29-34,46,47,49,52-56} The pore size distribution curves of the four carbon samples are given in Figure 2B and the pore size values are summarized in table 1. Remarkably, both the actual pore size and pore size distribution of the four samples is strikingly similar. The porosity of *all* four samples is dominated by small micropores centered at 6.8 Å. Additionally, all four samples have some pores centred at 8.5 and 12 Å (12.5 Å for sample nCN2600). Therefore, overall, the pore size of the four carbon samples, with respect to the pore systems present, is virtually identical. We have therefore succeeded in preparing, via a range of synthesis regimes, four highly microporous carbon samples for which all three indicators of

porosity (i.e., surface area, pore volume and pore size) are either virtually identical or vary within the expected experimental error ranges. As far as we know this is the first time that it has been possible to prepare a set of such N-free and N-doped porous carbons with closely matched porosity.

CO₂ uptake

The CO₂ uptake capacity of the four carbons, at ambient temperature and pressure range of 0 to 1 bar, is shown in Figure 3. The CO₂ storage capacity at 0.15 bar and 1 bar is summarized in Table 1. The uptake of the four samples shows significant variability and is in the range 2.8 – 4.3 mmol/g at 1 bar, and between 1 and 1.6 mmol/g at 0.15 bar. For pressure up to 1 bar (Figure 3), the order of CO₂ uptake is CKHP700-1 = SD2600 > Py2600 > nCN2600. Surprisingly, therefore, the N-doped carbons do not exhibit higher uptake than the N-free samples, and unexpectedly, the reverse is observed. Thus at 1 bar, the N-free samples, CKHP700-1 and SD2600, have CO₂ uptake of 4.2 and 4.3 mmol/g, respectively, while for the N-doped samples, nCN2600 and Py2600, it is lower at 2.8 and 3.4 mmol/g, respectively. The picture is similar at 0.15 bar where the N-free sample, CKHP700-1, has the highest uptake of 1.7 mmol/g, sample SD2600 and Py2600 have similar uptake of 1.3 mmol/g, and the N-doped nCN2600 sample has the least uptake of 1.0 mmol/g. The presence of N therefore offered no advantage with respect to CO₂ uptake capacity. Nevertheless, sample Py2600, which has a higher N content (12.4 wt%) had better CO₂ uptake than the lower N content sample (nCN2600). The apparent superior CO₂ uptake of the N-free samples compared to their N-doped analogues despite similar porosity for both sets of samples is, however, intriguing and goes beyond simply suggesting that the presence of N in porous carbons does not necessarily improve the adsorption of CO₂. Our findings are generally in agreement with those of Sevilla *et al*⁴⁶ and Titirici and co-workers,⁴⁷ but run counter to the conclusions of Xing *et al*.⁴⁸ We however believe that the conclusions of the work by Xing *et al*⁴⁸ did not have the benefit of a proper analysis of the pore size of the studied carbons and that the overall conclusion may be altered once changes in pore size are considered.

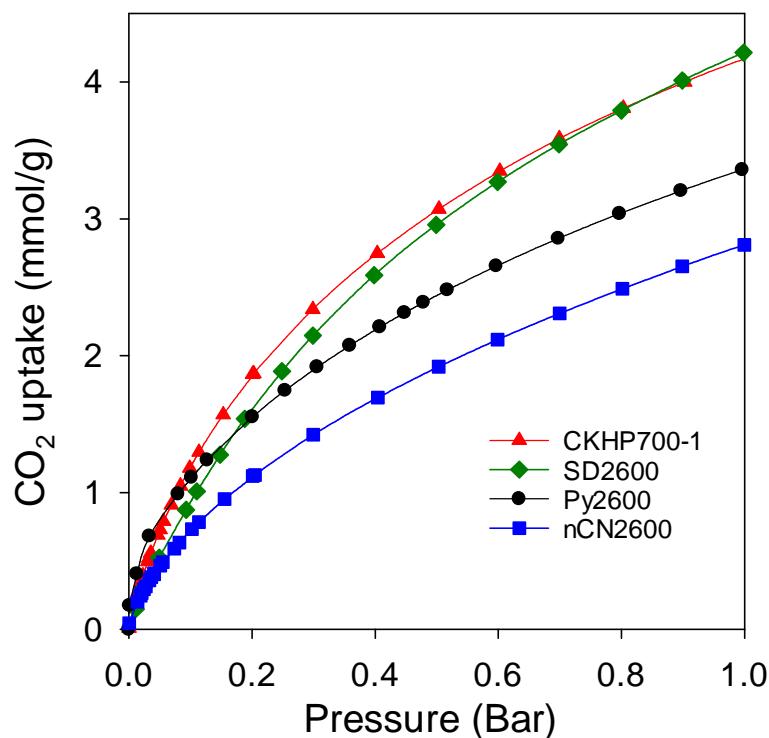


Figure 3. Low pressure (0 – 1 bar) CO₂ uptake isotherms at 25 °C for N-doped and N-free carbons. See experimental section for sample designation.

Our results not only show no positive influence of N-doping on CO₂ uptake but appear to suggest that there is a negative effect. To properly understand the trends in CO₂ uptake of our study carbons, we determined the isosteric heat of CO₂ adsorption (Q_{st}). The heat of CO₂ adsorption is a measure of the strength of adsorbent–adsorbate interactions that play an important role in the uptake of CO₂ onto carbons especially at low pressure (≤ 1 bar). The isosteric heat of adsorption was determined using the CO₂ uptake isotherms obtained at 0 °C and 25 °C, based on the Clausius-Clapeyron equation. Plots of Q_{st} as a function of CO₂ uptake are presented in Figure 4, and the Q_{st} values at a storage capacity of 0.7 mmol/g are summarised in Table 2. The Q_{st} (at low CO₂ uptake of 0.7 mmol/g) varies in the range of 27.8 – 29.4 kJ/mol, which is similar to that previously reported for N-doped carbons,^{19,21,57,58} Sample Py2600 has the highest Q_{st} of 29.4 kJ/mol due presumably to its high N content. On the other hand, sample *n*CN2600 has a Q_{st} of 27.8 kJ/mol,

which is slightly lower than that of the N-free samples; ca. 28.4 kJ/mol for both CKHP700-1 and SD2600. It is therefore apparent that the presence of N does not have a significant influence on the Q_{st} . It is also likely that the relatively high Q_{st} values observed for the N-free samples are due to the presence narrow micropores of size 6.8 Å. We have previously shown that pore size plays a key role in determining Q_{st} for N-free carbon samples.⁵⁶

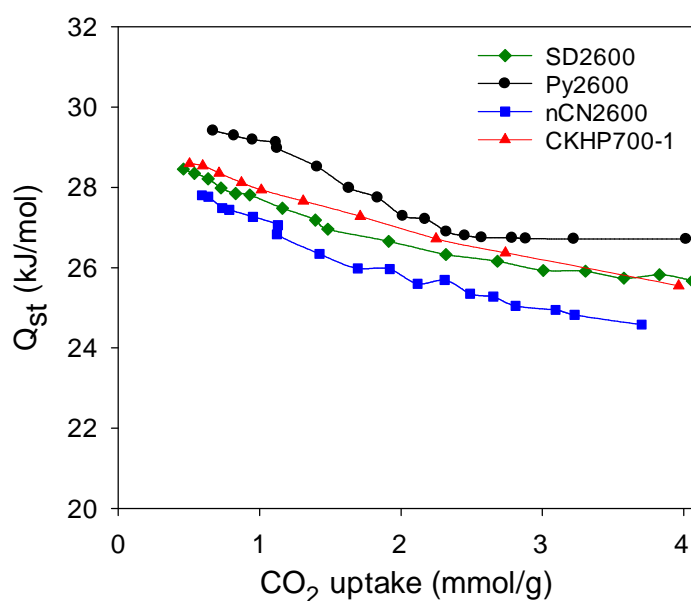


Figure 4. Isosteric heat of CO₂ adsorption (Q_{st}) as a function of CO₂ uptake for N-doped and N-free carbons. See experimental section for sample designation.

Table 2. Isosteric heat of CO₂ adsorption (Q_{st}) and micropore volume distribution for N-doped and N-free carbons

Sample	Heat of adsorption ^a (kJ/mol)	Proportion (%) of micropore volume in pore size range		
		6 – 7.5 Å	7.5 – 10 Å	10 – 20 Å
nCN2600	27.8	42.5	13.3	44.2
Py2600	29.4	71.1	12.2	16.7
CKHP700-1	28.5	80.1	11.5	8.4
SD2600	28.3	79.5	11.6	8.9

^aHeat of CO₂ adsorption at uptake of 0.7 mmol/g.

The picture that emerges from consideration of the porosity, CO₂ uptake and Q_{st} data is that whilst the presence of N might increase the strength of interaction with the pore walls, this does not necessarily translate to improved CO₂ uptake. It appears that the porosity (especially the pore size) plays a more important role in determining the CO₂ capture than the presence of N. The data discussed so far begs the question – why do the N-free samples have better uptake than their N-doped analogues? In an attempt to answer this question, we explored the slightest variations in the micropore size distribution of the four carbon samples. This was done by considering the proportion of micropore volume that arises from pores within three size ranges, namely, 6 – 7.5 Å, 7.5 – 10 Å and 10 – 20 Å as shown in Table 2. We first note that the micropore volume of the N-free samples, CKHP700-1 and SD2600, is dominated by pores of size between 6 and 7.5 Å, which contribute 80% of the micropore volume. The contribution from larger micropores is ~ 11.5% (7.5 – 10 Å) and 8.5% (10 – 20 Å). Indeed, a close comparison of the micropore size distribution curves of samples CKHP700-1 and SD2600 (Figure S1) shows that they are similar. On the other hand, compared to the N-free samples, the N-doped sample (Py2600) has a slightly higher proportion (i.e., 16.7%) of micropore volume from 10 – 20 Å pores, and the rise occurs at the expense of volume from 6 – 7.5 Å whose proportion drops to 71.1% while the proportion of 7.5 – 10 Å remains largely unchanged at 12.2% (Figure S2). We believe that this very slight change in proportion of micropore volume from small to larger pores is the cause of the lower CO₂ uptake of sample Py2600 compared to the N-free samples. The apparent shift to larger micropores is more pronounced for sample *n*CN2600 for which only 42.5% of the micropore volume arises from 6 – 7.5 Å, while 44.2% is from pores of size 10 – 20 Å, and 7.5 – 10 Å pores contribute 13.3% (Figure S3). We believe that this significant shift to larger micropores, which is not immediately apparent from the overall PSD (Figure 2) is responsible for the lower CO₂ uptake of sample *n*CN2600. This detailed analysis of the micropore volume distribution of samples with apparently similar pore size shines new light on the critical role played by pore size, and confirms that the size of pores is far

more important than the presence of N in determining CO₂ uptake. In particular our findings show that the presence of N cannot compensate for ‘unfavourably’ sized pores. As far as we know, such a detailed analysis of micropore size has hitherto not been reported.

The efficiency of pore channels in the capture and storage of CO₂ can be assessed by considering the CO₂ uptake density, given in $\mu\text{mol}/\text{m}^2$ in Table 1. At 0.15 bar, the uptake density is lowest ($1.02 \mu\text{mol}/\text{m}^2$) for sample *n*CN2600, followed by sample Py2600 ($1.31 \mu\text{mol}/\text{m}^2$). The N-free samples, SD2600 and CKHP700-1 have higher uptake density of 1.50 and $1.71 \mu\text{mol}/\text{m}^2$, respectively. A similar trend in uptake density is observed at 1 bar with the N-doped samples, *n*CN2600 and Py2600 having lower values of 2.9 and $3.5 \mu\text{mol}/\text{m}^2$, respectively, compared to $4.5 \mu\text{mol}/\text{m}^2$ for CKHP700-1 and $5.0 \mu\text{mol}/\text{m}^2$ for SD2600. It is clear that the uptake density closely follows the trend in pore size, with samples that have a higher preponderance of 6 – 7.5 Å pores achieving greater density irrespective of the presence or absence of N. To further elaborate on the greater importance of pore size in determining CO₂ uptake density, we compared the present carbons with N-free carbonaceous materials with porosity that arises predominantly from sharply distributed small (5 – 7.5 Å) pores, and which are virtually free of any pores larger than 7.5 Å (Supporting Figure S4). The samples, namely, CKHP600-2 and CKHP600-2-C5 have sharply distributed pores of size 6.8 and 5.8 Å, respectively, and virtually no other pores (Supporting Figure S4 and Table S1). Indeed, 96% of the micropore volume arises from 6 – 7.5 Å pores for sample CKHP600-2, and from 5 – 7 Å pores for sample CKHP600-2-C5. This proportion of small pores is much higher than for the other four study samples; 42.5% for *n*CN2600, 71.1% for Py2600, and ~80% for SD2600 and CKHP700-1 (Table 2). (Sample CKHP600-2 was prepared in a similar fashion to CKHP700-1, except that the heating was at 600 °C for a period of 2 h, while CKHP600-2-C5 was obtained by compaction of CKHP600-2 at 371 MPa, a compaction pressure equivalent to 5 tons).⁵⁶ The expectation was that such carbons should show a clear increase in CO₂ uptake density due to their optimally sized pore channels. This is indeed what is observed (Table S1)

wherein, at 0.15 and 1 bar, the uptake density for sample CKHP600-2 is 2.34 and 5.50 $\mu\text{mol}/\text{m}^2$, respectively, which is much higher than that of the study materials. Furthermore, compaction of CKHP600-2 slightly reduces the pore size from 6.8 to 5.8 Å for sample CHKP600-2-C5. This decrease in pore size to more optimal 5.8 Å pores is also reflected in the CO_2 uptake density that increases further to 2.71 and 6.4 $\mu\text{mol}/\text{m}^2$ at 0.15 and 1 bar, respectively, for sample CKHP600-2-C5. The clear effect of pore size on CO_2 uptake density is also apparent when the density is given as a function of the pore volume, i.e., in mmol/cm^3 , (Table S2). The overall picture that emerges is that CO_2 uptake at low pressure is critically dependent on the pore size, while the presence of N does not appear to have any meaningful influence. On the other hand, at high pressure (20 bar) the CO_2 uptake (Supporting Figure S5) and uptake density (Table S3) of the study carbons is very similar due to the fact that the key variable is the surface area. Thus in order to obtain carbon materials with improved CO_2 uptake at low pressure (≤ 1 bar) it is essential to prepare samples that only possess optimally sized small micropores. The challenge is how to ensure that such materials also have the highest possible surface area.⁵⁸⁻⁶⁰

The adsorption of CO_2 at low pressures, such as those investigated in this study, is relevant to the capture of CO_2 from flue gas streams of fossil fuel power stations. Under flue gas stream conditions, the selectivity of an adsorber for CO_2 is crucial given that flue gas streams are rich in nitrogen. Thus it is essential for adsorbent materials to have high selectivity for CO_2 (i.e., a high CO_2/N_2 selectivity ratio). In this regard, it has previously been claimed that N-doping of carbons enhances the CO_2/N_2 selectivity ratio. We therefore compared the selectivity of the present N-free (CKHP700-1) and N-doped (Py2600) samples; two samples with very closely matched porosity. We first compared the CO_2 uptake of the carbons with N_2 sorption at 25 °C and 1 bar as shown in Figure 5. The CO_2 uptake, 3.4 mmol/g (Py2600) and 4.2 mmol/g (CKHP700-1) is, as expected, much higher than the amount of N_2 sorbed, i.e., 0.16 and 0.17 mmol/g for Py2600 and CKHP700-1, respectively (Figure 5). The equilibrium CO_2/N_2 adsorption ratio (at 1 bar) is thus very high for

both samples, being 20 and 26 for Py2600 and CKHP700-1, respectively, which is significantly superior to previously reported N-free or N-doped activated carbons,^{12,16,18,61,62} a finding we ascribe to the optimal pores of the present carbons. Although both the N-free and N-doped sample have very high equilibrium CO₂/N₂ adsorption ratio, the selectivity of the N-free sample is higher, i.e., the presence of N offers to apparent advantage.

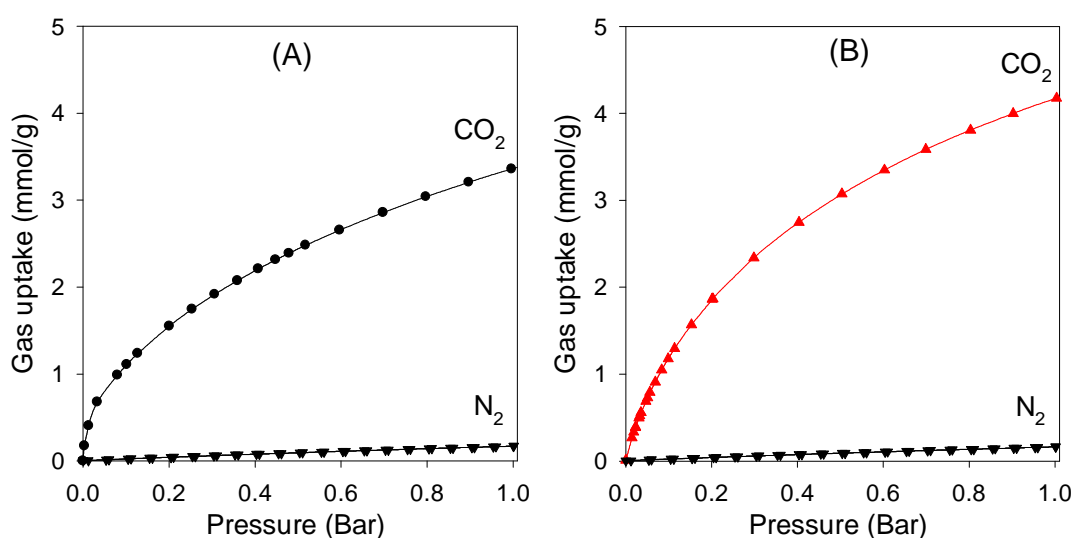


Figure 5. Comparison of low pressure CO₂ and N₂ uptake isotherms at room temperature for (A) N-doped sample Py2600 and (B) N-free sample CKHP700-1. The comparison gives a CO₂/N₂ adsorption ratio, at 1 bar, of 20 for Py2600 and 26 for CKHP700-1.

To be sure we also determined the selectivity for CO₂ using initial rates of CO₂ and N₂ adsorption (Supporting Figure S5). The selectivity calculated from initial rates was relatively similar at 82.6 for Py2600 and 88.6 for CKHP700-1, once again confirming that N-doping offered no advantage. Moreover, from a more practical point of view, and considering the fact that industrial flue gas streams contain a relatively small proportion of CO₂ (ca. 15%) and a much larger amount of N₂, we determined the relative uptake of CO₂ at 0.15 bar and N₂ uptake at 0.85 bar. This determination was achieved using the so-called ideal adsorbed solution theory (IAST) model, which can be applied in estimating the relative uptake (or selectivity) of adsorbents for any two

gases in a binary gas mixture.⁶³ The estimated selectivity for CO₂ from the IAST model (using the correlation $S = n(\text{CO}_2) p(\text{N}_2) / (n(\text{N}_2) p(\text{CO}_2))$, where S is selectivity for CO₂, n is uptake of CO₂ or N₂ in mmol/g, $p(\text{N}_2)$ is 0.85 and $p(\text{CO}_2)$ is 0.15) was 49 for Py2600 and 63 for CKHP700-1, once again confirming that N-doping offered to advantages. Indeed, the N-free CKHP700-1 sample appears to have higher affinity for CO₂ over N₂ regardless of the method used to compute the selectivity. It is likely that the superior selectivity of sample CKHP700-1 is due to the presence of a higher proportion of 6 – 7.5 Å (Table 2 and Figure S3). This further emphasises the greater importance of pore size in determining not only the amount of CO₂ adsorbed, but also the selectivity. Contrary to our findings, a previous study by Zhao *et al*⁶⁴ found that N-doping and the presence of metal ions improved the selectivity for CO₂ over N₂. However, the study⁶⁴ did not include a careful analysis of the effects of pore size. Indeed, based on the porosity data provided,⁶⁴ the claimed improvements in selectivity can be explained by changes in level of microporosity (and therefore pore size).

Conclusions

Highly microporous carbon materials with very closely matched porosity have been prepared via a range of synthesis methods, including activation of a variety of carbon precursors (biomass, polypyrrole or carbon nanotube superstructures) and carbonisation of an organic salt (Potassium hydrogen phthalate). This enabled the preparation of a series of carbons with closely matched porosity but which are either N-free or N-doped, in an attempt to conclusively elucidate the relative influence of N-doping and pore size on the CO₂ uptake capacity of carbons at low pressure (≤ 1 bar). The carbon materials, both N-free and N-doped exhibited similar total surface area (920 ± 60 m²/g), while their micropore surface area range was even narrower (860 ± 40 m²/g), values that are $\pm 5\%$ of each other and within the repeatability range (or experimental error) of the porosity measurements. The micropore volume of all the carbons was virtually identical at 0.39 – 0.40 cm³/g. The carbons allowed a simple and straightforward analysis of the influence of N-doping of

carbons on CO₂ uptake without any ambiguities associated with changes in surface area and pore volume. Our findings show that N-doping has no beneficial effect on the adsorption of CO₂. In contrast, we show that the low pressure adsorption of CO₂ on carbons is to a much greater extent very sensitive to the pore size, and in particular to the slightest changes in micropore size distribution within the pore size range of 5 – 10 Å. Furthermore, we also show that the pore size exerts a far greater influence on both the isosteric heat of CO₂ adsorption and the selectivity for CO₂ over N₂. Our findings on the influence of N-doping are in contrast to many previous claims on the benefits of N functionalities on carbon. However, many of these previous reports lacked a rigorous analysis of the pore size, and the conclusions may have been different had they had the benefit of such an analysis.

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Supporting Information Available: Two tables with comparative porosity and CO₂ uptake data, including for samples CKHP600-2 and CKHP600-2-C5. Six additional figures; Pore size distribution curves, high pressure CO₂ uptake isotherms, and curves used to calculate initial rates of relative adsorption of CO and N₂. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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TOC Graphic

