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N-doped carbon aerogels for carbon dioxide (CO$_2$) capture

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The N-doped carbon aerogel materials were investigated to explore their potential use in carbon dioxide (CO$_2$) capture. Carbon aerogels were prepared from a nitrogen-containing polymer precursor using urea as nitrogen source into the polymer matrix through the sol-gel method. CO$_2$ capture performances were evaluated from 273 to 298K at 1 bar. CO$_2$ adsorption is influenced by the micropores and amount of a nitrogen-containing the samples. N2 adsorption isotherms have showed different structures of these carbon materials. CO$_2$ adsorption capacities up to 3.6 mmol/g (298K) and 4.5 mmol/g (273K) were achieved. Both texture and surface chemistry affect the CO$_2$ capture performance of the adsorbents.

Key word: Adsorption, carbon dioxide (CO$_2$), urea, carbon, aerogel, N-doped.

INTRODUCTION

Global warming is caused mainly by greenhouse gas emissions such as methane (CH$_4$) and carbon dioxide (CO$_2$). These gases are gaining more attention due to their potential environmental and socio-economic negative consequences. Among the technologies proposed to reduce CO$_2$ emissions, adsorption is considered as a very promising technology for CO$_2$ capture since adsorbents have been discovered (Choi et al., 2009). These materials have a high adsorption capacity, great selectivity, good mechanical properties and remain stable over repeated adsorption–desorption cycles (Choi et al., 2009). Different types of solid sorbents have been, or are currently being investigated as potential adsorbents for CO$_2$ capture, including carbon-based sorbents (Zou et al., 2002), supported carbonates (Gregory et al., 2006) and zeolites (Jerome et al., 2008; Simone et al., 2004). Studies have shown some limitations of these materials either because of their low adsorption capacity. The introduction of new functional groups leading to several different configurations of these sorbents, including amine-functionalized porous carbons, organic resins and polymers offer promising alternatives (Jason et al., 2008; Zhijian et al., 2008). The incorporation of basic nitrogen

groups into the carbon framework ensures an improved adsorption/absorption for acidic gases (Foad et al., 2000; Pels et al., 1995).

Porous carbon materials used for CO$_2$ capture are mostly prepared by post-synthetic amine modification or ammonia treatment (Plaza et al., 2007) which leads to materials lacking stability and, in addition, the reagents are corrosive, with the same disadvantages as for modified silica and zeolites. Alternatively, nitrogen containing porous carbons can be prepared directly from nitrogen-rich precursors. Porous nitrogen-enriched carbons from melamine-formaldehyde resins using fumed silica had been prepared (Pevida et al., 2008). Porous carbons monolith using L-lysine as nitrogen source showed maximum CO$_2$ adsorption capacity of 3.13 mmol/g under 1 atmosphere at 298 K (Hao et al., 2010). Highly porous N-doped carbon activated by KOH (Sevilla et al., 2011) adsorbed CO$_2$ from 2.7 to 3.9 mmol/g at 298K. The structural characterizations and CO$_2$ adsorption on the resulting carbons indicated that CO$_2$ uptake was sometimes independent of the specific surface area but closely related to the micropore volume and the N content of the carbons. It was also observed that direct pyrolysis of these precursors usually results in bulk carbon products with less porosity (Takashi, 2000).

In the present work, we synthesized monolith N-doped carbon aerogels with sol-gel method using urea and resorcinol-formaldehyde as nitrogen and carbon precursor, respectively. Carbon aerogels are highly

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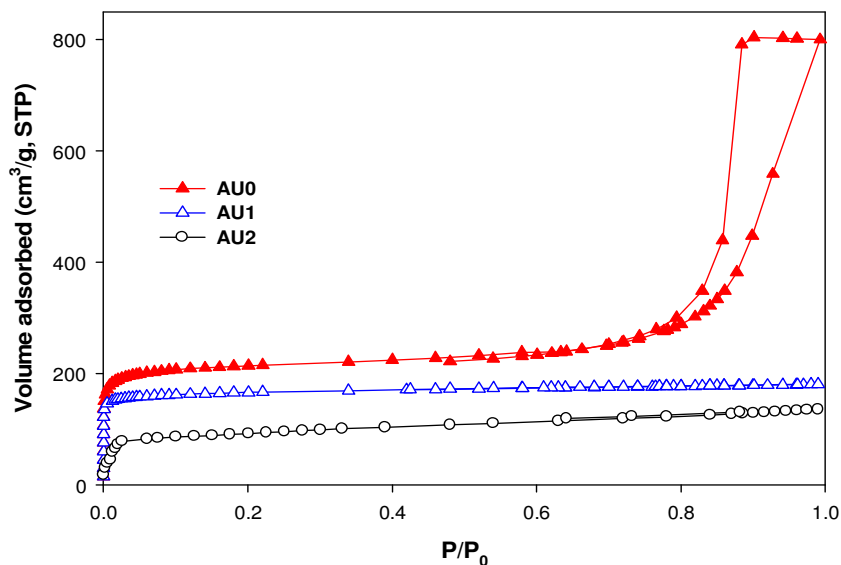
Figure 1. Adsorption-desorption isotherms of N-doped and carbon aerogels.

porous materials with a network structure consisting of interconnected sphere-like nodules whose sizes are regulated by the synthesis conditions (Elkhatat and Al-Muhtaseb, 2011). Here, we investigate the use of urea as nitrogen-containing precursors to introduce nitrogen groups on the surface of standard carbon aerogels. Urea can be hydroxymethylolated by the addition of formaldehyde to the amino groups. This occurs by a series of reactions that lead to the formation of mono- and di-methylolureas (Park et al., 2011; Dalin et al., 2011). The complex surface nitrogen functionalities can be obtained after pyrolysis when those precursors are incorporated into sol–gel polymerization. This is part of the first report on the N-doped aerogel material by sol gel method and can lead to more applications.

MATERIALS AND METHODS

Sample preparation

3.7 g of resorcinol and different amounts of urea 1 to 2 g were dissolved in 5 g of water and catalyst was added (weight ratio: Resorcinol / sodium Carbonate, R/C = 500). After stirring for 20 min, 5.1 ml of formaldehyde was added while stirring for 30 min at room temperature. Sol–gel polymerization of the mixture was carried out in a sealed glass cylinder by holding the mixture at 358K for 72 h in the oven. Acetone was selected as the drying solvent for ambient drying because of its low surface tension (20.66 dyn / cm) and its low boiling point (329K) which reduces the shrinkage of Resorcinol-Fromaldehyde-Urea (RFU) gels during drying (Jun et al., 2006). The wet gelling was performed at room temperature for 3 days, and then RFU gels were dried completely at ambient conditions for 72 h. After drying, RFU aerogel particles were placed in a quartz boat and heated to 1073K, ramp 278K / min under inert nitrogen (N_2) atmosphere in a tubular furnace for 2 h. The samples were denoted, respectively as AU0; AU1 AU2, where the numbers indicate the molar ratio of resorcinol/urea in the sample.

Characterization

Nitrogen adsorption isotherms were measured at 77K on ASAP 2010 volumetric analyzers (Micromeritics, Inc., GA). The BET (Brunauer-Emmett-Teller) specific surface area was calculated from nitrogen adsorption isotherms in the relative pressure (P/P_0) range of 0.05-0.2. The total pore volume was estimated from the amount adsorbed at a relative pressure (P/P_0) of ~0.99. The CO_2-adsorption isotherms of the AU-i series were measured using a Micromeritics ASAP 2020 static volumetric analyzer at 298 and 273K. Before adsorption measurements, all samples were degassed at 473K ensuring that the residual pressure fell below 3 μmHg. It was then cooled down to 273 and 298K, followed by the introduction of CO_2 into the system. The CO_2-adsorption capacity in terms of adsorbed volume under standard temperature and pressure (STP) was then recorded.

RESULTS AND DISCUSSION

Characterization

According to the International Union of Pure and Applied Chemistry (IUPAC), six types (Type I to VI) isotherms are used to describe different porous and materials interactions and four types of hysteresis loops (Types H1-H4) for texture of the adsorbent (Thommes, 2010). The N_2 adsorption and desorption isotherms of carbon aerogel and N-doped carbon aerogel displayed in Figure 1, show different types of isotherms. The sample AU0 type IV with H2 hysteresis typically observed with more complex pore structure in which network effect is important (Thommes, 2010). Unfortunately, we do not have images from scanning electron microscopy.

Adsorption isotherms of Type I (AU1 and AU2) are observed when the pores size of the carbon materials are in micro order and the potential of interaction between the

Table 1. Physical and chemical characteristics of carbon and N-containing carbonaerogel.

Samples	Physical properties				Chemical properties			
	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_t (cm^3/g)	N (wt%)	O (wt%)	H (wt%)	C (wt%)
AU0	746.7	0.19	1.05	1.24	0	10.82	0.81	88.37
AU1	576.5	0.18	0.10	0.28	0.51	19.35	0.60	79.54
AU2	321.8	0.13	0.08	0.21	1.44	17.68	0.50	80.38

S_{BET}: Surface area calculated by BET (Brunauer-Emmett-Teller) method. V_t = total volume at P/P_0 = 0.995; V_{meso} = volume of mesopore (V_t-V_{micro}).

surface of the carbon and N_2 is high. Thus, N_2 isotherms exhibited a high nitrogen uptake at low relative pressures (P/Po < 0.1), corresponding to the filling of micropores.

The N-doped carbon aerogels AU1, AU2 showed the lowest nitrogen uptake and also, their surface areas reduced considerably from 746.7 m^2/g (AU0) to 576 (AU1) and 314 m^2/g (AU2) when the molarratio of resorcinol/urea (r/u) increased corresponding to less developed porosity.

Table 1 shows the physical and chemical characteristics of N-containing carbon aerogels. The nitrogen content increased from 0.51 to 1.44% with the ratio of resorcinol/urea (r/u). We did not expect to get more residual nitrogen-content in sample AU2 than AU1. This very low range of value was also observed at this high temperature (1073K) because nitrogen was consumed which was in good agreement with the literature (Hongwei et al., 2012; Zhangxiong et al., 2012). We have not been able to use other techniques such as; Fourier transform infrared (FTIR) and x-ray photoelectron spectroscopy (XPS) to properly investigate bonding of nitrogen. Concerning theporosity of the structure, the pore size distribution of the samples were made up mostly of 0.7 nm for AU0 and AU1 but larger fractions of mesopores with pore diameters of up to 2 nm for AU0 and 1.2 nm for AU2 were obtained. The total pore volume decayed with addition of urea from 1.24 to 0.28 cm^3/g together with the volume of micropores from 0.19 to 0.13 cm^3/g.

The same trend was observed with the volume of the mesopores which decreased significantly from 1.05 to 0.08 cm^3/g. We therefore concluded that urea inhibited the development of mesopores. The percentage of other atoms such as oxygen, hydrogen and carbon did not change considerably between carbon aerogel and N-doped carbon aerogel.

CO_2 adsorption

Figures 2, 3 and 4 show the isotherms for CO_2 adsorption at 298 and 273K for the aerogel and N-doped carbon aerogels. The adsorption increased from 2.7 to 3.6 mmol/g at room temperature and 4 to 4.5 mmol/g at 273K. The highest value obtained at the ambient temperature was superior to what we observed in the literature (3.2 mmol/g) for N-doped monolith carbon material (Hao et al., 2010) but slightly inferior for other N-doped porous carbon material (3.9 mmol/g) with 1700 m^2/g surface area after activation with KOH (Sevilla et al., 2011). Our samples were prepared without anyactivation, just a conventional sol-gel recipe with Na_2CO_3 catalyst in few amounts (R/C = 500). The N-doped aerogel carbon AU1 had a better adsorption compared to the N-doped carbons AU2. Despite its high surface area and total pore volume AU0 adsorbed lesser than N-doped carbon. Table 1 has showed that N-content in AU2 was higher than AU1 but no CO_2 capacity adsorption. The difference of adsorption of N-doped carbon aerogel would not be attributed only to amount of nitrogen containing the sample but also to the micropore and pore size.

AU2 had more nitrogen content but lesser micropore and pore size (1.2 nm) than AU1 and AU0 though it is known that narrow pores are favorable to CO_2 adsorption. The isosteric heats of adsorption (Qst) for CO_2 (Figure 4) as calculated from the adsorption isotherms at 273 and 298K using the Clausius–Clapeyron equation confirmed the nitrogen content of the samples. The initial Qst values of 24.8 and 33.57 kJ/mol were shown for AU1 and AU2, respectively which decreased with the amount adsorbed. The values were not so high but indicated a little strong adsorbent–adsorbate interaction between the N-containing carbon framework and CO_2 molecules.

In this work, we confirmed also the theory observed by several authors (Plaza et al., 2007; Pevida et al., 2008; Hao et al., 2010; Sevilla et al., 2011; D'Alessandro et al., 2010; Zhangxiong et al., 2012) that the presence of basic N groups leads to an improvement of the adsorption of acidic gases such as CO_2. This could be due to the strong pole–pole interactions between the large quadrupole moment of CO_2 molecules (Lifeng and Ralph, 2011) and the polar sites associated with N groups coupled with the sample porosity (Sevilla et al., 2011). By comparing the properties of AU2 and AU0, we noted that the higher value of adsorption of AU2 was at low pressure due to the presence of nitrogen and not to its micropore until 300 mmHg, while AU1 gave a lower nitrogen content and micropore near to AU0. Table 2
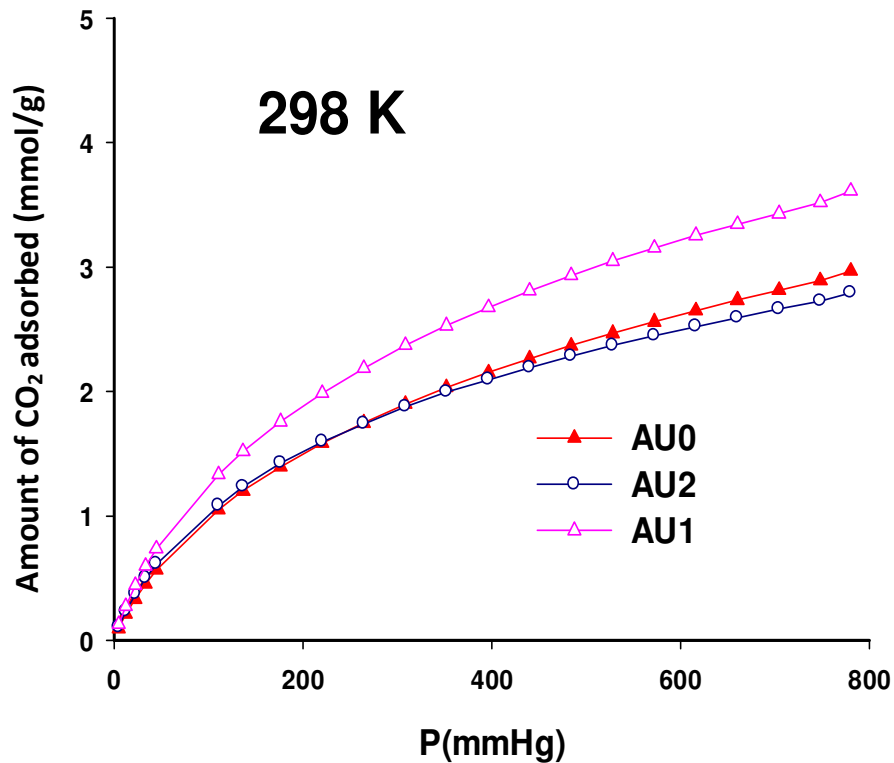
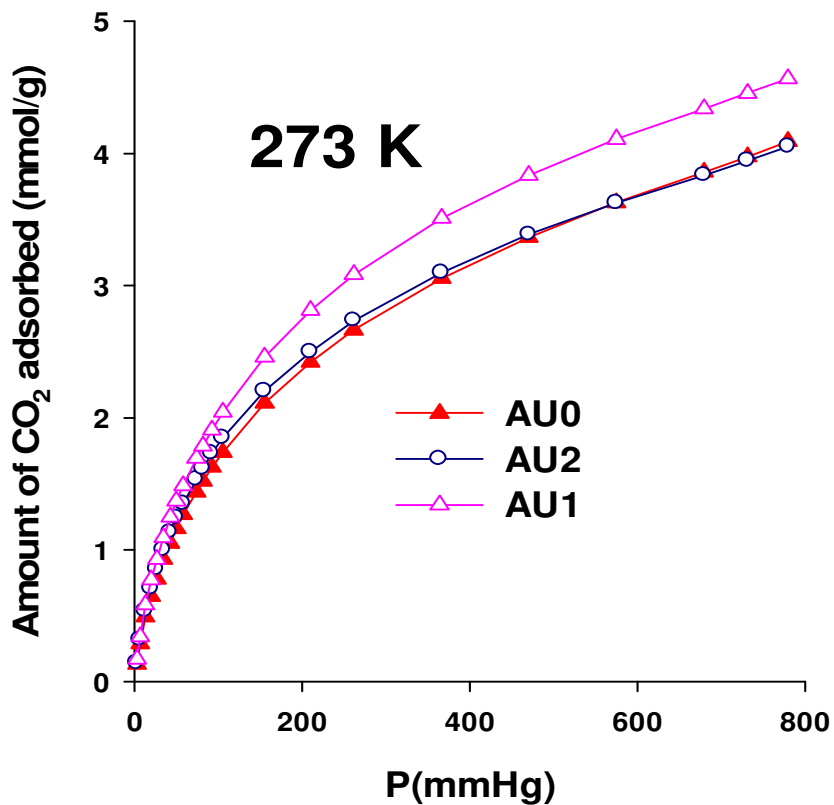**Figure 2.** CO$_2$ adsorption capacity of N-doped and carbon aerogel at 298K.

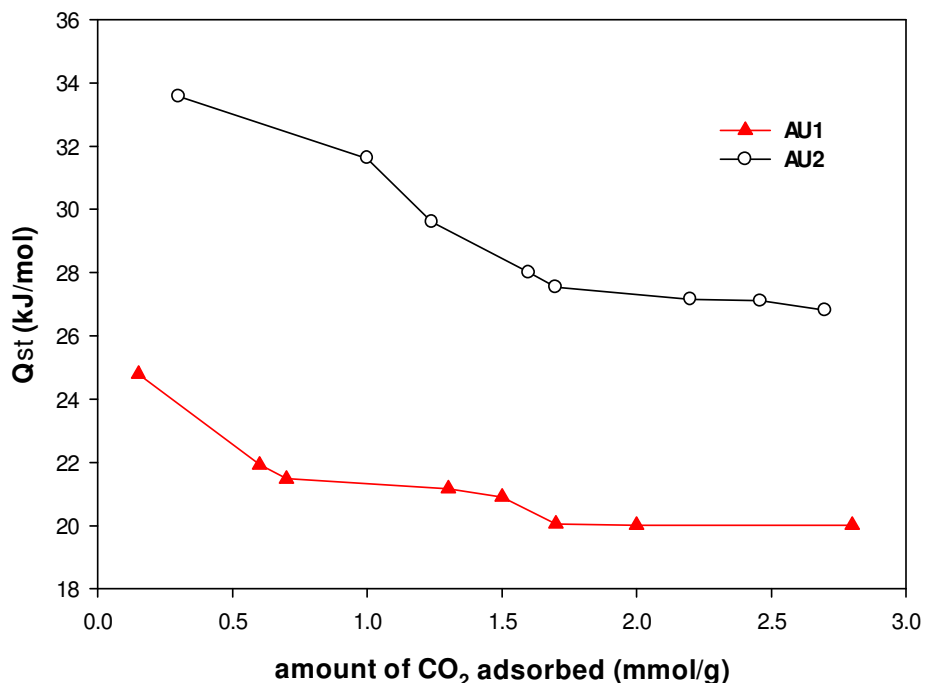**Figure 3.** CO$_2$ adsorption capacity of N-doped and carbon aerogel at 273K.

Figure 4. Isosteric heat of CO_2 adsorption (Qst) as function of amount of CO_2 adsorbed.

Table 2. CO_2 adsorption capacities of nitrogen-containing porous carbons observed in the literature at 25°C and 1 Atm.

Origin and N-doped carbon materials	Nitrogen content wt (%)	Capacity (mmol/g)	References
Melamine-formaldehyde	3.15	2.25	(Pevida et al., 2008)
Phenol-formaldehyde-lysine	1.91	3.13	(Hao et al., 2010)
Polypyrrole-Based Porous	10.1	3.9	(Sevilla et al., 2011)
Urea-formaldehyde-resorcinol	0.51	3.6	This work

shows a summary of some values of CO_2 adsorbed cited in the text.

Conclusion

N-doped carbon aerogel materials with different structures have been synthesized by a classical sol-gel method, with urea as a doped precursor. N_2 isotherms showed a difference of pores development. CO_2 adsorption experiment was affected by the nitrogen content and the micropore structure. The CO_2 adsorption and pore structures increased the amount of urea and the N-doped structure adsorbed more than the non-doped carbon aerogel.

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