



Facile Preparation of Nitrogen-Doped Activated Carbon for Carbon Dioxide Adsorption

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ABSTRACT

Nitrogen-doped activated carbons with high surface areas obtained from resorcinol and formaldehyde resins were evaluated as CO₂ adsorbents in a simulated flue gas stream under anhydrous and humid conditions. These carbons were prepared using two approaches, namely ammonia treatment without nitric acid pre-oxidation and amination after pre-oxidation. The pre-oxidation of activated carbons considerably enhanced the nitrogen incorporation during the amination process. The amination temperature affects the content and type of nitrogen incorporated onto the carbon surface, as determined by X-ray photoelectron spectroscopy, which enhances the specific adsorbent-adsorbate interaction for CO₂ in humid conditions. The presence of H₂O in the feed gas significantly decreased CO₂ adsorption for a very low nitrogen content of virgin activated carbon. A sample prepared via the amination of pre-oxidized carbon at 700°C (NORF700) exhibited excellent tolerance to moisture and the highest CO₂ capacity of 2.10 mmol/g in a 7% CO₂/83% N₂/10% H₂O wet stream at 50°C and 130 kPa. The high performance of NORF700 was ascribed to its high surface area, adequate micropore volume, and high amounts of pyridinic-like and pyrrole-like nitrogen species. The results indicate that nitric acid pre-oxidation followed by ammonia treatment at 700°C is an appropriate process for preparing adsorbents for CO₂ separation in post-combustion applications.

Keywords: Activated carbon; Ammonia treatment; CO₂ adsorption.

INTRODUCTION

Due to global climate change, the increased concentrations of greenhouse gases have become a concern. Among greenhouse gases, carbon dioxide (CO₂), released by the combustion of fuels and from certain industrial and resource extraction processes, makes the largest contribution to anthropogenic climate change (Plaza *et al.*, 2008). To reduce CO₂ emissions at industrial sites, the development of materials and technologies for CO₂ capture and sequestration has attracted a lot of attention in the past decade (Plaza *et al.*, 2007). For the post-combustion process, conventional monoethanolamine (MEA)-based solvent and wet scrubbing systems have been widely used for over 60 years, but they are energy intensive due to the required large amount of water (Arenillas *et al.*, 2005). The drawbacks of capturing CO₂ using the MEA process are high corrosion potential,

large MEA losses due to vaporization and degradation, and high energy consumption. To regenerate the solvent, a typical energy penalty incurred for the MEA capture process is an estimated 14% of the net power output of the plant (Rao and Rubin, 2002). Numerous alternatives, such as cryogenic separation, membrane separation, micro algal bio-fixation, and adsorption, are available for sequestering CO₂ from flue gases from the combustion of fossil fuels (Thiruvenkatachari *et al.*, 2009). Adsorption is attractive due to its low energy requirement, low cost, and good cycle performance. Recently, a number of porous adsorbents, such as metal-organic frameworks (MOFs), porous silica, zeolite, and activated carbons (ACs), have been developed for CO₂ capture. For MOFs, the major problems are their powder form and poor chemical and thermal stability, which are major obstacles to their effective use in realistic conditions. Amine-surface-modified or amine-impregnated porous silica (e.g., MCM-41, MCM-48, and SBA-15) materials lack stability over many cycles (Chang *et al.*, 2003; Hiyoshi *et al.*, 2005; Bhagiyalakshmi *et al.*, 2010). Although zeolitic imidazolate frameworks exhibit a high affinity for CO₂ molecules at low pressures and a higher selectivity for CO₂ from other relevant fuel gases, their use in CO₂ capture

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often suffers from structural instability and inefficient CO₂ selectivity in the presence of water, limiting their widespread use (Wang *et al.*, 2008). In contrast to the poor adsorption capacity of zeolites in the presence of moisture, carbon materials are relatively insensitive to moisture and are suitable candidates for CO₂ capture due to their pore structure and surface chemistry properties. The basic surface of carbon materials ensures a good adsorption for CO₂ since CO₂ is a weak Lewis acid (electron acceptor) that can interact with electron donors, such as nitrogen surface groups. Recently, basic nitrogen groups have been incorporated onto AC frameworks for enhancing CO₂ adsorption (Gray *et al.*, 2004; Plaza *et al.*, 2009; Plaza *et al.*, 2011). Nitrogen-containing functionalities can be introduced in the carbon matrix via a reaction with nitrogen-containing reagents (i.e., NH₃, urea, and amines) or the preparation of a carbon from a nitrogen-containing precursor (i.e., carbazole, melamine, acridine) (Stoeckli *et al.*, 1996; Lopez *et al.*, 2000; Carrott *et al.*, 2001; Plaza *et al.*, 2011; Plaza *et al.*, 2009). Plaza *et al.* (2010) modified AC with gaseous ammonia at temperatures from 400 to 900°C and found that the optimum temperature was 800°C, at which CO₂ adsorption capacity and nitrogen incorporation reached their maximum values. For gaseous ammonia to be strongly adsorbed at ambient conditions, the use of an adsorbent with an acidic surface is required. AC does not fully meet the above requirement since its surface acidity is insufficient. However, the surface chemistry of AC is quite easy to modify and can lead to the formation of strong interactions between gaseous ammonia and AC. Due to the small size (3 Å) and basic chemistry of ammonia gas, effective adsorption of NH₃ requires an acidic adsorbate surface and specific interactions between NH₃ molecules and the adsorbate surface, including hydrogen bonding, acid-base reactions, and complexation. AC can be given an acidic surface by heating it in an air flow (Le Leuch *et al.*, 2007) or oxidizing it using an oxidizing agent (Tamon *et al.*, 1996). Using an oxidizing agent such as nitric acid is a convenient way to form acidic groups on AC, since nitric acid has been shown to be a very effective oxidizing agent for the introduction of a significant number of oxygenated acidic functionalities in the form of carboxylic and phenolic hydroxyl groups onto the carbon surface (Puri, 1970).

Most post-combustion power plant flue gases include 68–75% N₂, 10–15% CO₂, 5–10% H₂O, 2–5% O₂, and trace amounts of NO_x and SO_x. The overwhelming majority of published research deals with dry feed gas, even though real flue gas contains a high level of saturated water vapor. The present study thus investigates the influence of N doping on the textural properties and surface basicity strength of AC applied to CO₂ adsorption from a simulated moist flue gas. A comprehensive study of the kinetic CO₂ adsorption under dry and wet gas streams was conducted using a wide range of carbon materials, including virgin carbon, carbon with NH₃ gas heat treatment without nitric acid pre-oxidation, and carbon with nitric acid pre-oxidation and heat treatment with NH₃ gas at various temperatures.

EXPERIMENTAL PROCEDURE

Preparation of Resorcinol-Formaldehyde AC

In a typical synthesis of aqueous organic gel, 5.71 g of resorcinol (R) and 0.14 g of sodium hydroxide were dissolved in a solvent mixture of ethanol (38.00 g) and deionized water (36.00 g) with magnetic stirring at 25°C. After dissolution, 2.01 g of 37 wt.% formaldehyde (F) was added and the mixture was stirred until a homogeneous solution was obtained. After curing (3 days at 50°C under vacuum), the dried polymer was heated at 400°C (5 h) under an N₂ atmosphere, and thus was carbonized into char. The obtained char was ground in an agate mortar and mixed with aqueous KOH solution (char:KOH concentration of 1:4 g/g) and distilled water (10 mL water per 2 g KOH). The mixture was kept at 85°C for 4 h under stirring and then dried at 110°C for 8 h. The activated char was carbonized at 800°C under N₂ flow at a flow rate of 100 mL/min and a ramping rate of 5 °C/min. Finally, the carbonized carbon was cooled and washed in 0.1 M HCl solution to remove residual KOH, and further washed with distilled water several times until the solution pH reached 7. The product (denoted as RFAC) was collected by filtration and dried in an oven at 110°C for 12 h.

Surface Modification Using NH₃ Gas

For preparing oxidized AC, 1.00 g of the dried resorcinol-formaldehyde AC was oxidized with 6 N HNO₃ at 80°C for 8 h (ratio of 1 g carbon/10 cm³ HNO₃ solution). The oxidized samples were then thoroughly washed with water to remove excess acid and the water-soluble products of oxidation, and finally dried at 110°C for 6 h. The acid treatment resulted in the formation of oxygenated AC.

For surface modification with NH₃ gas (amination) with oxidation, the obtained oxidized AC was loaded into the furnace, heated in an NH₃/N₂ mixture (80/20% v/v) with a heating rate of 10°C/min from room temperature until the defined amination temperature, and then held for 2 h. After heat treatment, the furnace was cooled to 100°C, and the NH₃/N₂ mixture flow was switched to N₂. The furnace was then allowed to cool down to room temperature. The NH₃/N₂ mixture and N₂ flow rates were both set at 50 cm³/min. The carbons obtained with pre-oxidation, denoted by the letter O, followed by NH₃ gas heat-treatment at 600, 700, and 800°C were designated NORF600, NORF700, and NORF800, respectively. To study the effect of pre-oxidation on the properties of the samples, an AC (denoted as NRF700) was prepared via amination treatment at 700°C without nitric acid pre-oxidation.

Characterizations of Samples

Ultimate analysis was carried out using an elemental analyzer (Elementar, Vario EL) to determine the chemical composition of the carbon samples. The carbon, hydrogen, and nitrogen content of the samples were determined directly, and the oxygen content was obtained by subtracting total content from C, H, and N. The chemical states of the nitrogen element of the samples were determined at room temperature using X-ray photoelectron spectroscopy (XPS) (Kratos Axis, Ultra DLD) with an Al K α source. For calibration, the C 1s electron binding energy was set to 285.0

eV and the distributions of N-containing functionalities were quantified after fitting the XPS N1s peaks into Gaussian-Lorentzian component profiles. The FTIR spectra of the samples were measured using a FTIR spectrometer (PerkinElmer, FTIR-2000). 0.1 g of AC was encapsulated in 1 g of KBr as the testing pellet. Moreover, a diffuse reflectance infrared Fourier transform spectroscopy, DRIFTS, was adopted to observe directly the interaction between activated carbons and adsorbent (carbon dioxide), to study in-situ FT-IR spectra of activated carbon after exposure to various environments. In situ DRIFTS measurements were performed using a PerkinElmer FTIR spectrometer (spectrum GX) and a diffuse reflectance accessory (Harrick Scientific, DRP-PE9) with a reaction cell (Harrick Scientific, HVC-DRP-3). The sample was placed in an airtight cell, equipped with a ZnSe window, had connections for inlet and outlet gas flows controlled by mass-flow controllers and the cell temperature was maintained by a heating element and a thermocouple, providing the feedback to a temperature controller to maintain the temperature constant. A total of 128 scans were recorded per spectrum over the range 4000–800 cm^{-1} at a resolution of 4 cm^{-1} . To improve the reflectivity of the samples, the samples were diluted with KBr and the ratio of KBr to sample was 20/1. A spectrum of KBr recorded in N_2 was set as background. The textural characterization of the samples was determined from the N_2 adsorption/desorption isotherms conducted in a volumetric apparatus (Micromeritics, ASAP 2020). The AC was degassed at 473°C in a vacuum for a period of at least 4 h prior to measurements. The nitrogen adsorption/desorption isotherms were measured over a relative pressure (P/P_0) range of approximately 10^{-3} to 0.995. The Brunauer-Emmett-Teller (BET) surface area of the AC (S_{BET}) was calculated from N_2 adsorption isotherms with the BET equation using adsorption data in the P/P_0 range of 0.06 to 0.2. The total pore volumes (V_{pore}) were estimated from the adsorbed N_2 amount at $P/P_0 = 0.973$. The pore size distribution (PSD) in the micro- and mesopore regions was determined by applying the density functional theory (DFT) method based on nitrogen adsorption data.

Dynamic Adsorption Capacity of Carbon Dioxide

CO_2 breakthrough experiments were performed in a stainless tubular column (i.d.: 20 mm; length: 120 mm) equipped with a porous plate located 30 mm from the base of the column, which was placed vertically inside a tubular furnace. 0.20 g of AC powder was used to get the required breakthrough capacity. In a typical experiment, adsorbents were regenerated prior to each breakthrough test by heating the stainless tubular column up to 150°C for 1 h while purging with 100 NmL/min of N_2 . The stainless tubular column was then cooled to 50°C. After pretreatment, the desired flow of N_2 and the selected CO_2 flow were added to the mixing tank as an N_2/CO_2 mixture (83/17 % v/v) with a total gas flow rate of 100 NmL/min. Since the moisture was contained in a coal-fired combustion stream, the adsorbent performance measurements were conducted under moist feed mode. To create moist conditions, saturated water vapor was obtained by passing N_2/CO_2 gas through a small-scale

water tank in a constant temperature water bath at 50°C to produce an $\text{N}_2/\text{CO}_2/\text{H}_2\text{O}$ mixture (83/10/7 % v/v) with a total gas flow rate of 100 NmL/min. The carbon dioxide concentration of the outlet gas stream was measured by a BABUC BSO103 CO_2 continuous monitoring system interfaced with a computer data acquisition program. The adsorption capacities of each carbon were calculated by integrating the area above the breakthrough curves, and from the total flow rate, CO_2 concentration in the inlet gas, flow rate, breakthrough time, and mass of carbon. The dynamic adsorption capacity is calculated from the breakthrough curve as:

$$Q_{\text{dyn}} = \frac{FC_{\text{in}} t_{\text{st}}}{M} \quad (1)$$

where Q_{dyn} is the dynamic adsorption capacity (mg/g-adsorbent), F is the total flow rate (mL/min), C_{in} is the concentration of CO_2 entering the column (vol.%), M is the mass of adsorbent loaded in the column (g), and t_{st} is the stoichiometric time corresponding to CO_2 stoichiometric adsorption capacity (min). The stoichiometric adsorption capacity is the area between the breakthrough curve and a line at $C_{\text{out}}/C_{\text{in}} = 1.0$.

RESULTS AND DISCUSSION

FTIR Spectra of Initial and Modified Samples

To investigate the effect of pre-oxidation on the functional groups present on the surface of the samples, a carbon denoted as ORFAC was prepared by the oxidation of nitric acid. By measuring the FTIR spectra of the samples before and after modification, surface functional groups formed or consumed during treatment can be obtained. Fig. 1 shows the results of FTIR measurements for initial carbon and surface-modified samples. In Fig. 1(a), there is a peak around 1020–1030 cm^{-1} for initial carbon (RFAC), which can be attributed to the C–O stretching of ethers. After pre-oxidation, peaks at 1729 and 1595 cm^{-1} and a broad band that extends from 900 to 1300 cm^{-1} appear for ORFAC. The peaks at 1729 and 1595 cm^{-1} are assigned to C=O group moieties (in carboxylic and lactone structures) and the broad band from 900 to 1300 cm^{-1} can be assigned to the C–O stretching and –OH bending modes of phenolic and carboxylic groups (Zawadzki, 1989). Amination treatment led to some changes in the spectra of the samples; bands related to carboxylic and phenolic structures diminished obviously and a peak at 1565 cm^{-1} , corresponding to the N–H group, was found for NRF700 and NORF700. Moreover, a 1604 cm^{-1} band that can be linked to the presence of a pyridine-like group was found for NORF700 (Mohammad *et al.*, 2010). It has been reported that the reaction of gaseous ammonia with carboxylic acid sites present on the carbon surface can form ammonium salts and through a dehydration or decarbonylation reaction may lead to pyrroles and pyridines, which has the formation of amides or nitriles groups as the intermediate step (Jansen *et al.*, 1994).

As shown in Fig. 1(b), the NORF series samples have similar absorption bands, with the only difference being

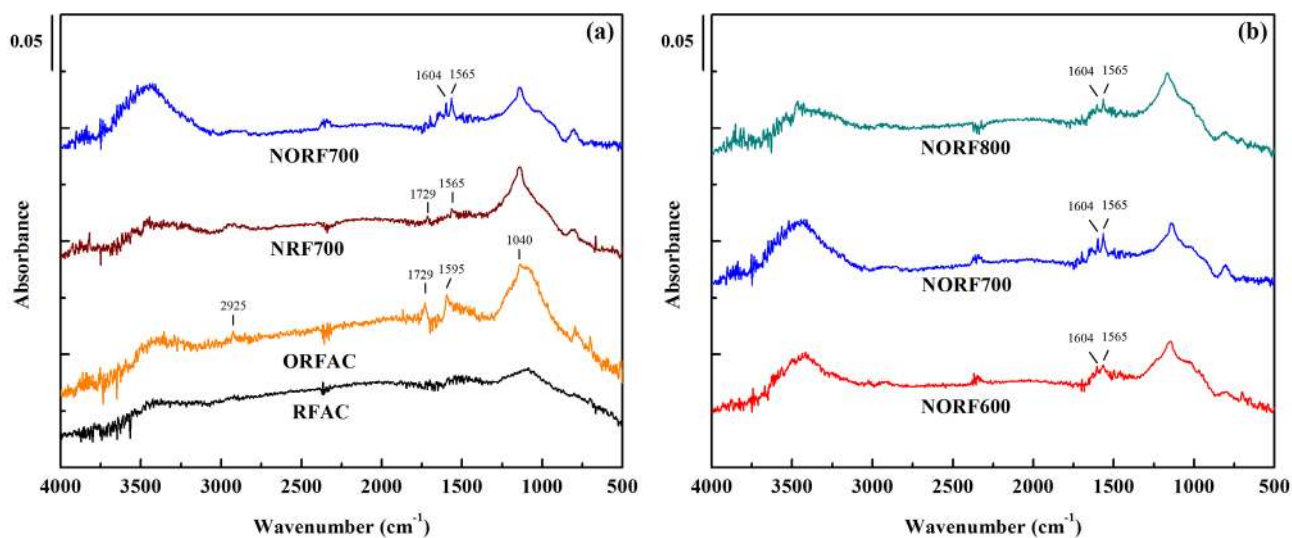


Fig. 1. FTIR spectra of initial and modified activated carbon samples.

their intensities, indicating small differences in the surface chemistry. A band at around 1565 cm^{-1} can be ascribed to the N-H group for all NORF samples. A comparison of spectra for samples with amination without preliminary oxidation (NRF700) and those with amination and oxidation (NORF series) shows obvious changes in the range of 3376 and 3294 cm^{-1} . The broad band in the 3376 to 3294 cm^{-1} region is associated with overlapping bands of O-H and N-H stretching vibrations, which might be related to the formation of hydrogen bonds between the adsorbed NH_3 molecules and oxygen surface groups (Gómez-Serrano *et al.*, 1994).

Textural Properties of Initial and Modified ACs

The N_2 adsorption-desorption isotherms for various AC samples are shown in Fig. 2. It is clear that the shapes of modified ACs are different from that of the initial AC. The major update of initial AC (RFAC) occurred at a relative pressure of around 0.2, and remained almost constant at higher relative pressures, indicating that RFAC was mainly a microporous material. For NORF800, the isotherm became a combination of I and II, indicating the presence of a number of mesopores. To determine the porosity development of the AC samples before and after modification, the pore size distributions, calculated using the DFT model, are shown in Fig. 3. As can be seen, all types of AC possessed micropores and mesopores. It can be observed that pre-oxidation followed by the ammonia process leads to the development of pores in the carbon and causes an increase in the numbers of ultramicropores ($< 0.7\text{ nm}$), supermicropores ($0.7\text{--}2\text{ nm}$), and mesopores ($2\text{--}50\text{ nm}$), especially for NORF800. The surface area, micropore area, pore volume, and average pore size of ACs are summarized in Table 1. The results show that after amination, the total surface area, micropore area, and pore volume of NRF700, NORF600, and NORF800 decreased compared to those of RFAC. NORF800 has the smallest S_{BET} value, micropore area, and pore volume of the NORF series, indicating that an amination temperature of 800°C is detrimental to textural development.

A comparison of the textural properties (see Table 1) between NRF700 (amination without preliminary oxidation) and NORF700 (pre-oxidation followed by amination) shows that pre-oxidation promotes the increases of the surface area, micropore volume, and pore volume of the sample. When the oxidized carbons were treated with ammonia at high temperatures, the NH_2 , NH , and atomic hydrogen radicals created during ammonia decomposition may have attached to the surface oxides and released CO_2 or CO (Pevida *et al.*, 2008), resulting in increased surface area and pore volume for NORF700. The mesopore volume for the modified ACs increased, especially for NORF700 and NORF800. This increase may be associated with the enlargement of micropores, indicating that mesopores and macropores increased with increasing temperature.

Nitrogen Content and Type of Nitrogen-containing Functionalities

Since CO_2 is an acidic gas, alkaline surface functional groups like nitrogen species on the AC surface improve the chemisorption of CO_2 from flue gas (Hsiao *et al.*, 2011). Elemental analysis (EA) and high-resolution XPS analyses were used to determine the nitrogen content and type of nitrogen-containing functionalities in the samples, respectively. The results obtained from EA presented in Table 2 show an increase of the nitrogen content after surface modification with amination, particularly for NORF carbons. For instance, the nitrogen content increased from less than 0.2 wt.% for initial carbon (RFAC) to 1.1 wt.% for NRF700 and 7.2 wt.% for NORF700. Moreover, the incorporation of nitrogen is significant for NORF700, which had 6 times more nitrogen than did NRF700, which was treated at the same temperature without pre-oxidation. The differences in nitrogen content between the NORF700 and NRF700 samples indicates that the presence of oxygen functionalities on the carbon surface before amination plays an important role in determining the degree of nitrogen incorporation into the surface, and that the pre-oxidation of carbons considerably enhances nitrogen incorporation during

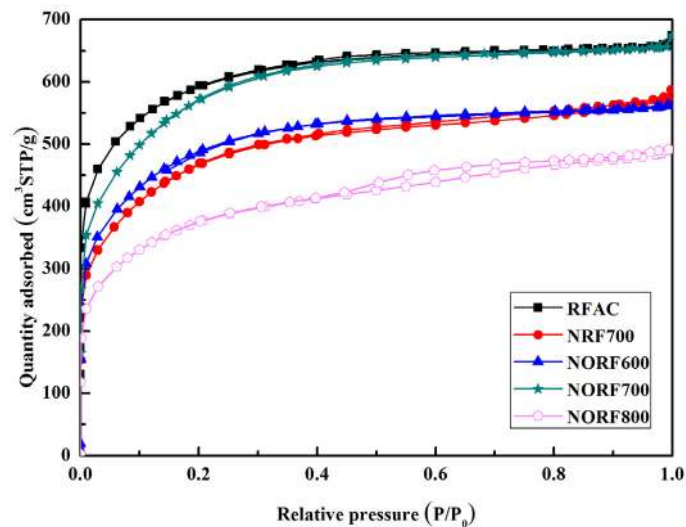


Fig. 2. N₂ adsorption-desorption isotherms of initial and modified activated carbon samples.

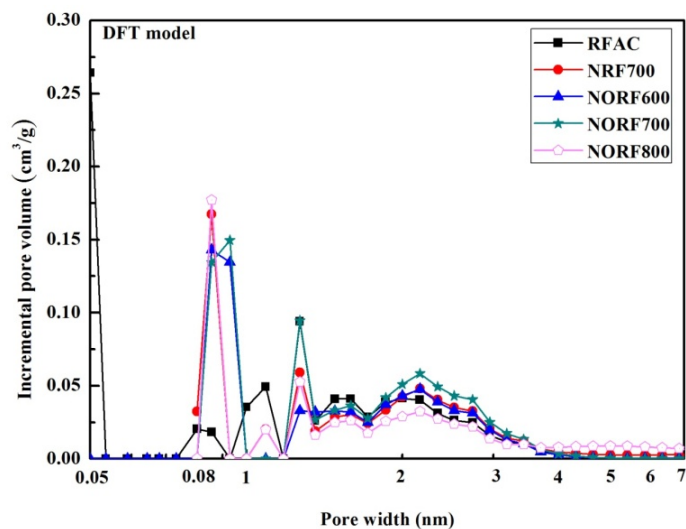


Fig. 3. Pore size distributions of various activated carbon samples obtained using DFT model.

Table 1. Textural properties of activated carbons obtained through surface modification of NH₃.

Sample	Surface area (m ² /g)		Pore volume (cm ³ /g)		Average pore diameter (nm)
	Total surface area (BET)	Micropore area ^a	V _{micro} ^a	V _{pore}	
RFAC	2054	1310	0.38	0.89	2.84
NRF700	1673	508	0.22	0.75	2.89
NORF600	1736	622	0.27	0.72	2.63
NORF700	2039	635	0.28	0.88	2.71
NORF800	1332	450	0.19	0.63	3.26

^a Values obtained using DFT model for micropore < 1.1 nm.

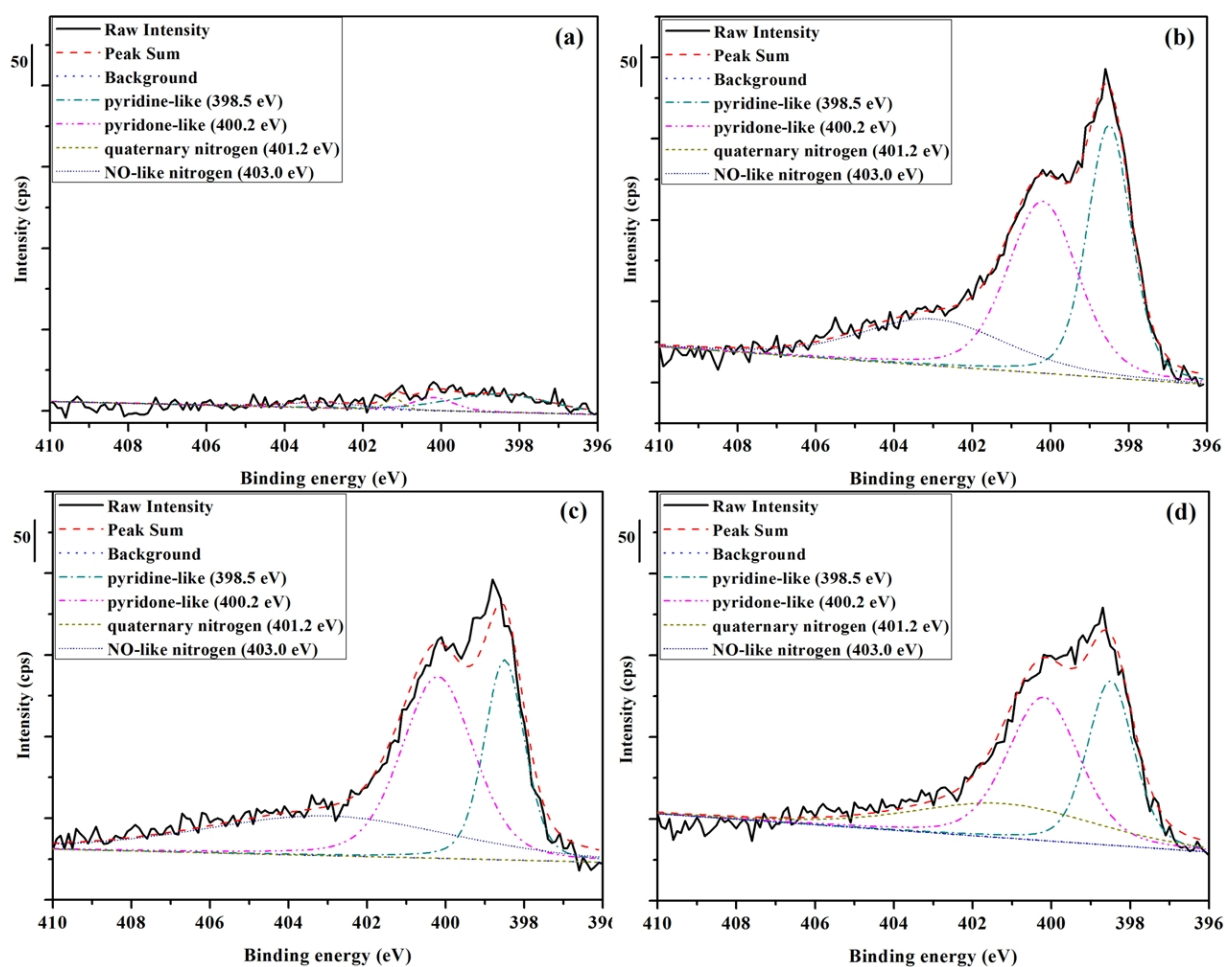
ammonia treatment (Table 2). It has been reported that the free radicals (such as NH₂, NH, and atomic hydrogen) created during ammonia decomposition may attach to the surface oxides or active sites present on the carbon surface to form nitrogen-containing functional groups (Stöhr *et al.*, 1991; Bota and Abotsi, 1994; Vinke *et al.*, 1994). Temperature also influences the amount of nitrogen incorporated into the carbon surface. For temperatures higher than 700°C,

less nitrogen was incorporated into the modified carbon in this study.

High-resolution N 1s spectra of various samples are shown in Fig. 4. Each of the XPS spectra was obtained using four Gaussian curves based on the four species of nitrogen reported in the literature. These nitrogen species could be assigned to pyridinic (N-6, 398.5 eV), pyrrolic/pyridone (N-5, 400.2 eV), quaternary (N-Q, 401.2 eV), and pyridine-

Table 2. Carbon, hydrogen, oxygen, and nitrogen content of samples obtained from elemental analysis.

Sample	Ultimate analysis (wt.%, dry basis)			
	C	H	N	O ^a
RFAC	81.80	2.02	< 0.20	16.17
NRF700	70.28	3.32	1.08	25.32
NORF600	50.24	3.15	4.99	41.70
NORF700	76.56	2.48	7.17	13.77
NORF800	53.48	3.74	3.98	38.79

^a Calculated by difference.**Fig. 4.** High-resolution fitted XPS spectra of N 1s peak of (a) RFAC, (b) NORF600, (c) NORF700, and (d) NORF800.

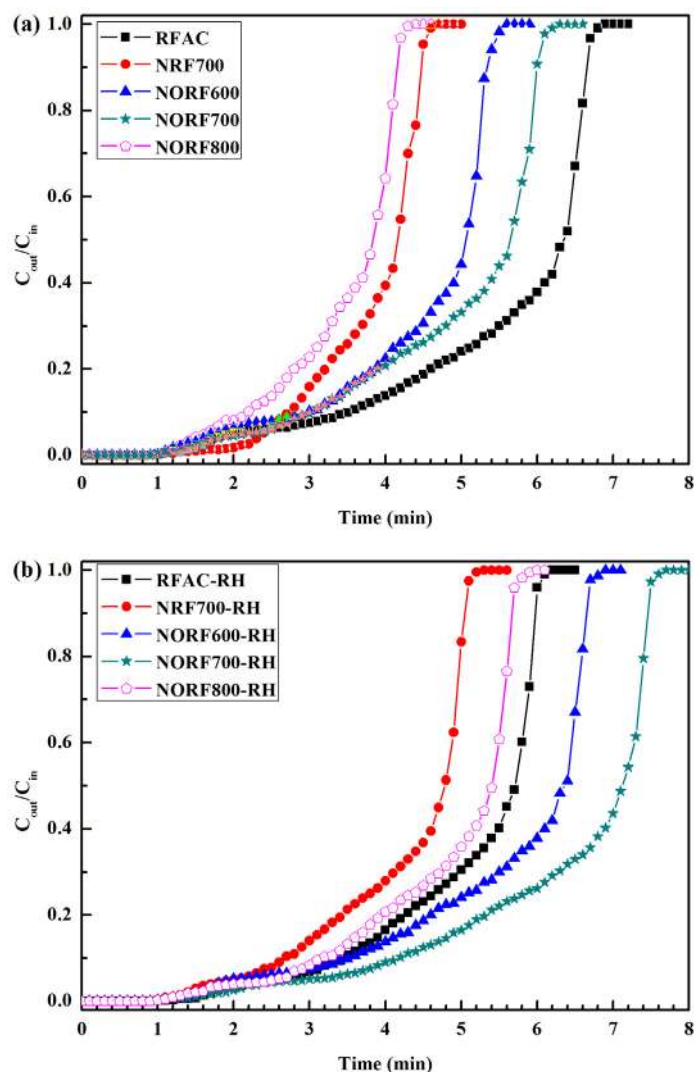
N-oxide (403.0 eV), respectively (Pinero *et al.*, 2003). The amount of various N functionalities on the samples was obtained by integrating the four individual curves, as shown in Table 3. As can be seen, amination treatment leads to an obvious change in the number and kind of nitrogen species in the samples. Amination increases the overall contribution of pyridinic (N-6) and pyrrolic/pyridone (N-5) for NORF600, NORF700, and NORF800. Taking into account that more nitrogen is incorporated for amination samples, the highest amount of nitrogen was obtained for NORF700. Moreover, more quaternary nitrogen, a very stable species, was found in NORF800 than in NORF600 and NORF700, indicating that pyridinic and pyrrolic functionalities transform into quaternary nitrogen at higher temperature.

Dynamic CO₂ Adsorption

Dynamic CO₂ adsorption and breakthrough in a 17% CO₂/83% N₂ stream under dry conditions and a 7% CO₂/83% N₂/10% H₂O stream under moist conditions are plotted as functions of time in Fig. 5 for various AC samples. As shown in Fig. 5(a), at the beginning of the anhydrous experiment, all the incoming CO₂ was adsorbed. After 1 min, the mass transfer zone reached the bed outlet and then CO₂ was detected in the effluent stream for RFAC, NRF700, NORF600, and NORF700. After 3–6 min, the bed became saturated and the effluent concentration of CO₂ was equal to that of the feed. RFAC had the broadest breakthrough curve, whereas NRF700 and NORF800 had the steepest curves, indicating that intraparticle diffusion was the mass

Table 3. Results of curve fitting of the contribution of nitrogen species to N 1s peak of initial and modified samples.

Sample	Binding energy (eV)				Total area
	398.5 N-6 (pyridinic)	400.2 N-5 (pyrrolic/pyridone)	401.2 N-Q (quaternary nitrogen)	403.0 pyridine-N-oxide	
RFAC	15.73	24.43	0.1	20.28	60.54
NORF600	412.70	374.52	0.1	226.41	1013.73
NORF700	360.63	588.37	0.1	443.57	1392.67
NORF800	338.10	459.44	278.76	0.1	1076.4

**Fig. 5.** Comparison of breakthrough curves of CO₂ adsorption for various activated carbon samples for (a) dry stream and (b) wet stream (adsorption at 50°C and total gas flow rate of 100 NmL/min).

transfer limiting mechanism. NRF700 and NORF800 exhibited high amounts of mesopores, which formed during the activation process; therefore, intraparticle mass transfer resistance was substantially reduced. From the breakthrough curve data, the dynamic adsorption capacities of obtained samples are given in Table 4. The adsorption performance of CO₂ follows the order: RFAC > NRF700 > NORF600 > NRF700 > NORF800. It is generally accepted that both textural properties and surface basicity strength influence the adsorption performance of CO₂. Therefore,

Table 4. CO₂ breakthrough capacity of initial and modified samples under dry and moist conditions.

Sample	Dry conditions (mmol/g)	Humid conditions (mmol/g)
RFAC	1.80	1.61
NRF700	1.19	1.25
NORF600	1.38	1.81
NORF700	1.56	2.10
NORF800	1.10	1.49

adsorption performance was correlated to specific surface area, pore volume, pore size, and number of nitrogen functional groups of the samples. A plot of the amount of CO₂ adsorbed under dry conditions versus micropore volume (including ultramicropores and supermicropores) is given in Fig. 6. There is a linear relationship between the amount of CO₂ adsorbed and the micropore volume. Based on the results of EA and XPS, RFAC has the lowest nitrogen content, implying that the surface basicity of AC is not beneficial for CO₂ adsorption under anhydrous conditions.

Fig. 5(b) shows the results of the breakthrough experiments for the separation of CO₂ from a 7% CO₂/83% N₂/10% H₂O wet stream (100% relative humidity (RH)) using five samples. The saturation time of the adsorption bed became longer compared to that for the dry condition, except for RFAC. This indicates that water on the surface significantly increases the breakthrough time for modified samples. Moreover, pre-oxidation followed by amination, especially at 700°C, resulted in better adsorbents. For amination, pre-oxidation of the carbon dramatically increases the adsorption capacity. For instance, a 1.05 times enhancement of the adsorption capacity is for NRF700; those for NORF600, NRF700, and NORF800 are 1.31, 1.34, and 1.35, respectively, as indicated in Table 4. Under wet conditions, much worse performance was obtained, with the 0.89 time decrease for RFAC, virgin carbon. The existence of moisture may greatly influence the CO₂ capture performance of low-nitrogen-content RFAC due to the competition for adsorption between water and carbon dioxide on the surface of RFAC. It has been reported that moisture adversely affects CO₂ uptake in a variety of physical adsorbents, such as zeolites and carbonic (Hsiao *et al.*, 2011). However, the highly humid flue gases, including 5–10% saturated water vapor, are treated in most of the post-combustion carbon captures projects (Ahn and Changha, 2004). Therefore, the development of new adsorbents for CO₂ removal from post-combustion flue gas should consider the tolerance to moisture. The reaction mechanisms between CO₂ and supported amine

groups producing ammonium carbamate and ammonium bicarbonate in dry and humid streams, respectively, are (daSilva and Svendsen, 2007):



Leal *et al.* (1995) found that one bidentate ammonium carbamate molecule converted into two monodentate ammonium bicarbonate molecules when water vapor was present in the gas feed, resulting in an obvious increase from 0.41 to 0.89 mmol/g using (3-aminopropyl)triethoxysilane/silica gel under a pure CO₂ flow with an RH of 100%. In the present study, the enhanced CO₂ adsorption for NORF600 and NORF700 in the humid stream may be attributed to the high nitrogen content. However, it should be pointed out that although NORF800 has a higher nitrogen content compared to that of NORF600, its CO₂ adsorption capacity is lower. These differences might be related to the types of nitrogen species on the AC surface. As shown in Table 3, both NORF600 and NORF700 have relatively high amounts of pyridinic-like nitrogen species (pyridine and pyridine-N-oxide) and pyrrole-like type nitrogen species compared to those of NORF800. In contrast, the carbon treated with pre-oxidation followed by ammonia treatment at the highest temperature (800°C), NORF800, had the highest amount of the most stable species (quaternary nitrogen), resulting in a lower CO₂ adsorption capacity than that of NORF600. Thus, the affinity between CO₂ and adsorbent depends not only on the amount of total nitrogen incorporated into the carbons but also on the type of nitrogen-containing functionalities introduced during the modification process. For comparison, the adsorption capacities of mesoporous silica and carbon materials obtained from the literature are given in Table 5. NORF700 has a higher CO₂ adsorption

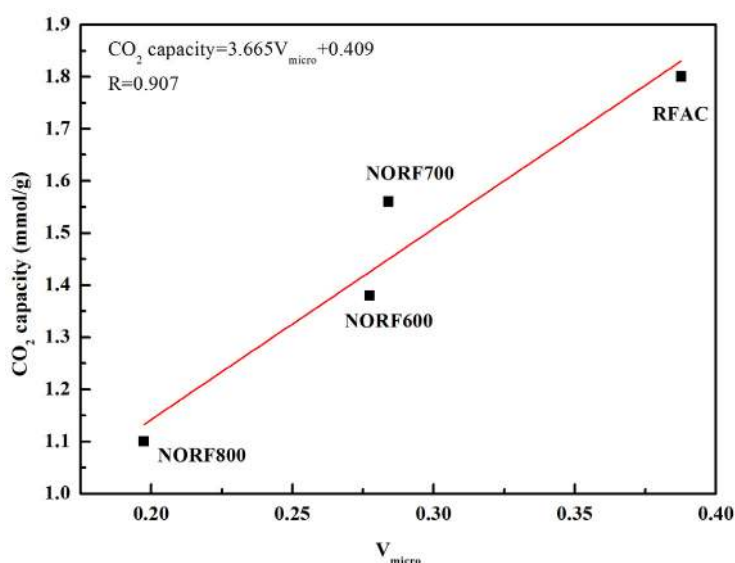


Fig. 6. Relationship between micropore volume and amount of CO₂ adsorbed on activated carbons under dry conditions.

Table 5. CO₂ adsorption capacity of various adsorbents.

Material	CO ₂ capacity (mmol/g)	Experimental conditions CO ₂ concentration	T (°C)	Reference
AC	0.25–0.8	17% (dry)	55	[33]
SWCNT	0.5–1.25	100% (dry)	35	[34]
MCM-48/AP	2.3	10% (100%RH)	25	[35]
SBA-15/TRI	1.8	15% (humid)	60	[36]
SBA-15/Aziridine polymer	4	10% (humid)	75	[37]
AC	2.7	10% (humid)	50	[25]
NORF700	2.1	10% (100 %RH)	50	This study

capacity than those of mesoporous silica and carbon evaluated under similar operating conditions (Na *et al.*, 2001; Cinke *et al.*, 2003; Huang *et al.*, 2003; Hiyoshi *et al.*, 2005; Drese *et al.*, 2009).

DRIFTS Study for NORF700

DRIFTS studies have been successfully applied in studying the sorption kinetics of physisorbed and chemisorbed species on the NORF700 sorbent surface under dry and wet conditions. All measurements were carried out on a ca. 50-mg fresh sample previously pretreated in situ in flowing N₂ (20 mL/min) at 150°C for 1 h. After pretreatment, the sample was purged in N₂ while being cooled to the desired adsorption temperature of 50°C. In case of dry condition, the desired flow of N₂ and the selected CO₂ flow were added to the mixing tank as an N₂/CO₂ mixture (83/17% v/v) with a total gas flow rate of 20 NmL/min. Fig. 7(a) showed the in-situ FT-IR spectra of NORF700 under three environments. It can be seen that the DRIFT spectra could be divided into three regions: 3800–3000 cm⁻¹, 2400–2300 cm⁻¹, and 1800–800 cm⁻¹. All spectra show a broad and strong absorption band at 3500–3000 cm⁻¹ with a maximum at around 3230 cm⁻¹, which is assigned to the stretching vibration of hydroxyl compounds from carboxyls, phenols or alcohols (Dandekar, *et al.*, 1998; Pradhan and Sandle, 1999; Boonamnuyvitaya, *et al.*, 2005). Upon heating sample to 150°C for 1 h a decrease of isolated OH stretching vibrations in the 3700–3750 cm⁻¹ (Aksoylu *et al.*, 2001), which are associated with free –OH modes and due to the adsorbed molecular water, was found for regenerated NORF700. Unlike the pretreatment and regenerated NORF700, several peaks arising from the remaining adsorbed water are observed for NORF700 exposure to N₂/CO₂ mixture, indicating that water is located at specific positions in the structure of NORF700. An intense and broad band in the region of 2370–2350 cm⁻¹ was observed, implying the adsorption of CO₂ was present on the surface of NORF700. There are three main bands in the 1800–800 cm⁻¹ range indicating the presence of surface oxygen groups: (i) a band at 1750 cm⁻¹ corresponding to C=O stretching vibration in carboxylic groups, lactones and anhydrides (Figueiredo *et al.*, 1999; Silva *et al.*, 2009; Zhang *et al.*, 2010), (ii) a band at 1600 cm⁻¹ attributing to C=C stretching vibration in aromatic rings of quinone and keto-enol groups (Figueiredo *et al.*, 1999; Silva *et al.*, 2009; Zhang *et al.*, 2010), and (iii) the broad band around 1100 cm⁻¹ assigning to the C–O stretching in carboxylic

groups, anhydrides, phenols, ethers and lactones (Figueiredo *et al.*, 1999; Silva *et al.*, 2009) or (C–O–C) stretching vibration in lactones and ethers (Shin *et al.*, 1997; El-Hendawy *et al.*, 2008). From the band at 1600 cm⁻¹ and through comparing in the cases of pretreatment, adsorption, and regenerated NORF700, it can be concluded that 1600 cm⁻¹ is present in all situations of NORF700.

To create moist conditions, saturated water vapor was obtained by passing N₂/CO₂ gas through a small-scale water tank in a constant temperature water bath at 50°C to produce an N₂/CO₂/H₂O mixture (83/10/7 % v/v) with a total gas flow rate of 20 NmL/min. The time of equilibration of the gaseous adsorbates with the sorbent was 15 min in all cases and only spectra under steady-state conditions were collected and shown. Rege and Yang (2001) used FTIR spectroscopy to study H₂O/CO₂ mixed gas on zeolite and alumina. They reported that the physisorbed CO₂ species appears in the region of 2370–2350 cm⁻¹ and several peaks correspond to the chemisorbed species appear in the region of 1700–1200 cm⁻¹, respectively. In generally, three basic absorption frequencies are observed in case of H₂O molecules, including a band of isolated OH stretching vibration in the 3690–3700 cm⁻¹, a broad band of hydrogen-bonded OH stretching vibration in the 3250–3400 cm⁻¹, and the H–O–H bending vibration band at 1645–1660 cm⁻¹ (Bertsch and Habgood, 1963). The DRIFTS spectra in Fig. 7(b) indicate the adsorption of 20 scem N₂/CO₂/H₂O mixture (83/10/7 % v/v) on NORF700 at 50°C. Exposure to H₂O-vapor/CO₂ yields bands of characteristic of physisorbed CO₂ (an intense and broad band in the region of 2370–2350 cm⁻¹). A comparison of Figs. 7(a) and 7(b) indicates that the introduction of H₂O-vapor results in the increase of intensity of physisorbed CO₂. Since the areas of the IR absorption peaks are proportional to molar adsorbed amounts, the physisorbed CO₂ molecules in wet stream are much more abundant than those of dry stream. Moreover, a prominent sharp band of H–O–H bending at 1645 cm⁻¹ and an intense and broad related to the H-bonded OH stretching between 3400–3000 cm⁻¹ were observed for NORF700 in wet condition. This was due to the increase in amount of H₂O molecules from N₂/CO₂/H₂O stream.

CONCLUSION

A series of nitrogen-doped AC samples was evaluated as potential adsorbents for separating CO₂ from post-combustion flue gas under dry and wet conditions. Two

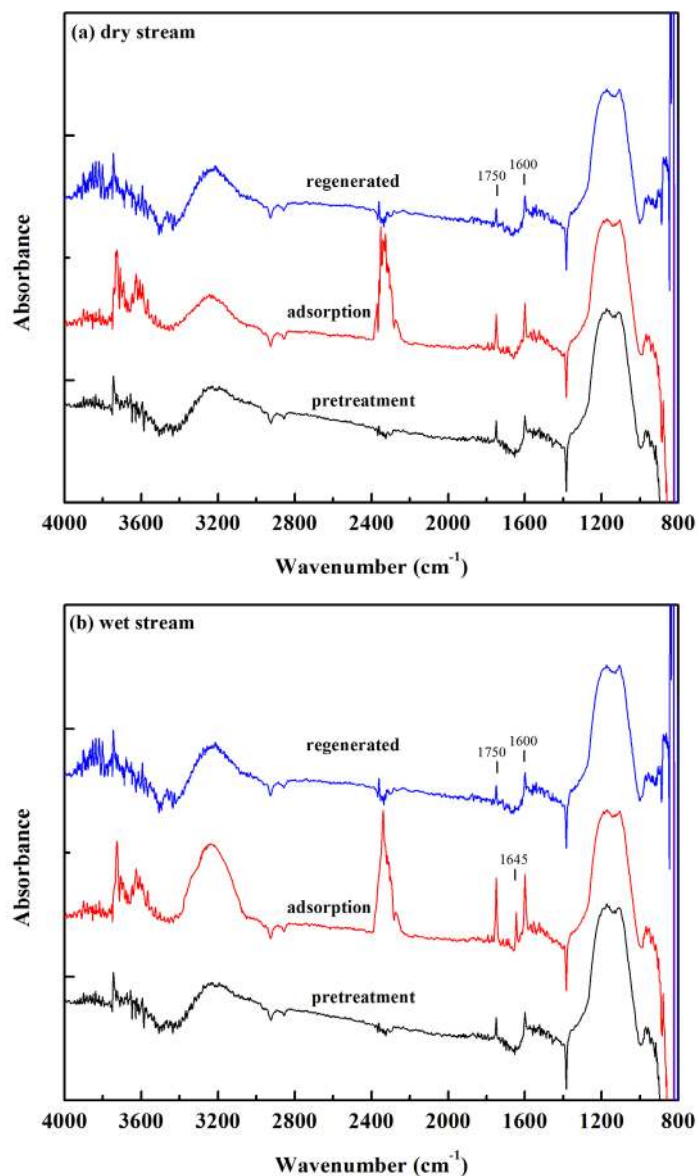


Fig. 7. DRIFT spectra of NORF700 recorded at 50°C after exposure to (a) N_2/CO_2 mixture (83/17 % v/v, 20 NmL/min) and (b) H_2O -vapor/ CO_2/N_2 (7/10/83 % v/v, 20 NmL/min) gas mixture for 15 min.

methods were employed to obtain nitrogen-doped AC samples, namely amination without nitric acid pre-oxidation and nitric acid pre-oxidation followed by amination at various temperatures. Preliminary oxidation significantly improves the nitrogen incorporation into the carbon surface during amination treatment. The increase of nitrogen content of the obtained samples was confirmed using FTIR, EA, and XPS. Amination temperature also influences the content and type of nitrogen incorporated onto the carbon surface. For temperature higher than 700°C, less nitrogen was incorporated into the pre-oxidized carbon. CO_2 breakthrough experiments performed under dry conditions demonstrated that the adsorption performance of CO_2 is closely related to the micropore volume of AC. The introduction of basic nitrogen surface groups, particularly through pre-oxidation followed by amination, significantly enhanced the adsorption ability of the carbon adsorbent towards CO_2 from a 7%

$CO_2/83\% N_2/10\% H_2O$ wet stream (100% RH). In contrast, the existence of moisture had a detrimental effect on CO_2 adsorption of very-low-nitrogen-content virgin AC due to the competition of adsorption between water and carbon dioxide on the surface. The NORF700 sample (pre-oxidation and amination at 700°C) had the highest CO_2 dynamic adsorption capacity of 2.10 mmol/g in a 7% $CO_2/83\% N_2/10\% H_2O$ wet stream at 50°C and 130 kPa. AC with an adequate micropore volume and high amounts of pyridinic-like nitrogen species (pyridine and pyridine-N-oxide) and pyrrole-like nitrogen species is responsible for the superior CO_2 adsorption performance. These results suggest that nitric acid pre-oxidation followed by amination treatment at 700°C is a promising surface modification process for the production of carbon-based CO_2 adsorbents for post-combustion power plant flue gases with 5–10% saturated water vapor.

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REFERENCES

- Ahn, H. and Changha, L. (2004). Effects of Capillary Condensation on Adsorption and Thermal Desorption Dynamics of Water in Zeolite 13X and Layered Beds. *Chem. Eng. Sci.* 59: 2727–2743.
- Aksoylu, A.E., Madalena, M., Freitas, A., Fernando, M., Pereira, R. and Figueiredo, J.L. (2001). The Effects of Different Activated Carbon Supports and the Modifications on the Properties of Pt/AC Catalysts. *Carbon* 39: 175–185.
- Arenillas, A., Smith, K.M., Drage, T.C. and Snape, C.E. (2005). CO₂ Capture Using Some Fly Ash-derived Carbon Materials. *Fuel* 84: 2204–2210.
- Bertsch, L. and Habgood, H.W. (1963). An Infrared Spectroscopic Study of the Adsorption of Water and Carbon Dioxide by Linde Molecular Sieve X. *J. Phys. Chem.* 67: 1621–1628.
- Bhagiyalakshmi, M., Yun, L.J., Anuradha, R. and Jang, H.T. (2010). Utilization of Rice Husk Ash as Silica Source for the Synthesis of Mesoporous Silicas and Their Application to CO₂ Adsorption through TREN/TEPA Grafting. *J. Hazard. Mater.* 175: 928–938.
- Boonamnuyvitaya, V., Sae-ung, S. and Tanthapanichakoon, W. (2005). Preparation of Activated Carbons from Coffee Residue for the Adsorption of Formaldehyde. *Sep. Purif. Technol.* 42: 159–168.
- Bota, K.B. and Abotsi, G.M.K. (1994). Ammonia: A Reactive Medium for Catalysed Coal Gasification. *Fuel* 73: 1354–1357.
- Carrott, P.J.M., Nabais, J.M.V., Carrott, M.M.L.R. and Pajares, J.A. (2001). Preparation of Activated Carbon Fibres from Acrylic Textile Fibres. *Carbon* 39: 1543–1555.
- Chang, A.C.C., Chuang, S.S.C., Gray, M. and Soong, Y. (2003). In-Situ Infrared Study of CO₂ Adsorption on SBA-15 Grafted with γ -(Aminopropyl)triethoxysilane. *Energy Fuels* 17: 468–473.
- Cinke, M., Li, J., Baushlicher, C.W., Ricca, A. and Meyyappan, M. (2003). CO₂ Adsorption in Single Walled Carbon Nanotubes. *Chem. Phys. Lett.* 376: 761–766.
- da Silva, E.F. and Svendsen, H.F. (2007). Computational Chemistry Study of Reactions, Equilibrium and Kinetics of Chemical CO₂ Absorption. *Int. J. Greenhouse Gas Control* 1: 151–157.
- Dandekar, A., Baker, R.T.K. and Vannice, M.A. (1998). Characterization of Activated Carbon, Graphitized Carbon Fibers and Synthetic Diamond Powder Using TPD and DRIFTS. *Carbon* 36: 1821–1831.
- Drese, J.H., Choi, S., Lively, R.P., Koros, W.J., Fauth, D.J., Gray, M.L. and Jones, C.W. (2009). Synthesis-structure-property Relationships for Hyperbranched Aminosilica CO₂ Adsorbents. *Adv. Funct. Mater.* 19: 3821–3832.
- El-Hendawy, A.A., Alexander, A.J., Andrews, R.J. and Forrest, G.G. (2008). Effects of Activation Prepared from Cotton Stalks. *J. Anal. Appl. Pyrolysis* 82: 272–278.
- Figueiredo, J.L., Pereira, M.F.R., Freitas, M.M.A. and Orfão, J.J.M. (1999). Modification of the Surface Chemistry of Activated Carbons. *Carbon* 37: 1379–1389.
- Gómez-Serrano, V., Acedo-Ramos, M., López-Peinado, A.J. and Valenzuela-Calahorra, C. (1994). Oxidation of Activated Carbon by Hydrogen Peroxide. Study of Surface Functional Groups by FT-i.r.. *Fuel* 73: 387–395.
- Gray, M.L., Soong, Y., Champagne, K.J., Baltrus, J., Stevens Jr, R.W., Toochinda, P. and Chuang, S.S.C. (2004). CO₂ Capture by Amine-enriched fly Ash Carbon Sorbents. *Sep. Purif. Technol.* 35: 31–36.
- Hiyoshi, N., Yogo, K. and Yashima, T. (2005). Adsorption Characteristics of Carbon Dioxide on Organically Functionalized SBA-15. *Microporous Mesoporous Mater.* 84: 357–365.
- Hsiao, H.Y., Huang, C.M., Hsu, M.Y. and Chen, H. (2011). Preparation of High-surface-area PAN-based Activated Carbon by Solution-blowing Process for CO₂ Adsorption. *Sep. Purif. Technol.* 82: 19–27.
- Huang, H.Y., Yang, R.T., Chinn, D. and Munson, C.L. (2003). Amine-grafted MCM-48 and Silica Xerogel as Superior Sorbents for Acidic Gas Removal from Natural Gas. *Ind. Eng. Chem. Res.* 42: 2427–2433.
- Jansen, R.J.J. and van Bekkum, H. (1994). Amination and Ammoxidation of Activated Carbons. *Carbon* 32: 1507–1516.
- Le Leuch, L.M. and Bandosz, T.J. (2007). The Role of Water and Surface Acidity on the Reactive Adsorption of Ammonia on Modified Activated Carbons. *Carbon* 45: 568–578.
- Leal, O., Bolivar, C., Ovalles, C., Garcia, J.J. and Espidel, Y. (1995). Reversible Adsorption of Carbon Dioxide on Amine Surface-bonded Silica Gel. *Inorg. Chim. Acta* 240: 183–189.
- Lopez, M.C.B., Martinez-Alonso, A. and Tascon, J.M.D. (2000). Microporous Texture of Activated Carbon Fibres Prepared from Nomex Aramid Fibres. *Microporous Mesoporous Mater.* 34: 171–179.
- Mohammad, S.S., Wan, M.A.W.D., Amirhossein, H. and Ahmad, S. (2010). A Review on Surface Modification of Activated Carbon for Carbon Dioxide Adsorption. *J. Anal. Appl. Pyrolysis* 89: 143–151.
- Na, B.K., Koo, I.K., Eum, H.M., Lee, H. and Song, H.K. (2001). CO₂ Recovery from Flue Gas by PSA Process Using Activated Carbon, Korean. *J. Chem. Eng.* 18: 220–227.
- Pevida, C., Plaza, M.G., Arias, B., Feroso, J., Rubiera, F. and Pis, J.J. (2008). Surface Modification of Activated Carbons for CO₂ Capture. *Appl. Surf. Sci.* 254: 7165–7172.
- Pinero, E.R., Amoros, D.C. and Solano, A.L. (2003). The Role of Different Nitrogen Functional Groups on the Removal of SO₂ from Flue Gases by N-doped Activated Carbon Powders and Fibres. *Carbon* 41: 1925–1932.
- Plaza, M.G., Pevida, C., Arenillas, A., Rubiera, F. and Pis,

- J.J. (2007). CO₂ Capture by Adsorption with Nitrogen Enriched Carbons. *Fuel* 86: 2204–2212.
- Plaza, M.G., Pevida, C., Arias, B., Feroso, J., Arenillas, A., Rubiera, F. and Pis, J.J. (2008). Application of Thermogravimetric Analysis to the Evaluation of Aminated Solid Sorbents for CO₂ Capture. *J. Therm. Anal. Calorim.* 92: 601–606.
- Plaza, M.G., Pevida, C., Arias, B., Feroso, J., Rubiera, F. and Pis, J.J. (2009). A Comparison of Two Methods for Producing CO₂ Capture Adsorbents. *Energy Procedia* 1: 1107–1113.
- Plaza, M.G., Pevida, C., Martin, C.F., Feroso, J., Pis, J.J. and Rubiera, F. (2010). Developing Almond Shell-derived Activated Carbons as CO₂ Adsorbents. *Sep. Purif. Technol.* 71: 102–106.
- Plaza, M.G., Garcia, S., Rubiera, F., Pis, J.J. and Pevida, C. (2011). Evaluation of Ammonia Modified and Conventionally Activated Biomass Based Carbons as CO₂ Adsorbents in Postcombustion Conditions. *Sep. Purif. Technol.* 80: 96–104.
- Pradhan, B.K. and Sandle, N.K. (1999). Effect of Different Oxidizing Agent Treatments on the Surface Properties of Activated Carbons. *Carbon* 37: 1323–1332.
- Puri, B.R. (1970). *Chemistry and Physics of Carbon*, Walker Jr. P.L. (Ed.), Marcel Dekker, New York, p. 191–282.
- Rao, A.B. and Rubin, E.S. (2002). A Technical, Economic, and Environmental Assessment of Amine-based CO₂ Capture Technology for Power Plant Greenhouse Gas Control. *Environ. Sci. Technol.* 36: 4467–4475.
- Rege, S.U. and Yang, R.T. (2001). A Novel FTIR Method for Studying Mixed Gas Adsorption at Low Concentrations: H₂O and CO₂ on NaX Zeolite and γ -alumina. *Chem. Eng. Sci.* 56: 3781–3796.
- Shin, S., Jang, J., Yoon, S.H. and Mochida, I. (1997). A Study on the Effect of Heat Treatment on Functional Groups of Pitch Based Activated Carbon Fiber Using FTIR. *Carbon* 35: 1739–1743.
- Silva, A.M.T., Machado, B.F., Figueiredo, J.L. and Faria, J.L. (2009). Controlling the Surface Chemistry of Carbon Xerogels Using HNO₃-hydrothermal Oxidation. *Carbon* 47: 1670–1679.
- Stoeckli, F., Centeno, T.A., Fuertes, A.B. and Muniz, J. (1996). Porous Structure of Polyarylamide-based Activated Carbon Fibres. *Carbon* 34: 1201–1206.
- Stöhr, B., Boehm, H.P. and Schlögl, R. (1991). Enhancement of the Catalytic Activity of Activated Carbons in Oxidation Reactions by Thermal Treatment with Ammonia or Hydrogen Cyanide and Observation of a Superoxide Species as a Possible Intermediate. *Carbon* 29: 707–720.
- Tamon, H. and Okazaki, M. (1996). Influence of Acidic Surface Oxides of Activated Carbon on Gas Adsorption Characteristics. *Carbon* 34: 741–746.
- Thiruvengkatachari, R., Su, S., An, H. and Yu, X.X. (2009). Post Combustion CO₂ Capture by Carbon Fibre Monolithic Adsorbents. *Prog. Energy Combust. Sci.* 35: 438–455.
- Vinke, P., van der Eijk, M., Verbree, M., Voskamp, A.F. and van Bekkum, H. (1994). Modification of the Surfaces of a Gasactivated Carbon and a Chemically Activated Carbon with Nitric Acid, Hypochlorite, and Ammonia. *Carbon* 32: 675–686.
- Wang, B., Cote, A.P., Furukawa, H., O’Keefe, M. and Yaghi, O.M. (2008). Colossal Cages in Zeolitic Imidazolate Frameworks as Selective Carbon Dioxide Reservoirs. *Nature* 453: 207–211.
- Yu, C.H., Huang, C.H. and Tan, C.S., (2012). A Review of CO₂ Capture by Absorption and Adsorption. *Aerosol Air Qual. Res.* 12: 745–769.
- Zawadzki, J. (1989). IR Spectroscopy in Carbon Surface Chemistry, In *Chemistry and Physics of Carbon*, Vol. 21, Thrower, P.A. (Ed.), Marcel Dekker, New York, p. 180–200.
- Zhang, Z., Xu, M., Wang, H. and Li, Z. (2010). Enhancement of CO₂ Adsorption on High Surface area Activated Carbon Modified by N₂, H₂ and Ammonia. *Chem. Eng. J.* 160: 571–577.

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