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Enhancement of CO_2 adsorption on high surface area activated carbon modified by N_2, H_2 and ammonia

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ABSTRACT

The activated carbons (ACs) with high surface area were modified separately by using ammonia aqueous solution impregnation and microwave irradiation in an atmosphere of N_2 or H_2 in order to improve their adsorption properties toward CO_2. The modified ACs were characterized, and the surface chemical properties of the ACs were determined separately by FTIR, Boehm titration and X-ray photoelectron spectroscopy (XPS) methods. The isotherms of CO_2 on the modified ACs were measured. Results showed that after surface modification, the contents of elements C and N of the samples increased, while that of the element O of the samples decreased in comparison with the original AC. Correspondingly, the amounts of the surface basic groups of the modified ACs increased, while those of the surface acidic groups decreased as compared to the original AC. The use of microwave irradiation in an atmosphere of N_2 to modify the carbon can make the total basic groups of the surfaces of the ACs be the highest among the modified ACs. As a consequence of that, the modified AC samples had higher adsorption capacities of CO_2 than the original AC, and the more the surface basic groups of the ACs, the higher the adsorption capacity of the ACs for CO_2. The amount adsorbed of CO_2 on the modified AC by the microwave irradiation in the atmosphere of N_2 was up to 3.75 mmol/g at 1 atm and 293 K, having an increase of 28% in comparison with the original AC.

1. Introduction

CO_2 is a ubiquitous species that has received much attention recently because of its greenhouse gas effect. Fossil fuels as non-renewable resources are the major source of energy for the coming few decades in global. The burning of fossil fuels produces around 21.3 billion tons of CO_2 per year and thus leads to severely adverse impacts on the environment, like air pollution and global warming [1]. Therefore, the development of an efficient and economical way to reduce the emission of CO_2 from energy production is becoming increasingly urgent to control carbon dioxide concentration in the earth's atmosphere. The removal of CO_2 from industrial emissions has become essential in the fight against climate change [2]. Currently, a variety of methods, such as membrane separation, chemical absorption and adsorption, have been proposed to sequester CO_2 from the flue gases from the combustion of fossil fuels. Thereinto, the adsorption is considered as one of the most promising technologies in the commercial and industrial applications because of the low energy requirement, cost advantage, and ease of applicability over a relatively wide range of temperatures and pressures [3]. However, the success of this approach is dependent on the development of a low cost adsorbent with a high CO_2 selectivity and adsorption capacity. Hence, recently, there have been many research activities which were focused on development of novel adsorbents such as metal-organic frameworks (MOFs) for CO_2 adsorption or surface modification of adsorbents such as zeolite, molecular sieve 4A and activated carbon (AC) for enhancing CO_2 adsorption.

Walton et al. [4] studied the CO_2 adsorption on Y and X zeolites, and reported that after the zeolites were modified by alkali metal cation exchange, their adsorption capacities for CO_2 were improved. Othman et al. [5] synthesized hydrotalcite by co-precipitation using a metal nitrate precursor and potassium carbonate with a Mg:Al ratio of 3:1, and found that CO_2 adsorption was improved when the Mg–Al hydrotalcite was coated on commercial zeolites. Yavuz et al. [6] prepared gallium (10 mol% substituted for Al) substituted hydrotalcites (Ga-SHT), and then modified the Ga-SHT using an impregnation of potassium carbonate aqueous solution. It was found that the resulting K_2CO_3-promoted calcined Ga-SHT-1 had a very good performance of CO_2 adsorption. Chang et al. [7] used ç-(aminopropyl)triethoxysilane (APTS) to modify SBA-15, and reported that the CO_2 adsorption on the amine-grafted SBA-15 was greatly improved. Yang and his co-workers [8] synthesized amine surface modified silica xerogel and MCM-48 materials,

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and found that the prepared sorbents were able to selectively bind the acidic gases CO_2 and H_2S due to presence of large amounts of basic amine groups on their surfaces. In addition, activated carbon (AC) was also considered as a highly potential adsorbent for CO_2 adsorption. Grande et al. [9] investigated the adsorption equilibrium of five pure gases (H_2, CO_2, CH_4, CO and N_2) on AC, and demonstrated that CO_2 was the most adsorbed gas followed by CH_4, CO, N_2, and H_2. They suggested that the AC was suitable for selective removal of CO_2 and CH_4 present in off-gases from the steam reforming of methane for hydrogen production. Arenillas et al. [10] prepared low cost carbon materials derived from fly ash, and impregnated them with organic bases. The results showed that the addition of polyethylene glycol (PEG) enhanced the CO_2 adsorption capacity and reduced the time taken for the sample to reach equilibrium. Drage et al. [11] produced two nitrogen enriched carbons from the chemical activation of urea-formaldehyde and melamine-formaldehyde resins using K_2CO_3, and then found that the carbons prepared by chemical activation were much more effective for CO_2 adsorption compared to that generated by physical activation. Thote et al. [12] synthesized an in situ nitrogen enriched carbon by chemical activation using zinc chloride followed by physical activation using CO_2. The results showed that the CO_2 breakthrough adsorption capacity of the nitrogen enriched carbon was two times higher than that of the commercially available ACs. Maroto-Valer et al. [13] prepared ACs with anthracites, and then modified the ACs by NH_3 heat treatment and polyethylenimine (PEI) impregnation. Finally, it was found that the CO_2 capture capacity of the modified ACs was improved due to introduction of alkaline nitrogen groups on the surface. However, Plaza et al. [14] used a commercial AC as a preliminary support, and then tried to modify the AC by using impregnation to make amine be coated on the surfaces of AC. Unfortunately, it was found that the adsorption capacity of the modified AC for CO_2 decreased because of drastic reduction of the microporous volume of the modified AC caused by amine impregnation.

The objective of this work is to investigate the enhancement of CO_2 adsorption on ACs with high surface area modified by using microwave irradiation under N_2 or H_2 flows and ammonia impregnation. The textural structures of the modified ACs with high surface area were characterized. The surface oxygen-containing groups, surface acidity/basicity strengths and the contents of elements on the surfaces of the ACs were further analyzed by Fourier transform infrared spectroscopy (FTIR), Boehm titration and X-ray photoelectron spectroscopy (XPS) separately. The isotherms of CO_2 on the modified ACs were measured. The influence of the surface chemistry of the modified ACs on their adsorption capacities for CO_2 was discussed and reported here.

2. Experimental

2.1. Materials and instruments

Original AC with high surface area was purchased from Tangshan Solid Carbon Co. Ltd. of Hebei (Hebei, China). The particle size was in the range of 300–400 mesh.

Magnetic suspension balance RUBOTHERM was supplied by Germany. Its precision was 0.000001 g. ASAP 2010 sorptometer was supplied by Micromeritics Company, USA. Microwave accelerated reaction system Mars5 was supplied by CEM Company, USA.

2.2. Modification of ACs

The original AC with high surface area was demineralized with the concentrated HF (0.1 mol/L) and HCl (0.1 mol/L) acids (ash content 0.1 wt%) for 3 h, separated by filtration, and then washed with deionized water until the aqueous solution showed a pH value of 7. After that, the AC was dried at 383 K for 24 h for surface modification.

2.2.1. Surface modification of ACs by ammonia impregnation

Firstly, 50 mL of ammonia aqueous solution (3 mol/L) was added to 0.5 g of the original AC placed in a 100 mL glass beaker, and then the glass beaker was placed in a thermostated bath and shaken for 24 h at room temperature. Secondly, the prepared sample was put into an evacuated vessel placed in an oil bath whose temperature was 250 °C until the ammonia evaporated completely. After that, the mixture was washed with deionized water and filtered until the filtrate showed a pH value of 7. Finally, the sample was dried at 383 K for 24 h. The obtained sample was denoted as AAC.

2.2.2. Surface modification of ACs by using microwave irradiation in the atmosphere of nitrogen

Firstly, 0.5 g of the original AC was put in a quartz reactor, and then the quartz reactor was placed inside a multimode resonant microwave cavity. Secondly, the sample in the quartz reactor was heated using microwave irradiation with an input power of 600 W in a nitrogen atmosphere for 5 min, and then cooled-down. Finally, the obtained sample was labeled as NAC.

2.2.3. Surface modification of ACs by using microwave irradiation in the atmosphere of hydrogen

Firstly, 0.5 g of the original AC was put in a quartz reactor, and then the quartz reactor was placed inside a multimode resonant microwave cavity. Secondly, the sample in the quartz reactor was heated using microwave irradiation with an input power of 600 W in a hydrogen atmosphere for 30 min, and then cooled-down. Finally, the obtained sample was labeled as HAC.

2.3. Pore structure characterization

The textural parameters of all the ACs studied were determined by nitrogen adsorption experiments at the liquid nitrogen temperature 77 K with the help of ASAP 2010 instrument equipped with commercial software of analysis and calculation. The samples were separately degassed at 523 K for 5 h in a vacuum environment before the nitrogen adsorption measurements. The specific surface area was calculated from the adsorption isotherm using the standard Brunauer–Emmett–Teller (BET) equation, using a nitrogen molecule surface area of 0.162 nm^2. The pore size distribution (PSD) was determined using Density Functional Theory (DFT) based on statistical mechanics. The total pore volume was evaluated by converting the adsorption amount at $p/p_0 = 0.95$ to a volume of liquid adsorbate. The micropore area and volume were obtained using the *t*-plot method of Lippens and de Boer to the adsorption data. The mean micropore diameter was calculated from the Hovath–Kawazoe (H–K) equation. The mean mesopore diameter was measured from the Barrett–Joyner–Halenda (BJH) model. The average pore diameter $D_p = 4V_p/S_{BET}$ (assuming a cylindrical shape of pores) was calculated from the BET surface area and pore volume.

2.4. Boehm titration

The Boehm titration method can be used to determine the number of surface functional groups. 1 g sample of a given AC was weighed carefully and placed into a vial containing 25 mL of each of the following 0.1 mol/L aqueous solution: hydrochloric acid, sodium hydroxide, sodium carbonate, sodium bicarbonate and sodium ethoxide, respectively. These vials were then sealed, stirred by shaking for 48 h at 25 °C and filtered. Then, 5 mL of each filtrate was pipetted and the excess base or acid contained therein was titrated with HCl or NaOH, respectively. The suspensions were continuously influxed with purified helium gas to eliminate atmospheric CO_2 and stirred throughout the measurement. The titration was performed using an automatic Metrohm 702 Titrino titrator (Metrohm, Switzerland) at the pH range of 2.0–11.0. The numbers of different acidic sites were then calculated assuming that NaOH neutralizes carboxylic, hydroxylic (phenolic) and lactonic groups, Na_2CO_3 neutralizes carboxylic and lactonic groups, $NaHCO_3$ neutralizes only carboxylic groups, and sodium ethoxide neutralizes carbonyl groups (in aqueous solutions). The number of basic sites could be calculated from the amount of HCl that reacted with the basic groups of the carbon surfaces [15].

2.5. X-ray photoelectron spectroscopy (XPS)

XPS was used to determine the number and type of functional groups presented on the surfaces of the modified ACs. A PHI5300 X-ray photoelectron spectrometer with a nonmonochromatized Al Kα radiation (1486.6 eV) was used for this analysis. The source was operated at 15 kV and 34 mA. Prior to examination, the samples were dried at 100 °C under vacuum for 2 h to remove adsorbed contaminants. XPS was run in retarding mode using survey pass energy of 89.45 eV and multiplex pass energy of 35.75 eV. The vacuum in the analysis chamber was always better than 5×10^{-10} Pa. Atomic ratios were calculated from the XPS survey spectra after correcting the relative peak areas by sensitivity factors based on the transmission characteristics of the Physical Electronics XPS apparatus.

2.6. Fourier transform infrared spectroscopy (FTIR)

The surface organic FTIR spectra were taken with a Bruker 550 FTIR instrument. Data acquisition was performed automatically using an interfaced computer and a standard software package. The samples were dried under vacuum at 150 °C prior to be mixed with KBr powder. The samples were run in ratio mode allowing for subtraction of a pure KBr baseline. The sample chamber was kept purged with nitrogen during the entire experiment. The spectrometer collected 64 spectra in the range of 400–4000 cm^{-1}, with a resolution of 4 cm^{-1}.

2.7. CO_2 adsorption measurement

The CO_2 adsorption–desorption isotherms at 298 K and 328 K were obtained separately on a RUBOTHERM magnetic suspension balance. The initial activation of the AC and the modified ACs were carried out at 523 K for 10 h in a vacuum environment. He (Ultra high purity, U-sung) was used as a purge gas in this study. The adsorption and the desorption processes were both carried out using high purity CO_2 (99.999%) gas. The buoyancy measurement was performed using ultra high purity He (99.999%) gas. A feed flow rate of 60 mL/min and 30 mL/min of CO_2 and He, respectively, were controlled with a mass flow controller (MFC) to the sample chamber. Both adsorption and desorption processes were conducted at the same temperature within a pressure range of 0–30 bar. The temperature of the sorption chamber can be adjusted and maintained constant by an internal temperature sensor. And the pressure can be changed stepwise through the gas flow rate.

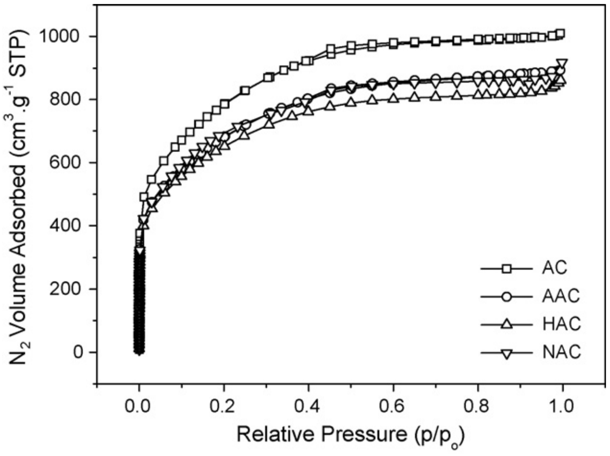

Fig. 1. N_2 adsorption–desorption isotherms of ACs.

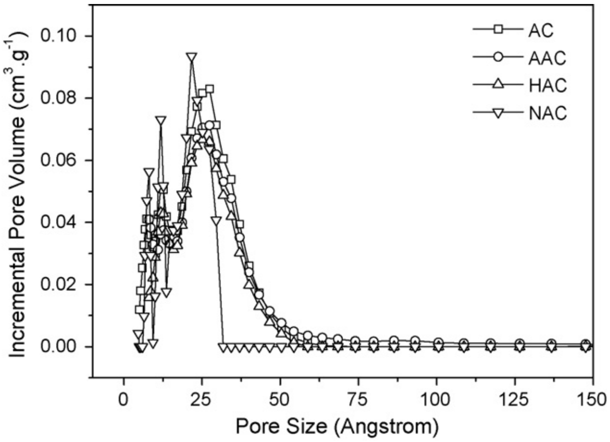

Fig. 2. DFT pore size distribution for ACs.

3. Results and discussion

3.1. Textural properties

Fig. 1 presents the adsorption–desorption isotherms of N_2 on the AC, AAC, HAC and NAC. It can be seen from Fig. 1 that the tested ACs all show the type I isotherm, indicating that there are mainly micropores in the AC materials. Fig. 2 shows the DFT pore size distributions for the ACs. It indicates that the ACs have mainly micropores and also have some mesopores. Table 1 lists the structure parameters of the ACs. The data in Table 1 indicated that the BET surface area and total pore volume of the AAC, HAC and NAC became somewhat smaller compared to the original AC, which may be due to the collapse of the pore walls at high temperatures [16]. The surface

Table 1
Porous structure parameters of the ACs.

Sample	BET surface area ($m^2 g^{-1}$)	Micropore area ($m^2 g^{-1}$)	Micropore volume ($cm^3 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	Average pore diameter (nm)	Micropore diameter (nm)	Mesopore diameter (nm)
AC	2829	2664	1.38	1.55	2.19	0.533	2.69
AAC	2461	2270	1.17	1.38	2.77	0.532	2.77
HAC	2350	2218	1.14	1.30	2.79	0.532	2.79
NAC	2546	2409	1.12	1.47	2.86	0.528	2.86

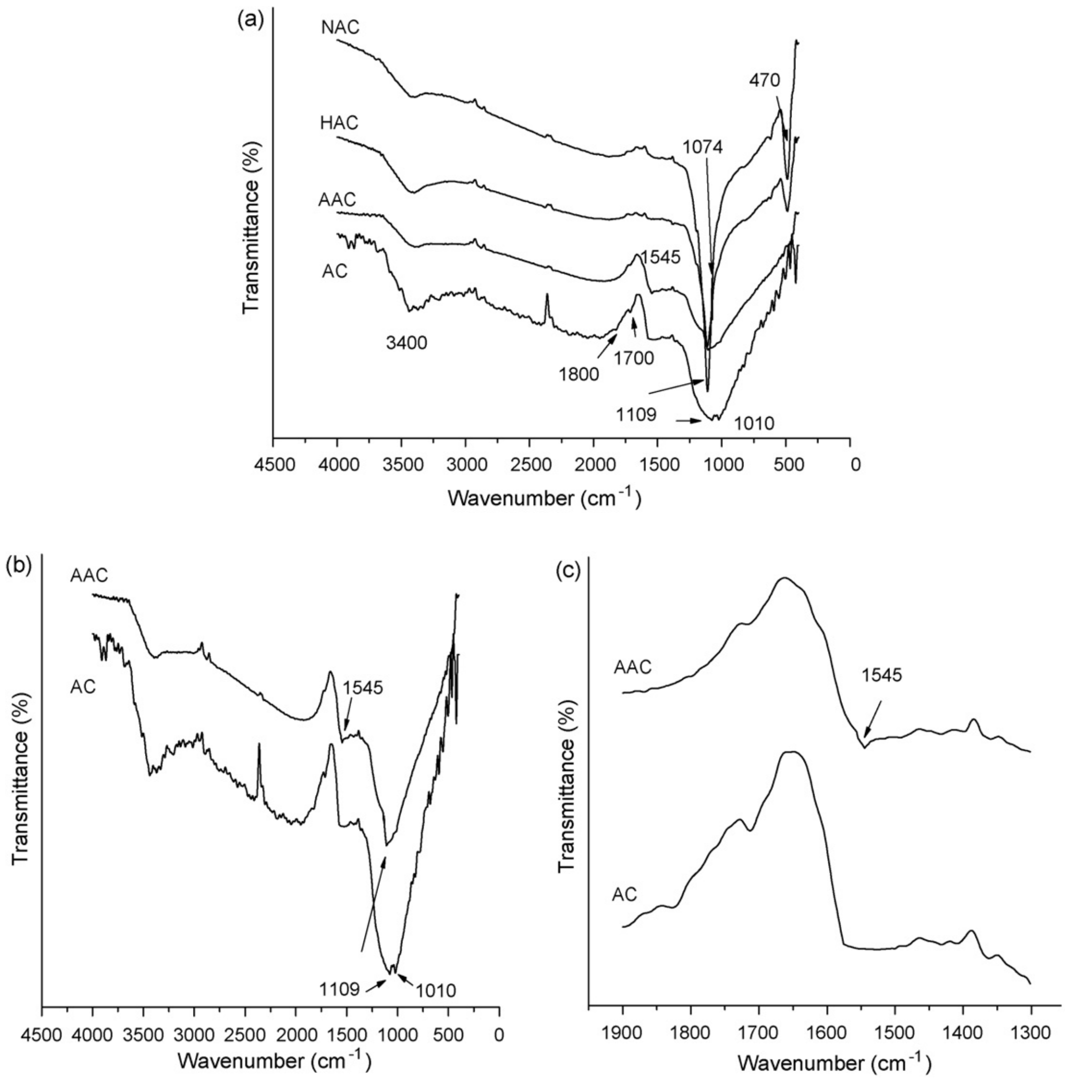

Fig. 3. (a) FTIR spectra for the original AC and the modified ACs. (b) The enlarged spectra of sample AC and AAC between 4000 and 400 cm^{-1}. (c) The enlarged spectra of sample AC and AAC between 1900 and 1300 cm^{-1}.

area of the ACs followed the order: AC > NAC > AAC > HAC. The average pore diameter of the modified samples increased somewhat as compared to the original AC.

3.2. FTIR and Boehm titration

Fig. 3a shows FTIR spectra of the original AC and the modified ACs. On the one hand, the spectra of these samples show some marked similarities. For example, the spectra of all ACs show presence of bands at 3000–2700, 1750–1630, and 1600–1450 cm^{-1}, which could be assigned to aliphatic C–H stretching modes, C=O (carboxylic and lactones), C=C, respectively. It suggests that they could possess similar groups on their surfaces. On the other hand, the spectra of these samples show some differences. For example, the spectra of the modified ACs were different from that of the original AC in that (1) the peak at around 3400 cm^{-1} which was assigned to carboxylic group O–H stretching [17,18] was more pronounced on the AC than those on the modified ACs, indicating that the content of the carboxylic group on the AC was higher than those on the modified ACs; (2) the peak at 1109 cm^{-1} for the modified ACs was more evident than that for the AC, as shown in Fig. 3a as well as Fig. 3b, which corresponded to the C–O bond stretching of CH_2–OH units; and (3) a new band related to N-containing species (at 1545 cm^{-1}, cyclic amides [19]) was observed in the spectrum of the AAC as shown in Fig. 3c, implying that the use of ammonia modification produced new nitrogen surface complexes [20,21]; (4) for the samples NAC and HAC two peaks at 1074 and 470 cm^{-1} assigned to the vibrational modes CN and C–N–C [16], respectively, of the amine group were also detected on the spectrums of the NAC and HAC, as shown in Fig. 3a, suggesting that some basic groups

Table 2
Boehm titration of surface groups on different activated carbons.

ACs	Carboxyl (mmol/g)	Lactone (mmol/g)	Hydroxyl (mmol/g)	Carbonyl (mmol/g)	Total basic (mmol/g)
AC	0.071	0.053	0.162	0.143	0.294
AAC	0.010	0.105	0.056	0.054	0.551
HAC	0.010	0.100	0.048	0.048	0.614
NAC	0.015	0.056	0.038	0.000	0.714

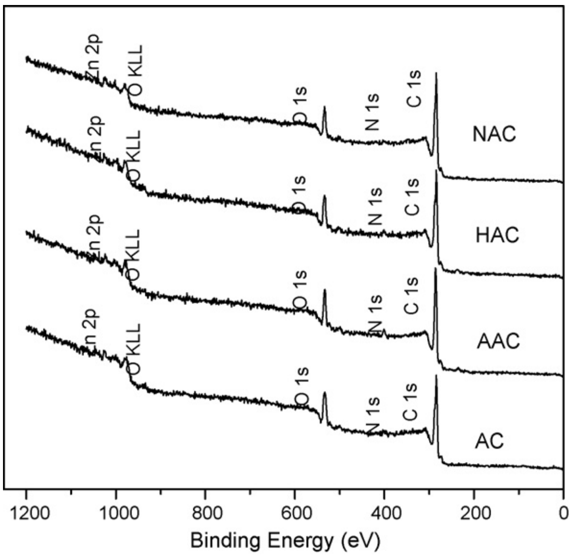

Fig. 4. XPS spectra of the AC samples.

were formed during the microwave treatment; (5) the intensity of the bands in the carbonyl region (1700 + 1800 cm^{-1}) on the spectrum of the HAC and NAC decreased, indicating that the content of carbonyl on the two samples decreased as compared to that on the AC, as shown in Fig. 3a; and (6) there was a shoulder peak at 1010 cm^{-1} assigned to $C{=}O$ on the spectrum of the AC, while there was no shoulder peak at 1010 cm^{-1} on the spectrum of the modified ACs, as shown in Fig. 3a.

Table 2 lists the surface acidity and basicity strengths of the modified ACs as obtained via the Boehm titration method. The data in Table 2 indicated that after ACs were modified separately by using the ammonia impregnation and the microwave irradiation in the atmosphere of H_2 or N_2, the amounts of the basic groups on the surfaces of the modified ACs became more, while the amounts of the acidic groups got fewer in comparison with that on the original AC. It indicated that the surface modification of the ACs with the ammonia impregnation and the microwave irradiation in the atmosphere of H_2 or N_2 can obviously increase the total basic groups on the surfaces of the ACs. The amounts of the surface basic groups on the ACs followed the order: NAC > HAC > AAC > AC.

It should be mentioned that the use of N_2 to modify the carbon surfaces can make the total basic groups on the carbon surfaces the highest and the total acidic groups of the carbon surfaces the lowest within the modified ACs. This is because activated carbon is a good microwave absorber, and it receives microwave energy directly through dipole rotation and ionic conduction. During microwave treatment in a N_2 atmosphere, the temperature of the ACs rapidly and uniformly rises, and as a consequence, the acidic groups on the carbon surfaces would be decomposed and removed in the form of CO or CO_2 [22,23], and meanwhile some N from N_2 atmosphere may be reacted with the carbon surfaces to form nitrogen-containing complexes. As a result, the relative content of basic groups on the NAC increased obviously.

3.3. X-ray photoelectron spectroscopy (XPS) analysis

The surface binding and elemental speciation of the AC samples were analyzed by X-ray photoelectron spectroscopy (XPS). Fig. 4 shows the XPS spectra of the samples. It can be seen that there were four distinct peaks due to the existence of carbon, oxygen, nitrogen and zinc. Table 3 shows the XPS results of the ACs concerning the surface elemental compositions. The amounts determined for C, O, N and Zn were calculated from the corresponding peak areas divided by the appropriate sensitivity factors (0.314 for C, 0.733 for O, 0.499 for N and 2.768 for Zn).

Table 3
Surface composition from XP spectra.

Samples	Atomic concentration (%)			
	C (%)	O (%)	N (%)	Zn (%)
AC	79.50	17.11	1.80	1.59
AAC	81.81	14.47	2.51	1.21
HAC	83.75	11.61	2.96	1.68
NAC	84.58	11.32	2.22	1.89

The data in Table 3 indicated that after the AC samples were modified by using the ammonia impregnation and the microwave irradiation in the atmosphere of N_2 or H_2, the N atomic concentration on their surfaces increased, while the O atomic concentration on their surfaces decreased. This is because the temperature of the ACs rapidly and uniformly rises during microwave treatment, and thus, the acidic oxygen-containing groups on the carbon surfaces would be decomposed and removed in the form of CO or CO_2 [22,23] if the microwave treatment of the AC is in the N_2 atmosphere, or in the form of CO or CO_2 and H_2O if the microwave treatment of the AC is in the H_2 atmosphere. On the other hand, nitrogen is usually present in the form of thermally stable quaternary groups contained within the aromatic structure of the carbon layer planes, and hence its remove seem more difficult in comparison with the decomposition and removal of the acidic oxygen-containing groups during microwave treatment. As a result, the relative content of O decreased, while the relative content of N on the NAC and HAC increased, which would improve the basicity of the surfaces of the HAC and NAC. As to the AAC treated by ammonia impregnation, since its treatment temperature was lower, 110–250 °C, only a few acidic oxygen-containing groups that were originally present on the carbon surfaces would be removed. Thus, the O atomic concentration of the AAC was higher than that of the HAC and NAC. The O atomic concentration of the sample surfaces followed the order: AC > AAC > HAC > NAC.

Since the original AC was prepared by activation with $ZnCl_2$, element Zn is present in all the ACs. The slight decrease of Zn content on the surface of AAC may result from the removal during ammonia impregnation.

Generally, the higher the oxygen atomic concentration of carbon surfaces, the greater its surface acidity was [24]. Therefore, it could be deduced that the surface acidic strength of the samples studied followed the order: AC > AAC > HAC > NAC, which corresponded to the order of total acid concentrations of the samples studied as shown in Table 3.

3.4. Isotherms of CO_2 on the modified ACs

Figs. 5 and 6 show separately the isotherms of CO_2 on the AC and modified AC samples at 298 K and 328 K in the range of the pressures from vacuum to 30.0 bar. It can be seen that the amounts adsorbed of CO_2 on all the samples decreased with temperature, and the lower the temperature, the larger the amounts adsorbed of CO_2. It indicated that physical adsorption dominated the CO_2 adsorption within the ACs. More importantly, it was observed that the modified ACs had higher adsorption capacities of CO_2 compared to the original AC, and the amounts adsorbed of CO_2 on these ACs followed the order: NAC > HAC > AAC > AC. It meant that after surface modification, the adsorption capacities of the modified ACs for CO_2 were improved. It was noticed that there was no apparent relationship between the sample surface area and its adsorption capacity for CO_2. In addition, it was found that the more the total basic groups on the surfaces of the modified AC, the higher its adsorption capacity of CO_2. In other words, the less the total acidic

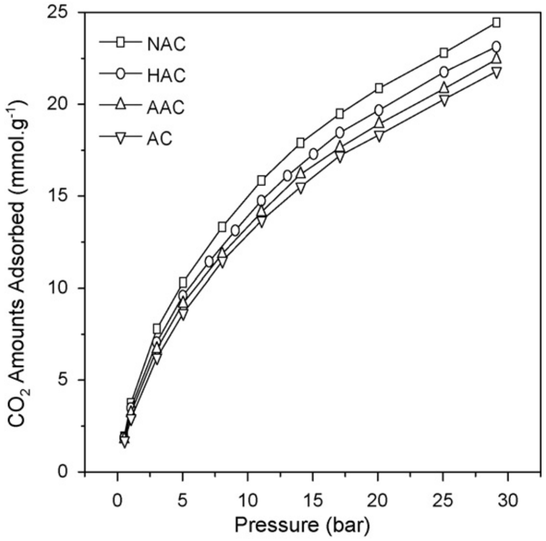

Fig. 5. Isotherms of CO_2 on different ACs at 298 K.

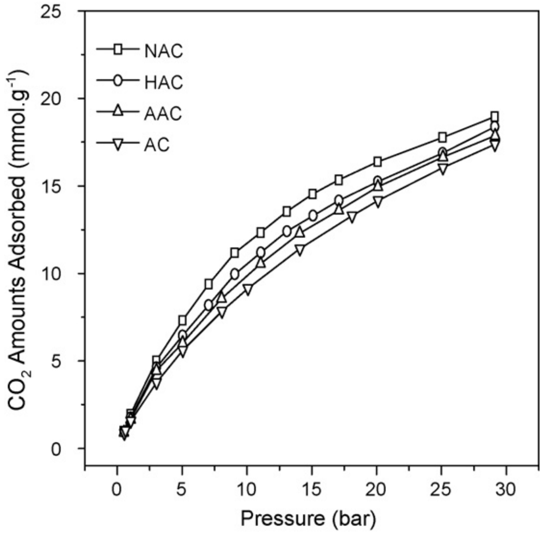

Fig. 6. Isotherms of CO_2 on different ACs at 328 K.

groups on the carbon surfaces, the higher the adsorption capacity of the ACs for CO_2, as indicated in Table 2. Since CO_2 is one kind of acidic gas, and possesses a strong quadrupole moment, the increase in the basicity of carbon surfaces will strengthen the interaction of CO_2 with the surfaces of the ACs, especially with nitrogen having moderately strong quadrupole, and thus the adsorption capacity of the ACs for CO_2 is improved. Generally speaking, the basicity of the carbon comes from the basic groups or basic nitrogen-containing groups on the surfaces of the ACs. That there are more basic nitrogen-containing groups on the surfaces would produce more adsorption sites for CO_2 adsorption. In addition, the decrease of acidic oxygen-containing groups on the carbon surfaces would facilitate the production of more basic groups on the surfaces. The order of the adsorption capacity of these ACs for CO_2 is nearly in agreement with the order of the total basic group concentrations on the carbon surfaces. Thus it was inferred that the surface basic chemical groups on the AC samples played a key role in the enhancement of CO_2 adsorption. Therefore, in order to improve the adsorption performance of the ACs for CO_2, the application of surface modification to increase the surface basic groups and decrease the acidic oxygen-containing groups surfaces are effective.

For comparison, Table 4 lists the adsorption capacities of some adsorbents reported by other investigators and available in present work for CO_2 adsorption. A comparison of these data in Table 4 indicates that the modified AC samples have a higher adsorption capacity of CO_2 than some materials, such as zeolite 13X and MOFs at 1 atm pressure and 298 K. Furthermore, it should be mentioned that at higher pressure, the adsorption capacity of the NAC for CO_2 was up to 20 mmol/g at 30 bar, which was higher than those of MOFs [32] and MIL-53 [33].

In order to describe the CO_2 adsorption behaviour on these ACs clearly, the Langmuir equation was used to fit the isotherms. The Langmuir model can be represented as follows [34]:

$$q_i = \frac{q_{\max} K P_i^*}{1 + K P_i^*} \tag{1}$$

or

$$\frac{P^*}{q} = \frac{1}{q_{\max} K} + \frac{P^*}{q_{\max}} \tag{2}$$

where q_i is the amount adsorbed in equilibrium with the concentration of adsorbate in gas phase (mg/g), $q_{\max}$ is the maximum adsorption amount (mg/g), P^* is the equilibrium pressure of the adsorbate in gas phase (bar), and K is the equilibrium constant of adsorption. In the model, $q_{\max}$ and K can be calculated from the linear plots of p/q versus p.

Table 5 presents the parameters of the Langmuir equation as well as the correlation coefficients (r^2) for the linear regression of the data presented in Figs. 5–6. The linear correlation of the data was good because the correlation coefficients r^2 were up to 0.99. It meant the adsorption behaviours of CO_2 on all four adsorbents can be well described by the Langmuir adsorption equation. The Langmuir isotherm model provides a good representation of the equilibrium data. The data in Table 5 also indicated that the $q_{\max}$ values of CO_2 on the NAC was the highest among the four

Table 4
Comparison of adsorption capacity of the modified ACs with those of various adsorbents (conditions: 1 atm and room temperature).

Adsorbent	Adsorption capacity (mmol/g)	Pressure (atm)	Temperature (K)	Reference
Zeolite 13X	1.77	1.0	293	[25]
All-silica DD3R zeolite	1.7	2.0	298	[26]
Activated carbon	1.5	1.0	298	[27]
AlPO4-14	2.0	1.0	300	[28]
MOF-505	3.3	1.0	298	[29]
Norit RB2	2.5	1.0	298	[30]
IRMOF-1	1.92	1.0	208	[30]
IRMOF-11	1.8	1.1	298	[30]
ZIF-100	1.05	1.0	298	[31]
AC	2.92	1.0	298	In present
AAC	3.22	1.0	298	In present
HAC	3.49	1.0	298	In present
NAC	3.75	1.0	298	In present

Table 5
Parameters obtained by fitting of Langmuir equation.

Adsorbents	Temperature (K)	Langmuir		
		$q_{\max}$ (mg/g)	K	r^2
AC	298	1258.5	0.0927	0.992
	328	1160.1	0.0583	0.995
AAC	298	1263.2	0.1010	0.991
	328	1208.2	0.0600	0.995
HAC	298	1301.8	0.1010	0.990
	328	1214.8	0.0631	0.997
NAC	298	1357.2	0.1080	0.993
	328	1219.7	0.0728	0.999

AC samples, and the maximum adsorption capacity $q_{\max}$ of those adsorbents became lower with the increase of temperature, suggesting that the adsorption of CO_2 on those adsorbents was physical adsorption.

4. Conclusions

The use of ammonia impregnation and microwave irradiation in the atmosphere of N_2 or H_2 to modify the AC can enhance its adsorption capacity of CO_2. When the AC was modified, the amounts of the basic groups on the carbon surfaces became more, while the amounts of the acidic groups got fewer as compared to the original AC. It meant that the surface modification brought about a variation in surface acidic/basic groups on the ACs. The amounts of the surface basic groups on the ACs followed the order: NAC > HAC > AAC > AC, suggesting that the use of microwave irradiation in the atmosphere of N_2 to modify the carbon surfaces can make the surface basic group concentration of the ACs the highest among these ACs. As a consequence of that, the modified ACs had higher adsorption capacities of CO_2 compared to the original AC. And the more the total basic groups on the surfaces of the carbon, the higher its adsorption capacity of CO_2. The amounts adsorbed of CO_2 on these ACs followed the order: NAC > HAC > AAC > AC. The amount adsorbed of CO_2 on the NAC was up to 3.75 mmol/g at 1 atm and 298 K, having an increase of 28% in comparison with the original AC with high surface area. The adsorption of CO_2 on all the four adsorbents can be well described by the Langmuir adsorption equation.

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References

[1] R. Heinberg, The Party's Over: Oil, War and the Fate of Industrial Societies, New Society Publishers, Gabriola Island, Canada, 2005.
[2] IEA Greenhouse Gas R&D Programme, CO_2 Capture and Storage, 2006.
[3] A. Duffy, G.M. Walker, S.J. Allen, Investigation on the adsorption of acidic gases using activated dolomite, Chem. Eng. J. 117 (2006) 239–244.
[4] K.S. Walton, M.B. Abney, M.D. LeVan, CO_2 adsorption in Y and X zeolite modified by alkali metal cation exchange, Micropor. Mesopor. Mater. 91 (2006) 78–84.
[5] M.R. Othman, N.M. Rasid, W.J.N. Fernando, Mg–Al hydrotalcite coating on zeolites for improved carbon dioxide adsorption, Chem. Eng. Sci. 61 (2006) 1555–1560.
[6] C.T. Yavuz, B.D. Shinall, A.V. Iretskii, M.G. White, T. Golden, M. Atilhan, P.C. Ford, G.D. Stucky, Markedly improved CO_2 capture efficiency and stability of gallium substituted hydrotalcites at elevated temperatures, Chem. Mater. 21 (2009) 3473–3475.
[7] A.C.C. Chang, S.S.C. Chuang, M. Gray, Y. Soong, In-situ infrared study of CO_2 adsorption on SBA-15 grafted with gamma-(aminopropyl)triethoxysilane, Energy Fuels 17 (2003) 468–473.
[8] H.Y. Huang, R.T. Yang, D. Chinn, C.L. Munson, Amine-grafted MCM-48 and silica xerogel as superior sorbents for acidic gas removal from natural gas, Ind. Eng. Chem. Res. 42 (2003) 2427–2433.
[9] C.A. Grande, F.V.S. Lopes, A.M. Ribeiro, J.M. Loureiro, A.E. Rodrigues, Adsorption of off-gases from steam methane reforming (H_2, CO_2, CH_4, CO and N_2) on activated carbon, Sep. Sci. Technol. 43 (2008) 1338–1364.
[10] A. Arenillas, K.M. Smith, T.C. Drage, C.E. Snape, CO_2 capture using some fly ash-derived carbon materials, Fuel 84 (2005) 2204–2210.
[11] T.C. Drage, A. Arenillas, K.M. Smith, C. Pevida, S. Piippo, C.E. Snape, Preparation of carbon dioxide adsorbents from the chemical activation of urea-formaldehyde and melamine-formaldehyde resins, Fuel 86 (2007) 22–31.
[12] J.A. Thote, K.S. Iyer, R. Chatti, N.K. Labhsetwar, R.B. Biniwale, S.S. Rayalu, In situ nitrogen enriched carbon for carbon dioxide capture, Carbon 48 (2010) 396–402.
[13] M.M. Maroto-Valer, Z. Tang, Y.Z. Zhang, CO_2 capture by activated and impregnated anthracites, Fuel Process. Technol. 86 (2005) 1487–1502.
[14] M.G. Plaza, C. Pevida, A. Arenillas, F. Rubiera, J.J. Pis, CO_2 capture by adsorption with nitrogen enriched carbons, Fuel 86 (2007) 2204–2212.
[15] H.P. Boehm, Surface oxides on carbon and their analysis: a critical assessment, Carbon 40 (2002) 145–149.
[16] J.M. Valente Nabais, P.J.M. Carrott, M.M.L. Ribeiro Carrott, J.A. Menéndez, Preparation and modification of activated carbon fibres by microwave heating, Carbon 42 (2004) 1315–1320.
[17] K.B. Pradhan, K.N. Sandle, Effect of different oxidizing agent treatments on the surface properties of activated carbons, Carbon 37 (1999) 1323–1332.
[18] P.J. Chen, S. Wu, Acid/base-treated carbons: characterization of functional groups and metal adsorption properties, Langmuir 20 (2004) 2233–2242.
[19] I. Sutherland, E. Sheng, R.H. Bradley, P.K. Freakley, Effects of ozone oxidation on carbon black surfaces, J. Mater. Sci. 31 (1996) 5651–5655.
[20] S. Biniak S, G. Szymański, J. Siedlewski, A. Światkowski, The characterization of activated carbons with oxygen and nitrogen surface groups, Carbon 35 (1997) 1799–1810.
[21] S. Andrzej, P. Maciej, B. Stanislaw, W. Mariusz, Influence of the surface chemistry of modified activated carbon on its electrochemical behaviour in the presence of lead (II) ions, Carbon 42 (2004) 3057–3069.
[22] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfao, Modification of the surface chemistry of activated carbons, Carbon 37 (1999) 1379–1389.
[23] D.M. Nevskaia, A. Santianes, V. Munoz, A. Guerrero-Ruiz, Interaction of aqueous solutions of phenol with commercial activated carbons: an adsorption and kinetic study, Carbon 37 (1999) 1065–1074.
[24] X. Li, Z. Li, Q.B. Xia, H.X. Xi, Z.X. Zhao, Effects of textural properties and surface oxygen content of activated carbons on desorption activation energy of water, Adsorpt. Sci. Technol. 24 (2006) 363–374.
[25] N. Konduru, P. Lindner, N.M. Assaf-Anid, Curbing the greenhouse effect by carbon dioxide adsorption with Zeolite 13X, AIChE J. 53 (2007) 3137–3147.
[26] S. Himeno, T. Tomita, K. Suzuki, S. Yoshida, Characterization and selectivity for methane and carbon dioxide adsorption on the all-silica DDR zeolite, Micropor. Mesopor. Mater. 98 (2007) 62–69.
[27] V. Goetz, O.P.A. Guillot, Carbon dioxide–methane mixture adsorption on activated carbon, Adsorption 12 (2006) 55–63.
[28] X.X. Zhao, X.L. Xu, L.B. Sun, L.L. Zhang, X.Q. Liu, Adsorption behavior of carbon dioxide and methane on $AlPO_4$-14: a neutral molecular sieve, Energy Fuels 23 (2009) 1534–1538.
[29] B.L. Chen, High H_2 adsorption in a microporous metal-organic framework with open metal sites, Angew. Chem. Int. Ed. 44 (2005) 4745–4749.
[30] R. Andrew. Millward, O.M. Yaghi, Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature, J. Am. Chem. Soc. 127 (2005) 17998–17999.
[31] B. Wang, A.P. Côté, H. Furukawa, M. Ókeeffe, O.M. Yaghi, Colossal cages in zeolitic imidazolate frameworks as selective carbon dioxide reservoirs, Nature 453 (2008) 207–211.
[32] Q.M. Wang, D.M. Shen, M. Bülow, M.L. Lau, S.G. Deng, F.R. Fitch, N.O. Lemcoff, J. Semanscin, Metallo-organic molecular sieve for gas separation and purification, Micropor. Mesopor. Mater. 55 (2002) 217–230.
[33] S. Bourrelly, P.L. Llewellyn, C. Serre, F. Millange, T. Loiseau, G. Férey, Different adsorption behaviors of methane and carbon dioxide in the isotypic nanoporous metal terephthalates MIL-53 and MIL-47, J. Am. Chem. Soc. 127 (2005) 13519–13521.
[34] M.X. Yu, Z. Li, Q.N. Ji, S.W. Wang, Su. Dagen, Y.S. Lin, Effect of thermal oxidation of activated carbon surface on its adsorption towards dibenzothiophene, Chem. Eng. J. 148 (2009) 242–247.