Article

Carbon Dioxide Adsorption on Porous and Functionalized Activated Carbon Fibers

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Abstract: Polyacrylonitrile-based activated carbon fibers (ACFs), modified using potassium hydroxide (KOH) or tetraethylenepentamine (TEPA), were investigated for carbon dioxide (CO$_2$) adsorption, which is one of the promising alleviation approaches for global warming. The CO$_2$ adsorption isotherms were measured, and the values of isosteric heat of adsorption were calculated. The results showed that the KOH-modified ACFs exhibited a great deal of pore volume, and a specific surface area of 1565 m$^2$/g was obtained. KOH activation made nitrogen atoms easily able to escape from the surface of ACFs. On the other hand, the surface area and pore volume of ACFs modified with TEPA were significantly reduced, which can be attributed to the closing or blocking of micropores by the N-groups. The CO$_2$ adsorption on the ACF samples was via exothermic reactions and was a type of physical adsorption, where the CO$_2$ adsorption occurred on heterogeneous surfaces. The CO$_2$ uptakes at 1 atm and 25 °C on KOH-activated ACFs reached 2.74 mmole/g. This study observed that microporosity and surface oxygen functionalities were highly associated with the CO$_2$ uptake, implying the existence of O-C coordination, accompanied with physical adsorption. Well cyclability of the adsorbents for CO$_2$ adsorption was observed, with a performance decay of less than 5% over up to ten adsorption-desorption cycles.

Keywords: carbon dioxide; activated carbon fiber; surface modification; adsorption; characterization

1. Introduction

The increase in the atmospheric carbon dioxide (CO$_2$) level has been almost guaranteed as being responsible for global warming and climate change. According to statistical data, the emission of CO$_2$ has mostly occurred from anthropogenic activities. In order to mitigate the increasing concentration of CO$_2$, several CO$_2$ capture technologies have been widely studied. Among them, adsorption techniques are effective processes to separate CO$_2$ from exhaust. Based on this, selecting appropriate adsorbents is very important, and many porous materials have been considered as potential candidates for CO$_2$ capture [1–5].

The affinity of the adsorbent surface to CO$_2$ molecules determines the adsorption capacities of CO$_2$ on the adsorbents. Several studies have shown that the CO$_2$ adsorption performance arises from the synergetic effect of the micropores and the surface nitrogen functionalities [6,7]. The porosity of activated carbons was highly associated with the activation temperature, rather than the activation time [8]. It was found that the adsorption capacity of gas at a lower pressure was controlled by ultramicropores, but micropores and mesopores became dominant at a higher pressure [8,9]. Nevertheless, Xing et al. [10] observed that in addition to the micropore volume and specific surface area of the carbons, the CO$_2$ uptake was dependent on other properties of the carbons. Maroto-Valer et al. [11] reported that the CO$_2$ adsorption capacity was positively associated with the microporosity of the carbons. They suggested that only pore sizes of less than 1.0 nm were effective in CO$_2$ adsorption at atmospheric pressure,
based on the molecular size of CO$_2$ being 0.209 nm. At present, a value of 0.33 nm is usually used as the kinetic diameter of CO$_2$ molecules [12-14]. Referring to the study of Im et al. [15], the hydrogen adsorption capacity was primarily subject to the pore volume, with a width of about 0.6-0.7 nm. Accordingly, several studies have found that high CO$_2$ capacity can mainly be attributed to the presence of small micropores (<0.8 nm) [16] or ultramicropores (<0.7 nm) [13], because the adsorption potential in the pores was enhanced. A high CO$_2$ capacity of 8.9 mmole/g at 0 °C and 1 bar on activated phenolic resin-derived carbon spheres has been obtained [16].

As a general rule, doping a Lewis-base onto the surface of adsorbents could improve their CO$_2$ adsorption capacities, because CO$_2$ is regarded as a weak Lewis acidic gas. Reacting with N-containing compounds was commonly a useful and effective method for providing Lewis-base active sites on the surface of adsorbents. The electron-donor properties induced by these N-functionalities could go towards CO$_2$ capture [17,18]. The CO$_2$ adsorption capacities on the polyetherimide impregnated activated carbons positively depend on the adsorption temperature, which is indicative of chemical adsorption [11]. The activated carbons modified at a high temperature with ammonium gas exhibited lower CO$_2$ capacities, which could be ascribed to the total or partial blinding of micropores by N-functionalities [11]. Plaza et al. [19] also found that alkylamine coating increased the nitrogen content and basic sites on the activated carbons, but the microporous volumes and the CO$_2$ adsorption capacities of the activated carbons were significantly decreased. Tetraethylenepentamine (TEPA) has been grafted onto the surface of carboxyl-rich porous carbons, and a nitrogen content of 11.56 wt% was obtained [20]. Although the CO$_2$ uptake achieved was about 3.2 mmole/g at 25 °C and 1 bar, the N-rich adsorbents were not heat-treated such that the N-functionalities might be unstable, and would probably be released under desorption with high temperatures.

It has been shown repeatedly that nitrogen atoms, possessing a pair of lone electrons, can act as a Lewis base and are able to facilitate the adsorption of CO$_2$ through the interactions between the quadrupole moment of CO$_2$ molecules and the polar N-species [6]. Specifically, the nitrogen groups on the adsorbents that have a basic character were amine groups and imine groups, so the presence of these groups would lead to higher CO$_2$ capacities, probably partially from chemisorption [11]. Hao et al. [21] also reported that pyrrolic N might function as polar sites for CO$_2$ capture. As for pyridonic N, its nitrogen atom is positioned just next to the −OH group, such that this nitrogen atom is surrounded with a higher electron density and behaves as a strong Lewis base [22], promoting a high CO$_2$ adsorption capacity.

Even though most studies have utilized acid-base interactions to interpret the high CO$_2$ adsorption capacities of N-rich carbons, Xing et al. [10] proposed another point of view. They thought that the importance of the hydrogen-bonding interactions between the CO$_2$ molecules and the hydrogen atoms on the N-doped carbons should be taken seriously, as they may override the effects of acid-base interactions. Fan et al. [22] believed that the pyridonic N groups play an important role in CO$_2$ adsorption because the position of the N atom enhances its Lewis basicity, and the pole-pole interactions between the CO$_2$ molecules and the carbon surface. Bandosz et al. [23] suggested that, besides the nitrogen functionalities, the hydrogen bonding or polar interactions of CO$_2$ within the confined pores of carbonaceous adsorbents may originate from other heteroatomic functional groups. If these chemical interactions were inevitable, the adsorption phenomena would be complicated and the performance of the adsorbents in long-term applications could be unpredictable.

Among the known adsorbents, activated carbon fibers (ACFs) have unique characteristics compared with powder or granular activated carbons. A small fiber diameter ensures fast intraparticle adsorption kinetics, and the fibrous form is favored because of ease in handling when it is used in fabric or felt forms [24]. Recently, several special structures of carbon materials have been studied to serve as CO$_2$ adsorbents [25]. However, some have complicated manufacturing processes, some were expensive, and there was often a challenge in realizing mass production and commercialization. In terms of practical applications, ACFs should be a feasible adsorbent, and how to improve their CO$_2$ uptake is a relevant question. The studies regarding the CO$_2$ uptake of ACFs published in literature have almost
always focused on the discussion of capacities and porosity. Only a few studies have talked about the effect of the chemical properties of ACFs on CO\textsubscript{2} adsorption, and almost no studies have investigated the role of surface functional groups on CO\textsubscript{2} adsorption performance. Therefore, this paper is intended to investigate the material properties of ACFs modified with potassium hydroxide (KOH) or TEPA, determine their adsorption capacities of CO\textsubscript{2}, and discuss the dependence of CO\textsubscript{2} uptake on the primary parameters.

2. Materials and Methods

2.1. Preparation of theAdsorbents

One ACF in fabric form was supplied by Taiwan Carbon Technology Co. (Taichung, Taiwan), whose precursor was polyacrylonitrile (PAN), and it was denoted by ACF. The as-received ACF samples were modified with KOH (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) to increase the porosity or TEPA (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) to complement the nitrogen content. An appropriate amount of ACF sample was immersed in a KOH aqueous solution, where KOH:ACF = 2:1 (w/w). In order to make sure the ACF was completely filled with KOH solution, the solution was mixed in ultrasonic cleaning equipment for 10 min at room temperature, and then dried in an oven for 24 h at 100 °C. The mixture was heat-treated to 800 °C and kept for 1 h in a tubular furnace under flowing N\textsubscript{2}, at a heating rate of 10 °C/min. The obtained product was rinsed thoroughly using 1 M hydrochloric acid (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) and abundant deionized water to remove the excess KOH, and then dried in an oven at 100 °C for 24 h. This sample was denoted as aACF. The treatment with TEPA \((\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2)_2\text{NH}\) was carried out as follows. A portion of ACF sample was weighed and soaked with a liquor of TEPA solution (10 wt% in alcohol), with a ratio of 0.07 g/mL. The solution was sonicated in ultrasonic cleaning equipment for 90 min at 60 °C, and then dried in an oven for 24 h at 50 °C. Next, the mixture was thermal-treated at 500 °C for 1 h in a tubular furnace under flowing N\textsubscript{2}, at a heating rate of 10 °C/min. An amount of deionized water was used to clean the product to get rid of free TEPA, and was then dried in an oven at 100 °C for 24 h. This sample was denoted as nACF.

2.2. Characterizations

Surface textural characteristics of the adsorbents were acquired from the adsorption-desorption isotherms of nitrogen gas, measured at −196 °C, which was conducted using an accelerated surface area and porometry (ASAP) apparatus—Micromeritics ASAP 2020 (Norcross, GA, USA). Before the measurements, the samples were degassed at 350 °C for 24 h. The equilibrium interval for each adsorption point was set as 45 s. The specific surface area of each sample was determined using the Brunauer-Emmett-Teller (BET) method, which was denoted as \(S\text{\textsubscript\text{BET}}\). The total pore volume \((V_1)\) of the adsorbent was obtained from the adsorption amount of nitrogen gas at \(P/P_0 \approx 0.99\). The micropore volume (<2 nm, \(V\text{\textsubscript{mi}}\)), micropore area \((S\text{\textsubscript{mi}})\), ultramicropore volume (<0.7 nm, \(V\text{\textsubscript{ultra}}\)) and mesopore volume \((2 \sim 50 \text{ nm}, V\text{\textsubscript{me}})\) were calculated from the density functional theory (DFT) method. Field emission scanning electron microscopy (FESEM) was used to probe the morphology of the filaments using a microscope (Hitachi S-4800, Hitachi, Krefeld, Germany). To understand the surface chemistry of the adsorbents, X-ray photoelectron spectroscopy (XPS) was applied and a spectrophotometer (PHI 5000 VersaProbe II, ULVAC-PHI, Kanagawa, Japan) was used to measure the XPS spectra on the surface of the adsorbent. A scanning X-ray monochromator of Al source was used. The kinetic energy and electrons emitted from the top 1–10 nm of the sample surface were collected. C\textsubscript{1s} electron binding energy corresponding to graphitic carbon was set at 284.6 eV for calibration purposes. The XPSPEAK software (version 4.1, The Chinese University of Hong Kong, Hong Kong, China) was utilized for deconvolution of the XPS spectra, which was a nonlinear least squares curve-fitting program. Prior to quantification, a Shirley-type background was selected to be subtracted. After the baseline was subtracted, curve fitting was performed using a Gaussian
2.3. CO₂ Adsorption

The Micromeritics ASAP 2020 was also used to measure the adsorption isotherms of CO₂ gas on the adsorbents. To eliminate the humidity and some trace impurities adsorbed on the surface, the sample was outgassed at 350 °C for 24 h prior to the measurement. A circulating water bath was used to control the water temperature in the adsorption dewar, where the temperature was set at 25, 40, or 55 °C. The equilibration interval for each pressure point was set as 45 s. The experimental equilibrium data were fitted with the Freundlich equation (Equation (1)), which is a well-known empirical equation for describing adsorption phenomena taking place on a heterogeneous surface with a diversity of adsorption sites:

\[ q_e = K_F P^{1/n} \]  

where \( q_e \) (mmol/g) is the equilibrium adsorption capacity at each pressure point, \( K_F \) [(mmol/g)/(kPa)\(^{1/n}\)] is the Freundlich adsorption coefficient, \( p \) (kPa) is the gas pressure, and \( n \) is a constant associated with the curvature of the isotherm. The goodness of fit of the above isotherm model to the experimental data was quantified using two different error functions: the nonlinear regression coefficient (R\(^2\)) and the average relative errors (ARE). The value of R\(^2\) indicates the percentage of deviation that can be explained by this fitting equation. On the other hand, the deviation between the experimental adsorption data and the fitting values could be calculated by ARE according to Equation (2) [26], where \( q_{e,exp} \) and \( q_{e,cal} \) (mmol/g) are the experimental and calculated adsorption capacity, and \( N \) is the number of the measured data.

\[
\text{ARE} (\%) = \sum_{j=1}^{N} \left( \frac{|q_{j,exp} - q_{j,cal}|}{q_{j,exp}} \right) \times \frac{100}{N} 
\]

The adsorption-desorption cycle tests of the adsorbents were also measured using ASAP2020. The same adsorption processes were conducted repeatedly for ten cyclic runs to evaluate the feasibility of their practical application for CO₂ adsorption. The isosteric heat of adsorption (\( Q_{st} \), kJ/mol) was determined according to the Clausius-Clapeyron equation (Equation (3)), where \( A \) is the coefficient, \( R \) (=8.314 J/mol/K) is the universal gas constant, and \( T \) (K) is the adsorption temperature.

\[
\ln P = A - \frac{Q_{st}}{R} \left( \frac{1}{T} \right) 
\]
The decrease in $S_{\text{BET}}$, $V_t$ and $V_{\text{mi}}$ of ACF after TEPA modification could be attributed to the fact that the micropores were totally or partially blinded by N-functionalities [11]. The TEPA has a bulk and long-chain structure. Thus, the graft of TEPA on ACFs could hinder the gas molecules from getting access to the pores or depositing on the carbon surface. Moreover, if the TEPA was attached inside the pores of the ACFs, the pore would be filled with TEPA molecules and the available adsorption surface or volume would be reduced. Even though the surface area and pore volume of aACF was increased compared with the as-received ACF, the ratios of $S_{\text{mi}}/S_{\text{BET}}$, $V_{\text{mi}}/V_t$, and $V_{\text{ultra}}/V_t$ for aACF and nACF were less than those of ACF. On the other hand, the $V_{\text{me}}$ for aACF and nACF raised to 2 and 1.2 times of that of ACF, respectively. It is believed that TEPA modification would block half of the macropores and close one fourth of the micropores, based on the data shown in Table 1. Several investigations have reported that KOH activation mainly generates micropores [10]; the results in this study revealed that KOH activation not only created new pores, but also widened the existing ones such that the increase of pore volume covered all pore size ranges. Figure 1 illustrates the pore size distributions (PSD) of the ACFs samples in the micropore and mesopore ranges. The previous discussion is strongly supported by Figure 1. The insets (a) and (b) of Figure 1 clearly present that, compared with ACF, the peaks of the PSD for aACF have shifted to the right, and there is a new peak at about 0.5 nm. Although nACF also has a new peak at about 0.5 nm, all peaks on its PSD are weakened, especially in the pores smaller than 0.7 nm.

Table 1. Textural properties of the samples determined from the adsorption-desorption isotherms of N$_2$ at –196 °C.

| Sample | $S_{\text{BET}}$ (m$^2$/g) | $S_{\text{mi}}$ (m$^2$/g) | $V_t$ (cm$^3$/g) | $V_{\text{me}}$ (cm$^3$/g) | $V_{\text{mi}}$ (cm$^3$/g) | $V_{\text{ultra}}$ (cm$^3$/g) | $S_{\text{mi}}/S_{\text{BET}}$ | $V_{\text{mi}}/V_t$ | $V_{\text{ultra}}/V_t$ |
|--------|-----------------|-----------------|-------------|-----------------|-----------------|-----------------|-----------------|-------------|-----------------|
| ACF    | 966 ± 16        | 862             | 0.4635      | 0.0427          | 0.3472          | 0.1456          | 0.892           | 0.749       | 0.314           |
| aACF   | 1565 ± 26       | 1224            | 0.7357      | 0.1135          | 0.5028          | 0.2020          | 0.782           | 0.683       | 0.275           |
| nACF   | 797 ± 10        | 599             | 0.3848      | 0.0612          | 0.2610          | 0.0923          | 0.752           | 0.678       | 0.240           |

* Micro pore area, micropore volume, ultramicropore volume, and mesopore volume were determined by the density functional theory (DFT) method, where an ultramicropore was defined as a pore size less than 0.7 nm.
* Total pore volume ($V_t$) represented the single point total pore volume at $P/P_0 = 0.99$.

Figure 1. Pore size distributions of the activated carbon fiber samples obtained from the DFT method, where: inset (a) micropore range; inset (b) ultramicropore range.

Figure 2 shows the FESEM images of the adsorbents. The width of a filament of ACF was micro-scaled and the well-defined striations parallel to the fibrous axis were filled on the surface of the ACF (Figure 2a). The reaction with KOH made the longitudinal striations and corroded grooving more significant, and the surface of the filament was clean (Figure 2b). The redox reactions between various
potassium-based compounds with ACFs were responsible for the change in the morphology of the ACFs [27]. On the other hand, the TEPA modification of ACFs did not cause any perceptible variation in the filament appearance (Figure 2c).

**Figure 2.** FESEM images of the samples: (a) as-received ACF; (b) KOH-activated ACF (aACF); (c) TEPA-modified ACF (nACF).

Previous studies have shown that CO₂ adsorption capacities are closely linked to surface heteroatomic species of the adsorbents, especially to N-functionalities [11,19,29]. Accordingly, XPS was conducted to examine the surface chemical states. As seen from Figure 3a, the primary characteristic peaks in the survey scan spectra of the adsorbents are due to the photoelectrons of C₁s, O₁s, and N₁s. The KOH activation of ACF resulted in a significant loss of nitrogen atoms during activation (Figure 3b), consistent with findings from Xing et al. [10]. The surface of ACF consisted of 8.2 at% of O₁s and 2.4 at% of N₁s, where the nitrogen originated from its PAN precursor (Figure 3b). The nitrogen content on nACF was not significantly increased, which could be ascribed to it undergoing a heat treatment at 500 °C after immersion. Nevertheless, the results confirmed that the surface of ACF has been decorated with nitrogen-based groups from TEPA. Figure 3c–d show a comparison of the N₁s and O₁s regions for the adsorbents. It is evident that the major groups of N– and O-functionalities have transformed to others after modifications.

In order to understand the chemical bonding states, deconvolution of high-resolution XPS O₁s, and N₁s peaks of the adsorbents was carried out. Deconvolution of the O₁s region provided information on the distribution of the surface oxygen-functionalities. The optimal results were used to calculate the values of the atomic percent of oxygen-functionalities after curve fitting of the O₁s region for the samples (Figure 4a). Four distinct types of O-functionalities including –C=O (531.1 eV); R-O-C=O, O=C-NH₂, O=C-O=C=O, C-OH, R-O-R (532.3 eV), R-O=C=O, O=C-O-C=O (533.3 eV), and -COOH (534.2 eV), as well as the contribution of chemisorbed H₂O (536.1 eV), can be identified [30]. This indicated that the oxygen atoms on aACF were primarily present as –OH and C = O groups. It is noted that on the surface on nACF, the existence of a great amount of chemisorbed water was detected, which is likely to be related to the introduction of nitrogen functionalities.
Figure 3. The X-ray photoelectron spectroscopy (XPS) of the samples: (a) survey scan spectra; (b) atomic ratios; (c) N\textsubscript{1s} peaks; (d) O\textsubscript{1s} peaks.

Figure 4. Results of the fits of the high resolution X-ray photoelectron spectroscopy (XPS): (a) O\textsubscript{1s} region; (b) N\textsubscript{1s} region. The values were given in the atomic ratio (%) of total intensity.

The composition and the atomic percent of N-functionalities on the surface of the adsorbents are shown in Figure 4b. Six nitrogen-based compounds were identified [31], including the aromatic...
N-imines (395.7 eV), the pyridine-type N (398.4 eV), the pyrrolic N or pyridonic N (400.1 eV), the quarternary N (401.2 eV), the pyridine N oxides (402.4 eV), and the chemisorbed NO$_2$ (405 eV). Pyridonic N and pyrrolic N could not be differentiated from each other based on the current measurement technology [32]. In view of the fact that oxygen existed on the surface of the adsorbents and the pyrrolic N was much more unstable than pyridonic N at an elevated temperature [33], the functional groups occurring at 400.1 eV were probably pyridonic N. Arising from the precursor of ACF, the major N-functionalities were featured with the quarternary N and the pyridine type N. Even though the evolution of nitrogen took place significantly during the KOH activation process, pyridonic N was much more heat-resistant compared with other species. Since the nitrogen on the aACF originated totally from the ACF, it is believed that the pyridonic N was a more stable form. The distribution of N-functionalities on nACF displayed an increase in pyridonic N, which could be due to the functional groups in TEPA.

The TGA profiles are illustrated in Figure 5a, and the temperatures for the maximum rate of weight loss for ACF, aACF, and nACF were 600, 588, and 655 °C, respectively (in Figure 5b). Comparing the profiles of aACF with ACF, the oxidation resistance of the samples was not significantly changed after KOH activation. Possibly due to the total or partial blinding of micropores by N-functionalities, the oxidation resistance of ACF modified with TEPA was improved significantly.

![Figure 5](image-url)

**Figure 5.** The profiles of (a) thermogravimetric analysis (TGA) and (b) differential thermogravimetry (DTG) of the samples.

3.2. CO$_2$ Adsorption Performance

The adsorption equilibrium data of CO$_2$ on the adsorbents under a pressure of less than 120 kPa at different temperatures (25, 40, or 55 °C) are shown in Figure 6a–c. The equilibrium time for each measured point was held to 45 s after achieving the respective pressure value. The highest CO$_2$ uptake of 2.74 mmole/g was observed on aACF at 25 °C and 1 atm, which was higher than those of ACF (2.33 mmole/g) and nACF (1.61 mmole/g). As the adsorption temperature increased, the adsorbed amounts of CO$_2$ decreased. The temperature dependence of CO$_2$ adsorption capacity was consistent with the behavior of an exothermic reaction.
micropores by N-functionalities, the oxidation resistance of ACF... indicated that the micropores in the adsorbents could have a more important role than the nitrogen functionalities.

Figure 6. Adsorption isotherms of CO2 of the samples: (a) as-received ACF; (b) KOH-activated ACF (aACF); (c) TEPA-modified ACF (nACF) and (d) the isosteric heat of adsorption (\(Q_{st}\)) of CO2.

The nitrogen content, though, was limited; aACF exhibited the highest percentage of imine groups and pyridonic groups. The presence of these groups might lead to its higher CO2 capacities. This implied that the CO2 adsorption capacities might be subject to not only the nitrogen content but also the type and the location of N-functionalities \[6,21,34\]. According to the results of \(Q_{st}\) (Figure 6d), estimated from the adsorption data, the CO2 adsorption on aACF still behaved as a physical process. The calculated values of \(Q_{st}\) for all adsorbents were under 40 kJ/mol, indicative of physical adsorption in the low CO2 uptake range of 0.2–1.0 mmol/g. The values of \(Q_{st}\) decreased with increasing CO2 uptake, implying CO2 adsorption occurred on an energetically heterogeneous surface \[35\]. A linear relationship between \(Q_{st}\) and the CO2 uptake was observed if the logarithmic scale of the amount of CO2 adsorbed was used. The value of \(Q_{st}\) followed the order aACF > ACF > nACF, which indicated that the micropores in the adsorbents could have a more important role than the nitrogen functionalities.

The adsorption model has a significant effect on the characteristic of \(Q_{st}\) \[21\]. According to previous experience, the Freundlich model was selected to curve-fit the experimental adsorption data, and Figure 6a–c also portrays the fitted curves. The fitted results are summarized in Table 2. The values of R² were higher than 0.9993 and the ARE ranged from 1.0 to 2.4, indicating that the Freundlich equation provided a satisfactory fit for the adsorbents. The values of parameter \(n\) were greater than 1.3, implying the CO2 molecules had an affinity for the surface of the adsorbents. As seen from the data, the values of \(K_f\) and \(n\) varied inversely with adsorption temperature, but took on a similar tendency with the CO2 uptake.
Table 2. Curve-fitting of the Freundlich equation for the CO$_2$ adsorption data at different temperatures.

| Sample | Temperature (°C) | $K_F$ (mmole/g/kPa$^{1/n}$) | $n$  | $R^2$ | ARE (%) |
|--------|------------------|-------------------------------|------|-------|---------|
| ACF    | 25               | 0.134                         | 1.61 | 0.9997| 2.26    |
|        | 40               | 0.084                         | 1.52 | 0.9996| 2.37    |
|        | 55               | 0.052                         | 1.43 | 0.9995| 2.38    |
| aACF   | 25               | 0.164                         | 1.64 | 0.9998| 1.89    |
|        | 40               | 0.102                         | 1.54 | 0.9998| 1.76    |
|        | 55               | 0.063                         | 1.50 | 0.9993| 1.54    |
| nACF   | 25               | 0.089                         | 1.59 | 0.9998| 1.48    |
|        | 40               | 0.052                         | 1.47 | 0.9999| 1.06    |
|        | 55               | 0.031                         | 1.36 | 0.9999| 1.23    |

Further, in examining the correlation of CO$_2$ uptake at a lower pressure (0.15 atm) and at 25 °C with the physical and chemical properties of the adsorbents, it was obvious that the CO$_2$ adsorption capacity was highly associated with the micropores, especially the ultramicropore volume (Figure 7a–b), which indicated the importance of ultramicropores in CO$_2$ adsorption at low pressures. It is noteworthy that the CO$_2$ uptake changed positively with the surface oxygen content, but negatively with the surface nitrogen content (Figure 7c). In further analysis, for the N-functionalities, the percentage of NO$_2$ groups was the only significant factor influencing the CO$_2$ adsorption capacities (Figure 7d). However, for the O-functionalities, except for the –COOH group, all other O-groups were highly associated with the CO$_2$ uptake. This indicated that the O-C coordination could be an adsorption mechanism for CO$_2$ adsorption on ACFs, where the CO$_2$ molecules (as an acidic gas) prefer to bind to the surface O-functionalities of ACFs [36]. For the purpose of comparison, Table 3 shows the CO$_2$ adsorption capacities in this study and on various supporting materials, with or without modifications, from the literature. This comparison indicates that the CO$_2$ adsorption on ACFs in this research were comparable or superior to other porous carbons.

The adsorption technique applied in gas separation required the cyclic regeneration of the adsorbents. Thus, multiple CO$_2$ adsorption-desorption cyclic tests were conducted on the adsorbents to evaluate further practical applications. Figure 8 displayed ten cycles of adsorption-desorption experiments for CO$_2$ adsorption at 25 °C. Within each cycle, the adsorbents were desorbed by subjecting them to the conditions of a dynamic vacuum. The adsorption capacities of CO$_2$ were decayed by about 1.8% (ACF), 5.0% (aACF) and 2.1% (nACF) after 10 cyclic runs, respectively. Therefore, the adsorbents were judged to exhibit an excellent cyclability. The results presented in Figure 8 seem to suggest that the decay in adsorption efficiency was mostly taking place after the first adsorption cycle. It was expected that CO$_2$ molecules could get into all pores in the first adsorption cycle, especially the ultramicropores. When the adsorbents were desorbed in a vacuum, some CO$_2$ molecules could not escape effectively, most probably in the ultramicropores, because of the confinement effect. Thus, aACF, having the largest $V_{ultra}$, exhibited the highest decay of the adsorption capacity after the first adsorption cycle.
Figure 7. Correlation of equilibrium CO\textsubscript{2} uptake at CO\textsubscript{2} = 0.15 atm and 25 °C with the (a) BET surface area (S\textsubscript{BET}) and micropore area (S\textsubscript{mi}); (b) micropore volume (V\textsubscript{mi}) and ultramicro pore volume (V\textsubscript{ultra}); (c) surface N and O content; (d) NO\textsubscript{2} (%) in N-groups; (e) percentage of O-functionalities.

Table 3. Comparisons of CO\textsubscript{2} uptake on the adsorbents in this study with various supporting materials from the literature.

| Support Materials       | Surface Modification | S\textsubscript{BET} (m\textsuperscript{2}/g) | Concentration of CO\textsubscript{2} | Adsorption Temp. (°C) | CO\textsubscript{2} Uptake (mmole/g) | Reference |
|-------------------------|----------------------|---------------------------------|-------------------------------|----------------------|-----------------------------------|-----------|
| ACFs                    | KOH                  | 1565                            | 1 atm                         | 25                   | 2.74                              | This study|
| ACFs                    | KOH                  | 527–1720                        | 1 bar                         | 25                   | 1.9–2.6                           | [34]      |
| ACFs                    | KOH                  | 780                             | 1 atm                         | 25                   | ~1.0                              | [37]      |
| ACFs                    |                     | 1461                            | 1 atm                         | 25                   | 2.80                              | [38]      |
| ACFs                    |                     | 140–925                         | 1 atm                         | 20                   | 0.55–2.28                         | [39]      |
| ACFs                    |                     | 907–1914                        | 1 bar                         | 25                   | 0.6–0.7                           | [40]      |
| Carbon                  |                     | 1343                            | 1 bar                         | 25                   | 1.50                              | [14]      |
| Hierarchical carbon nanosheet | KOH              | 1556                            | 1 bar                         | 25                   | 3.10                              | [25]      |
| Carbon sphere           | Ethylenediamine     | 590                             | 1 atm                         | 25                   | 2.90                              | [41]      |
| Carbon                  | SOCl\textsubscript{2}, TEPA | 823                             | 1 bar                         | 25                   | 3.2                               | [20]      |
| Carbon                  | KOH, urea           | 862                             | 1 bar                         | 25                   | 2.91                              | [29]      |
| Silica-coated MWCNTs    | Polyethylene-imine  | 375                             | 1 bar                         | 25                   | 1.41                              | [42]      |
capacities of CO$_2$ were decayed by about 1.8% (ACF), 5.0% (aA$_F$) and 2.1% (nA$_F$) after 10 cyclic runs, respectively. Therefore, the adsorbents were judged to exhibit an excellent cyclability.

The results presented in Figure 8 seem to suggest that the decay in adsorption efficiency was mostly taking place after the first adsorption cycle. It was expected that CO$_2$ molecules could get into all pores in the first adsorption cycle, especially the ultramicropores. When the adsorbents were desorbed in a vacuum, some CO$_2$ molecules could not escape effectively, most probably in the ultramicropores, because of the confinement effect. Thus, A$_F$, having the largest V$_{\text{ultra}}$, exhibited the highest decay of the adsorption capacity after the first adsorption cycle.

Figure 8. Successive cyclic adsorption/desorption curves and the variation of adsorption capacities at 25 $^\circ$C: (a, b) as-received ACF; (c, d) KOH-activated ACF (aA$_F$); (e, f) TEPA-modified ACF (nA$_F$).

4. Conclusions

For ease in practical applications, microporous ACFs for CO$_2$ adsorption have been investigated. The KOH activation of ACFs generated increased pore volume, not only in the micropore but also in the mesopore ranges. A microporosity of 68% and ultra-micro-porosity of 28% were obtained in KOH-activated ACFs. Due to the total or partial blinding of micropores by N-functionalities, the TEPA-modified ACFs had a lower surface area and pore volume. Surface modification of ACFs gave rise to a change of the predominant surface functional groups. An increase in the amount of chemisorbed water on ACFs treated with TEPA should be the outcome of the introduction of polar nitrogen functionalities. The existence of basic nitrogen-containing functionalities was thought to lead to higher CO$_2$ uptakes; however, there was no explicit relationship between them in our findings. Instead, the O-functionalities showed a highly associated linear relationship between the functional groups and the CO$_2$ uptake. Despite this, the values of isosteric heat of adsorption still confirmed that in this study, the influence of micro-porosity on CO$_2$ adsorption was prevailing. Moreover, the ACF
samples exhibited excellent CO$_2$ capture cyclability. Further studies should aim to find the optimal conditions for KOH activation of ACFs in order to improve their CO$_2$ adsorption performance.

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