Preparation of potassium intercalated carbons by in-situ activation and speciation for CO₂ capture from flue gas

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A B S T R A C T

Nitrogen and/or sulfur doped carbons were extensively investigated as CO₂ adsorbents, however their performance in CO₂ capture from combustion flue gas, which is the largest stationary emission source, was less promising. Herein, potassium was used as a dopant for carbon, and a new series of materials, namely potassium intercalated carbons (PICs), were prepared sequentially by oxidation of mesoporous carbon, potassium ion exchange, and calcination. Based on results from FT-IR, XPS, TG-MS, etc., it was found the pre-loaded potassium interacted with the carbon matrix during calcination, enabled great flexibility in: (1) porosity adjustment by "in-situ activation", and (2) surface chemistry manipulation by potassium intercalation. Taking together, the optimized sample (PIC-700) showed fast and stable CO₂ uptake of 5.23 wt.% in flue gas conditions (40 °C, 1 bar, 15%CO₂), which is among the highest for carbon-based adsorbents. Such promising performance is directly related to the enhanced CO₂ affinity due to the presence of potassium dopants. Dynamic separation of CO₂ from 15%CO₂/85%N₂ showed similar adsorption capacity, and no performance decay could be observed during temperature swing cycles, demonstrating the great potential for the PICs for practical CO₂ capture applications.

1. Introduction

Lowering the carbon intensity of our economy is an unavoidable pathway to fight climate change. In this context, several options were proposed such as efficiency enhancement, transformation to more renewable energies, etc [1]. Among this toolbox, CO₂ capture and storage (CCS) was considered as a major player. It was estimated by IPCC that without CCS, costs of most solutions to achieve the 2 °C goal will increase dramatically if not unsuccessful [2]. CO₂ capture is an enabling technology in the entire CCS chain, but unfortunately, it is also the most costly step [3,4]. Currently, capturing CO₂ from combustion flue gas is the most urgent aspect as it provides solutions to carbon reduction to the largest stationary carbon emission source [5–7]. For such an application, amine scrubbing is a state-of-the-art technology that is now being demonstrated in large scale [8]. However, this process is highly energy intensive and environmentally risky (e.g. amine leakage, etc.) [9–13].

Adsorption by solid materials was regarded as an alternative approach for CO₂ capture [14–19]. This is mainly because the energy penalty and environmental footprint of this process may be considerably lower than amine scrubbing. A wide range of materials have been investigated as CO₂ adsorbents, e.g. amine modified silica [20,21], alkaline metal oxides [22,23], zeolites [24–26], metal-organic frameworks [27–29], etc. All of these materials have their own pros and cons, and optimized CO₂ capture performance in terms of adsorption capacity, selectivity, stability, and others is yet to be achieved.

Carbons have been widely employed as functioning materials because they are cheap, less toxic, and chemically inert [5,30–33]. As a CO₂ adsorbent, one promising property of these materials is their highly developed porosity, making them favorable for capturing CO₂ from high pressure/concentration sources [15,19,34]. On the other hand, in order to improve their performance at low pressure, e.g. CO₂ capture from combustion flue gas, hetero-atom doping is necessary to enhance their interaction with CO₂. In this context, nitrogen and sulfur were
extensively investigated as dopants, and the resulted carbons showed higher CO₂ adsorption capacity as compared with their un-doped counterparts [35,36]. However, the improvement is still limited, and most materials showed CO₂ uptakes of less than 1 mmol/g at flue gas conditions (40 °C, 15%CO₂ in 1 bar total pressure) [37,38]. One issue of these nitrogen or sulfur doped carbon could be attributed to their different requirement on carbonization temperature to maximize porosity and hetero-atom concentration of the resulted materials. To be more specific, textural properties of carbons are closely related to the decomposition of the used precursor, which is greatly accelerated at 600–800 °C, resulting in high porosity. However, the nitrogen and sulfur functionalities start to decompose at considerably lower temperature, which means only a part of these hetero-atoms can survive the carbonization process, leading to limited doping level and strengthened CO₂ affinity. In our previous work, potassium was used as a thermally stable dopant for carbons, and procedures were established for the preparation of a series of potassium tethered carbons (termed as PTC) [39]. It was found that following such a strategy, stronger and highly dispersed adsorption sites were induced onto the carbon surface, leading to carbons with very promising performance in CO₂ capture from flue gas. Herein, we report a series of similar but different carbon materials, namely potassium intercalated carbons (PICs), by calcination of PTC. Based on characterization results from FT-IR, XPS, TG-MS, N₂ physorption, etc., we found the calcination procedure led to in-situ activation of the carbon backbone and re-speciation of potassium sites, which greatly extended the flexibility on tuning the porosity, surface chemistry, and CO₂ adsorption performance of the resulted PICs. At optimized calcination temperature (700 °C), the sample PIC-700 showed fast and stable CO₂ uptake of 5.23 wt.% at flue gas conditions, which is among the highest for carbon-based materials.

2. Experimental

2.1. Materials

Resorcinol, p-phthalaldehyde, and Pluronic F127 were purchased from Aladdin Reagent (Shanghai) Co. Ltd. Potassium hydroxide (KOH), concentrated HNO₃ and H₂SO₄ were obtained from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used as received.

2.2. Preparation of samples

6.00 g F127, 1.76 g resorcinol and 2.24 g p-phthalaldehyde were added into a PTFE-lined autoclave, and then stirred using a glass rod until sticky paste was obtained. The autoclave was then sealed, heated at 250 °C for 8 h, and cooled to room temperature to obtain PR (a brownish solid). Mesoporous carbon (MC) was then prepared by carbonize PR in a tube furnace at 800 °C (5 °C/min) for 300 min under N₂ flow (400 cm³/min).

Modification of MC was firstly carried out by oxidation in a mixture of concentrated nitric acid and concentrated sulfuric acid (2:1, volume ratio) at 60 °C for 8 h, the solid was then extensively washed with de-ionized water and dried at 110 °C overnight to afford the oxidized MC (M-C-O x). Afterwards, potassium tethered carbon (PTC) was prepared by disperse 1 g M-C-O x in aqueous KOH solution (2 mol/L), stirred for 24 h, washed to neutral and dried overnight. PTC was then calcinated at 600, 700, and 800 °C for 300 min in N₂ flow to obtain PIC-x (x = 600, 700, and 800, corresponding to the used calcination temperature).

2.3. Characterization

2.3.1. CO₂ adsorption by thermal gravimetric method

10-20 mg samples were added in the sample pan of a TA Q50 thermal gravimetric analyzer, and was pre-treated at 115 °C (30 min) in Ar to remove any physically-sorbed H₂O and/or CO₂. After the temperature was cooled and stabilized at 40 °C, the feeding was switched to 15%CO₂/85%N₂, and the weight gain was used to calculate the adsorption capacity.

2.3.2. CO₂ isotherms

A Micromeritics Tristar II 3020 analyzer was used to measure the CO₂ adsorption isotherms at different temperatures. Before any tests, the samples were degassed at 200 °C for 2 h.

2.3.3. Dynamic CO₂ separation from N₂

Breakthrough curves were analyzed on a home-made fixed bed adsorber (6 mm, i.d.), where 0.20 g of sample was charged and sandwiched by quartz wool. This gives a bed length of 3.0 ± 1 cm, note such conditions may not be able to guarantee a high Péclet number, and thus the obtained results can be interpreted only from thermodynamic aspect, any analysis on adsorption kinetics should be carried out under conditions that any axial dispersion effect was negligible [41]. Adsorption was carried out by flowing 20 ml/min 15%CO₂/85%N₂ at 40 °C, and gas composition at the outlet was analyzed by a mass spectroscope. After adsorption, desorption was performed in Ar at 115 °C for 15 min, followed by the next adsorption-desorption cycle.

\[ \text{Chemical Reaction} \]

Scheme 1. Preparation of the potassium modified samples.
3. Results and discussion

The adsorbents reported in this paper were prepared by modification of mesoporous carbons as illustrated in Scheme 1. Firstly, the carbon precursor was synthesized by a solvent-free method. During the process, F127, resorcinol, and p-phthalaldehyde were mixed, and their self-assembly and copolymerization could be triggered by thermal treatment at 250 °C (Scheme 1A) [42]. This allowed the formation of a phenolic resin like polymer (named as PR, hereafter, Scheme 1B). Its chemical structure could be verified by FT-IR. As showed in Fig. S1, the broad adsorption bands at 3350 and 3650 cm⁻¹ were attributable to hydroxyl group. Meanwhile, absorption at 2800–3000 cm⁻¹ and 1450-1650 cm⁻¹ can be related to the C–H bonding and benzene ring of the phenolic resin backbone.

In the subsequent step, PR was carbonized in N₂ flow to afford a micro-mesoporous carbon, MC, for further modification (Scheme 1C). The optimum carbonization temperature was determined by TG-MS measurement on PR (Fig. S2). A rapid weight loss stage from ca. 300 to 400 °C followed by a slower weight loss stage up to ca. 750 °C can be observed. From the MS signals, the weight loss can be attributed to the formation of CO₂ and H₂O due to the decomposition of polymer backbone, which is in accordance with the thermolysis behavior of phenolic resin previously reported by Liu et al. [43] Based on the above, 800 °C was used for the carbonization of PR to assure the removal of most volatile components, this is very important to achieve highly reproducible preparation.

Modification of MC was carried out sequentially by: (1) oxidation in concentrated H₂SO₄/HNO₃ at 60 °C (M C–O x, Scheme 1D), (2) potassium tethering by ion exchanging (PTC, Scheme 1E), and (3) potassium intercalation by calcination of PTC (PIC-x, where x = 600, 700, and 800, corresponding to the calcination temperature, Scheme 1F). Surface functionalities of the samples at different preparation stages were characterized by FT-IR (Fig. 1A). MC showed featureless spectra according to our previous work [39], these groups served as anchoring functionalities were stable even after calcination at 700 °C.

In order to analyze the surface functionalities more clearly, XPS measurement was carried out. The obtained elemental survey spectrum showed in Fig. S3 corresponds well with the preparation steps, e.g. MC and M C–O x contain carbon and oxygen exclusively, while potassium could be detected in PTC and PICs. Fig. 1B–E shows the high resolution C1s spectra of the samples. According to Heo and co-workers, the spectra can be deconvoluted into four peaks, namely 284.8 eV for C–C bonding, 286.6 eV for C–O–C bonding, 288.0 eV for epoxy or C–OH bonding, and 289.0 for O–C = O bonding, respectively [46]. Table 1 summarizes the relative contents of these functionalities. In line with the FT-IR results, the amounts of oxygen-containing groups increased after oxidation due to the introduction of hydroxyl, carboxyl, and other groups. For PTC, the concentration and distribution of these groups did not change obviously as compared with M C–O x, which is expectable according to the general chemistry of ion exchange. Very interestingly, C–O bonding only slightly diminished after calcination as was evidenced by PIC-700 (Table 1). Since any hydroxyl and other organic groups containing oxygen should be decomposed during calcination, the observed high oxygen content clearly evidenced the presence of O–K⁺ species within the carbon matrix. As has been widely demonstrated, these heteroatom-bearing functionalities can improve CO₂ affinity of carbons, resulting in enhanced CO₂ adsorption, particularly at low pressures [39].

Our previous investigations demonstrated that CO₂ adsorption of PTC was jointly determined by: (1) porosity of the materials, and (2) speciation and dispersion of the potassium sites [39, 47, 48]. We assume that these properties could be influenced significantly during calcination, enabling more dimensions in tuning the performance of the PICs. Therefore, a TG-MS measurement was carried out on PTC to disclose the interaction between the tethered potassium and carbon backbone during calcination. From Fig. 2, weight loss below 150 °C could be attributed to the desorption of physically adsorbed moisture. Oxygen-containing functionalities such as hydroxyl and carboxyl started to decompose at temperatures higher than 200 °C, this also led to the conversion of the loaded potassium into K₂CO₃ [49]. With further increase of temperature to ca. 550 °C, generation of CO could be detected, indicating the oxidation of carbon matrix by reactions of K₂CO₃ + C = K₂O + 2CO and K₂O + C = 2K + CO. The constant weight loss at temperatures higher than 750 °C could be related to further gasification of the carbon matrix and evaporation of metallic potassium [50, 51].

The above process echoed perfectly by the ICP-OES results for the PIC-x samples. As could be found in Table 1, because of the gasification

<table>
<thead>
<tr>
<th>Sample</th>
<th>C–C (%)</th>
<th>C–O (%)</th>
<th>Epoxide/C–OH (%)</th>
<th>O–C=O (%)</th>
<th>ICP (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>76.09</td>
<td>11.9</td>
<td>5.35</td>
<td>2.65</td>
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<tr>
<td>MC–ox</td>
<td>76.79</td>
<td>12.47</td>
<td>5.38</td>
<td>5.36</td>
<td></td>
</tr>
<tr>
<td>PTC</td>
<td>76.59</td>
<td>12.86</td>
<td>6.47</td>
<td>4.08</td>
<td></td>
</tr>
<tr>
<td>PIC-600</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.44</td>
</tr>
<tr>
<td>PIC-700</td>
<td>85.42</td>
<td>8.94</td>
<td>2.38</td>
<td>3.27</td>
<td>3.03</td>
</tr>
<tr>
<td>PIC-800</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.25</td>
</tr>
</tbody>
</table>
of carbon matrix, the potassium content evolved gradually from 2.44 to 3.03 wt.% when the calcination temperature increased from 600 to 700 °C. However, calcination at 800 °C led to rapid decrease of potassium content to 2.25 wt.%, which was attributable to the formation and evaporation of metallic potassium. Based on the above, the interaction between the loaded potassium species and the carbon matrix could be regarded as an “in-situ activation” process [52-54], and thus influenced the micro-structure of the resulted PIC-x samples considerably: Firstly, new porosity can be generated due to the removal of carbon atoms and the mobility of potassium vapor within the graphite layer; On the other hand, compounds such as KC₈ might be formed by carbon atoms and the mobility of potassium vapor within the graphite layer; On the other hand, compounds such as KC₈ might be formed by 

Porosity of the samples was analyzed by N₂ physisorption at −196 °C. Fig. 3 illustrates the obtained isotherms and pore size distribution (PSD) curves of the parent MC and samples after different modification steps. According to the IUPAC classification, all of the isotherms showed combinative features of Type I and Type IV isotherms [40]. To be more specific, N₂ uptake increased rapidly at the low-pressure region (P/P₀ < 0.1), indicating the presence of abundant micropores probably generated by the thermal decomposition of the carbon precursors. At the same time, presence of mesopores can also be confirmed due to the observed hysteresis loops in a P/P₀ range of 0.4-0.7. The PSD curves indicate that micropores with average diameters of ca. 0.8 and 1.3 nm are predominant in all of the samples (inserts of Fig. 3). Due to the templating effect of F127, a wide peak in the 2.5–5.0 nm range was also observable. Modification of the carbons led to considerable changes on the surface areas. As can be found from Table 2, MC has a specific surface area (S_BET) of 790 m²/g and a total pore volume (V_total) of 0.50 cm³/g. Oxidation and potassium introduction led to the decrease of S_BET to 680 and 580 m²/g for M-C-O-x and PTC, respectively. This could be attributed to the alteration of porosity by the introduced surface functionalities. Very interestingly, due to the “in-situ activation” effect of potassium at elevated temperature, calcination led to recovery of porosity. For example, S_BET of PIC-700 achieved 917 m²/g, even higher than the parent MC. With the increasing of calcination temperature up to 800 °C, the specific surface area of PIC-800 increased to a promisingly high value of 1173 m²/g due to the enhancement of activation.

SEM images of the samples were showed in Figs. 4 and S4. The samples were composed from µm-scale particles with large amounts of pores and cavities, very typical for carbon materials derived from synthetic polymers [55]. TEM images of the samples revealed amorphous carbon multilayers for all the samples (Fig. 5). It is worthwhile to mention that from both the SEM and TEM images, uniform morphology could be observed in large domains, revealing the loaded potassium species dispersed evenly in the carbon matrix, and formation of any crystalline potassium salt was avoided. Structure of the samples was also confirmed by XRD. As can be seen from Fig. S5, peaks attributable to the (002) and (100) reflection of carbon can be observed at ca. 24° and 44°, respectively [56]. However, these peaks are of low intensity and highly broadened, indicating the low crystallinity.

CO₂ adsorption performance of the samples was evaluated firstly in a thermal gravimetric analyzer, 15% CO₂ balanced with N₂ was used in order to simulate flue gas. From Table 2, MC adsorbs only 2.25 wt.% CO₂ considerably lower than other carbon materials [15,19,57]. This result could be attributed to the micro-mesoporous structure, moderate surface area, and limited oxygen-containing groups of MC, as these properties were reported to be crucial for carbons to adsorb low concentration CO₂ [53]. After oxidation, CO₂ uptake of M-C-O-x increased to 2.88 wt.%, which demonstrated the importance of surface functionalities by considering its lower surface area as compared to that of MC. Enhancement of CO₂ uptake is more profound for potassium

<table>
<thead>
<tr>
<th>Sample</th>
<th>Textural properties</th>
<th>CO₂ uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S_BET (m²/g)</td>
<td>V_total (cm³/g)</td>
</tr>
<tr>
<td>MC</td>
<td>795</td>
<td>0.50</td>
</tr>
<tr>
<td>MC-ox</td>
<td>680</td>
<td>0.45</td>
</tr>
<tr>
<td>PTC</td>
<td>576</td>
<td>0.40</td>
</tr>
<tr>
<td>PIC-600</td>
<td>722</td>
<td>0.50</td>
</tr>
<tr>
<td>PIC-700</td>
<td>917</td>
<td>0.55</td>
</tr>
<tr>
<td>PIC-800</td>
<td>1173</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Fig. 2. TG-MS of PTC.

Fig. 3. N₂ isotherms (A) and pore size distributions (B) of the samples.

Table 2: Textural properties and CO₂ uptake of the samples.
modified carbons. PTC adsorbed 4.66 wt.% of CO₂, which could be further increased to 5.01 and 5.23 wt.% after calcination at 600 and 700 °C, respectively. Apart from the high adsorption capacity at flue gas conditions, these samples also showed fast adsorption kinetics, taking only ca. 10 min to reach adsorption equilibrium (Fig. S6). Further increase of the calcination temperature to 800 °C led to lower CO₂ uptake (4.15 wt.%) although the sample has higher surface areas. These observations clearly demonstrated that for these potassium modified carbons, the CO₂ adsorption capacities under flue gas conditions are closely correlated to their potassium contents (Fig. S7).

Fig. 6A showed the CO₂ adsorption isotherms of PIC-700 at different temperatures. CO₂ adsorption increased with the increasing of pressure, and decreased with the increasing of temperature. These observations correlates well with the exothermal nature of physical adsorption process. At 40 °C and 0.15 bar, the sample adsorbed 5.28 wt.% CO₂, which agreed well with the TGA measurement. Adsorption and desorption
branches of all the isotherms were overlapped, indicating the adsorption process is fully reversible, which is the pre-requisite for multi-cycle CO₂ capture.

Based on the isotherms, isosteric heat of adsorption (Qst) was calculated by applying Clausius-Clapeyron equation (Fig. 6B). Very interestingly, an initial Qst value of 65.0 kJ/mol was achieved (CO₂ uptake = 1.00 wt.%), which is considerably higher than those reported for nitrogen or sulfur doped carbons [58,59]. Qst decreased with the increase of adsorption capacity due to favorable occupation of stronger sites, but it remained at ca. 30 kJ/mol even at 8.80 wt.%. These results demonstrated that modification of the carbons with potassium could effectively strengthen the CO₂ affinity, which is responsible to their higher performance at flue gas conditions.

Cycling stability of PIC-700 was evaluated in TGA by carrying out adsorption at 40 °C in 15%CO₂-85%N₂ and desorption at 115 °C in pure Ar. As can be observed from Fig. 7A, the sample showed very stable performance with less than 5% decrease of CO₂ uptake in 50 cycles. Last but not the least, dynamic separation of CO₂ from flue gas was performed in a fixed bed adsorber using temperature swing mode, namely adsorption at 40 °C and regeneration at 115 °C for 15 min. Fig. 7B showed the breakthrough curves from 10 cycles, stable adsorption capacities of 5.04 ± 0.08 wt.% were obtained during the entire process, in good accordance to those obtained in TGA and isotherm measurement. Note the humps observed at ca. 60–80 s for CO₂ could not be regarded as breakthrough, and these were attributed to the slight change of ionization efficiency after switching the gas feed from Ar to the simulated flue gas. Furthermore, all the curves were overlapped indicating the fast kinetics were not compromised as well during prolonged cycles. We also carried out an addition TGA test that measured the adsorption capacity of PIC-700 in pure CO₂ (Fig. S8). It was found that with the increasing of temperature, the weight of the sample went back to its original value at ca. 190 °C. This is to say that when using pure CO₂ as the purging gas for desorption, CO₂ with nearly 100% purity could be obtained at ca.190 °C, and the temperature can be lowered if steam was used. Taking the above observations together, the PICs reported here showed promising performance in CO₂ capture from flue gas, which justified its great potential for practical applications. Future works will focus on the influence of moisture and other contaminants in practical flue gas.

4. Conclusion

We have successfully developed a series of new hetero-atom doped carbons, namely potassium intercalated carbons (PICs), for CO₂ capture from combustion flue gas. The materials were synthesized by calcining our previously reported potassium tethered carbons (PTCs, prepared by oxidation and potassium ion exchanging of mesoporous carbon) at elevated temperatures. It was found that the additional calcination step has profound impact on the structure and surface chemistry of the samples. On one hand, porosity could be effectively improved by an “in-situ activation” effect. This is because the pre-loaded potassium species decomposed to K₂CO₃, which led to oxidation of the carbon backbone, and the generated metallic potassium moved within the carbon layer and partially evaporated. On the other hand, high temperature allowed reaction between potassium and carbon, leading to highly-dispersed intercalation of potassium in the carbon matrix. Consequently, PICs showed adsorption enthalpy of higher than 30 kJ/mol at high CO₂ loadings, indicating effective enhancement on CO₂ affinity. In flue gas


