Effect of the SBA-15 template and KOH activation method on CO$_2$ adsorption by N-doped polypyrrole-based porous carbons

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Abstract
Nitrogen-doped carbons have attracted much attention due to their novel application in relation to gas storage. In this study, nitrogen-doped porous carbons were synthesized using SBA-15 as a template, polypyrrole as the carbon and nitrogen precursor, and KOH as an activating agent. The effect of the activation temperature (600–850°C) on the CO$_2$ adsorption capacity of the obtained porous carbons was studied. Characterization of the resulting carbons showed that they were micro-/meso-porous carbon materials with a well-developed pore structure that varied with the activation temperature. The highest surface area of 1488 m$^2$ g$^{-1}$ was achieved at an activation temperature of 800°C (AC-800). The nitrogen content of the activated carbon decreased from 4.74 to 1.39 wt% with an increase in the activation temperature from 600 to 850°C. This shows that nitrogen is oxidized and more easily removed than carbon during the activation process, which indicates that C-N bonds are more easily ruptured at higher temperatures. Furthermore, CO$_2$ adsorption isotherms showed that AC-800 exhibited the best CO$_2$ adsorption capacity of 110 mg g$^{-1}$ at 298 K and 1 bar.

Keywords: N-doped, SBA-15, polypyrrole, CO$_2$ adsorption

1. Introduction

Global warming, as a result of rapid industrialization and civilization, has caused unpredictable disasters such as droughts, floods, economic issues, disease, and the destruction of ecosystems and has thus endangered human life [1-3]. The main greenhouse gases that lead to global warming are carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O), fluorocarbons, perfluorocarbons, chlorofluorocarbons, and sulfur hexafluoride (SF$_6$) [3]. Among these gases, CO$_2$ is a key anthropogenic greenhouse gas closely linked to the global greenhouse effect. Thus, reducing CO$_2$ emissions is a priority in the fight against global warming.

In recent years, porous carbon materials have been widely employed as potential adsorbents in many fields, including gas adsorption, catalytic supports, supercapacitors, fuel cells, and lithium ion batteries. This is due to their high specific surface area, large pore volume, low preparation cost, high adsorption capacity, stable chemical and thermal performance, and because modifications are easy to design [4-9].

Mesopores come into play when the adsorbates are polymers, dyes, and vitamins, but a microporous structure is also important to adsorb small gas molecules. Thus, it is essential to control the pore structure of porous carbons [10]. Template methods are recognized as a suitable means of controlling the development of porosity in carbons. Porous carbons with a homogeneous structure and a uniform pore size can be prepared using soft templates, but this method places the following strict requirements on the precursor: (1) the precursor should have the form of a self-assembled nanometer-sized...
structure; (2) there must be a guide component to create the pores; (3) the components used to create the pores must tolerate the activation temperature; and (4) the carbon precursor must maintain its nanostructure during decomposition and removal of the pore-creating agents [11]. Additionally, it is not possible to control the size and shape of the products when using a soft template. However, hard-template sources such as ordered mesoporous silicate and zeolites are relatively abundant. In particular, SBA-15 is an efficient hard template due to its well-ordered hexagonal mesoporous structure.

Recently, the presence of certain functional groups containing electron-donating or electron-withdrawing heteroatoms, such as N, B, and Si, has been shown to improve the CO2 adsorption performance of carbon materials [12]. Nitrogen doping has attracted much interest due to the unique applications of N-doped carbons, particularly in gas adsorption, water purification, catalyst supports, and electrochemistry [13]. Conductive polymers are excellent carbon and nitrogen source materials. Specifically, the monomer of polypyrrole is a C, N five-membered heterocyclic molecule, which is a more common conductive polymer. Recently, it has been reported that polypyrrole can be used as a conductive polymer and combined with other materials as a carbon source and nitrogen source to prepare porous carbons. Thus, significant efforts have been made to synthesize N-doped porous carbons. Hard templating is often employed to prepare heteroatom-doped carbons due to the controllable pore structure and morphology of the obtained carbons and the homogeneous incorporation of nitrogen into the carbon frameworks.

In recent work, Wahby et al. [14] demonstrated that porous carbons with a high surface area can capture a large amount of CO2 [15]. KOH is usually used as a chemical activation agent because it produces activated carbon with an extremely high surface area, a predominantly microporous structure, and a narrow micropore distribution. Here, a series of N-doped porous carbons were synthesized using SBA-15 as the template, polypyrrole as the carbon and nitrogen precursor, and KOH as an activating agent. We expect that the porous carbon produced using this method will combine a high density of nitrogen functionality and a large surface area, thus displaying improved CO2 capturing outcomes.

The effect of the KOH activation temperature on the CO2 adsorption capacity of the obtained porous carbons was also studied at temperatures of 600, 700, 800, and 850°C. The prepared N-doped porous carbons had large specific surface areas (663–1488 m² g⁻¹) and, furthermore, these carbon materials showed relatively high CO2 adsorption capacities of up to 110 mg g⁻¹ at 298 K and 1 atm.

### 3. Results and Discussion

The external pore structure of the prepared activated carbons studied was observed using SEM and TEM, as shown in Fig. 2. The SBA-15 (Fig. 2a and b) and AC-800 morphology (Fig. 2c and d) morphologies were characterized using SEM. Fig. 2e shows TEM images of the AC-800 activated carbon. The AC-800 morphology is not similar to that of SBA-15, which consists of interconnected short bars to necklace-like connected spherical particles. Fig. 2b shows that SBA-15 has a well-ordered hexagonal mesoporous structure. This morphology provides a large pore canal that is essential for achieving good pore development and in which polypyrrole can react uniformly with KOH. As shown in Fig. 2c, AC-800 largely follows the pore structure of SBA-15, which indicates that the activated carbons have a replicated two-dimensional hexagonal mesoporous
The textural properties of the activated carbons prepared at different temperatures (600, 700, 800, and 850°C) were characterized from their nitrogen adsorption-desorption isotherms, as displayed in Fig. 3. The isotherm shape changes with an increase in the activation temperature from 600 to 850°C, which indicates a change in the porous structure of the activated carbons. All of the isotherms are basically identical as type I or IV, according to the IUPAC nomenclature, with the corresponding type of hysteresis loop, indicative of the mesoporous nature of the SBA-15 template, which indicates that polypyrrole was actually inserted inside of the SBA-15 channels. In addition, some micropores are present in the activated carbons, which may be a result of interaction in the carbon framework inducing a pore-wall collapse and blocking some of the mesoporous channels.

The pore-structure parameters of the activated carbons as a function of the activation temperature are summarized in Table 1. The synthesized activated carbons have high specific surface areas, large mesopore volumes, and large total volumes. The specific surface area increased with an increase in the activation temperature up to 1488 m² g⁻¹ (AC-800) and then decreased to 1235 m² g⁻¹ (AC-850). The pore diameter was controlled in the range of 2.42 to 3.77 nm and the pore volume increased significantly when increasing the activation temperature from 0.467 to 1.164 cm³ g⁻¹. Micropore formation can be attributed to thermo-decomposition of the carbon precursor (polypyrrole), while the mesoporous framework results from the replication of the SBA-15 template [16]. It was unusual to find that the mesopore volume of AC-800 is much lower than that of AC-850, whereas the specific surface area of AC-800 is much higher than that of AC-850. This may be due to the collapse of the template structure at high temperatures, resulting in the production of vast numbers of mesopores despite the greater activation of the carbon source at the higher temperatures. The micropores prevailingly derive from the activation of the carbon precursor, while mesopores mainly stem from the replication of the SBA-15 template. Furthermore, some mesopores will form due to the collapse of the thinner micropore walls in the carbon frameworks during the HF etching of the SBA-15 template as a result of the high temperatures achieved during this process [17].

For better characterization of the change in the pore structure of the activated carbons studied here, the pore size distributions in the micro-meso-pore regions are shown for the prepared porous carbons obtained using different activation temperatures. Fig. 4 shows the effect of the activation temperature on the pore size distribution of the prepared activated carbons. All of the carbons obtained at different activation temperatures possessed a mostly narrow pore size distribution mainly concentrated in the 0.5 to 2 nm range. On the one hand, mesopore formation arises from removal of the template; on the other hand, the micropores originate from the activation of the carbon source. In particular, AC-800 possesses a significant fraction of narrower micropores (<0.7 nm), which has an important effect on its gas capture properties.

The details of the textural properties and chemical compositions of the prepared activated carbons at different temperature are shown in Table 1. As shown in Table 1, the nitrogen content of the activated carbons decreased from 4.74 to 1.39 wt% as the activation temperature increased from 600 to
CO2 adsorption by N-doped polypyrrole-based porous carbons

Table 1. Pore structure parameters and elemental compositions of the prepared activated carbons at different activation temperatures from the N2 adsorption isotherms

<table>
<thead>
<tr>
<th>Sample</th>
<th>SBET (m² g⁻¹)</th>
<th>V_total (cm³ g⁻¹)</th>
<th>V_meso (cm³ g⁻¹)</th>
<th>D (nm)</th>
<th>Chemical composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N</td>
</tr>
<tr>
<td>AC-600</td>
<td>663</td>
<td>0.467</td>
<td>0.270</td>
<td>2.82</td>
<td>4.74</td>
</tr>
<tr>
<td>AC-700</td>
<td>1204</td>
<td>0.729</td>
<td>0.349</td>
<td>2.42</td>
<td>2.15</td>
</tr>
<tr>
<td>AC-800</td>
<td>1488</td>
<td>0.976</td>
<td>0.545</td>
<td>2.62</td>
<td>1.18</td>
</tr>
<tr>
<td>AC-850</td>
<td>1235</td>
<td>1.164</td>
<td>1.006</td>
<td>3.77</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Fig. 4. Micropore size distributions (a) and mesopore size distributions (b) of the prepared activated carbons at different activation temperatures.

850°C, which shows that nitrogen is oxidized and more easily removed than carbon during the KOH activation process [14]. This also indicates that C-N bonds are more easily ruptured at higher temperatures. Moreover, the existence of alkaline nitrogen functional groups favors increased CO2 adsorption.

The CO2 adsorption capacities of the activated carbons were measured using CO2 adsorption isotherms at 298 K, and the obtained results are shown in Fig. 5. All of the porous carbons show high CO2 adsorption capacities (at least 30 mg g⁻¹) in the order of AC-800>AC-700>AC-600>AC-850>SBA-15. This indicates that a relatively high activation temperature is favorable for CO2 adsorption. AC-800 exhibits the best CO2 adsorption capacity at 110 mg g⁻¹, which is attributed to its high surface area. As the carbon surface is the CO2 adsorption site and the pore volume is the volume available for trapping CO2, a large number of adsorption sites and a high trapping volume lead to a high CO2 adsorption capacity [18-20]. CO2 adsorption not only relies on the pore structure and surface area of the carbons but also on the surface functional groups. In this study, the prepared porous carbons contained basic nitrogen functional groups, which can act as chemical adsorption sites for CO2. The basic functional groups increase the surface interactions with acidic CO2 gas, thereby enhancing the CO2 adsorption capacity.

4. Conclusions

In summary, nitrogen-doped porous carbons were directly prepared from a polypyrrole carbon precursor, with SBA-15 serving as a template, via chemical activation with KOH. The effect of the activation temperature on the pore structure and CO2 adsorption capacity of the obtained porous carbons was studied. We found that the N-doped carbons had high surface

Fig. 5. CO2 adsorption capacities of the prepared activated carbons at different activation temperatures (at 298 K and 1 bar).
areas (up to 1488 m² g⁻¹), large pore volumes (up to ~1.164 cm³ g⁻¹), and porosities within the micropore–mesopore range.


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References