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One-pot synthetic method to prepare highly N-doped nanoporous carbons for CO_2 adsorption

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HIGHLIGHTS

- A one-pot synthetic method was used for the preparation of N-doped nanoporous carbons.
- Polypyrrole (PPY) were activated with NaOH under set conditions (NaOH/PPY = 2 and 4).
- N-doped activated carbon exhibited high specific surface areas (2169 m^2 g^{-1}).
- The carbons showed a very high CO_2 adsorption capacity of 177 mg g^{-1} at 298 K.

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ABSTRACT

A one-pot synthetic method was used for the preparation of nanoporous carbon containing nitrogen from polypyrrole (PPY) using NaOH as the activated agent. The activation process was carried out under set conditions (NaOH/PPY = 2 and NaOH/PPY = 4) at different temperatures in 600–900 °C for 2 h. The effect of the activation conditions on the pore structure, surface functional groups and CO_2 adsorption capacities of the prepared N-doped activated carbons was examined. The carbon was analyzed by X-ray photoelectron spectroscopy (XPS), N2/77 K full isotherms, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The CO_2 adsorption capacity of the N-doped activated carbon was measured at 298 K and 1 bar. By dissolving the activation agents, the N-doped activated carbon exhibited high specific surface areas (755–2169 m^2 g^{-1}) and high pore volumes (0.394–1.591 cm^3 g^{-1}). In addition, the N-doped activated carbons contained a high N content at lower activation temperatures (7.05 wt.%). The N-doped activated carbons showed a very high CO_2 adsorption capacity of 177 mg g^{-1} at 298 K and 1 bar. The CO_2 adsorption capacity was found to be dependent on the microporosity and N contents.

1. Introduction

Over the past two decades, porous carbons, such as activated carbons, activated carbon fibers, nanoporous carbon, carbon nanofibers and graphene, have attracted considerable attention as gas adsorbents owing to their highly developed porosity, extended surface area, and the hydrophobicity of their surface chemistry, thermal stability and low cost [1–8]. In particular, reducing CO_2 emissions has attracted increasing attention owing to their deleterious global environmental effects. Up to now, commercial CO_2 capture technologie is very expensive and energy intensive. Improved technologies for CO_2 capture are needed to achieve a low energy penalty [8–10]. Among the different methods for CO_2 capture, considerable effort has been made to improve its adsorption.

A range of carbon materials have been used for CO_2 capture. Porous carbons are a non-oxide porous material with significant scientific and technological applications in CO_2 adsorption. Two different approaches have been adopted to improve the CO_2 adsorption capacities of porous carbons. One simple approach is to incorporate superficial basic sites that improve the interaction of CO_2 (acidic gas) with the carbon surface. Currently, these basic sites consist of nitrogen functional groups incorporated through a reaction of porous carbons with different nitrogen-containing compounds (e.g. ammonia, amines, etc.) [10–15]. Recently, several authors have examined a simpler route for the creation of basic centers using nitrogen-rich compounds as the precursors for the fabrication of N-doped carbons [12,13]. Another strategy to enhance CO_2 capture capacity is to fabricate porous carbons with a

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tailored pore structure suitable for CO_2 adsorption. Recent research has shown that activated carbons with a large population of pores, 1–2 nm in size, exhibit better CO_2 adsorption performance than those with narrower micropores or with a mesoporous pore network [14,15].

Porous carbons with these pore characteristics can be obtained by chemical activation and carbonization using different types of precursors with KOH and a template [8]. Park et al. reported the preparation of porous carbon materials that exhibited high CO_2 adsorption capacities from a weak acid acrylic cation exchange resin using the MgO-template method [16].

In this study, very high CO_2 adsorption capacities (1 bar and 298 K) of highly porous N-doped activated carbons were prepared for CO_2 capture using polypyrrole (PPY) as the carbon precursor and NaOH as the activating agent. The activation process was carried out under fixed activation conditions at different temperatures (600–900 °C). The effect of the activation conditions on the pore structure, surface functional groups and CO_2 adsorption capacities of the prepared N-doped activated carbons was examined.

2. Experimental

2.1. Materials and method

PPY was prepared using $FeCl_3$ as an oxidizing agent. 0.3 M of distilled pyrrole was added to a solution of 0.5 M of $FeCl_3$. The resulting reaction mixture was stirred continuously at 5 °C to obtain polypyrrole [17]. The product was filtered and washed thoroughly with methanol, and the sample was dried under vacuum for more than 24 h at room temperature. The final PPY yield was approximately 100%. The polypyrrole was activated chemically by heating a PPY and NaOH mixture (NaOH/PPY at a weight ratio of 2 or 4) to 600–900 °C (heating rate: 3 °C min^{-1}, holding time: 2 h) under N_2. The activated samples were then washed several times with HCl (10 wt.%) to remove any inorganic salts, and then washed with distilled water until a neutral pH was reached. Finally, the activated carbons was dried in an oven at 120 °C. The activated carbons thus synthesized is denoted as PN-*a*-*b*, where *a* is the NaOH/PPY weight ratio and *b* the activation temperature (in °C). Fig. 1 shows a schematic diagram of N-doped activated carbons formation steps using a NaOH activation method.

2.2. Characterization

The textural properties of the samples were determined by physically adsorbing N_2 at 77 K using a surface area analyzer (BEL, Japan). The N_2 adsorption on the samples was used to calculate the specific surface area using the Brunauer–Emmett–Teller (BET) equation. The total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of approximately 0.995, and the micro- and mesopore structures were analyzed using the Horvath–Kawazoe (H–K) and BJH (Barrett–Joyner–Halenda) equations, respectively. The morphologies of the samples were analyzed by scanning electron microscopy (SEM, Hitachi S-4200) and transmission electron microscopy (TEM, JEM2100F, JEOL). X-ray photoelectron spectroscopy (XPS, ESCALAB220i-XL VG Scientific, UK) was performed using monochromatized Al *Kα* X-ray radiation as the X-ray source for excitation to confirm the nitrogen content.

A CO_2 adsorption test was conducted under ambient conditions of 273 K and 298 K at both low (1 bar) and moderate pressures (30 bar, BEL, Japan). In each experiment, approximately 0.1 g of the sample was loaded into a stainless chamber. Before the measurements, the samples were degassed at 573 K for 12 h to obtain a residual pressure $<10^{-6}$ mmHg. After the chamber was cooled to room temperature, CO_2 was introduced until a pressure of 30 bar was reached. Ultrahigh purity grade (99.9999%) CO_2 was used to exclude the effects of moisture and other impurities. Finally, a

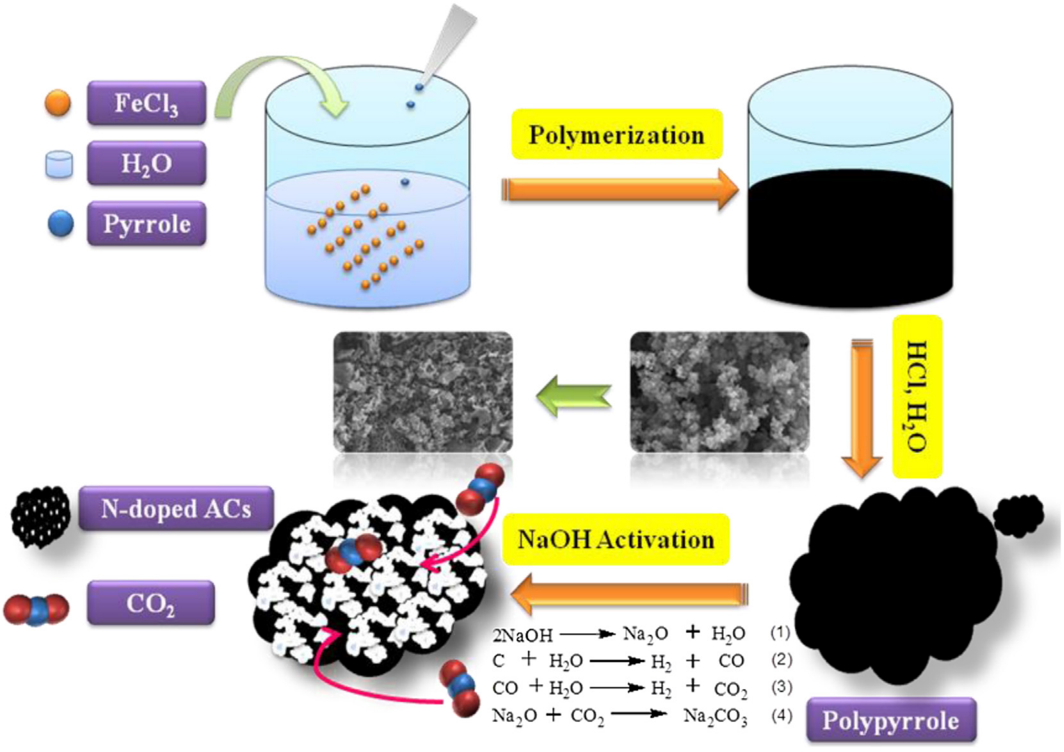

Fig. 1. Schematic diagram of the preparation of N-doped activated carbon formation steps for CO_2 capture.