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Heteroatom self-doped activated biocarbons from fir bark and their excellent performance for carbon dioxide adsorption

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ABSTRACT

A series of cost-effective heteroatom-doped porous carbons has been developed from the agricultural by-products of fir bark by a two-step carbonization and activation process. The morphology, chemical characterization and texture properties were investigated by thermogravimetric analysis (TG), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectrometry (XPS), elemental analysis (EA), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and N_2 adsorption-desorption at 77 K. The results show that fir bark is a suitable precursor for preparing heteroatom-doped activated carbon, corresponding to hetero-oxygen (2.05–7.35 wt. %) and nitrogen (0.8-1.5 wt. %) doping. The lab-made AC materials derived from fir bark, with a surface area of 1377 m^2/g, showed a very excellent sorption performance for CO_2 up to 7 mmol/g and 5.2 mmol/g at 273 K and 298 K up to 1 bar, which was significantly higher than the commercial carbon materials and were among the highest compared with other biomass based ACs. The high CO_2 uptakes, moderate heat of adsorption (Qst), good selectivity show that the high performance activated carbons for CO_2 capturing at low pressure can be prepared by KOH activation of fir bark.

1. Introduction

Carbon dioxide is a major greenhouse gas emitted by the combustion of fossil fuels (coal, oil and natural gas) [1], and it results in the greenhouse effect and a change in the global climate. The concentration of CO_2 in the atmosphere has been increasing at a terrifying pace due to higher demands for global consumption of fossil energy [2,3]. Therefore, the control of CO_2 emission is a momentous matter for improving the global climate. For CO_2 capture, principal methods are processes of absorption in amines, adsorption on porous solids, cryogenic distillation and membrane separation [4,5]. However, considering intensive energy consumption and the corrosively in the regeneration process, the development of new and suitable adsorbent materials for selective carbon dioxide adsorption and capture is one of the fundamental tasks and also very urgent [4]. These materials should possess a large CO_2 adsorption capacity (suitable pore texture development), a high affinity and selectivity toward CO_2, a stability during rapid adsorption-desorption cycles, fast kinetics and low heat of adsorption, a tolerance for moisture and of course inexpensive [5]. To date, the most commonly studied porous solid adsorbents are zeolites [6], covalent organic frameworks (COFs) [7,8], carbon gels [9], activated carbons [10–13], metal-organic-frameworks (MOF) [14,15], and porous of organic polymers (POPs) [16,17].

Among these materials, activated carbons (AC) possess excellent pore structure and are regarded as one of the most porous adsorbents, attracting wide research interest in hydrogen storage [18,19] and carbon dioxide capture [20–23]. AC has the characteristic feature of high specific surface area (S_{BET}), large micropore volume (V_{mic}), favorable pore size distribution (PSD), thermal and chemical stability, capability for rapid adsorption and stability for large-scale production and fast kinetics [18,19]. As is known to all, ACs can be prepared by pyrolysis from a variety of carbon-containing source materials. Many kinds of ACs derived from bamboo [3,19], sawdust [1], Corncob [2], leaves [10,12], palm shells [13], coconut shell [20,24], rice husk [23], polymers [25], anthracites [26], etc., have been prepared by physical and/or chemical activation for CO_2 adsorption. The important role of micropore size and volume of ACs on CO_2 capture has been widely accepted [20–23]. In addition to micropores, heteroatom (N, B, P, S, and O) doping is another possible factor that may influence the CO_2 adsorption behavior.

Among them, N and/ or O doped activated carbons have gained increasing interest over the last decade, mainly because doping carbonaceous materials with nitrogen and oxygen is an effective way to modify their surface chemistry and improving their CO_2 adsorption

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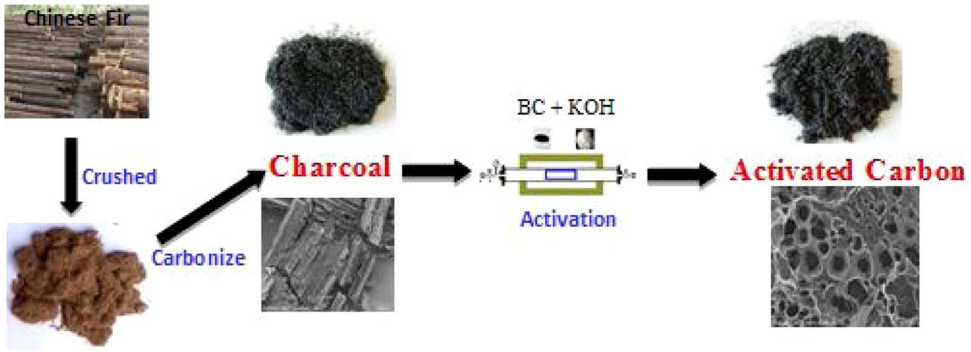

Fig. 1. Schematic illustration of the complete synthesis route of the AC samples.

performance. Kowalewski et al. [27] reported N-doped sample exhibited higher selectivity and Qst than non-N-doped counterpart. Recently, Nandi et al. [28] presented high initial isosteric heats of adsorption (Qst) values 65.2 kJ/mol, indicate strong adsorbent–adsorbate interaction between the N-containing carbon framework and CO_2 molecules. Ashourirad et al. [29,30] found that the CO_2-philic sites (N and O) are the key parameters for selective CO2 adsorption over N_2 and CH_4. Liu and Wilcox [31] theoretically analyzed the positive effect role of oxygen-containing groups in CO_2 capture. Overall, the role of heteroatom involving sites, particularly N- and O- containing groups in CO_2 capture, mainly because the changing of the geometry of the pore surface and the charge distribution of the surface. The N and O can be introduced predominantly in two ways to fabricate N/O-doped activated carbons, namely, from carbonization/activation of N/O-enriched precursors or from post-treatment with a N/O source, such as urea, melamine, ozone, plasma oxidation, etc. However, negative impact of the post-treatment on CO_2 storage has demonstrated by several authors due to the blocking of the pores in ACs. Therefore, reasonable efforts have been devoted to developing heteroatom self-doped carbon materials.

At present, there are many studies on the development of biomass adsorbents, *e.g.*, biomass materials derived from domestic wastes, industrial wastes, agricultural and forestry by-products due to their wide availability, low cost, and renewability [20–24]. The fir tree is one of the most abundant trees all over the world, and it is of high economic value as a renewable natural resource that is widely used in building, furniture and medicine. Fir bark is a sort of common forestry waste, and it is currently poorly valued. In most cases, vast fir bark will be burned as garbage and produce ash and hazardous gaseous pollution products. If the deciduous bark could be employed as a carbon source to synthesize super activated carbon, one could acquire high-value-added products for diversification and growing carbonaceous applications [18,27]. Another advantage is that fir bark is a natural heteroatom-containing precursor in which the introduction of nitrogen/oxygen-containing functional groups has little effect on the pore structures, and these functional groups are highly dispersed either on the surface or in the carbon matrix.

This present work used fir bark as a raw material to prepare heteroatom self-doped activated carbons, using KOH as the activation agent for carbon dioxide capture. This material would not only generate value-added products from forestry waste but also offer a potentially cost-effective alternative to commercial ACs. The aim of this experiment was to investigate the impact of the weight ratio of KOH/bark charcoal and to characterize the ACs from fir bark.

2. Experimental

2.1. Materials

Chinese fir (Cunninghamia lanceolata) bark obtained from a commercial plantation area in Fujian province, China, was repeatedly cleaned with tap water until the color of the leachate was clear and then oven dried for 24 h at 103 °C. The bark was crushed and sieved through a number 10 mesh (approximately 2 mm).

The potassium hydroxide (KOH) and HCl reagents purchased were analytic grade and used without further purification or treatment. All of them were from Tianjin Fuchen Chemical Reagents Factory (China).

2.2. Activated carbon synthesis

ACs were prepared by two steps. First, the powder was carbonized at 450 °C for 1 h under pure nitrogen environment and gradually increased temperature (5 °C/min); the flow rate of nitrogen was 500 ml/min. After cooling down to room temperature, the carbonaceous precursor was obtained. Subsequently, the carbonaceous precursor powder and KOH were physically mixed with 1:0.5–6 mass ratio (wt.%), and introduced into a nickel crucible. A muffle furnace (KDF, 80-plus) was used for heat-treating under a stream of nitrogen (500 ml/min) at a constant heating rate (3 °C/min) up to the final activation temperature 700 °C and kept for 2 h. After cooling down to room temperature under nitrogen flow, the activated carbon was washed first with 1 M HCl, followed with Soxhlet for 48 h. Finally, the AC was dried in an oven for 24 h, and a very pure activated carbon (AC) material was obtained and designated ACBKx, where x represents the KOH/carbon mass ratio. The synthesis route was presented in Fig.1.

2.3. Physicochemical characterization of the materials

2.3.1. TG analysis

The TG curves representing the carbonization and activation processes at the weight ratio W = 4 were obtained by thermogravimetric analyses (TGA, SDT-Q600, NETZSCH, Germany). The samples were heated from room temperature to the final temperature of 1000 °C at a rate of 10 °C/min under an atmosphere of N_2 maintained at a flow rate of 20 ml/min.

2.3.2. Morphology analysis

The surface morphology of the samples was carried out using scanning transmission electron microscopy (SEM) observations (FEG SEM Hitachi S 3400, Japan) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100 at an accelerating voltage of 200 kV).

2.3.3. Chemical characterization

The surface functional groups of the AC samples were investigated by Fourier transform infrared (FTIR) spectroscopy. The spectra were measured between 4000 and 400 cm^{-1}. The elemental analysis was determined by an elemental analysis Vario EL from Elementar (Elementar Analysensysteme, Germany) and an X-ray photoelectron spectrometer (XPS) from a SPECS XPS (XPS; SPECS XPS system, Berlin,