



The formation of novel carbon/carbon composite by chemical vapor deposition: An efficient adsorbent for enhanced desulfurization performance



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ABSTRACT

Carbon species were grown on surface of prepared Ni based biomass carbon to form a novel carbon/carbon composite by thermal chemical vapor deposition (CVD) of methane without extra catalyst, which is different from the regular preparation method. Methane was adsorbed on the surface of metal Ni firstly, and then decomposed to elemental carbon via a sequence of free radical reactions. The produced carbon was dissolved into the metal catalyst. The CNTs are then formed by precipitation of carbon atoms on the surface of the catalyst. The physical–chemical properties of prepared new composite materials are characterized to illustrate the successful growth of carbon species on the porous carbon. The composite exhibited abundant pore structure and large surface area, and then was used as adsorbent for adsorption of sulfur dioxide. The sulfur capacity of the composites is 7.3 mg/g, which is higher than that of biomass carbon support with 2.2 mg/g. The results indicated that the prepared samples exhibited the well performance on sulfur dioxide adsorption.

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1. Introduction

Adsorption is considered to be one of most effective method for the pollutant removal. The adsorption efficiency is mainly affected by the adsorbent. Among them, carbonaceous materials have been extensively investigated for the adsorption of sulfur dioxide, which is controlled by the property of adsorbent such as pore texture parameters and surface functional groups. Therefore, many modification methods of carbon adsorbents had been investigated to strengthen their interaction with target pollutants [1–3]. Chemical and thermal treatment methods are used commonly to introduce some functional groups on the carbon surface and change surface chemistry characteristics or adjust pore structure of the adsorbents, respectively [4–9].

Due to the dual advantage of the composite material, it attracts much attention in the different application field. Among the different carbon materials, activated carbon has been investigated extensively due to its advantage of density, and rapid adsorption capability. In the meanwhile, carbon nanotubes exhibit the excellent characteristics of the large surface area and abundant porous

structure. Therefore, the couple of carbon nanotubes (CNTs) on activated carbon surface to form the new composite with unique physical, chemical and electronic properties could be attractive for their potential applications in environmental remediation.

Chemical vapor deposition (CVD) technique is the dominant method to synthesize CNTs in substrates like activated carbon fibers [10], activated carbon [11–13] and porous supports such as MgO [14–16], Al₂O₃ [17,18] and SiO₂ [19]. Fe, Co, and Ni have been widely used as the most effective catalysts for the CVD growth of carbon nanostructure [20,21]. The abundant pore structure and the large surface area offer the advantage for the dispersion of metal catalyst, which is favorable for the growth of CNTs and can enhance nanotube yield [22,23].

This study is focused on the synthesis of carbon species on as-prepared biomass carbon by chemical vapor deposition (CVD) using methane as the carbon source to form the novel carbon/carbon composite. The carbon support is prepared by catalytic carbonation of biomass in the presence of nickel catalyst, and then used as support for the formation of CNTs upon the surface of carbon to enhance adsorptive capacity. The preparation method is different from the regular method for the growth of CNT in the presence of Ni particles catalysts. The physical properties of prepared new composite materials are characterized to illustrate the successful growth of carbon nanotube on the porous carbon. In addition, the

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composite with abundant pore structure and large surface area was used as adsorbent for adsorption of sulfur dioxide.

2. Material and methods

2.1. Preparation of the carbon/carbon composite

2.1.1. Preparation of biomass based carbon support

Biomass based carbon was prepared from the precursor of corn cob, which was used as support for the growth of CNT. The original corn cob was dried at 120 °C for overnight, then crushed and sieved to 80–200 mesh. The carbon prepared with Ni(NO₃)₂ catalyst show the best adsorption capacity [24]. In addition, according to the report, metal Ni catalyst result in the best growth rate of carbon nanotube by CVD method [25]. Therefore, Ni(NO₃)₂ is selected as the catalyst in the article.

The carbon support were prepared by catalytic carbonation of pretreated corn cob using Ni(NO₃)₂ as catalyst. 10 g pretreated raw materials are mixed with Ni(NO₃)₂ solutions in the different mass ratio and stirred for different time at different impregnation temperature to make the nickel disperse into corn cob. So it is advantageous for the catalyst to play a better catalytic role in the carbonization stage. Subsequently, the mixture is dried at 120 °C for overnight to remove free water and then heated to the 500 °C with 10 °C/min and keeps at different temperature for 90 min under nitrogen atmosphere at 0.5 L/min. The impregnation parameters (temperature, time, and catalyst ratio) are investigated in this article.

2.1.2. Growth of CNTs on biomass carbon support

CNTs were synthesized in fixed bed reactor (vertical furnace) at different temperatures (500–700 °C) by CVD method. In a typical growth experiment, 1 g pretreated biomass based carbon was located in stainless steel tube, subsequently heated to 600 °C with the increase rate of 10 °C/min, and then kept at this temperature for 90 min with H₂ flow of 50 mL/min. All gases were controlled by differential mass flow controllers (MFC). In the following, the sample was heated to different temperature from 500 to 700 °C under N₂ flow of 100 mL/min, and kept at this temperature for 15 min to stabilize the samples before the addition of carbon source. And then, the flow of methane at 50 mL/min was introduced into the reactor for the growth of CNTs.

2.2. Characterization of the composite sample

The surface morphologies and main elements content of the samples were characterized by the scanning electron microscopy (SEM) (Hitachi, S-3000N) and energy dispersive X-ray spectrometer (EDS). X-ray diffraction (XRD) (Rigaku D/max-2500 diffractometer with Cu K α radiation) was used to acquire the composition of samples. Fourier transform infrared spectroscopy (FTIR) (Bruker Tensor 27 spectrometer) which is obtained in the range of (500–4000) cm⁻¹ by combination sample with KBr to interpret the surface structure of samples. Pore texture parameters are measured by

nitrogen adsorption at 77 K on a Micromeritics ASAP 2020 sorptometer.

2.3. The adsorption performance

The adsorption performances of prepared samples are evaluated by the methylene blue (MB) capacity (GB/T12496.8-1999) and iodine value (GB/T12496.10-1999). The SO₂ adsorption capacity was evaluated by breakthrough test under dry condition.

The desulphurization performance of prepared carbon samples is test in vertical tube furnace with internal diameter of 7 mm for the stainless steel column. All gas controlled by the MFC are merged into gas mixer firstly, and then flowed into the reactor. The outlet gas was adsorbed with KOH solution to reduce the discharge of harm gas. The standard cylinder was used for the preparation of the simulated coal gas. 1 g prepared carbon samples are used for test with SO₂ (1000 ppm), 8% O₂, N₂ as carrier gas with flow rate of 100 mL/min. The SO₂ gas sample is collected at certain interval time and monitored using handy flue gas analyzer (ZYF-6800P). The adsorption capacity of SO₂ was calculated by Eq. (1) and (2). And the adsorption efficiency is acquired by Eq. (3).

$$\Delta q_n = \frac{10^{-6}Q}{2m} (t_n - t_{n-1}) [(C_{SO_2}^0 - C_{SO_2}^n) + (C_{SO_2}^0 - C_{SO_2}^{n-1})] \quad (1)$$

$$q_n = \sum \Delta q_n \quad (2)$$

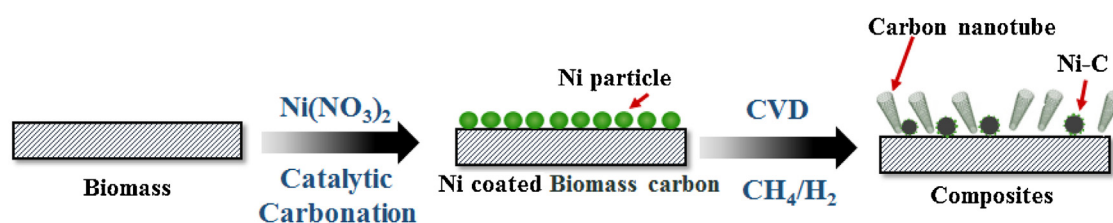
$$\eta = \frac{10^6 m q_n}{C_{SO_2}^0 Q t_n} \times 100\% \quad (3)$$

Among them: q_n , q_{n-1} —The cumulative adsorption capacity of SO₂ when sampling at n times and $(n-1)$ times (mg/g); t_n , t_{n-1} —The cumulative time when sampling at n times and $(n-1)$ times (min); $C_{SO_2}^{n-1}$, $C_{SO_2}^n$ —the outlet concentration of SO₂ when sampling at $(n-1)$ times and n times (ppm); $C_{SO_2}^0$ —the inlet concentration of SO₂ (ppm); Q —flow rate of flue gas (mg/min); m —mass of carbon samples (g); η —adsorption efficiency (%).

3. Results and discussion

3.1. The preparation conditions

The mixture of biomass with catalyst is advantageous for the catalyst to play a better catalytic role in the carbonization stage to form the porous carbon with the high surface area. Furthermore, the large surface area and high porosity of carbon support could prevent catalyst particle coalescence and produce well dispersion of catalyst particles [26,27]. Therefore, a new method was proposed to prepare the composite by catalytic carbonization of biomass firstly to form porous carbon, and then growth of CNTs on the biomass carbon support without the additional catalyst to form composite. The preparation process of the composite can be presented in Scheme 1. The catalyst play dual role during this preparation course: one side, it is favorable to the porous carbon support; on the other side, the remaining catalyst on the surface of carbon support could be used for the growth of CNTs.



Scheme 1. The preparation process of carbon/carbon composite.

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