Influence of Base Additive on Nanoporous Carbon Materials via HTC for Catalyst Support

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Abstract: Nanoporous support materials were successfully synthesized from biomass via hydrothermal carbonization with base additives. This research study the effect of hydrothermal temperature (160-200 °C), hydrothermal time (4-24 h) and influence of base additive (NaOH, KOH, Na_2CO_3 and K_2CO_3) have been chosen in order to improve the surface structure. The samples have been characterized by scanning electron microscopy, nitrogen sorption, Fourier transform infrared spectroscopy and X-ray diffraction. The experimental results revealed that hydrothermal carbonization process and acid addition have effect on the properties of catalyst support. The results indicated that hydrothermal process at 200°C for 12 h and activation with KOH at 900°C for 2 h, exhibited the highest surface area, porosity and pore volume leading to increased distribution of metal on the carbon support.

Keywords: Biomass, Nanoporous carbon, Catalyst support, Hydrothermal carbonization.

1. Introduction

Sustainable and renewable materials are required in all aspect of energy and environment because of decreasing of the resource. Most research focuses on synthesis or production of biofuel, solar energy, use of biomass for energy and resources such as activated carbon [1]. Activated carbons applications in water treatment in most industry such as food [2, 3], pharmaceutical, petroleum [4], automobile [5], nuclear [6], [7], and biofuel. Furthermore, activated carbon with high porosity are used extensively for adsorption of small sized molecule. Treatment system is necessary for increasing of pore size to containing large molecules requires adsorbents with mesoporous content [8].

Carbon with high mesoporous surface areas have utility in many applications, for example in chromatography, dye removal from water, electronic capacitor, lithium batteries, bio-catalyst, electro-catalyst, support materials, etc. [9] Synthesis of activated carbons from biomass has been carried out using physical (CO_2, stream, etc.) and chemical (typically, $ZnCl_2$, acid and base) activation [10]-[16].

Hydrothermal carbonization was the generally used in recent years for energy and materials processing to delivering desirable properties to hydrochar (high concentration of oxygenated functional groups (OFG) and low degree of aromatization) [6], [7], [17], [18].

In this research, there is interesting to investigate the influence of base additive to activated the high porosity of the activated carbon by using cattail leave as raw material. Cattail leave is one of the most common weeds in Thailand. Cattail grow rapidly and can be breed in large numbers in water source. It has an impact on the environment and waste water. Cattail leave is a biomass composed of 38.5% cellulose, 37.6% hemicellulose, 12.8% lignin and 11.1% ash [19]. Objective of this research, to synthesis and investigate the morphology, functional group and porosity of the activated carbon in different kind of base (NaOH, KOH, Na_2CO_3 and K_2CO_3) activation.

2. Materials and Methods

2.1. Material Preparation

Activated carbons prepared by used Cattail leaves (*Typha angustifolia*) as carbon source from nature. Cattail leaves was washed by water to remove the impurities and cut in to 2.5 cm then dried at 90°C for 24 h, mesh and sieved for separated powder and fiber. Cattail leave powder was used to synthesis the activated carbon in this research.

2.2. Hydrothermal Treatment

Teflon autoclave was filled with 30 g cattail leaves powder and 60 mL deionized water. The hydrothermal held in range of temperature at 160, 180 and 200 °C for 4, 8, 12 and 24 h. The hydrothermal treated product (hydrochar) was cool in room temperature and were dried at 90 °C for 24 h.

2.3. Chemical Activation

The activated carbons were prepared by used base (NaOH, KOH, Na_2CO_3 and K_2CO_3) activation. Precursor were mixed with 4 M base solution and stirred for 3 h. The mixture was loaded in to quartz boat and positioned inside aluminum tube that was place in horizontal tube furnace for carbonization process. Carbonization temperature was used at 900 °C for 2 h and 10 °C/min heating rate under nitrogen atmosphere at a flow rate of 100 cc/min. The products were rinsed by used hydrochloric acid (0.1 mol/L) and washed with deionized water until a pH of 7 was obtained. Finally, the activated carbons were dried at 105 °C for 12 h.

2.4. Characterization

The surface morphology of the activated carbons prepared at the optimum conditions was identified by scanning electron microscopy (SEM) (Zeiss EVO MA10) operated at 10 kV. Fourier Transform Infrared spectroscopy (FT-IR) (Perkin Elmer Spectrum Two) was used to determine the function group on surface of sample. The porosity and surface area were calculated by applying the Brunauer-Emmett-Teller (BET) model.

3. Results and Discussions

Fig. 1a and 1b shows yield of hydrochar products trough hydrothermal process at different temperatures and times. The increase of reaction temperature leads to a significant decrease of solid yield due to moisture content in the structure was eliminated and the composition of the hemicellulose component and some of cellulose and lignin. Increasing of temperature from 160 °C to 200 °C reduced the yield on average by 30%. The yield of hydrochar significantly decreases with temperature. The higher temperature causes a relatively increase of solid mass loss, which can be due to the greater effect of water in hydrolysis reaction. The temperature of 200 °C seems to show the least of yield. When the reaction time is longer than 12 h, the yield increases. Within the investigated parameters, longer residence times resulted in yield of hydrochar increase due to re-polymerization reaction of decomposition biopolymer. The biopolymer are reformed into carbon, which reduces the surface area of hydrochar. The reaction time provided the decomposition of biomass less than temperature.

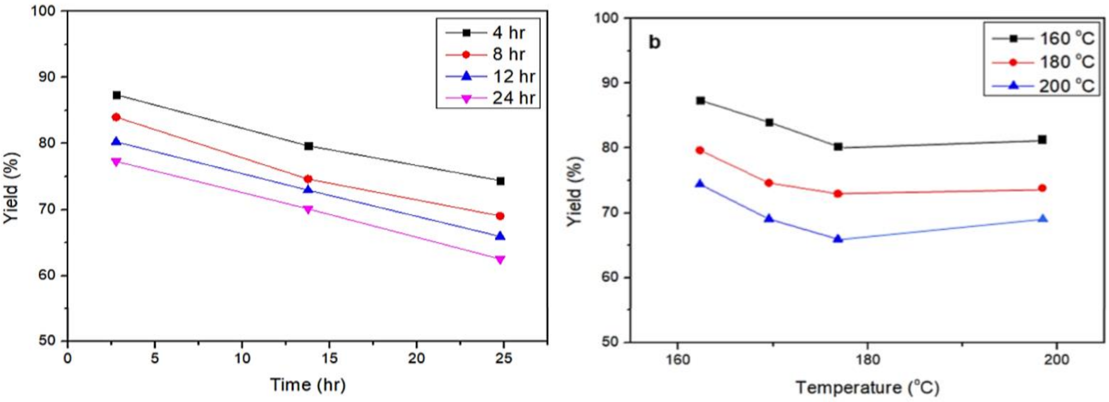

Fig. 1. Yield of hydrochar through hydrothermal process at different (a) times and (b) temperatures.

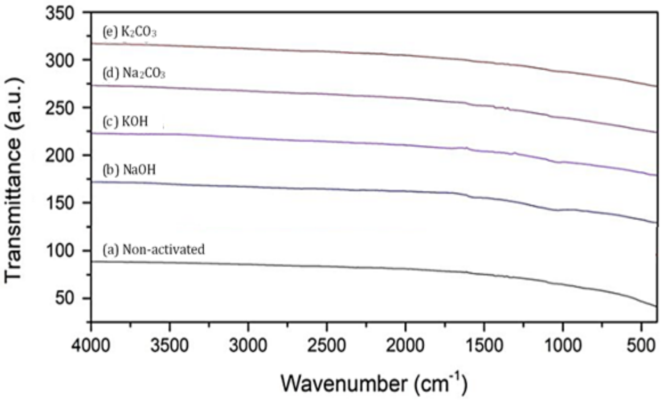

Fig. 2. FTIR spectra of carbon activated by (a) Non-activated, (b) NaOH, (c) KOH, (d) Na_2CO_3 and (e) K_2CO_3.

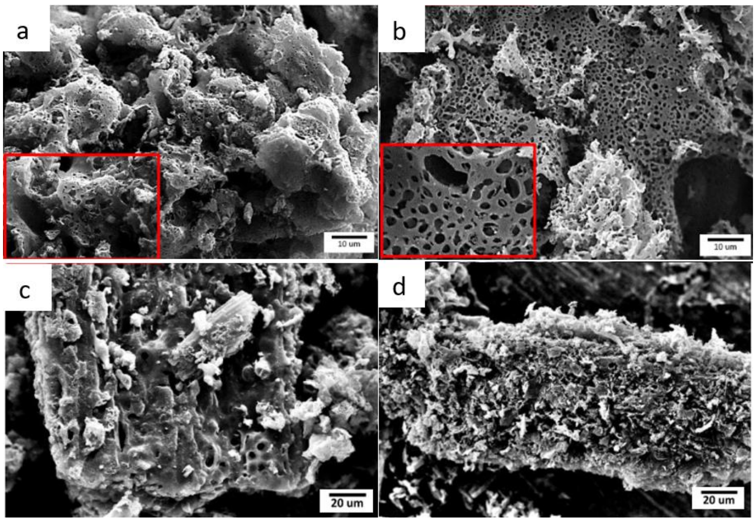

Fig. 3. SEM image (500x) of activated carbon through hydrothermal carbonization process and activated by base (a) NaOH, (b) KOH, (C) Na_2CO_3 and (d) K_2CO_3.

Fig. 2 shows FTIR spectra of non-activated carbon and carbon activated by 4 M concentration base NaOH, KOH, Na_2CO_3 and K_2CO_3 at 900 °C for 2 h. Functional group on the surface of activated carbon have degradation form base cause α and β-aryl ether of lignin turn into gas phase and water-soluble substance, and dehydration from base additive generated porosity inside the activated carbon. Hemicellulose, cellulose and lignin have degradation and generated the -OH group form -OK group on the surface. After rinse by water after activated by base cause an ion exchange, K^+ is disappear and left -OH at the surface of activated carbon.

Morphology of prepared activated carbon shown as scanning electron micrograph in Fig. 3 (a-d). After activated the hydrochar by chemical activation with base significant change on the surface morphology can be found in different kind of base. Base activation can be increase pore size and porosity depend on the dissociation of base. Comparation of hydroxy and carbonate group, carbonate base have too influence to the pores because amount of base dissociation cause the pore fracture. In the other way, hydroxy base have an appropriate influence to size increasing of pores and KOH activated exhibits a great porosity and distribution.

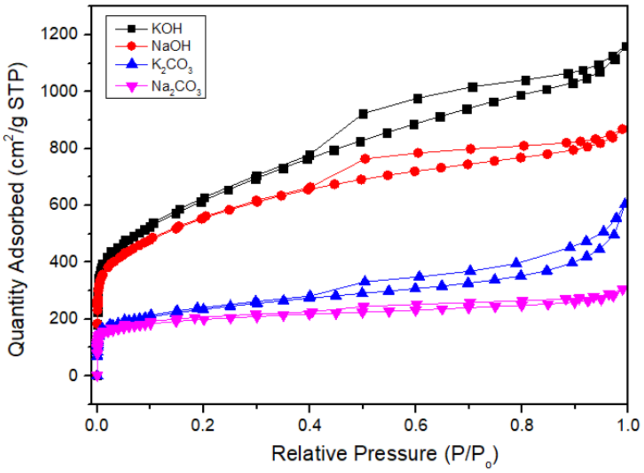

Fig. 4. Nitrogen sorption isotherm of activated carbon.

Nitrogen sorption isotherms of activated carbon shown in Fig. 4. Base activated carbon present typical (I+IV) isotherms according to the IUPAC classification. The major nitrogen adsorption occurs at relative pressures in range of 10^{-6}-0.999. A horizontal adsorption at 0.3 P/P_0 ratios, suggesting that the mesopores dominant in all activated carbon there exist some micropores because of large hysteresis loop and high deviation from the plateau region in isotherm plot. Activated carbon used hydroxy base (NaOH and KOH) have higher deviation and laugher hysteresis loop than activated carbon used carbonate base (Na_2CO_3 and K_2CO_3). Activated carbon by used KOH additive exhibited highest surface areas at 2162 m^2g^{-1}.

4. Conclusions

The hydrothermal temperature and base activation are mainly affected on the morphology and porosity of synthesized activated carbon. Hydrothermal carbonization at 200 °C for 12 h was the best condition in this work. The temperature is the mainly effect to the solid yield and structural properties of activated carbon. Increasing of the temperature cause decreasing of hydrochar yield above 30% from decomposed of hemicellulose and cellulose. The base activation has an effect to the porosity of activated carbon. Tar and gas compositions from degradation of hemicellulose and cellulose was expose and increase the pore size of activated carbon. Carbon activated by KOH could be generate the highest pore volume in this research.

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