Effects of thermal treatment on carbon cryogel preparation for catalytic esterification of levulinic acid to ethyl levulinate

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ABSTRACT

Organic catalyst, especially derived from lignocellulosic biomass, is currently being developed for application in reaction engineering. Lignin, a major constituent in biomass, is highly potential as carbon- based -derived catalyst. Carbon cryogel was prepared from acidic lignin-furfural mixtures via sol-gel polycondensation. The effect of carbonization and calcination on carbon cryogel preparation has been investigated in this study. The carbon cryogels were characterized using surface area analyzer and NH_3-TPD. Based on the carbonization and calcination studies, the total surface area and acidity of the selected carbonized cryogel were 214.2 m^2/g and 11.3 mmol/g, respectively while calcined cryogel were 426.5 m^2/g and 16.1 mmol/g, respectively. The selected carbon cryogels were further characterized using TGA, FTIR, XRD and FESEM-EDX. Overall, the characterization results revealed calcined cryogel has higher thermal stability and stronger acid sites. Subsequently, the performance of calcined carbon cryogel prevailed in catalytic esterification of levulinic acid to ethyl levulinate. The esterification reaction was further investigated at different catalyst loading (5 to 35 wt%), molar ratio of ethanol to levulinic acid (5 to 30), time (1 to 8 h) and temperature (78 to 170 °C). At the optimum conditions, calcined cryogel evinced 87.2% and 86.5 mol% of levulinic acid conversion and ethyl levulinate yield, respectively.

1. Introduction

Various types of homogeneous and heterogeneous catalysts including acid and base (organic and inorganic), metal oxide, and non-metal oxide [2,5,10,28,42,45] are being synthesized. More recently, there is a prevalence of biomass-derived catalysts for application in green chemical processes [6,13,19,27,37]. In fact, carbon has been widely explored in the development of catalyst [20,34] instead of being used as merely adsorbents only [1,14,18]. Carbon is suitable as catalyst support due to its high surface area and thermal stability [4,11,12,16]. The two properties are essential in various types of reactions especially at high temperature.

Carbon cryogel synthesized from lignin and furfural has been shown to have potential as an organic solid acid catalyst [43]. Carbon gel has been explored via synthesis of phenol or resorcinol with formaldehyde [30,39,41] and performed well in many applications including as a catalyst. The replacement of chemicals such as phenol with lignin or tannin and formaldehyde with furfural or hydoxymethylfurfural (HMF) could be another alternative for producing carbon gel. The structure of carbon gel depends on the feedstock and reaction mixture conditions to obtain wide range of carbon gel products. The properties of carbon cryogel from lignin and furfural may also be influenced by the heating and gel synthesis conditions. Thermal treatment is one of the important factors that influence the carbon properties for catalytic applications.

Ethyl levulinate is derived from levulinic acid (LA) via esterification with ethanol in the presence of acid catalyst [9,24,28]. Besides, ethyl levulinate has also been derived using carbohydrate and furfuryl alcohol [17,25,36,47,49]. The direct production of ethyl levulinate from carbohydrate and furfuryl alcohol shows potential alternative for deriving bio-fuel based products from a renewable source such as biomass [46,50]. Alkyl levulinate can be used as fuel-additives [3,24,28] to improve the engine performance, fuel stability, and quality by reducing carbon monoxide and nitrogen monoxide emissions. Besides, ethyl levulinate can also be applied as a precursor for production of γ-valer-olactone (GVL) [17], dubbed as advanced bio-fuel. Thus, carbon cryogel with good surface properties signified its potential as acid catalyst in esterification of LA to alkyl levulinate.

Therefore, the objective of this study is to investigate the effects of carbonization and calcination temperature and time to determine the optimum parameters for producing carbon cryogel. The carbon cryogel was characterized using surface area analyzer (BET), temperature programmed desorption (TPD), thermogravimetric analyzer (TGA), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and field emission scanning electron microscopy with energy dispersive

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X-ray spectrometry (FESEM-EDX). In addition, selected carbon cryogel was further studied as solid acid catalyst for the esterification of LA to ethyl levulinate.

2. Experimental

2.1. Chemicals and reagents

Sulfuric acid, H_2SO_4 (95–97%) was purchased from QRec, New Zealand, lignin and alkali were purchased from Sigma-Aldrich Co., United States and furfural was purchased from Merck, Germany. The chemicals were used to synthesize the gel for preparation of carbon cryogel. As for the catalytic testing in esterification reaction, levulinic acid and ethanol were used as the main feedstocks. All chemicals in this part were purchased from Merck, Germany with analytical grade and used as received including the standard of ethyl levulinate, which was used for peak identification and analysis.

2.2. Synthesis and preparation of carbon cryogel

The gel was synthesized according to previous method [43]. Lignin, furfural and water mixtures were mixed according to 1:1:1 ratio. The mixture was mixed with 8 M H_2SO_4 as acid catalyst in the reaction conducted at 90 °C for 30 min. The gels produced was cooled and then, immersed in *t*-butanol for solvent exchange and further rinsed with *t*-butanol to displace excess liquid. The gel was pre-frozen and then freeze dried for 8 h to form cryogel. Finally, the cryogel was either carbonized in inert atmosphere or calcined in ambient air to compare the effect on carbon cryogel preparation. The effect of carbonization temperature was studied between 300 and 700 °C at 5 h, while the range of calcination temperature was investigated between 300 and 550 °C at 4 h. As for carbonization and calcination time, the cryogel was studied between 1 and 5 h at selected carbonization and calcination temperature, respectively. The selected carbonized and calcined carbon cryogel were characterized to study the physical and chemical properties.

2.3. Characterization of carbon cryogel

The surface areas of the carbonized and calcined cryogel were calculated based on the Brunauer–Emmett–Teller (BET) method using the nitrogen adsorption and desorption analysis (Micromeritics and Surfer) at −196 °C. The acidity of the carbon cryogel was measured using NH_3-TPD (Micromeritics AutoChem II 2920 V4.03) with thermal conductivity detector (TCD) and gas flowrate of 10% NH_3/He up to 900 °C. The cryogel, carbonized cryogel and calcined cryogel were further characterized with TGA, FTIR and FESEM. TGA was used to study the thermal stability and main composition of samples. The analysis was conducted using Perkin Elmer TGA 7 instrument at temperature ramp of 10 °C/min from 30 to 900 °C under nitrogen flow. FTIR was used to analyze the chemical bonding of the product using Perkin-Elmer Spectrum with KBr pellet. The spectra obtained were observed at IR range of 650 to 4000 cm^{-1}.

XRD was applied to analyze the phase structure of the carbon cryogel by using a Bruker D8 Advance diffractometer system (Cu Kα radiation, 40 kV, 30 mA) for angle 2θ between 10° to 80°. The morphology of cryogel and carbon cryogel was observed using FESEM (ZEISS Supra 35VP with GEMINI column) at 500 ×, 10 kV. The energy dispersive X-ray spectrometry (EDX) was used to measure the weight composition of C, O and S.

2.4. Esterification of levulinic acid

The carbonized and calcined cryogel were tested for esterification of levulinic acid in a reflux condenser at reflux temperature of ∼78 °C for 10 h with 19:1 M ratio of ethanol to levulinic acid and 15 wt% catalyst

loading. The manipulated variables for ethyl levulinate production were further investigated over selected carbon cryogel either carbonized or calcined cryogel. The variables are carbon cryogel loading (5–35 wt%), ethanol to levulinic acid molar ratio (5–30), reaction time (1–8 h) and reaction temperature (78–170 °C). The selected carbon cryogel was further studied for the reusability of catalyst on the esterification reaction. The carbon cryogel used was washed and recovered via filtration. The recovery of carbon cryogel was conducted by mixing the used catalyst with an ethanol and water mixture (1:10) and stirred vigorously (300 rpm) for 2 h. After slow stirring (100 rpm) for 24 h, the mixture was washed with water and filtered. The catalyst was oven dried for 24 h at 110 °C and returned to subsequent cycles.

The yield of ethyl levulinate was calculated using a. GC-FID 7820A gas chromatograph system (Agilent Technology) The GC was equipped with HP-5 column (length, 30.0 m; diameter, 320.0 μm) with the following conditions: injector temperature, 270 °C; column temperature, 80 °C (13 °C/min) → 170 °C (40 °C/min) → 300 °C; carrier gas, nitrogen (1.0 mL/min). High Performance Liquid Chromatography (HPLC) from Agilent Technology (1260 Infinity) was used to detect the peak of levulinic acid and measure peak concentration. The conditions of the HPLC analysis are as follows: UV detector (210 nm) was used with Hi-Plex H column (length, 300 mm; diameter, 7.7 mm) at 60 °C, auto injector (20 μL injection volume) and mobile phase of 5 mM H_2SO_4 (0.6 mL/min).

The percentage of yield and conversion were calculated based on the standard concentration of ethyl levulinate and levulinic acid, respectively with the aid of prepared standard calibration curves. The EL yield and levulinic acid conversion were calculated using Eqs 1 and 2.

$$\text{EL yield (mol. \%)} = [(C_E \times V_p)/1000/M_E)/(W_i/M_L)] \times 100 \tag{1}$$

$$\text{Conversion (\%)} = [W_i-((C_L \times V_p)/1000)]/W_i \times 100 \tag{2}$$

where, C_E and C_L are the final product concentration of ethyl levulinic and levulinic acid (mg/L), respectively, M_E and M_L are the molecular weight of ethyl levulinic and levulinic acid (g/mol), respectively, V_p is the final volume of product (L), and W_i is the weight of levulinic acid (g).

3. Result and discussion

3.1. Effect of carbonization and calcination of cryogel

Fig. 1(a) and (b) present the effect of temperature and time on carbonized cryogel. From Fig. 1(a), the surface area increases when cryogel is carbonized from 300 up to 600 °C but decreases slightly when the temperature further increases to 700 °C. The carbonization process enlarges the surface area of the carbonized cryogel since the sample decomposes and reduces the particles size. Besides, the increase in surface area is also due to the formation of pores on the carbon surface. At 300 °C, small surface area (27.4 m^2/g) is obtained due to relatively low heating supplied to the cryogel for organic decomposition and restructuring of the carbon bonding to reduce particle size and increase pore formation. At 600 and 700 °C, the small difference in surface area is due to low decomposition of organic compound and slow increment of pore formation. Large surface area is required for carbon cryogel to act as catalyst for reaction to occur.

High total acidity is obtained at different carbonization temperature although the strength of the acidity somewhat reduces with increasing temperature. The carbonization temperature is selected at 500 °C as the carbonized cryogel corresponds to both large surface area (330.4 m^2/g) and acidity (12.3 mmol/g). The effect of carbonization time prevails as the surface areas increases with increasing heating time as depicted in Fig. 1(b). The surface area increases with carbonization time from 102.5 m^2/g to 330.5 m^2/g for 2 h and 5 h, respectively. Even at constant temperature, the surface area increases as continuous energy is supplied to change the carbon structure and increase pore formation. Sufficient