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A novel peat biochar supported catalyst for the transesterification reaction

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ABSTRACT

In the present study, the peat, as solid waste, was utilized as the support to prepare carbon solid base catalyst for biodiesel production from palm oil. The chemical and structural properties of catalysts were examined by thermogravimetric analysis (TGA), scanning electron microscope (SEM), energy dispersive spectrometer (EDS), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), N_2 adsorption/desorption and the Hammett indicator method. The results indicated that 30K/PB-600 catalyst exhibited the highest catalytic activity (the maximum biodiesel yield of 98.6% was acquired) owing to its highest total basicity. Besides, the stability of the catalyst during reaction was also demonstrated. After 9 repeated use, the catalyst could still possess a rather high catalytic activity (biodiesel yield of 81%). The little deactivation of catalyst was mainly owing to K^+ ions leached into reaction media. Therefore, biochar derived from peat could prove to be an appropriate material for catalyst synthesis.

1. Introduction

Due to the increasing urgent concern about greenhouse gas emissions and other environmental pollutions, the use of alternatives to fossil fuels has drawn more attention in recent years [1]. Biodiesel, as a sustainable, renewable and non-toxic biofuel biofuels, can be produced via the transesterification of animal/vegetable oils with C_1/C_2 alcohols [2,3]. Conventionally, biodiesel is synthesized through transesterification using homogeneous base catalysts (KOH, CH_3CH_2ONa, etc.) [4]. Although, these catalysts have high catalytic activity and biodiesel yield, they are corrosive for the reactors, and their separation is very tedious [5]. To solve these problems, solid base catalysts have been drawn much attention because of their less corrosion, low environmental pollution, and easy separation [6,7]. To date, various kinds of heterogeneous basic catalysts have been synthesized and successfully utilized for biodiesel production, such as alkaline earth oxides, zeolites, hydrotalcite, and anion exchange resins [8–11]. However, only a few of them can be used on industrial scale owing to the synthesis cost [12]. With respect to this problem, many researchers began to use wastes materials (such as animal bones, shells, and ash) as feedstocks to synthesis cost-effective catalyst [13–19].

Biochar, as a solid residue formed in the pyrolysis of biomass, can be produced on a scale ranging from large industrial facilities to individual farms [20]. Due to its relatively high chemical stability, contents of surface functional groups and special porosity and surface chemistry, biochar can be directly utilized as an adsorbent, catalyst as well as catalyst support [21,22]. Specifically, Dehkhoda et al. [23] have used hardwood biochar as the support for the synthesis of solid acid catalysts, and it exhibited high catalytic activity for the esterification reaction. Rao et al. [24] have explored partially carbonized de-oiled canola meal derived biochar catalyst and used it in the esterification reaction. The maximum conversion could reach 93.8%. Dong et al. [25] have used the biochar catalyst which pyrolysis-derived by douglas fir in the esterification reaction, and biodiesel yield of 99% was acquired. Peat is an accumulation of partially decayed plant organic matter formed under water saturated wetland conditions over millennial timescales [26]. Peatlands are considered as an important global carbon sink, covering above 3% of the world's land surface [27]. Peatlands are carbon-rich and have higher heating value of peat (>15 MJ/kg), which makes peat an energy source of interest as a biofuel [28]. On this purpose, the pyrolysis of peat can not only produce bio-oil and syngas but also acquire by-product biochar.

Recently, the use of activated carbon loaded with different potassium salts for biodiesel production is of great interest

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[29–34]. Since the utility of biochar as a precursor for activated carbon has been studied, extending its application as a possible carbon precursor to load with different potassium salts for catalyzing the production of biodiesel would not only help the commercialization of biodiesel production, but also increase the environmental viability of the pyrolysis process.

In this paper, peat biochar (PB) was selected as the support to load K_2CO_3 for the transesterification reaction. There is no information in the literature concerning the use of peat biochar originating from peatlands as support for catalyst synthesis. The as-prepared catalyst products were characterized by TGA, SEM, EDS, FTIR, XRD, N_2 adsorption/desorption and the Hammett indicator method. Effect of the K_2CO_3 loading, activation temperature, methanol/oil molar ratio, reaction time, reaction temperature and catalyst amount on the catalyst activity were investigated. Furthermore, the reusability study of the catalyst was also conducted.

2. Experimental

2.1. Materials

Peat was collected from the peatland in the Changbai Mountain range (China). Commercial edible-grade palm oil (the acid number of palm oil was 1.19 mg KOH/g (ASTM D-974) and the acid value of the feedstock was low enough for effective base catalyzed transesterification reaction [35]) was purchased from the local supermarket (Guangzhou, China). Potassium carbonate (99%), tetrahydrofuran (99.8%) and methanol of analytical grade (99.5%) were supplied by Sigma-Aldrich Chemical Co. Ltd.

2.2. Catalyst preparation

The dried peat was calcined at 600 °C for 2 h within nitrogen atmosphere to acquire the PB. As-synthesized PB was subsequently sieved with diameter grades of 0.15–0.18 mm.

The catalysts were synthesized using wet impregnation method [36]. K_2CO_3 impregnating solution was prepared with various concentrations (20 wt%, 30 wt% and 40 wt%). Typically, to prepare 20 wt% K_2CO_3 loaded catalyst, 2 g of K_2CO_3 powder was added slowly to 60 ml of water and subsequently added 8 g of dried PB. The mixture was stirred at 600 rpm for 3 h, and it was dried at 105 °C for 12 h, and finally calcined at 500–700 °C for 2 h within nitrogen atmosphere.

The as-prepared catalysts were designated as σK/PB-T, where σ and T represented the K_2CO_3 loading (wt%) and the activation temperature, respectively.

2.3. Catalyst characterization

Thermogravimetric analysis was performed using a SDT Q600 thermogravimetric analyzer between 30 °C and 700 °C. The sample morphology and elemental chemical analysis were conducted on a QUANTA 200, and the accelerating voltage was 20 kV. Backscattered electron and secondary electron and detectors were used to take the micrographs. Crystalline structure of the catalyst was studied by X-ray diffractometry (XRD-Bruker; D8 Advance) coupled with Cu Kα radiation. Textural characteristics were analyzed by adsorption N_2 using an Autosorb1-MP Quantachrome. Specific surface area and total volume were calculated using the BET and BJH methods. The basic strength of the catalysts was determined by the Hammett indicator method, expressed by an acidity function ($H\_$) [37]. The used indicators were as follows: neutral red ($H\_ = 6.8$), bromothymol blue ($H\_ = 7.2$), phenolphthalein ($H\_ = 9.8$), 2,4-dinitroaniline ($H\_ = 15.0$), and 4-nitroaniline ($H\_ = 18.4$). The total basicity of the catalysts was measured by the method of Hammett indicator-benzene carboxylic acid (0.02 M anhydrous methanol solution) titration. The FTIR spectra were performed on a Bruker equipment, Alpha model. Spectra were collected in the range of 500–4000 cm^{-1} region.

2.4. Transesterification experiment

The transesterification reaction was performed using a 150 ml 3-necked flask equipped with a water cooled condenser, a thermocouple thermometer, and a magnetic stirrer. The flask was first filled with an appropriated amount of catalyst, methanol and 30 g of palm oil. The catalytic tests were carried out at 65 °C under mechanical stirring of 700 rpm. After reaction, the biodiesel (fatty acids methyl ester, FAME) was analyzed by gas chromatography. The biodiesel yield was calculated through the following expression [38]:

$$\text{Yield} = (\text{weight of biodiesel} \times \%\text{FAME})/(\text{weight of oil}) \times 100\%$$

Where % FAME refers to the concentration of FAME obtained by gas chromatography analysis.

2.5. Catalyst reusability

The catalysts stability was investigated by consecutive reuses. After completing the reaction, the catalysts were filtered and washed thoroughly with tetrahydrofuran. Subsequently, the washed catalysts were dried in an oven at 110 °C for 12 h. The recovered catalysts were used for transesterification of palm oil under similar reaction conditions to measure its activity in a number of cycles.

3. Results and discussion

3.1. Catalyst characterization

The SEM images of the PB and 30K/PB-600 catalyst are presented in Fig. 1. From Fig. 1a, PB exhibits a porous structure, indicating its large specific area and high porosity. Fig. 1b shows the detailed morphologies of the as-prepared 30K/PB-600 catalyst. The 30K/PB-600 catalyst shows larger and more irregular blocks which proved that K compounds covered on the PB surface.

EDS analysis of the PB and the 30K/PB-600 catalyst are listed in Table 1. To determine the elemental analysis exactly, several typical points were selected for each sample. As observation, the main components of PB were C, Al_2O_3 and SiO_2. For the 30K/PB-600 catalyst, the K content of the three points ranged from 17.91% to 19.19%, which indicated that the loaded potassium was well dispersed on the PB.

The FTIR spectra of PB and the 30K/PB-600 catalyst were shown in Fig. 2. The peak from 700 to 900 cm^{-1} attributed to tetrahedral Al—O [39]. The peak at 1037 cm^{-1} was corresponding to the Si—O stretching and Si—O—Si vibrations [40]. The peak at 1457 should be attributed to carbonate species [36]. The peak at around 1640 cm^{-1} was due to —OH groups of water molecules adsorbed onto the surface of the catalyst. The peak observed at 3600 cm^{-1} was attributed to the hydroxyl stretching vibration to aluminum [41]. The peak at around 3430 cm^{-1} of the 30K/PB-600 catalyst could be due to the stretching vibrations of Al—O—K groups and —OH groups of water molecules [36,42].

Fig. 3 displays the XRD patterns of PB and K/PB catalysts. For fresh PB, the peaks at $2\theta = 21°, 27°, 43°, 50°, 60°, 68°$ were assigned to the characteristic peaks of quartz. The peaks at $2\theta = 20°, 30°, 39°$ and $48°$ were corresponding to the characteristic peaks of C. The peaks appeared at $2\theta = 28°$ was indexed to the characteristic peaks of Al_2O_3. When loaded with K_2CO_3, the intensities of main peaks of