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Mixed and ground KBr-impregnated calcined snail shell and kaolin as solid base catalysts for biodiesel production

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ABSTRACT

Mixed and ground activated snail shell and kaolin catalysts impregnated with KBr were investigated. The snail shell and kaolin were calcined, mixed, and ground prior to immersion with KBr solution and subsequent activation at 500 °C for 3 h. The precursor and catalysts were characterized by thermal gravimetric analysis, Fourier transform infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, and Brunauer–Emmett–Teller surface area. The catalytic performance of the prepared catalysts was evaluated by transesterification of soybean oil with methanol. The effects of various parameters on biodiesel yield were investigated. A biodiesel yield of 98.5% was achieved using the catalyst prepared by 40% KBr-immersed, mixed, and ground snail shell and kaolin, which were activated at 500 °C. The transesterification conditions were as follows: reaction temperature, 65 °C; reaction time, 2 h; methanol-to-soybean oil molar ratio, 6:1; and catalyst amount (relative to the weight of soybean oil), 2.0 wt%. The solid catalyst could be reused for four times, and biodiesel yield remained over 73.6% for the fourth time.

1. Introduction

The declining fossil fuel resources, along with the gradual global climate warming and pollution caused by fossil fuels, has spurred the development of renewable alternative energy sources. Non-toxic, renewable, high-cetane number, biodegradable, high-flash point, and environmentally friendly biodiesel has emerged as a substitute for traditional fossil fuels [1–3]. According to the Association of American Material Experiment (ASTM), biodiesel refers to vegetable oils and animal fats or other renewable biological resources as raw materials through the transesterification production of long carbon chain fatty acid ester [4–6].

Among the biodiesel preparation methods, the transesterification reaction with conventional catalysts surpasses the traditional homogeneous acid and alkali catalyst transesterification [7–11]. This process, which uses traditional acid and base catalysis, is the most commonly used technique for biodiesel production. This technique is characterized by easy operation, mild conditions, short reaction time, and high yield. However, the development of transesterification reaction is limited by its highly corrosive catalyst, which is also difficult to separate and purify, in addition to other factors such as the generation of large amounts of industrial waste water and environmental pollution. Thus, the exploration of an environmental-friendly catalyst is becoming a research hot spot in recent years. To overcome the aforementioned disadvantages, heterogeneous solid catalysts have long been investigated. Solid alkali catalysts have attracted much attention because of their high biodiesel yield, fast reaction rate, easy separation from products, and high catalytic activity, which indicate their good prospects for development [12,13].

A solid base refers to compounds in a reaction that can provide electron, exhibit chemical adsorption acid, or discolor the acidic indicator of solids. Biodiesel production by solid base catalysts has been reported in recent years. These catalysts include molecular sieve solid base catalysts, such as Na–X [14] and CaO/NaY [15] molecular sieves, anion exchange resin catalyst [16,17], metal oxides, such as CaO·MgO and SrO [18–23], supported solid base catalyst [24–29], and resin-type solid base catalysts [30,31]. Among the solid base catalysts, CaO exhibits active catalytic performance, mild reaction conditions, readily available raw materials, low cost,

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non-corrosiveness, and high recyclability in transesterification reaction. In addition, calcium, such as egg shell, shell, and bone, is naturally abundant. Boro et al. [21] prepared a series of Li doped egg shell derived CaO for biodiesel production from nonedible oil feedstock. Under optimum reaction conditions, biodiesel yield reached 94%. Liu et al. [22] through numerous experiments compared the catalytic activities of $K_2CO_3/\gamma-Al_2O_3$, $KF/\gamma-Al_2O_3$ with CaO. Results show that CaO had better reusability and maintained high activity even after 20 uses. Additionally, the activity of $K_2CO_3/\gamma-Al_2O_3$, $KF/\gamma-Al_2O_3$ is reduced after use that significantly affected biodiesel yield. The right amount of water content also significant affected the biodiesel yield in this experiment, because it increased the basic characteristics of the CaO active site. Boey et al. [32,33] calcined crab shells as biodiesel transesterification catalyst and performed a statistical analysis using central composite design. Analytical results show that catalyst concentration, reaction temperature, catalyst amount, catalyst concentration, and methanol-to-oil molar ratio are the most important factors affecting biodiesel purity. Moreover, the catalyst reusability test showed that the catalyst could be used 11 times without losing its activity. Viriya-empikul et al. [34] calcined mollusk shells of snail at 800 °C for 2 h–4 h. CaO was formed at temperatures above 800 °C, with the product of calcination as catalyst for biodiesel transesterification reaction, and the conversion rate reached over 90% after 2 h. Experimental results show that the surface area of the catalyst affected the catalyst performance. Boro et al. reported the use of Mumbai local shell shad as catalyst under the following conditions: calcinations temperature, 800 °C; catalyst amount, 3 wt %; methanol/oil ratio, 9:1; and activation temperature, 65 °C ± 5 °C. They obtained 93.3% yield. Rezaei et al. [35] used discarded mussel shells as a catalyst by calcinations at different temperatures. Instrumental analytical results showed that the catalyst had high catalytic activity at 1050 °C. Under optimal reaction conditions, the biodiesel purity and yield were 100% and 94.1%, respectively. The results showed that the activity of the recycled catalyst was deactivated because of the reduced amount of Ca on the surface. Given the instability and poor recycling rate of the produced catalyst, a low-cost, environment-friendly, high-catalytic performance, and reusable solid base catalyst should be established.

Kaolin, another natural substance [36], is good catalyst for biodiesel production, but it does not exhibit high catalytic activity when used alone. To enhance the high-catalytic performance of CaO and kaolin catalyst, experiments have been performed to prepare a highly efficient, inexpensive, green, environmentally friendly solid base catalyst. The present study mixed and ground different proportions of kaolin and snail shells after high-temperature calcination. Then, the catalyst was immersed with different K+ concentrations solution, because K+ show good catalytic performance. Numerous studies have reported on the load of K+ such as MgO [37], CaO [38], ZrO [39], SiO_2 [40], shell [41], and so on. Qiu F. et al. used a solid base nanocatalyst prepared by ZrO_2 loaded with C4H4O6HK and achieve the biodiesel yield of 98.03% [39]. Jairam S. et al. Used KI-impregnated calcined oyster shell as a solid catalyst for transesterification of soybean oil and achieved a maximum conversion of 95% [41]. But none of them achieved a maximum conversion of 98%. KBr solution was used in this study because of its better solubility. The ground mixture was soaked in KBr to load K+ and then calcined to obtain high activation. The resulting catalyst showed good morphology and high dispersion of the active component for efficient biodiesel preparation under mild conditions. This high-performance catalyst did not produce saponification and emulsification during the catalytic reaction. The prepared catalysts were characterized by thermal gravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and Brunauer–Emmett–Teller (BET) methods. The effects of catalyst preparation conditions and various reaction variables on the biodiesel yield were also investigated. The stability and reusability of the prepared catalyst were also determined.

2. Experimental

2.1. Material

Commercial edible-grade soybean oil was purchased from the local supermarket. (Shanghai, China) and used without further purification. Snail shells were collected from the local seafood market. Kaolin, n-hexane, KBr, and anhydrous methanol were of analytical reagent grade and purchased from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China). Methyl laurate (internal standard) was of chromatographic grade and purchased from Sinopharm Chemical Reagent Co. Ltd. Anhydrous methanol were AR grade and purchased from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China) ($H_2O \leq 0.05\%$).

2.2. Catalyst preparation

First, the residue inside the collected snail shell was removed, and the shell was washed with hot water and placed in an oven at 100 °C for 12 h. The snail shells were then dried and calcined in a muffle furnace at 700 °C–900 °C for 3.5 h. The kaolin was calcined in a muffle furnace at 800 °C for 10 h to remove hydroxyl. Then, the calcined kaolin and snail shell were ground at different ratios using a mortar. The ground catalyst were added to different concentrations of KBr solution for 3 h–6 h with warm water, then filtrated and placed in a drying oven at 110 °C for 12 h. Finally, the dried catalyst was calcined in a muffle furnace for 3 h at 450 °C–650 °C to activate the catalyst performance. The prepared catalysts were ground and stored in desiccator until further use.

2.3. Catalyst characterization

TGA, XRD, SEM, FTIR, XPS, and BET were applied to evaluate the change in the structure and morphology of the fresh and used catalysts. The weight loss behavior of KBr supported on ground kaolin and snail shell during activation was measured using a thermobalance (TA Q5000IR). Samples were heated to 800 °C at a heating rate of 10 °C/min under N2 flow. The XRD pattern of the catalyst was studied on an X-ray diffractometer (X, Pert PW 3040/60) at 2θ angle, with scan range of 10°–80°. The XRD patterns of the catalyst were obtained with Cu Kα radiation (k = 0.15406 nm) at 40 kV, 30 mA, scan speed of 4.0°/min, and scan range of 10°–80°. Functional groups attached to the catalyst surface were determined by FTIR (Nicolet 6700), which used the KBr pellet technique which recorded in the 4000 cm^{-1}–400 cm^{-1} range with a resolution of 4 cm^{-1}. Furthermore, the morphology was observed on a ultra-resolution field-emission scanning electron microscope (Model S-3400N Hitachi). The chemical composition of the major elements present in the catalysts material were analyzed by XPS (Model ESCALAB 250, Thermo-VG Scientific). The specific surface area, mean pore diameter, and pore volume were determined the BEt method (model: ASAP2020M+C).

2.4. Transesterification reaction and method of analysis

The transesterification reaction of soybean oil with methanol was performed in a 500 mL three-neck round-bottomed flask equipped with a mechanical stirring bar, a thermometer, and reflux condenser. The typical reaction procedure was as follows. First, 50 mL (45.6 g) of soybean oil, 13 mL anhydrous methanol