



A novel waste water scale-derived solid base catalyst for biodiesel production



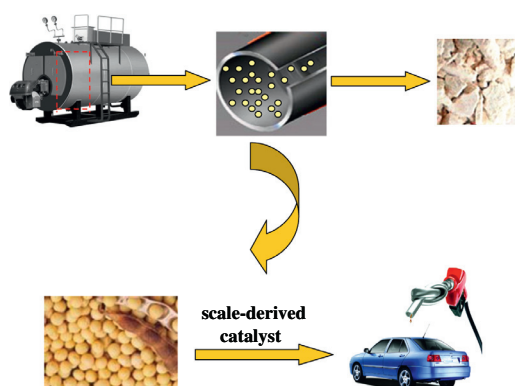
Pingbo Zhang, Qiuju Han, Mingming Fan*, Pingping Jiang

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, PR China

HIGHLIGHTS

- Successful usage of waste scale as a novel catalyst.
- New species $\text{CaO-MgO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ from waste scale for biodiesel production.
- The $\text{CaO-MgO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ catalyst not only exhibits a favorable catalytic performance but also has perfect reusability.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel waste water scale-derived catalyst was prepared through calcining the waste water scale and used as an active and stable catalyst for the production of a clean and green alternative fuel–biodiesel via transesterification reaction of soybean oil with methanol. The effect of calcination temperature in range of 200–1000 °C on the catalytic activity was investigated. The maximum biodiesel yield reached about 93% under the optimal condition. Acceleration of the catalytic activity of water scale-derived catalyst for biodiesel synthesis was also studied. In addition, the transesterification reaction mechanism was proposed. Operational simplicity, low cost of catalyst used, high yields, wide applicability and reusability are the key features of the waste water scale-derived catalyst. The results suggest that the waste water scale-derived catalyst is a promising catalyst for a green and durable biodiesel production process.

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1. Introduction

With energy crisis and environmental issues, biodiesel, the environmentally sound renewable resource, has attracted an increasing amount of attention in recent years. Because biodiesel is made from natural, renewable sources such as new and used vegetable oils and animal fats [1–5]. In addition, compared with

fossil fuels, it leads to much less emission of greenhouse gases, such as particulates, nitrogen oxides, sulphur, and volatile organic compounds [6].

Biodiesel is produced from plants oils or animal fats through a transesterification reaction with methanol or alcohol [7,8]. The conventional catalysts applied in the transesterification reaction are homogeneous catalysts, such as strong acids and strong bases [9]. However, acidic catalysts (such as H_2SO_4) will corrode the equipment [10] and the reaction rates are relatively slow [11]. Alkaline catalysts (such as NaOH , KOH , and NaOCH_3) are generally

* Corresponding author. Tel.: +86 510 85917090; fax: +86 510 85917763.

E-mail address: fanmm2000@126.com (M. Fan).

sensitive to water and free fatty acid of oils [10]. Both of them are very difficult to separate from the reaction mixture and must be neutralized and washed at the end of reaction, which cannot be recycled [12]. As heterogeneous catalysts can be easily removed from the liquid products [13] and avoid producing large amount of wastewater contributing to polluting the environment, they have an exciting potential for improving the economics of biodiesel production [14]. Peterson and Scarrah [15] reported that alkaline-earth metal oxides, notably calcium oxide, were used as heterogeneous catalysts for the production of biodiesel. Among the reported heterogeneous catalysts, CaO shows an active catalytic performance in transesterification reaction [7]. Moreover, it shows potential in biodiesel production from the economic point of view. Because CaO can be obtained from the wastes consisting of CaCO₃ [16], such as waste eggshell [17], oyster shell [18], shrimp shell [19], mud crab shell [20], mollusk shell [21], and fish scale [22], which is a kind of innovation involved in making utilization of wastes, saving resources, and improving economic efficiency.

In northern China, heating groundwater (such as well water and springs) containing some minerals can produce waste water scale. The derivatives of waste water scale are composite metal oxide with the main content CaO. In this work, we present a novel waste water scale-derived catalyst by calcining method to enhance the basic strength in tandem with the surface properties of the catalyst. The waste water scale and its derivatives used as heterogeneous catalysts for biodiesel production were investigated via transesterification of soybean oil with methanol. Furthermore, the possible mechanism of transesterification was proposed.

2. Experimental

2.1. Materials and catalyst preparation

Water scale was obtained from home kitchens in Lianyungang city, eastern China. All chemicals were of analytical grade and used as received. Refined soybean oil was procured from local market. Water waste scale was washed thoroughly with distilled water several times to remove the impurities and followed by drying in hot air oven at 105 °C for about 24 h. The dried water scales were subsequently ground to fine powder and calcined in a muffle furnace at different temperatures ranging from 200 °C to 1000 °C for 2.5 h to prepare the novel catalysts.

2.2. Catalyst characterization

Elemental analyses were determined by atomic absorption spectroscopy (AAS). Thermogravimetric analysis (TGA) was performed with a STA409 instrument in dry air at a heating rate of 15 °C/min. X-ray diffraction (XRD) patterns were carried out with a Bruker D8 Advance powder diffractometer using Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA from 10° to 90° with a scan rate of 4°/min. The microstructures were collected on scanning electronic microscope (SEM) at 2.0 kV (Hitachi S-4800, Japan).

The basic strength of the catalyst was measured with Hammett indicators, including neutral red ($pK_{BH^+} = 6.8$), phenolphthalein ($pK_{BH^+} = 9.8$), Nile blue ($pK_{BH^+} = 10.1$), and 2,4-dinitroaniline ($pK_{BH^+} = 15.0$) [23,24]. The basicity of the catalyst was determined by method of Hammett indicator–benzene carboxylic acid (0.02 mol/L anhydrous methanol solution) titration [24,25]. Additionally, the total basicity and basic strength of the catalyst was also detected by temperature programmed desorption of carbon dioxide (CO₂-TPD) with an AutoChem 2920. About 0.1 g of catalyst was pretreated under a helium stream at 700 °C for 2 h. Subsequently the catalyst was saturated with CO₂ for 1 h at room temperature. After flushing with He flow for 30 min, the catalyst was

heated from room temperature to 900 °C with a heating rate of 10 °C/min and the desorbed CO₂ was detected with a thermal conductivity detector [26–28].

2.3. Catalytic activity tests and biodiesel analytical methods

Water scale-derived catalysts were used in transesterification reactions carrying out in a batch reactor for the catalytic activity. Soybean oil and methanol were placed in a round-bottom glass flask equipped with a reflux condenser. Next, the designated amount of prepared catalyst was placed in and stirred at 50–80 °C for 2–6 h. After the reaction, centrifugation was used to separate the layers (methyl ester, glycerol, and catalyst).

The product was directly measured by gas chromatography. Then, the treated sample (0.2 μ L) was injected into the GC-122 gas chromatograph, which was equipped with a SE-54 capillary column (0.32 mm \times 30 m). The column temperature was kept at 160 °C for 2 min, raised to 220 °C at a rate of 10 °C/min, then to 260 °C at a rate of 8 °C/min, and finally maintained at this temperature for 10 min.

The internal standard method for determining the yield of biodiesel was used, with methyl salicylate as internal standard. In our work, the composition of biodiesel was 56.5% methyl linoleate, 23.2% methyl oleate, 10.6% methyl palmitate, 6.6% methyl linolenate and 3.1% methyl stearate from the gas chromatogram.

The mass concentration of biodiesel was obtained by the GC and the yield of biodiesel was calculated by the following equation:

$$\begin{aligned} \text{Yield} &= \frac{m_{\text{actual}}}{m_{\text{theoretical}}} \approx \frac{C_{\text{esters}} \times n \times V_{\text{esters}}}{m_{\text{oil}}} \times 100\% \\ &\approx \frac{C_{\text{esters}} \times n \times V_{\text{oil}}}{m_{\text{oil}}} \times 100\% \approx \frac{C_{\text{esters}} \times n}{\rho_{\text{oil}}} \times 100\% \end{aligned}$$

where both m_{actual} (g) and $m_{\text{theoretical}}$ (g) are the actual mass and theoretical mass of biodiesel; m_{oil} (g) is the mass of soybean oil; n is the diluted multiple of biodiesel; C_{esters} (g/mL) is the mass concentration of biodiesel; ρ_{oil} (g/mL) is the density of soybean oil; V_{esters} (mL) and V_{oil} (mL) are the volumes of biodiesel and soybean oil, respectively [29–31].

2.4. Catalytic activation

The catalytic activation of water scale-derived catalysts was as follows. A certain proportion of methanol and catalyst were added in the flask equipped with a reflux condenser and stirred for 1.5 h at 25 °C for activation. Then, a proportional amount of soybean oil was added to the mixture and stirred [32]. The transesterification reaction conditions and post treatment were as the above reaction procedure.

3. Results and discussion

3.1. Catalyst characterization

The elemental analysis for water scale found Ca 38.7%, Mg 0.14%, and Fe 0.0049% by weight percentage. Thermal stabilities of water scale were investigated by TGA in Fig. 1. The result showed that carbon dioxide was decomposed from the precursor with a further weight loss of 43% between 600 and 770 °C. Above 800 °C, the weight loss remained constant. From these results, it could be indicated that carbonate was completely converted to metal oxide by calcining at 800 °C. Therefore calcination at 800 °C or higher temperature was selected.

Catalytic activity for transesterification is closely related to the basic strength [33–35] and basicity of the catalyst, the basic strength and basicity of various catalysts were depicted in Table 1

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