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# Potential of using ceramics wastes as a solid catalyst in biodiesel production

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## ABSTRACT

Reusing waste products is one of the milestones of progress toward environmental sustainability; producers can add value by reusing waste products. This study reports that ceramics wastes (CWs) are suitable raw materials for preparing a solid-base catalyst for biodiesel production. This study synthesized biodiesel from soybean oil using transesterification over a CWL-800-2. CWL-800-2 can be used directly for biodiesel production without being further dried or thermal pretreated, avoiding the usual activation of solid catalysts at high temperature. The effects of the calcination temperature and duration, methanol/oil ratio and catalyst amounts on the conversion are also reported in this paper. The solid base catalyst was highly active, air-insensitive and can be reused for at least four cycles without loss of activity. The catalysts were characterized using XRD, FE-SEM, FTIR, BET and the Hammett indicator method.

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## 1. Introduction

Currently, both human population and urbanization are increasing worldwide; consequently, the quantity of waste generated by agricultural, industrial, and municipal sources is steadily increasing [1]. Numerous methods exist for recycling waste materials. For example, the raw materials may be extracted and reprocessed, and the wastes can be transformed to new materials by subjecting them to chemical reactions. When considering any waste management hierarchy, one must recall the three essential principles: reduce, reuse, recycle; these principles facilitate minimization of the quantities of waste materials that must be sent to disposal sites [2–4].

Nowadays, homogeneous basic catalysts are most preferred in the commercial production of biodiesel because of their low cost and high availability [5,6]. Although homogeneous catalysts are the most common catalysts for catalyzing transesterified animal or plant oils into biodiesel, they possess severe problems; for example, some catalysts cannot be recovered or reused; some catalysts have high cost and low efficiency and generate large amounts of wastewater [7,8]. In general, the purification of biodiesel produced through homogeneous catalysis requires a vast quantity of water. Using heterogeneous catalysts could definitely improve biodiesel production processes and alleviate some problems associated with homogeneous catalysts. Heterogeneous solid-base catalysts are

advantageous because they can be easily separated and are recyclable, ecofriendly, and environmentally benign [9–11].

Ceramics wastes (CWs) are abundant, cost effective sources of Al and Si; they contain large amounts of Si and Al compounds (such as  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}_x$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ), along with small quantities of impurities. Because CWs contain both Si and Al components, CWs can be employed as inexpensive raw materials for synthesizing high-value catalysts [12]. In recent years, some interesting studies have successfully modified the structures of various surface metal oxide species in order to optimize the catalytic properties of these materials for specific applications. Potential advantages include high reusability, high ease of separation from the product, modifiable catalyst properties, increased stability, and ease of storage. Modified catalyst host materials are mainly associated with two distinctive properties: (1) have large specific surface areas, which enable high loading of base sites and (2) during processing, can be easily separated from the reaction medium. In this context, some recently developed Li-based catalysts have been proven to display unexpected catalytic properties and stability [13–16]. Dai et al. [17] prepared a  $\text{LiAlO}_2$  catalyst through solid-state reaction that could enhance the conversion of oil to biodiesel. Wang et al. [18] realized a significant improvement in catalytic activity by using  $\text{SiO}_2$  and  $\text{Li}_2\text{CO}_3$ ; they successfully loaded large quantities of reactants to basic sites. CWs have considerable potential for commercialization as prepared catalysts given their high yield and ease of control as well as low cost.

As an alternative to current commercial catalysts, this paper reports an effective and affordable waste materials-based method for biodiesel production. Aided by a simple solid-state reaction,

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the present study utilizes CWs to prepare solid-base catalysts, with  $\text{Li}_2\text{CO}_3$  as the activating agent.

## 2. Materials and methods

### 2.1. Materials

The heptadecanoic acid methyl ester, ACS-grade methanol, and reagent-grade  $\text{Li}_2\text{CO}_3$  were purchased from Uni-Onward Co. (Taiwan), ECHO Chemical Co. (Miaoli, Taiwan), and Shimakyu's Pure Chemicals (Osaka, Japan), respectively. Soybean oil, castor oil, canola oil, olive oil, Rapeseed oil and Cocoa ester were purchased from Great Wall Enterprise Co. (Taiwan). Ceramics wastes was picked in the National Taichung University of Education

### 2.2. Catalyst preparation

The catalyst was prepared using a solid-state reaction. A 5 g of CWs powder was added to an aqueous solution containing 9 g of  $\text{Li}_2\text{CO}_3$ . The as-prepared solution was dried at 120 °C for 24 h. Finally, the CWs and  $\text{Li}_2\text{CO}_3$  mixing powder was thoroughly ground and calcined at 800 °C in air for 4 h. The as-prepared sample was washed with 700 ml of anhydrous methanol and dried at 95 °C under a vacuum for 1 h to remove adsorbed base sites from the catalyst surface. The as-prepared catalysts were labeled on the basis of the calcination temperature (500–800 °C) and calcination durations (1–4 h), for example, CWL-500-1, CWL-800-4).

### 2.3. Reaction procedures

The conversion of soybean oil to biodiesel was performed in a 250 ml flat-bottomed flask, equipped with a reflux condenser and a magnetic stirrer. The reactor was initially filled with 12.5 g of soybean oil, which was heated to 65 °C for 2 h while stirring at 300 rpm. The reactant was stirred evenly to avoid splashing in the flask at the stirring speed. The timing of the reaction was initiated as soon as the mixture of the methanol and catalyst was added into the reactor. The effects of the molar ratio of methanol to oil (12:1–36:1) and catalyst/oil weight ratio (2–8 wt%) on the conversion of triglycerides to biodiesel were investigated. All of the experiments were performed at atmospheric pressure. After the transesterification reaction, DI water was added into the reaction mixture to stop the reaction [15]. The water contents have a significant inhibiting effect on the transesterification of glycerides with alcohols that use alkaline or acid catalysts, because water causes the reaction change to saponificate. The biodiesel and glycerol layers were easily separated because of differing densities of 0.86 and 1.126 g/cm<sup>3</sup>, respectively. A supernatant was filtered through a common paper filter, and excess methanol and water were then evaporated before to fatty acid methyl ester (FAME) analysis.

### 2.4. Catalyst characterization

Hammett indicators were used to assess the basic strength of the as-prepared catalyst ( $H_-$ ): 2 mL of Hammett indicators were added to each catalyst sample (~100 mg) and shaken. Then, the mixture was allowed to equilibrate for 2 h; equilibrium can be confirmed through the lack of further changes in the color of the mixture. The phases of the resulting products were analyzed using a powder diffractometer (AC MXP18, Tokyo, Japan,  $\lambda = 1.54056 \text{ \AA}$ ) at 295 K from 20° to 80° (step interval = 0.02°). In addition, the microstructure of the as-prepared catalyst was observed through field-emission scanning electron microscopy energy-dispersive spectroscopy, (FESEM-EDS; JEOL, JSM-7401, Tokyo, Japan). Moreover, the particles' specific surface areas were assessed through nitrogen adsorption by using a surface area

analyzer (BET; Micromeritics, Gemini 2370 C) and by applying the Brunauer–Emmett–Teller (BET) equation. Finally, the magnetization curves and hysteresis loop of the samples were obtained using a vibrating sample magnetometer (model 4HF ADI) at room temperature under a maximum field of 18 kOe.

### 2.5. Analytical methods

The biodiesel purity of the product, expressed in terms of the concentration of fatty acid methyl esters (FAMES), was evaluated through gas chromatography (Thermo Trace GC Ultra, Thermo Co., Austin, Texas, USA). The employed gas chromatography system included a 30 m (length)  $\times$  0.25 mm (internal diameter)  $\times$  0.25  $\mu\text{m}$  (film thickness) capillary column (Tr-biodiesel (F), Thermo Co.), a flame ionization detector, a programmable column oven, and a programmable temperature injector. The temperature in the column oven was programmed as follows: the initial temperature was 120 °C; it then increased to 220 °C at 30 °C/min and further increased to 250 °C at 10 °C/min. The injector temperature was programmed as follows: the initial temperature was 90 °C for 0.05 min; it then increased to 260 °C at 10 °C/min. The carrier gas was nitrogen (flow rate = 2 mL/min). The conversion was determined per the following equation. Conversion % =  $\frac{\sum A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\%$  where  $\sum A$  is the total area of all peaks from C14:0 to C24:0 and  $A_{EI}$  is the heptadecanoic acid methyl ester IS area.  $C_{EI}$  and  $V_{EI}$  are the concentration (mg/mL) and volume (L) of the heptadecanoic acid methyl ester solution added to the sample, respectively;  $m$  represents the sample mass (mg).

## 3. Results and discussion

### 3.1. Characterizations of as-prepared catalyst

The XRD spectra of the samples obtained at calcination temperatures of 500–800 °C are illustrated in Fig. 1. At 500 °C, strong diffraction peaks were observed in  $\text{SiO}_2$  (JCPDS 078–1253). However, the intensity of the  $\text{SiO}_2$  phase substantially decreased at 600 °C. The observed diffraction peaks were characteristic of  $\text{Li}_4\text{SiO}_4$  and  $\text{LiAlO}_2$ . Upon calcination at 700 °C, CWs and  $\text{Li}_2\text{CO}_3$  undergoing decarbonization processes leads to the formation of  $\text{Li}_4\text{SiO}_4$  (JCPDS 020-0637) and  $\text{LiAlO}_2$  (JCPDS 044-0224). The catalyst products' spectra were very similar; their main crystalline structures corresponding to CWs were transformed to mixtures of crystalline  $\text{Li}_4\text{SiO}_4$  and  $\text{LiAlO}_2$  phases after solid-state synthesis with  $\text{Li}_2\text{CO}_3$ . In each sample, the primary active site for the reaction was the mixture of crystalline  $\text{Li}_4\text{SiO}_4$  and  $\text{LiAlO}_2$ .

Fig. 2 shows the XRD analysis of four catalyst products prepared with calcination durations of 1, 2, 3 and 4 h at 800 °C. The  $\text{Li}_4\text{SiO}_4$  and  $\text{LiAlO}_2$  phases appeared with calcination, and the main crystalline structures of these catalysts, which corresponded to CWs, were transformed to  $\text{Li}_4\text{SiO}_4$  and  $\text{LiAlO}_2$  phases after solid-state synthesis with  $\text{Li}_2\text{CO}_3$ . Both  $\text{Li}_4\text{SiO}_4$  and  $\text{LiAlO}_2$  followed distinct calcination durations (i.e., 1–4 h). All calcinations had  $\text{Li}_4\text{SiO}_4$  and  $\text{LiAlO}_2$  diffraction peaks, but the intensities of the diffraction peaks increased with increasing calcination duration. Weak  $\text{Li}_4\text{SiO}_4$  and  $\text{LiAlO}_2$  diffraction peaks followed 4 h of calcination. This is because with increases in calcination duration,  $\text{Li}_4\text{SiO}_4$  and  $\text{LiAlO}_2$  begin to agglomerate, which tends to block the  $\text{Li}_4\text{SiO}_4$  and  $\text{LiAlO}_2$  phases. That has been calcined for an excessively long period is likely due to the loss of  $\text{Li}_4\text{SiO}_4$  and  $\text{LiAlO}_2$  phases through sublimation into and agglomeration inside the structure [6]. As a result, regardless of the calcination duration, the  $\text{Li}_4\text{SiO}_4$  and  $\text{LiAlO}_2$  phases were observed for all trials in the present study.

When the reaction temperature reached the melting point of  $\text{Li}_2\text{CO}_3$  (650 °C),  $\text{Li}_2\text{CO}_3$  entered a molten state. Within the temperature range 800–900 °C, the following equation

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