# Transesterification of palm oil to fatty acids methyl ester using K$_2$CO$_3$/palygorskite catalyst

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## ARTICLE INFO

## ABSTRACT

In the present study, palygorskite (PA) was served as the support for loading K$_2$CO$_3$ to prepare cost-effective solid base catalyst for biodiesel production. X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), energy dispersive spectrometer (EDS), N$_2$ adsorption/desorption and the Hammett indicator method were used to characterize the physico/chemical of the catalysts. The effects of catalyst preparation conditions (such as the loading of K$_2$CO$_3$ on the PA and the active temperature), reaction conditions (such as reaction time, methanol-to-oil molar ratio and catalyst loading) and the catalyst reusability were studied in detail. The experimental results revealed that the highest biodiesel yield of 97.0% was obtained using the 40K/PA-550 catalyst (the loading of K$_2$CO$_3$ on the PA was 40 wt.% and the calcination temperature was 550 °C) under optimum reaction condition (reaction time of 3.5 h, catalyst loading of 5 wt.% and methanol-to-oil molar ratio of 12:1) due to its highest total basicity. Moreover, after reusing for more than 8 cycles, the catalyst can still possess a rather high biodiesel yield (above 80%). The deactivation of catalyst was mainly owing to K$_2$O leaching to the product and the decreased surface area of the catalyst during consecutive use.

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## 1. Introduction

Biodiesel as a renewable, sustainable and biodegradable biofuel can be typically produced through the transesterification of animal/vegetable oils with C$_1$/C$_2$ alcohols, together with glycerol by-product [1]. Generally, biodiesel production used homogeneous base catalysts such as K or Na hydroxide in the transesterification reaction [2,3]. However, removal of the used homogeneous base catalyst and purification of biodiesel are difficult due to the occurrence of saponification and emulsification. And the by-product glycerol is easy to be contaminated by the K or Na salts which make it unable to directly use as a commodity [2]. Furthermore, the generated alkaline wastewater must be treated before disposal. To circumvent these issues, the use of heterogeneous base catalysts can commonly possess several outstanding advantages including ease of separation, none toxicity, none corrosion and less environ-mental pollution [4]. Presently, a variety of heterogeneous base catalysts are used such as metal oxides, composite metal oxides, zeolites, hydrotalcites, anion exchange resins, lipase immobilized on/in various supports and so on [5–10]. However, only a few of them were being used on commercial scale because of the catalyst synthesis cost.

To address this problem, many researchers used natural sources (such as rocks) or solid wastes (such as shells, ash, and animal bone) as raw materials for catalyst synthesis [11–16]. Natural clays such as dolomite, hydrotalcite, sepiolite, and bentonite are abundant in the nature. The low cost and relative high surface to volume ratios could allow them to serve as catalyst supports for the biodiesel synthesis [1,2,17,18]. Palygorskite (PA also known as attapulgite) is an aluminum–magnesium silicate clay mineral which is abundant in nature. Different types of PA are differentiated from each other on the basis of the element that is dominant in its composition. PG has large surface area, excellent chemical stability and strong adsorption properties. Due to its unique crystalline structure, morphological and physico-chemical properties, PA has been used in the chemical industry, agriculture, surface

coatings and environment purposes, as well as in catalysis (as catalyst or catalyst support) [19–22]. Liang et al. [23] used the natural clay minerals palygorskite as immobilization agents to significantly decrease the phytoavailable Cd concentrations in paddy soils. Chen et al. [24–26] successfully used PA as catalyst support for catalytic cracking of biomass tar or benzene and $CO_2$ reforming of toluene. Zhang et al. [23] used PA as the catalyst support to immobilize peroxophosphotungstate, and the immobilized catalysts were successfully applied in epoxidation of soybean oil. However, to the best of our knowledge, the application of PA in other catalytic processes (such as the transesterification reaction) was less widely explored. Suppose that direct utilization of the PA as a support to implement base active sites may acquire more active catalyst for the transesterification reaction.

Among the bases for heterogeneous catalyst, potassium salts (such as $K_2CO_3$) has shown high catalytic activity in the transesterification reaction and could be supported on $\gamma$-$Al_2O_3$, bentonite, activated carbon and hydroxyapatite as solid base catalysts [12,17,18,27–29]. Few literatures have been reported on using PA-supported alkaline catalyst to synthesize solid catalyst for biodiesel production till date.

On the basis of the above considerations, in this study, we utilize the PA-supported alkaline catalyst for the first time to design and prepare cost-effective and stable catalytic systems for biodiesel production. The physico/chemical properties of the resulting catalysts were characterized by XRD, TGA, FTIR, SEM-EDS, $N_2$ adsorption/desorption and the Hammett indicator method. The effects of catalyst preparation conditions (i.e., the loading of $K_2CO_3$ on the PA and the active temperature), reaction conditions (i.e., reaction time, methanol-to-oil molar ratio and catalyst loading) on the catalytic performance and the catalyst reusability were also investigated.

## 2. Experimental

### 2.1. Materials

PA (particle size < 0.074 mm) was purchased from Anhui Mingguang Guoxingaotu Co. in China. Methanol, $K_2CO_3$ and tetrahydrofuran were obtained from Tianjin Kelmel. Refined palm oil was provided by a local market. Fatty acid profile of palm oil is given in Table 1 and characteristics of palm oil are shown in Table 2, respectively. As listed in Table 2, the acid value and water content of the feedstock were low enough for effective base catalyzed transesterification reaction [30].

### 2.2. Catalyst preparation

The PA was washed several times with deionized water, and dried overnight at 90 °C. The PA-supported catalysts were synthesized using wet impregnation method. Typically, in order to prepare 20 wt.% $K_2CO_3$ loaded catalyst, 2 g of $K_2CO_3$ powder was added slowly to 50 ml of water to prepare aqueous solution. This solution was subsequently added to 8 g of dried PA and mixed with constant magnetic stirring at 600 rpm for 4 h, and then it was dried at 105 °C for 12 h followed by 4 h calcination at 450–750 °C. The

**Table 1**
Fatty acid profile of palm oil.

| Fatty acid | Structure | Composition (wt.%) |
|---|---|---|
| Myristic acid | C14:0 | 3.2 |
| Palmitic acid | C16:0 | 64.5 |
| Stearic acid | C18:0 | 6.9 |
| Oleic acid | C18:1 | 20.2 |
| Linoleic acid | C18:2 | 4.1 |

**Table 2**
Characteristics of palm oil.

| Property | Test method | Unit | Value |
|---|---|---|---|
| Acid number | ASTM D-974 | mg KOH/g | 1.29 |
| Saponification number | AOCS Cd 3a-94 | mg KOH/g | 191 |
| Water content | ASTM D-1123 | wt.% | 0.02 |
| Mean molecular mass | GB 5530-85 | g/mol | 887.17 |
| Density (15 °C) | EN ISO 3675 | kg/m$^3$ | 912 |

as-synthesized catalysts were designated as $a$K/PA-$T$, where $a$ and $T$ represented the $K_2CO_3$ loading (wt.%) and the calcination temperature, respectively.

### 2.3. Catalyst characterization

Thermogravimetric analysis (TGA) was performed using a Stanton Redcroft STA-780 thermal analyser between 30 and 850 °C. Samples weighing between 25 and 35 mg were placed in a nickel crucible. Runs were carried out in a static air atmosphere at a heating rate of 10 °C/min.

The X-ray diffractometer (XRD-Bruker; D8 Advance) patterns of the several catalysts were analyzed using a powder coupled with Cu K$\alpha$ radiation.

The FTIR spectra were recorded on a Shimadzu IR-Prestige-21 spectrometer at room temperature. The spectra were obtained after accumulation of 20 scans at a resolution of 2 cm$^{-1}$ between 500 and 4000 cm$^{-1}$. Powder samples were prepared by dispersing the samples in KBr (sample/KBr ratio of 1:150) and compressing the mixture to form disks.

The porous characteristic of the samples were evaluated by performing $N_2$ adsorption–desorption measurements using a BELSORP-max instrument at −196 °C. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method on the basis of the nitrogen adsorption data in the $p/p_0$ range corresponding to the linear region of the BET plot. The BJH method was used to calculate the pore volume and pore size distribution. Prior to the measurement, the sample in the glass adsorption tube was degased at 150 °C under a $N_2$ flow for 6 h.

Scanning electron microscopy (SEM) studies were conducted on a QUANTA 200 (FEI Company, Hillsboro, OR, USA), normally operating at 20 keV and equipped with a Microanalyzer (EDAX) to perform energy dispersive spectroscopy (EDS). Both secondary electron and backscattered electron detectors were used to take the micrographs.

The basic property of the catalysts was evaluated by the Hammett indicator method and expressed by an acidity function (H_) [31]. 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). Basicity of the catalysts was measured by the method of Hammett indicator-benzene carboxylic acid (0.02 mol L$^{-1}$ anhydrous methanol solution) titration.

The amount of catalyst elements in biodiesel product was determined using the inductively coupled plasma optical emission spectrometer (ICP–OES), Perkin–Elmer Optima 3000 V. The operation conditions for ICP–OES analysis were as follows: the sample flow rate was 1.5 ml/min; plasma power was 1000 W; plasma, auxiliary and nebulizer gas flow rates were 10, 0.6 and 0.65 L/min, respectively.

### 2.4. Transesterification reaction

The transesterification reaction was carried out in a 150 ml 3-neck flask with a condenser and a thermocouple thermometer. The transesterification reaction was represented as: