



# Influence of fuel type on microwave-enhanced fabrication of KOH/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> nanocatalyst for biodiesel production via microwave heating



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## ABSTRACT

Microwave irradiation has attracted a great deal of attention when it comes to synthesis of organic and inorganic materials. In the present study, a microwave heating system was utilized to prepare KOH/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> nanocatalysts via combustion method, so as to produce biodiesel from canola oil. Moreover, the effect of carbon content of fuels such as urea, ammonium acetate, glycerol and diethylene glycol used in the combustion reaction on the properties of the synthesized nanocatalysts was evaluated. The samples were analyzed by XRD, FTIR, TGA, BET-BJH, FESEM, and EDX techniques, with their basicity levels evaluated by Hammett indicator. The results showed that the combustion temperature tends to decrease with an increase in carbon content of fuel. Accordingly, the supports synthesized by urea and ammonium acetate exhibited the best crystalline structures. However, all samples showed Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> structure during impregnation by KOH and calcination step. The samples prepared by urea and ammonium acetate, as fuel, presented appropriate percentages of material-to-parent solution ratio, bringing about higher activities. Among them, the KOH/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> synthesized by urea had the largest surface area and activity, so that it succeeded to convert 83.5% of canola oil to biodiesel via microwave irradiation at microwave power of 450 W, methanol-to-oil molar ratio of 12, catalyst concentration of 4 wt. %, and reaction time of 60 min. The sample showed high reusability when it was calcined at 700 °C after each round of reaction.

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## 1. Introduction

Nowadays, biodiesel represents a promising alternative energy source that can reduce environmental problems such as air pollution, greenhouse gas generation and global warming. Biodiesel containing long-chain fatty acid methyl esters (FAMES) is usually produced by transesterification of triglycerides by short-chain alcohol in the presence of a catalyst; homogeneous basic catalysts such as KOH and NaOH are common choices in this regard [1]. However, these catalysts have some drawbacks such as sensitivity to free fatty acid (FFA) and water in feedstock, the need for several purification and neutralization steps, and environmental problems associated with the process-generated wastewater. On the other hand, although homogeneous acidic catalysts are insen-

sitive to quality of feedstock, the catalysts tend to raise severe environmental problems, corrode equipment, and end up with very low reaction rates [2]. Consequently, heterogeneous basic catalysts have been used for biodiesel production [3]. Many studies were performed on the activity of basic catalysts where the alkaline earth metal oxides, especially calcium oxide (CaO), showed high activity and basicity in the transesterification reaction [4,5]. Nevertheless, the catalysts presented low stability in air and reaction medium [6]. One way to overcome these problems is to use a support with high stability that establishes strong bonds with CaO [7–9]. As an alkali earth aluminate, calcium aluminate (general formula: Ca<sub>x</sub>Al<sub>2y</sub>O<sub>x+3y</sub>) can be a suitable choice for this purpose. Calcium aluminate contains several phases such as CaAl<sub>2</sub>O<sub>4</sub> (CA), Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (C<sub>3</sub>A), CaAl<sub>4</sub>O<sub>7</sub> (CA<sub>2</sub>) and Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> (C<sub>12</sub>A<sub>7</sub>), with CA and C<sub>12</sub>A<sub>7</sub> being the two major phases long been used in cement and steel industries [10]. CaO–C<sub>12</sub>A<sub>7</sub> catalyst was prepared by chemical synthesis and thermal activation from sodium aluminate solution and calcium hydroxide emulsion and investigated in

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biodiesel production [11,12]. It showed high activity (more than 94%) at a temperature of 65 °C, catalyst concentration of 5–6 wt. %, methanol-to-oil molar ratio of 15–18, and reaction time of 3–4 h. The sample was also prepared by solid-state reaction and utilized to undertake transesterification of *Argemone mexicana* oil to biodiesel where high activity and stability was detected [13]. Tao et al. [14] studied the activity of mesostructured  $\text{KF}/\text{Ca}_x\text{Al}_2\text{O}_{(x+3)}$  synthesized via solvent-evaporation strategy for the transesterification reaction. They reported that the sample calcined at 700 °C for 3 h showed high total active basicity and basic strength where 98% of soybean oil was converted to biodiesel at a temperature of 60 °C, catalyst concentration of 6 wt. %, methanol-to-oil molar ratio of 18, and reaction time of 5 h.

Calcium aluminate is usually synthesized by wet chemical methods, especially the combustion method [10], whereas other methods such as sol-gel [15,16], co-precipitation [11,12] and solid state reaction [13] are utilized for biodiesel production heterogeneously. However, the combustion method (CM) has gained much larger deals of attention as it saves energy and time and results in rapid nucleation and growth, suppression of undesired phases, and high purity and homogeneous structure of final powder at nano scale [17]. There are several parameters influencing the reaction such as the type of fuel, fuel-to-oxidizer ratio, use of excess oxidizer, ignition temperature and source, gelling temperature and amount of water contained in precursor mixture [18,19]. The type of fuel is a major parameter in CM as it imposes significant effects on the reaction temperature generated in this process [20,21]. Surprisingly, barring some sketchy reports, no systematic study has been undertaken on the effects of different fuel for preparation of calcium aluminate.

Nowadays, microwave irradiation serves as an ignition source which is considerably utilized in CM, replacing conventional heating systems (furnace). This is because microwave irradiation can uniformly heat a substance throughout the reaction container, leading to a more homogeneous nucleation and shorter crystallization time [22]. In microwave combustion method (MCM), heat is generated into the material as a result of microwave radiation/material molecules interaction, while in conventional combustion synthesis, heat is transferred to sample surface from where it starts to distribute throughout the sample slowly. Microwave irradiation has also fascinated a significant interest in chemical reactions such as biodiesel production because of less energy consumption, short reaction and separation time, faster kinetics, higher yield and relatively simple manipulations [23–27]. Microwave-assisted biodiesel production using homogeneous catalysts has been widely evaluated in contrast to that with heterogeneous catalysts [28–31]. To the best of our knowledge, a study on the effect of calcium aluminate, when used as a support, on biodiesel production process is yet to be reported.

In this study, the effect of different fuel types (urea (U), ammonium acetate (AA), glycerol (G) and diethylene glycol (DEG)) on the preparation of calcium aluminate using MCM was evaluated. The produced calcium aluminate was then loaded by potassium components as active phase for microwave-assisted biodiesel production from canola oil. The samples were characterized by XRD, FTIR, TG, BET surface area, EDX and FESEM techniques. In addition, the samples had their basicity examined by Hammett indicator method. Finally, the reusability of optimal sample was evaluated.

## 2. Materials and methods

### 2.1. Materials

Aluminium nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), calcium nitrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), potassium hydroxide (KOH) and methanol

( $\text{CH}_3\text{OH}$ ) of chemical grade were purchased from Merck. Used as fuel, urea ( $\text{CH}_4\text{N}_2\text{O}$ ), ammonium acetate ( $\text{C}_2\text{H}_5\text{NO}_2$ ), glycerol ( $\text{C}_3\text{H}_8\text{O}_3$ ) and diethylene glycol ( $\text{C}_4\text{H}_{10}\text{O}_3$ ) were also purchased from Merck. All materials were used as received without any further purification. Moreover, canola oil was supplied from local supplier.

### 2.2. Catalyst preparation

In order to prepare calcium aluminate samples, aluminum nitrate (10 mmol) and calcium nitrate (5 mmol) were dissolved in distilled water to prepare an initial solution onto which fuel solution was loaded under vigorous stirring at room temperature for 45 min until a clear transparent solution was obtained. Metal nitrate salts and the fuels were chosen by considering total reducing and oxidizing agent valences of the raw materials, with metal nitrate-to-fuel molar ratio being stoichiometric (33.35 mmol U, 18.2 mmol AA, 14.3 mmol G and 10 mmol DEG). The solution was heated at 80 °C to form a gel; it was then placed in a domestic microwave oven (Daewoo, Model No. KOC9N2TB, 900 W, 2.45 GHz) and exposed to microwave energy for 10 min. Accordingly, the precursor mixture started to boil and underwent evaporation followed by decomposition with the evolution of gases. When the solution reached the point of spontaneous combustion, an exothermic reaction began at the ignition temperature, generating a certain amount of heat manifested in the maximum temperature or temperature of combustion. Therefore, the solution vaporized and instantly became a solid as were labeled as CA(U), CA(AA), CA(G) and CA(DEG). Generally, amino acids can serve as a complexing agent for the metal ion in the solution, and also serve as fuel for the synthesis of nano-crystalline metal oxides. The samples as support were used for the next step without any thermal treatment.

The KOH-containing calcium aluminate was synthesized by impregnation of as-prepared calcium aluminate with different fuels in presence of KOH. For this purpose, the supports were mixed by KOH aqueous solution (35 wt. %) at 80 °C for 2 h and then dried at 110 °C for overnight and finally calcined at 700 °C in ambient air for 4 h. The obtained powders were labeled as KCA(U), KCA(AA), KCA(G) and KCA(DEG).

### 2.3. Catalyst characterization

The X-ray diffraction was utilized to determine the crystalline phase of the samples using UNISANTIS/XMP 300 by means of Cu K $\alpha$  radiation operating at 45 kV and 80 mA within the scanning range of 10–60°. Surface-active functional groups of as-prepared catalysts were determined by Fourier Transform Infrared Spectrometry (FTIR) in the range of 400–4000  $\text{cm}^{-1}$  using a SHIMADZU 4300 (Japan) spectrometer. Incomplete decomposition of nitrate and fuels during the combustion synthesis of supports was determined by TG analysis using an Evolution STA apparatus (SETARAM, France) in atmosphere medium operated in the range of 50–800 °C at a heating rate of 20 °C/min. Utilizing a PHS-1020 apparatus (PHSCHINA, China), BET-BJH technique was used to determine specific surface area, mean pore size and pore volume of KOH-containing calcium aluminate catalysts. The catalysts were degassed at 180 °C for 12 h prior to the analysis. The morphology and surface structure of all samples were accomplished through Field Emission Scanning Electron Microscopy (FESEM) using a MIRA3 FEG-SEM (TESCAN, Czech republic) equipped with a VEGA II Detector (Czech Republic, TESCAN) to undertake energy dispersive X-ray (EDX) analysis to quantify surface composition. Basic strength of KOH-containing calcium aluminate catalysts ( $\text{H}_+$ ) was determined by using Hammett indicators. About 300 mg of the sample was shaken with 1 mL of a solution of Hammett indicators

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