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Comparative assessment of the ability of a microwave absorber nanocatalyst in the microwave-assisted biodiesel production process

Hamed Nayebzadeh ^{a, c, *}, Naser Saghatoleslami ^a, Mohammad Haghghi ^{b, c},
 Mohammad Tabasizadeh ^d, Ehsan Binaeian ^e

^a Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, P.O. Box 9177948974, Mashhad, Iran

^b Chemical Engineering Faculty, Sahand University of Technology, P.O. Box 51335-1996, Sahand New Town, Tabriz, Iran

^c Reactor and Catalysis Research Center (RCRC), Sahand University of Technology, P.O. Box 51335-1996, Sahand New Town, Tabriz, Iran

^d Department of Biosystems Engineering, Faculty of Agriculture, Ferdowsi University of Mashhad, P.O. Box 9177948974, Mashhad, Iran

^e Department of Chemical Engineering, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran

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ABSTRACT

In this study, a carbon-supported KOH/Ca₁₂Al₁₄O₃₃ nanocomposite was fabricated via the microwave combustion method, in which dextrose was used as a carbon source, and its activity in the microwave-assisted transesterification reaction as a microwave absorption material was assessed. The samples were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetry, Brunauer–Emmett–Teller (BET), field-emission scanning electron microscopy, and energy dispersive X-ray analyses. The results showed that the carbonate and noncarbonate samples had a calcium aluminate (Ca₁₂Al₁₄O₃₃) structure as a support. Different carbon groups were formed during preparation of the carbon-supported KOH/Ca₁₂Al₁₄O₃₃ nanocomposite, which improved its surface area and porosity. Although the samples presented similar basicity, the carbonated nanocomposite exhibited twice as much activity as the KOH/Ca₁₂Al₁₄O₃₃ nanocatalyst for conversion of canola oil to biodiesel in the microwave-assisted transesterification reaction at 270 W microwave power. The nanocomposite with a larger pore size made active sites easily accessible and exhibited higher catalytic ability where the conversion of 98.8% was obtained under the optimized conditions of 270 W microwave power, methanol/oil molar ratio of 15, 4 wt% of the nanocomposite, and 30 min of reaction time. The carbon-supported nanocatalyst can be reused for at least four times with less reduction in activity. Furthermore, the obtained biodiesel showed that it met the standard values (EN 14214 and ASTM D-6751) with respect to the density, kinematic viscosity at 40 °C, acid number, and flash point.

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1. Introduction

Nowadays, researchers attempt to accelerate the reaction to reduce the requirement time for obtaining products.

Therefore, the conventional heating systems were replaced by new technologies such as microwave, ultrasonic, and super/subcritical processes. The microwave heating technique has been successfully used in various chemical processes such as nanomaterial synthesis, solid-state chemistry, nanotechnology, and organic chemistry. Microwave irradiation rapidly and homogeneously increases the temperature of a reaction medium such that the higher reaction rate and selectivity of the ensuring products can be

* Corresponding author.

E-mail addresses: hamed.nayebzadeh@mail.um.ac.ir, H.nayebzadeh@yahoo.com (H. Nayebzadeh).

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obtained by choosing appropriate microwave parameters [1,2].

Biodiesel production is one of the chemical reactions that can be performed by microwave irradiation, in which the reaction and separation times are reduced significantly from hours to minutes. Biodiesel is commonly produced by transesterification of edible and nonedible oils in the presence of short chain alcohol, where methanol is usually used because of its high activity and low price, using a catalyst. To further increase the compatibility of the biodiesel production process with the environment, heterogeneous catalysts are suggested instead of homogeneous catalysts [3,4]. Some heterogeneous catalysts such as CaO [5–7], NaOCH₃ [8], NaNH₂ [9], heteropolyacid catalyst [10,11], and sulfated zirconia [12] have been examined in the microwave-assisted transesterification reaction (MTR). In addition to strong stability and less leaching of active phases of catalysts in the reaction mixture, high specific surface area, strong base strength, and high concentration of base sites are characteristics of an active transesterification catalyst [13].

Alkaline earth aluminates with formula M_xAl_{2y}O_{x+3y} (M = Ca, Mg, Sr, and Ba) as active and stable support may be an appropriate choice for use in the biodiesel production because it can be easily synthesized via the microwave combustion method (MCM) with a high surface area in very short time. The activity of a MgO/MgAl₂O₄ nanocatalyst synthesized by the combustion method was studied in the biodiesel production and yield of 95.7% was obtained under the conditions of 110 °C, methanol/oil molar ratio of 12, 3 wt% of the catalyst, and reaction time of 3 h [14]. The CaO/Ca₁₂Al₁₄O₃₃ catalyst also converted 98.7% of vegetable oil to the biodiesel at 65 °C, 1:10 oil/methanol ratio, and 6 wt% of the catalyst for 3.5 h [15]. The KF/Ca_xAl₂O_(x+3) catalyst was evaluated to catalyze the transesterification reaction of soybean oil with methanol [16]. The yield of 98% was obtained under the conditions of 60 °C, methanol/oil molar ratio of 18, 3 wt% of the catalyst, and 5 h of reaction time when the catalyst showed less stability. In our previous work, KOH/calcium aluminate was successfully synthesized by the MCM and showed high activity in the transesterification reaction of canola oil [17]. However, no study has so far been done on the activity of these catalysts in the MTR.

It is well known that using microwave absorbing materials is important for further accelerating the reaction rate. If the catalyst is a strong microwave absorber material, it can gather the microwave irradiation and the "microwave hot spots" would be consequently formed [18]. Therefore, carbonated catalysts can have an opportunity to achieve the highest reaction rate, which have been examined in a few studies for biodiesel production via the esterification reaction [18,19]. However, according to the best of best knowledge, carbonated alkaline earth aluminate catalyst prepared via a simple MCM has not been used for biodiesel production via the MTR.

The triple objectives of this study were as follows: first, to develop an experimental procedure for preparation of a KOH-containing Ca₁₂Al₁₄O₃₃/C nanocomposite as a high active microwave absorbing material via the simple MCM; second, to evaluate the influence of absorbed microwave

energy on the rate of transesterification reaction; and third, to obtain a sample with high stability in the MTR for industrial application. The samples (carbonated and non-carbonated) were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG), BET–Barrett–Joyner–Halenda (BJH), field-emission scanning electron microscopy (FESEM), and energy dispersive X-ray (EDX) analyses, and their basicity was evaluated by the Hammett indicator method. Finally, the MTR parameters were optimized.

2. Materials and methods

2.1. Catalyst preparation

Ca₁₂Al₁₄O₃₃ (CA) was prepared by the MCM using urea as fuel with stoichiometric compositions, according to the concepts of propellant chemistry. For this purpose, 12 mmol Ca(NO₃)₂·4H₂O, 14 mmol Al(NO₃)₃·9H₂O, and 55 mmol urea were dissolved in 40 mL distilled water and the mixture was heated on the hotplate at 80 °C under stirring to form viscous gel. Then, the mixture was placed in the microwave oven (Daewoo, Model No. KOC9N2TB, 900 W, 2.45 GHz) and irradiated for 10 min. After evaporation of remained water and exhaustion of the gases, the mixture was flamed for a few seconds and fume white powder was synthesized. The CA/C nanocomposite was synthesized as described above where dextrose (13.75 mmol) was used instead of urea. Finally, the brown powder was prepared when no flame was observed.

Finally, the samples were impregnated by the KOH where 1 g of each sample was mixed with 35.6 mL of a 0.1 M KOH aqueous solution and heated at 80 °C to form gel. After drying at 110 °C overnight, the solution was calcined at 800 °C for 3 h under argon medium. The samples were labeled as KCA and KCA/C. The catalyst preparation routes are shown in Fig. S1 of the Supplementary Material (SM).

2.2. Catalyst characterization

The crystalline phase of the samples was detected by XRD analysis using a Unisantix XMD 300 by means of Cu K α radiation operating at 45 kV and 80 mA with scanning range of 10–70°. The active surface functional groups of the synthesized nanocomposites were evaluated by the FTIR in the range of 400–4000 cm⁻¹ using a Shimadzu 4300 (Japan) spectrometer. The decomposition of raw materials and fuels during catalyst preparation was analyzed by thermogravimetry analysis (TGA). The TGA was performed using an evolution STA (SETARAM, France) instrument in the range of 50–800 °C at a heating rate of 20 °C/min under the airflow. The specific surface area, mean pore size, and pore volume of the nanocomposites were assayed using a PHS-1020 (Phschina, China) apparatus by the BET–BJH methods. FESEM analysis was accomplished to study the morphology and surface structure of the nanocomposites using MIRA3 FEG-SEM (TESCAN, Czech Republic). The distribution of elements in the samples was quantified by EDX technique using a VEGA II detector (TESCAN). The basic strength of the solid bases (H₊) was determined by using Hammett indicators. The indicators used were as follows:

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