

IN SITU TRANSESTERIFICATION OF MICROALGAE OVER KOH SUPPORTED ON MESOPOROUS CeO₂ CATALYST

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Abstract

In this study, a mesoporous CeO₂ with large surface area and uniform pore size distribution was synthesized using Brij35 as a surfactant. The solid base catalyst KOH/CeO₂ prepared by impregnation method was used to produce biodiesel from *Chlorella vulgaris* biomass by *in situ* transesterification. The characteristics of the catalysts were analysed by the X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analyzer and Fourier Transform infrared spectroscopy (FT-IR). The effects on biodiesel yield of catalyst preparation conditions and transesterification parameters were investigated. The optimum preparation conditions of solid base catalyst KOH/CeO₂ were as follows: 50 wt% loading of KOH, 350 °C of calcination temperature and 3 h of calcination time. At the optimal transesterification conditions of catalyst content of 14% wt%, methanol to biomass ratio of 6 mL/g, reaction temperature of 60 °C and reaction time of 8 h, the highest biodiesel yield could achieve 92.9%.

Keywords: Microalgae; Biodiesel; KOH/CeO₂; Solid base catalyst.

1. Introduction

With the rapid development of industry and the increasing demand for transportation, traditional sources of energy such as petroleum and coal have been excessively consumed, resulting in the serious environment destruction. Biodiesel has aroused great interest as an alternative energy source to nonrenewable fuels [1-2]. Biodiesel is defined as the fatty acid methyl esters (FAME) produced by transesterification, the feedstock for biodiesel can be vegetable oils, animal fats, waste cooking oil and microalgae oil [3-5]. Compared to traditional fuels, biodiesel has better property such as bio-degradable, no-toxic, and low carbon emission [6]. Therefore, biodiesel is an ideal clean energy for the replacement of traditional energy.

The range of raw materials to prepare the biodiesel is wide. Due to the edible oil clashes with the food, this feedstock has caused heated argument [7]. Compared with terrestrial plants, there are some advantages for microalgae as the raw materials. As a lower phytoplankton, microalgae have high photosynthetic efficiency, causing a rapid grow and a high biomass production [8]. Moreover, microalgae have a high oil content. The lipid content of some microalgae is up to 20%~70% [9]. Since the cultivation process of microalgae is not restricted by region and season, microalgae can grow everywhere, avoiding the occupation of crops land [10]. Based on the above features, microalgae are recognized as promising feedstock for biodiesel. Microalgae biodiesel technology covers a number of sport technique segments, including the screening, cultivation and harvesting of microalgae, the extraction and transesterification of microalgae lipid [11]. The lipid in microalgae is usually extracted by organic solvents, such as methanol, chloroform [12-14]. Due to the volatility and toxicity of organic solvents, this method causes the high cost for biodiesel production as well as environment pollution. Recently, in

situ transesterification (direct transesterification) method has been developed, as it combines lipid extraction and transesterification into a one step process [15]. Compared to the conventional two-step method, the in situ transesterification simplifies the process of biodiesel production. In addition, it reduces the use of organic solvents and consumption of energy, giving an environment-friendly economic routine [16].

In the process of the transesterification reaction, catalysts play an important role. The homogenous catalysts such as H_2SO_4 and $NaOH$ have been applied in the transesterification reaction so far [17-18]. However, the homogenous catalysts are difficult to be separated from the product. The purification of the product requires a large amount of water, resulting in the emission of waste water. In addition, the homogenous catalyst has high requirement for the quality of raw materials and it causes serious corrosion of equipment [19]. Since heterogeneous catalyst is easier to be recycled and reused, it simplifies the biodiesel production process and reduces the production cost. The application of heterogeneous catalyst in the preparation of biodiesel is widely studied [20]. Liu et al. synthesized a nano-solid base catalyst ($K/ZrO_2/\gamma-Fe_2O_3$) with weak magnetism and used it for transesterification of soybean oil to produce biodiesel, the biodiesel yield reached above 93.6 wt% and the magnetic catalyst was reused in six cycles without remarkable loss in catalytic activity [21]. Saba et al. prepared $KOH/ZSM5$ for transesterification of sunflower oil, the FAME yield could reach 95.1% under optimal conditions and the catalyst remained high catalytic activity after four times' reuse [22].

As an inexpensive rare earth oxide, CeO_2 is commonly used in catalytic systems as a catalyst or as a carrier for catalyst. For instance, CeO_2 and modified CeO_2 were used as catalysts by Venkatesh for the transesterification of *Pongamia pinnata* oil [23]. Farias et al. reported that CeO_2 supported on bentonite was used for ethylic transesterification [24]. CeO_2 was also mixed with other metal oxides such as CaO , MgO for transesterification of different oils [25-26]. However, the studies on mesoporous CeO_2 used as catalyst carrier for transesterification have never been reported.

In this study, a mesoporous CeO_2 with large surface area and uniform pore size distribution was synthesized using Brij35 as a surfactant. The solid base catalyst KOH/CeO_2 prepared by impregnation method was used to produce biodiesel from *Chlorella vulgaris* biomass by *in situ* transesterification. The purpose of this study was to investigate the characteristics of the CeO_2 carrier. The optimal synthesis condition of the catalyst for the transesterification reaction was investigated. Furthermore, the optimal transesterification reaction conditions were studied and the effect of the reaction parameters was evaluated.

2. Materials and methods

2.1. Materials

C. vulgaris powder was purchased by Shandong WudiLvqi Biological Engineering Company (Binzhou, China). Heptadecanoic acid methyl ester and FAME standards were obtained from J&K Scientific (Beijing, China). Polyoxyethylene ether (Brij35) was procured from Macklin (Shanghai, China). $(Ce(NH_4)_2(NO_3)_6)$, ethanol, ammonia solution (25wt%), potassium hydroxide (KOH), methanol and n-hexane were obtained from Sinopharm (Shanghai, China). All reagents used were of analytical grade. The water used in the experiment was deionized water.

2.2. Catalyst preparation

Firstly, mesoporous CeO_2 carrier was synthesized through the soft-templating approach using polyoxyethylene ether (Brij35) as a surfactant [27]. 20.0 g of Brij35 was dissolved in 50% ethanol, then 10.97 g of $Ce(NH_4)_2(NO_3)_6$ was added by stirring to form a homogeneous solution with the molar composition of Brij35/ $Ce(NH_4)_2(NO_3)_6$ of 2:1. Ammonia of 25wt% was added drop-wise to the solution until the final pH value of the aqueous solution was maintained at 9.0~10.0. The mixture was stirred for 3 h and aged for 2 d. The yellow precipitate was recovered by suction filtration, followed by washing thrice with deionized water and ethanol, respectively. The precipitate was then heated in an oven at 80°C under vacuum. Finally, the dried material was calcined at 350°C for 4 h in a muffle furnace to obtain mesoporous CeO_2 carrier.

The KOH/CeO₂ catalysts with different KOH loadings (35, 40, 45, 50, 55wt%) were prepared by impregnation of the CeO₂ with an aqueous solution of KOH. The mixture was stirred for 2h and then dried at 100°C for 12 h. The impregnated precursor was calcined in a muffle furnace to obtain the KOH/CeO₂ solid catalyst.

2.3. In situ transesterification

The transesterification reactions were carried out in a 250mL three neck round-bottom flask with a condenser. 5 g of dry microalgae, 20 mL of hexane, a certain proportion of methanol (4- 12 mL/g) and amounts of the catalyst KOH/CeO₂(12-20 wt%) were added to the neck flask. The neck flask was put in a water bath with vigorous stirring to a preset temperature (50-70°C) for a preset time (2- 10 h). After the completion of the reaction, the mixture was cooled to room temperature and filtered to remove the residues. 20 mL of hexane was added to the filtrate to extract the FAME product, this step was repeated three times. The obtained hexane layer was transferred to a clean flask and evaporated to obtain the biodiesel. The FAME content in the sample was directly analyzed by gas chromatography. The conversion efficiency of lipid to FAME was expressed as weight of FAMEs compared with weight of total convertible lipids [28].

2.4. Biodiesel sample analysis

The composition of biodiesel was analyzed using a gas chromatography-mass spectrometer (Shimadzu, Japan) equipped with a flame-ionization detector (FID) and a Rxi-Wax capillary column (30m × Φ 0.25 mm × 0.25 μ m). The injector temperature was 250°C, the oven temperature was set at 160°C and held for 1 min, and then it was increased to 200°C at the rate of 5°C/min before the temperature increase to 230°C at rate of 2°C/min and held for 5 min. The detector temperature was set at 260°C. Helium was used as carrier gas at a flow rate of 1.0mL/min.

2.5. Catalyst characterization

Fourier transform infrared (FT-IR) spectra of the samples were performed using ALPHA-T Fourier Transform Infrared Spectrometer (BRUKER Corp, Germany) from 400 cm⁻¹ to 4000 cm⁻¹. X-ray diffraction (XRD) was carried out on D/MAX-rA instrument (Rigaku Corp., Japan). Nitrogen adsorption and desorption isotherms of CeO₂ were studied using the ASAP2020 analytical system (USA). The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method and the mesopores volume and pore size distribution were calculated by the Barrett-Joyner-Halenda (BJH) method from the desorption curve of the isotherm.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. BET and N₂ adsorption-desorption isotherm

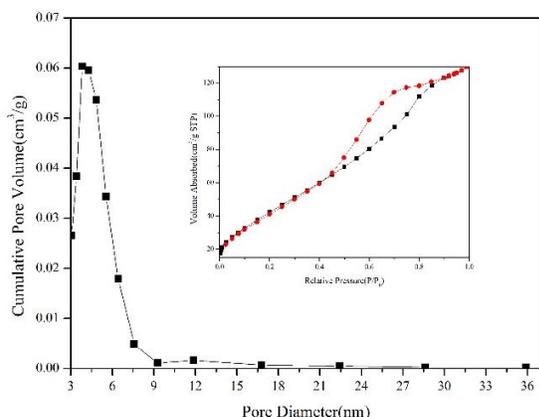


Fig.1. (a) Pore size distribution curve and (b) Nitrogen adsorption-desorption isotherm of CeO₂

The BET result of the CeO₂ showed that the carrier had a surface area of 160.04 m²/g, a pore volume of 0.187 m³/g and an average pore diameter of 3.817nm. Fig.1 shows the N₂ adsorption/desorption isotherm and pore diameter distribution of CeO₂. The pore diameter distribution indicated the CeO₂ carrier possessed mesoporous pore with a pore size that mainly distributed in 3-9 nm. According to the IUPAC classification, the N₂ adsorption/desorption isotherm of the CeO₂ belonged to type IV with a notable H₂ hysteresis loop, revealed that the carrier was typical of mesoporous materials.

3.1.2. FT-IR

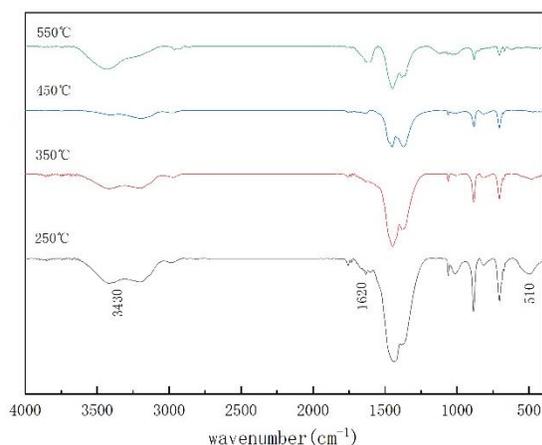


Fig.2. The FT-IR absorption spectra of KOH/CeO₂ calcined in different temperatures

3.1.3. XRD

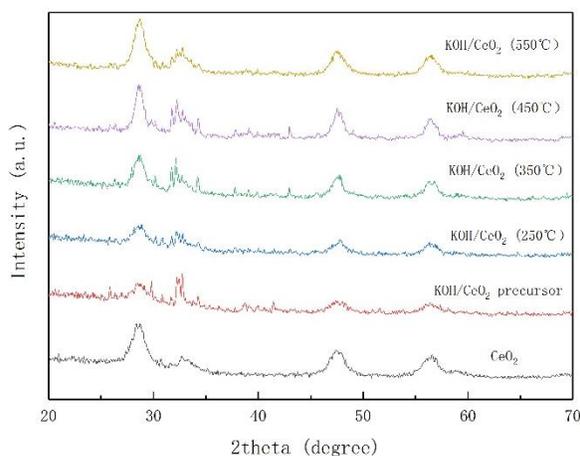


Fig.3. XRD patterns of CeO₂, uncalcined KOH/CeO₂ precursor and calcined KOH/CeO₂ at different temperatures

The FT-IR absorption spectra of KOH/CeO₂ calcined in different temperatures was represented in Fig.2. The broad band at 3430 cm⁻¹ attributed to the presence of the O-H stretching vibration. The peak appeared at 1603 cm⁻¹ can be assigned to the bending vibration of O-H. The peaks appeared at 700-1500 cm⁻¹ was due to the presence of C-H, -CH₂- and C-O-C vibration in the polyoxyethylene ether (Brij35) structure. The peak at 510 cm⁻¹ corresponded to the characteristic stretching of Ce-O bond [29]. As can be seen in Fig.2, the intensity of absorption peak decreased with the calcination temperature increases, which indicated that the calcination temperature had influence on the structure of catalyst.

Fig. 3 shows that the XRD patterns of CeO₂, uncalcined KOH/CeO₂ precursor and calcined KOH/CeO₂ at different temperatures. All samples showed diffraction peaks at $2\theta = 28.5^\circ, 33.1^\circ, 47.5^\circ$ and 56.4° , which corresponded to the characteristic cubic fluorite structure of CeO₂. After loading with KOH, the diffraction peaks of CeO₂ almost disappeared, which proved that KOH had been loaded on the CeO₂ surface successfully. As can be seen, the diffraction peak related to the KOH phase has not been found, which might be due to high dispersion of K⁺ species. With increasing calcination temperature from 250°C to 550°C, the intensities of diffraction peaks of CeO₂ gradually increased, indicating that the calcination temperature had influence in the distribution of KOH on the surface of CeO₂.

3.2. Catalytic performance for biodiesel production

3.2.1 Effect of preparation conditions on the FAME yield

The effects of various preparation conditions include KOH loading amount, calcination time and calcination temperature on catalytic performance were investigated in the microalgae transesterification. The transesterification reactions were carried out at a catalyst content of 14 wt.%, a methanol to biomass ratio of 6 mL/g, a temperature of 60°C and a reaction time of 8 h.

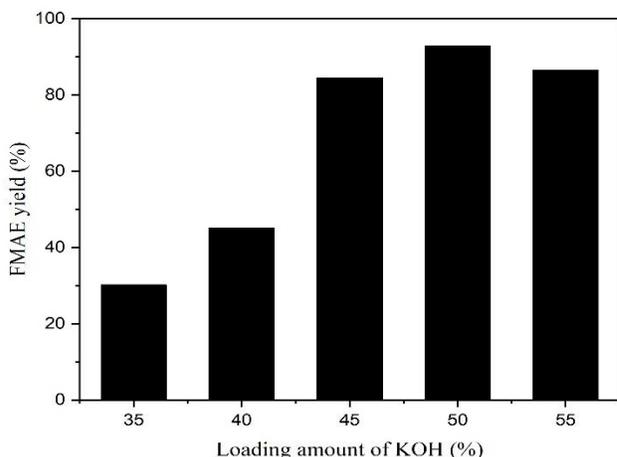


Fig.4. Effects of KOH loading amount on FAME yield (%)

A series of KOH/CeO₂ catalysts with KOH loading from 35 to 55 wt% calcined at 350°C for 3 h were prepared. As shown in Fig.4, as the KOH loading increased from 10 wt% to 30 wt%, the biodiesel yield increased from 30.2% to 92.9%. However, the biodiesel yield decreased as the KOH loading exceeded 50wt %.The increase of biodiesel yield was attributed to the formation of active sites with the increase of KOH loading. As the KOH loading continued to increase, the active sites on the surface of the carrier gradually approach saturated and agglomerated on the

carrier partially, resulting in the decrease in catalyst activity , which caused the reduce of biodiesel yield. Therefore, the optimum loading amount of KOH was 50wt%.

The influence of calcination temperature of the KOH/CeO₂ catalyst was studied with the calcination temperature ranging from 250°C to 650°C.

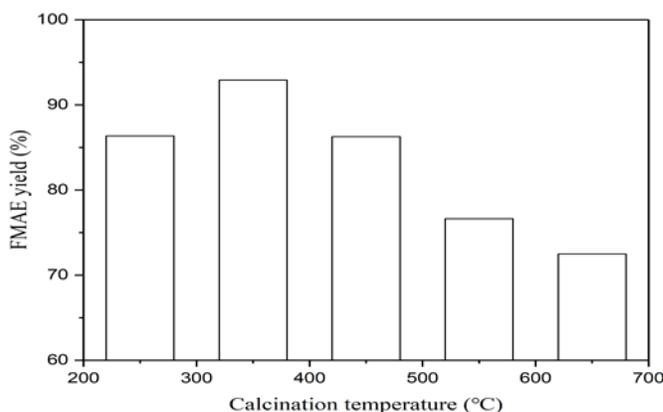


Fig.5. Effects of calcination temperature on FAME yield (%)

Fig.5 shows that the biodiesel yield increased from 86.3% to 92.9% as the calcination temperature of the catalyst increased from 250°C to 350°C. However, the biodiesel decreased after the calcination temperature exceeded 350°C. Previous research had documented that, K₂O formed by decomposition of KOH as calcination temperature exceed 600°C, which contributed to the strong basic activity in transesterification reaction [30]. In this study, the FT-IR and XRD results indicated that the calcination temperature had influence on the structure of mesoporous CeO₂.

When the calcination temperature exceeded 350°C, it may lead to the sintering of catalyst surface, resulting in the reduction of the specific surface area. Therefore, the appropriate calcination temperature was 350°C.

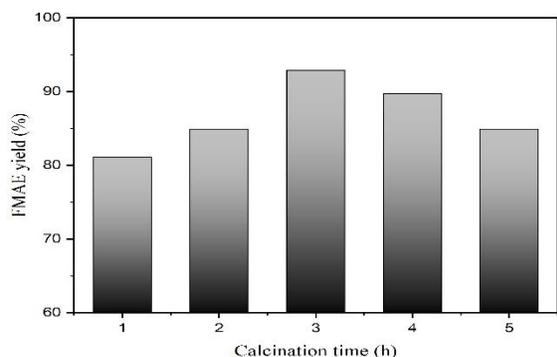


Fig.6. Effects of calcination time on FAME yield (%)

In order to determine the effect of calcination time for the catalyst preparation, the calcination time was varied within the range of 1 – 5 h. Fig.6 shows that the biodiesel yield increased from 81.1% to 92.9% as the calcination temperature of the catalyst increased from 1 h to 3h. However, the biodiesel decreased after the calcination temperature exceeded 3 h. Excessive time would result in the catalyst surface sintering. Thus, the best calcination time for catalyst preparation was 3h.

3.2.2. Effect of transesterification conditions on the FAME yield

The optimum preparation conditions of solid base catalyst KOH/CeO₂ were as follows: 50 wt% loading of KOH, 350°C of calcination temperature and 3 h of calcination time. The KOH/CeO₂ prepared in the optimum conditions was applied to research the influence of reaction conditions on the biodiesel yield.

3.2.2.1. Effect of catalyst content

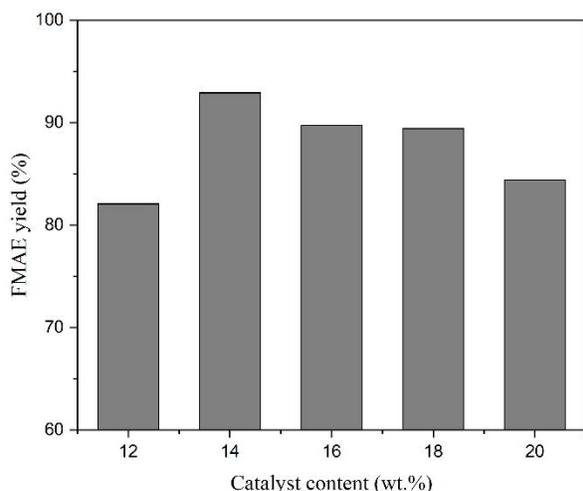
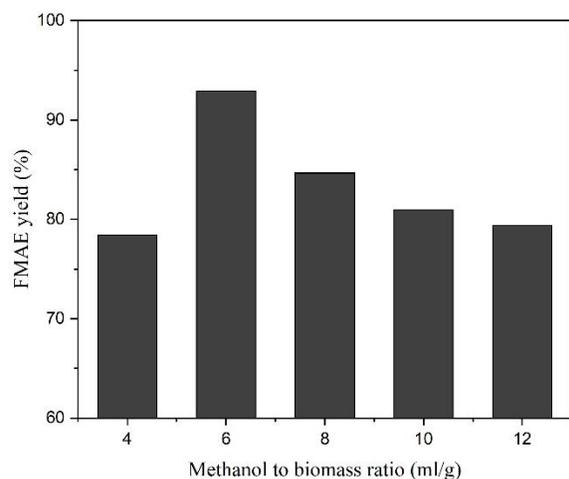


Fig.7. Effects of catalyst content on FAME yield (%)

To study the effect of catalyst content, transesterification reactions were performed with different amounts of the catalyst (12-20wt%) at a methanol to biomass ratio of 6 mL/g, a temperature of 60°C and a reaction time of 8 h. Fig.7 shows that the biodiesel yield increased from 44.0% to 92.9% as the catalyst amount increased from 10 wt% to 14 wt%. However, the biodiesel yield decreased slightly with the catalyst amount further prolonged to. It was probably because the excessive catalyst caused saponification. Therefore, the optimal mass ratio of the catalyst was 14wt%.

3.2.2.2. Effect of methanol/oil molar ratio



The biodiesel yield under various methanol to biomass ratios was showed in Fig.8 with catalyst content of 2wt% and the temperature of 60°C after reacting for 8h. The biodiesel yield increased from 78.4% to 92.9% as the methanol to biomass ratio increased from 4 mL/g to 6mL/g. The dilution of the oil and catalyst concentration caused by excess methanol explained the decrease of biodiesel yield. Therefore, the optimum methanol/oil molar ratio was 6:1.

Fig. 8. Effects of methanol to biomass ratio on FAME yield (%)

3.2.2.3. Effect of reaction temperature

To investigate the optimum reaction temperature, transesterification reactions were carried out with various reaction temperature (50, 55, 60, 65, 70°C) at a methanol to biomass ratio of 6 ml/g, a catalyst amount of 14 wt% and a reaction time of 8 h. As shown in Fig.9, the biodiesel yield increased from 75.1% to 92.9% with the reaction temperature increased from 50°C to 60°C. However, the biodiesel yield decreases to 82.0% as the catalyst amount increased to 70°C. Because the boiling point of methanol is 64.7°C, methanol would volatilize from the reaction system when the reaction temperature exceeded 64.7°C, resulting in the loss of methanol and a decrease in biodiesel yield. Thus, 60°C was considered as the appropriate reaction temperature.

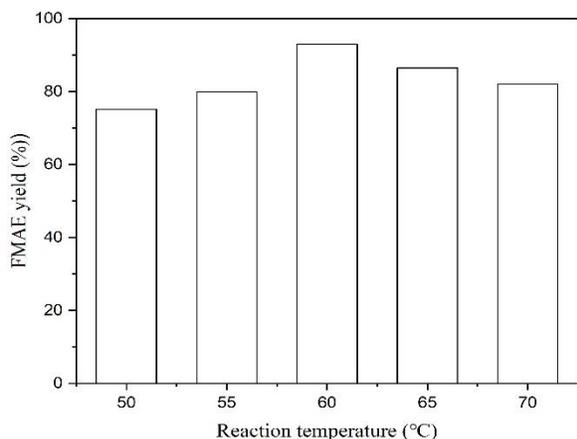


Fig.9. Effects of reaction temperature on FAME yield (%)

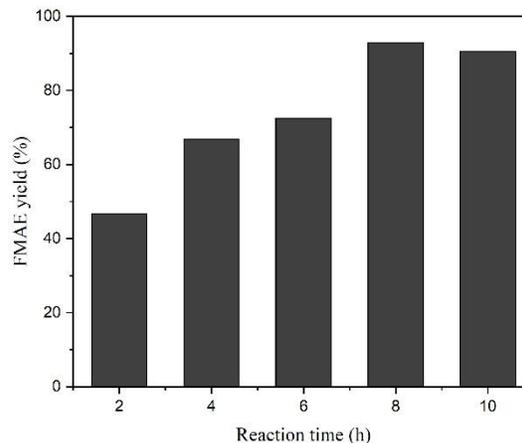


Fig.10. Effects of reaction time on FAME yield (%)

3.2.2.4. Effect of reaction time

The optimal reaction time was investigated with the reaction time ranging from 2 h to 10 h. Fig.10 presented that the biodiesel yield increased rapidly from 46.8% to 92.9%. However, when the reaction time increased to 10 h, the biodiesel yield was not significantly improved. The slightly decrease of the biodiesel yield may be due to the degradation of long-chain unsaturated fatty acids [28]. Therefore, 8h was chosen as the optimum reaction time.

4. Conclusion

In this paper, a mesoporous CeO₂ was successfully synthesized using Brij35 as a surfactant. The BET result showed that the mesoporous CeO₂ had the advantages of large surface area and uniform pore size distribution. The solid base catalyst KOH/CeO₂ was prepared by impregnation method and used to produce biodiesel from *Chlorella vulgaris* biomass by *in situ* transesterification. The optimum preparation conditions of solid base catalyst KOH/CeO₂ were as follows: 50 wt% loading of KOH, 350°C of calcination temperature and 3 h of calcination time. The highest yield of biodiesel of 92.9% was achieved at the optimal reaction condition of 14 wt% of catalyst content, 6 mL/g of methanol to biomass ratio and at 60°C for 8 h. KOH/CeO₂ catalyst is a promising solid base catalyst for the high catalytic activity and low cost.

Acknowledgements

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