

Research Article

3D Hollow Mg-Ca-Al Hydrotalcite-Like Compounds Doped with KF for Catalytic Transesterification

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Received 8 October 2022; Revised 7 February 2023; Accepted 9 February 2023; Published 27 February 2023

Academic Editor: Vikranth Kumar Surasani

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Herein, a kind of three-dimensional hollow Mg-Ca-Al hydrotalcite-like compounds (HTLCs) microsphere was prepared by self-assembly of hydrotalcite-like nanosheets. Mg-Ca-Al HTLCs microsphere (MS) has large specific surface area and large pore size, and the modification of KF·2H₂O increases numerous alkaline active sites on the surface of the catalyst. The prepared catalyst has excellent catalytic effect for the production of biodiesel by transesterification. Under the optimal conditions of the catalyst addition amount which accounts for 2% of the weight of oil, the biodiesel yield of the best catalyst is as high as 92% within 30 minutes. This article also provides a paradigm of a rational structural design for regulating the morphology of HTLCs.

1. Introduction

At present, the energy crisis of declining fossil fuels and the environmental crisis of the increasing carbon dioxide content in the atmosphere is intensifying. One promising key to solve these troubles is making the development of new environmentally friendly, renewable, and green alternative fuels [1, 2]. Since the energy release performance of biodiesel is similar to that of petrochemical diesel, it presents excellent environmental compatibility and biodegradability. Therefore, biodiesel is considered to be a reliable alternative for fossil fuel diesel [3, 4]. The production of biodiesel is important for the sustainable development and security of energy [5, 6].

The main method for the production of biodiesel is the transesterification reaction of animal fats or vegetable oils with short-chain alcohols, and the alcohol most commonly used is methanol [7, 8]. Traditionally, biodiesel is mostly produced by homogeneous base catalysis. Same as all the homogeneous bases or acid catalysts [9], the disadvantages are that the catalyst is difficult to recycle and prone to

saponification and the purification of the product will generate a large amount of waste water [10]. Therefore, solid base catalysts have been rapidly developed due to the properties of easy separation and high catalytic efficiency. At present, the mainly reported solid base catalysts include metal oxides, hydrotalcite compounds, supported solid bases, and anion exchange resins. As a new type of functional materials, hydrotalcite and hydrotalcite-like compounds have been concerned by researchers because of their special layered structure, tunable composition, and structure [11].

Hydrotalcite-like compounds (HTLCs) are a kind of inorganic materials with layered microstructure, and their usual chemical formula is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A_{x/n}]^{n-} \cdot mH_2O$ [12], which sometimes also is named as layered double hydroxide (LDH). The positively charged laminates of HTLCs are mainly composed of divalent and trivalent metal cations, while anions and water balance the charges between them. The divalent and trivalent metal cations are present uniformly in the laminate structure [13, 14]. Researchers adjusted the structure and function of the material by changing its chemical compositions, synthesis parameters, and preparation conditions

[15, 16]. However, the apparent basicity of HTLCs materials is weak, which is not conducive to catalyze the transesterification reaction with a low reaction yield. Therefore, researchers used alkali metal salts to modify the HTLCs' solid base catalyst to achieve the goal of high-efficient catalytic reaction. In recent years, compared with the traditional hydrotalcite with two-dimensional (2D) plate-like structure, the hydrotalcite with a three-dimensional (3D) structure has more extensive application potential in the fields of catalysis, adsorption, electrochemistry, and biomedicine due to their good stability and multifunctional chemical properties, which has attracted numerous scientific researchers to conduct in-depth research [17–20].

Synthesis of HTLCs with three-dimensional layered structures generally requires the self-assembly of lamellae with uniform size and good crystallinity [21]. However, hydrotalcites synthesized by conventional methods usually exhibit stone block and platelet morphology [22]. Therefore, many researchers have used auxiliary means, such as adding a third substance (template and surfactant) or changing the solvent to control the growth of hydrotalcite lamellae, thus inducing the lamellae to self-assemble to form 3D lamellar structures. Shao et al. [23] fabricated LDHs with 3D multilayer structure using SiO_2 as a sacrificial template, which can be completely hydrolyzed by alkali dissolution induction. However, the results showed that the crystallinity and crystal form of the production were affected by post-processing (template removal process) [24–26]. In addition, similar studies reported showed the disadvantages of too many postprocessing steps and sensitive experimental conditions. Therefore, developing a one-step synthesis of HTLCs with the three-dimensional (3D) structure without postprocessing is required.

In this work, HTLCs' microsphere with 3D structure was synthesized by one-step high-temperature solvothermal method [27] and then modified by $\text{KF}\cdot 2\text{H}_2\text{O}$. The structure and morphology were characterized by several measurements methods, which confirmed its three-dimensional spherical structure. The prepared catalyst was used for the transesterification reaction to produce biodiesel, and the results showed that the catalysts presented excellent catalytic activity.

2. Experimental

2.1. Chemicals. $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ was purchased from Xilong Chemical Co., Ltd. $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{KF}\cdot 2\text{H}_2\text{O}$, $\text{CO}(\text{NH}_2)_2$, and CH_3OH were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). These reactants are analytically pure and used without further purification. Soybean oil was purchased from the local market (Nanjing, China). Deionized water was used throughout the experiment.

2.2. Preparation and Modification of $\text{KF}/\text{Mg}-\text{Ca}-\text{Al}$ HTLCs MS. $\text{Mg}-\text{Ca}-\text{Al}$ HTLCs MS was synthesized by the simple one-step hydrothermal method. Urea (36 mmol) and citric acid (2.4 mmol) were dissolved in a mixed solution of

ethanol and water (60 mL), in which the volume ratio of ethanol/water was 1 : 1. The solution was stirred and different proportions of $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ were added to form a stable solution; then, the obtained suspension was agitated for 2 hours and transferred into hydrothermal kettle lined with tetrafluoroethylene and kept at 443 K for a certain period; after hydrothermal kettle was naturally cooled, the resulting suspension was filtered, and the resulting solid product was washed with deionized water to a pH value of 7~8 for the filtrate. Finally, $\text{Mg}-\text{Ca}-\text{Al}$ HTLCs MS was obtained after dried overnight at 333 K.

The prepared HTLCs MS was calcined at a specific temperature (723~923 K) for 3 hours to convert them to $\text{Mg}-\text{Ca}-\text{Al}$ composite metal oxides. Then, we grind the obtained oxide with certain amounts of $\text{KF}\cdot 2\text{H}_2\text{O}$ by adding a small amount of water, and the obtained mixture was dried at 333 K overnight to obtain $\text{KF}/\text{Mg}-\text{Ca}-\text{Al}$ HTLCs MS.

2.3. Catalyst Characterization. The catalyst was characterized by X-ray diffraction (XRD, Bruker-AXS D8, Cu target, $2\theta = 5\sim 80^\circ$, scanning speed: $10^\circ/\text{min}$), scanning electron microscopy (SEM, Inspect F50, FEL, USA), Fourier transform infrared spectroscopy (FT-IR, Nicolet 5700), and N_2 adsorption-desorption analysis (Beshide 3H-2000PS1).

2.4. Transesterification Reactions and Product Analysis. The transesterification reaction was carried out in a batch reactor at atmospheric pressure with reflux equipment. The reaction conditions were as follows: reaction temperature was 338 K and the molar ratio of alcohol/oil was 12 : 1. Catalysts, which were prepared with different addition ratios of calcium and magnesium, calcination temperature, hydrothermal time, and KF loading ratio, were tested. After the reaction, the solid-liquid mixture was cooled and centrifuged to recover the solid catalyst. The liquid phase was separated and the upper layer was the target product biodiesel phase, while the lower layer was the byproduct glycerol phase. The yield of biodiesel was determined by external standard method using a GC9790 II gas chromatograph (Fuli Instruments, Zhejiang, China) with DB-5Ht capillary column and flame ionization detector (FID).

3. Results and Discussion

3.1. Characterization of the Catalysts

3.1.1. XRD Analysis. Figure 1 shows the X-ray diffraction patterns of a series of $\text{KF}/\text{Mg}-\text{Ca}-\text{Al}$ HTLCs MS synthesized with different hydrothermal times (a), Ca/Mg addition ratios (b), and calcination temperatures (c). It could be seen that the diffractions at 2θ of 11.58° , 23.29° , 34.80° , 38.63° , 46.77° , 60.77° , and 62.06° were correspond to the characteristic diffraction peaks of hydrotalcite-like crystalline surfaces (003), (006), (009), (015), (018), (110), and (113), respectively [28]. These characteristic peaks indicated the successful preparation of $\text{Mg}-\text{Ca}-\text{Al}$ HTLCs. However, the diffractions at about $2\theta = 45.01^\circ$,

55.88° could be attributed to potassium compounds, which implied that KF was successfully loaded.

Meanwhile, it could be seen from Figure 1(a) that, with the prolonging of hydrothermal time from 12 h to 36 h, the intensity of characteristic diffractions enhanced, which means the regularity of the hydrotalcite-like layered structure has increased. In Figure 1(b), it could be found that the intensity of characteristic diffractions with the lamellar structure were decreasing with the increasing Ca/Mg feeding ratio, which demonstrated that the introduction of Ca²⁺ might affect the formation of the lamellar structure of hydrotalcite materials, since the size of Ca²⁺ was larger than Mg²⁺ and would cause a certain degree of deformation of the laminate in the process of compounding with Mg-Al. Therefore, too much Ca²⁺ may inhibit the formation of the laminate. Simultaneously, excess Ca²⁺ was more likely to mainly form CaCO₃, whose characteristic diffractions were at ~29.88°, 31.35°, and 42.77° [29] and showed less activity during the transesterification. In similar, the higher HTLCs' calcination temperatures also led to the formation of CaCO₃ species, which was proved by Figure 1(c), as the characteristic diffractions of them increased with the calcination temperature. Apart for this, other details in XRD patterns were similar. Both the parameters affect the structure and properties of the catalyst and would finally affect their activities [30], and the detailed results are shown in the following sections.

3.1.2. SEM Analysis. The SEM images of the prepared HTLCs MS, the calcined HTLCs MS, KF/Mg-Ca-Al HTLCs MS, and the HTLCs prepared without the addition of the template agent (citric acid) are shown in Figure 2. By comparing Figures 2(a) and 2(d), it could be seen distinctly that, due to the addition of citric acid, the original hydrotalcite with randomly stacked lamellar morphology (Figure 2(d)) was transformed into microsphere structure in a regular shape (Figure 2(a)). As shown in Figures 2(b) and 2(c), after the calcination (at 773 K) and further loading modification, the structure of the spheres was still maintained. Although the lamellar structure might be destroyed when the catalyst was calcined at high temperature, it was regained during the loading process based on the "memory effect" [31]. Compared with the morphologies shown in Figures 2(a)–2(c), it could be seen that the calcination did not destroy the 3D microsphere structure, so did the KF loading process. This demonstrated that the spherical structure of the material was retained during the process of high-temperature calcination and KF loading, which implied that this material had the certain stability.

3.1.3. FT-IR Analysis. A series of catalyst samples with different KF loading amounts were analyzed by FT-IR, and the results are shown in Figure 3. It could be seen from the figure that all samples had a broad and strong absorption peak at ~3460 cm⁻¹, which was the hydrogen-oxygen bond stretching vibration peak of -OH or the bending vibration peak of interlayer water molecules [32]. The peak near 1380 cm⁻¹ was caused by the C-O asymmetric stretching vibration in CO₃⁻, indicating that the layered structure of

hydrotalcite was the carbonate ion intercalation structure [33]. The peaks in the low wavenumber range from 500 cm⁻¹ to 800 cm⁻¹ were the vibration peak of M-OH and the stretching peak of O-M-O [34].

3.1.4. BET Analysis. Specific surface area and pore diameter analysis were performed for the KF/Mg-Ca-Al HTLCs MS (Ca/Mg = 1 : 1, hydrothermal time: 24 h, Mg-Ca-Al HTLCs calcined at 773 K, and KF load ratio of 1 : 1). The adsorption-desorption isotherm of the catalyst is shown in Figure 4. It shows a type III isotherm, belonging to the isotherm of macroporous solid materials. The specific surface area based on the BET method was 3.04 m²/g and the average pore diameter was 104 nm, which belonged to the macroporous category. Combined with the SEM images, it was inferred that the catalyst had the hollow microsphere structure and accumulation pores. The large pores were favorable for oil macromolecules to enter them and participate in the reaction on the catalyst surface, so it was beneficial for reaction to get a higher yield.

3.2. Catalytic Transesterification Performance

3.2.1. Effect of Catalyst Preparation Conditions on Biodiesel Yield. As shown in Figure 5(a), the FAME yield obtained was decreased by the catalysts prepared with hydrothermal time longer than 24 h. Combined with Figure 1(a), it could be deduced that much more CaCO₃ were formed when hydrothermal time were over 24 h, and CaCO₃ was not an effective catalyst support beside HTLCs [35]. So, it could infer that 24 h was the best hydrothermal time for the catalyst preparing.

As previous work showed Ca/Mg ratios would affect the catalysts activity [29], different Ca/Mg feeding ratios on the catalytic efficiency are presented in Figure 5(b). It can be seen that the highest yield of biodiesel was obtained by Ca/Mg of 1 : 1. Combined with the XRD patterns in Figure 1(b), it could be inferred that laminate structure was benefit for the catalyst activity, and too little Ca²⁺ dosing amount may not lead the Ca²⁺ embedded in the laminate, while too much Ca²⁺ were not conducive to the formation of catalyst lamellar structures and increased the amount of CaCO₃. Therefore, 1 : 1 was a proper Ca/Mg addition ratio in the preparation process for the higher catalytic activity.

Figure 5(c) shows the FAME yield catalyzed by KF/Ca-Mg-Al HTLCs MS with different calcining temperatures. The catalytic activity was the best when the calcination temperature was 773 K. Beyond 773 K, the catalysts' activity was dropped. This might be caused by the reason that when the calcined temperature was over 773 K, the composite metal oxides produced by the decomposition of hydrotalcite started to sinter and form a spinel structure [36], which prevented the recovery of the layered structure and resulted in a decrease in catalytic activity. Figure 5(d) shows the influence of KF loading on FAME yield. It could be found that the FAME yield increased dramatically with the increase of KF loading content, which indicated that the introduction of KF had greatly enhanced the activity of the catalyst. In particular,

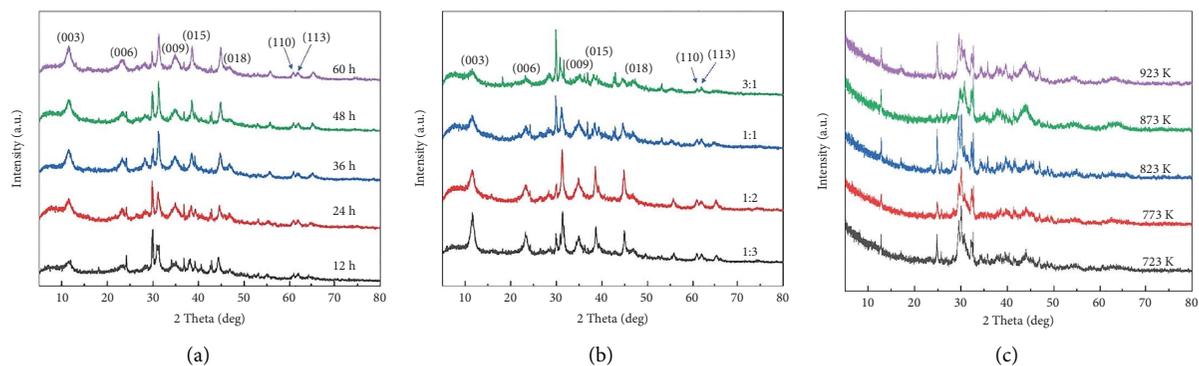


FIGURE 1: XRD patterns of KF/Mg-Ca-Al HTLCs MS catalysts with (a) different hydrothermal times, (b) Ca/Mg addition ratios, and (c) calcination temperatures (other conditions: Ca/Mg = 1 : 1, hydrothermal time: 24 h, and Mg-Ca-Al HTLCs calcined at 773 K).

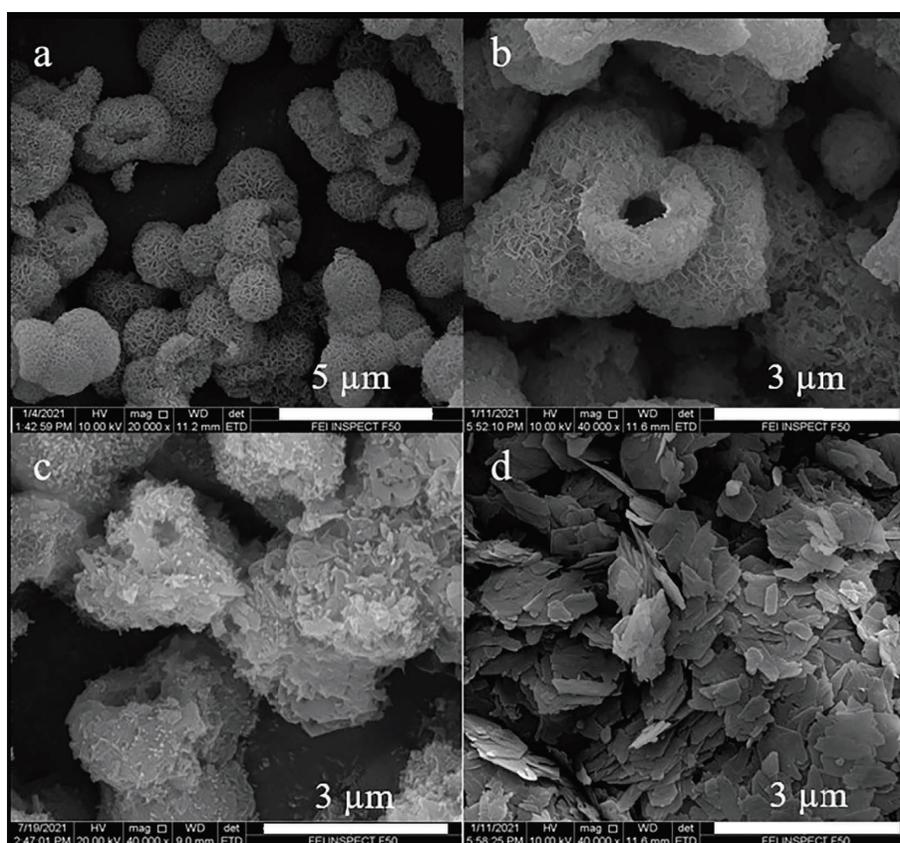


FIGURE 2: SEM images of (a) Mg-Ca-Al HTLCs MS, (b) calcined Mg-Ca-Al HTLCs MS (calcined at 773 K), (c) KF/Mg-Ca-Al HTLCs MS (HTLCs MS calcined at 773 K), and (d) Mg-Ca-Al HTLCs prepared without the addition of citric acid.

when the loading ratio of KF/HTLCs reached 1 : 1, the yield of biodiesel obtained more than 90% in a very short reaction time of 30 min, which achieved the goal of fast reaction.

3.2.2. The Influence of Reaction Conditions on the Yield of FAME. With the optima catalyst, the impact of reaction time and catalyst amount of transesterification on the yield of FAME was further optimized. According to our former studies, temperature of 338 K and methanol-to-oil molar ratio of 12 was chosen as a fixed parameter.

Figure 6(a) shows the FAME yield of different reaction time periods, and it could be found that the FAME yield did not increase much over 30 min, which indicated that the reaction was close to the equilibrium point around 30 min. Therefore, 30 min was chosen to be the optimal reaction time. Figure 6(b) shows the effect of catalyst dosage on the FAME yield. It could be seen that although the FAME yield reached 97% when the catalyst adding amount was 4%, the FAME yield was 92% when the catalyst adding amount was only 2%. Therefore, 2% was chosen as the optimal catalyst adding amount.

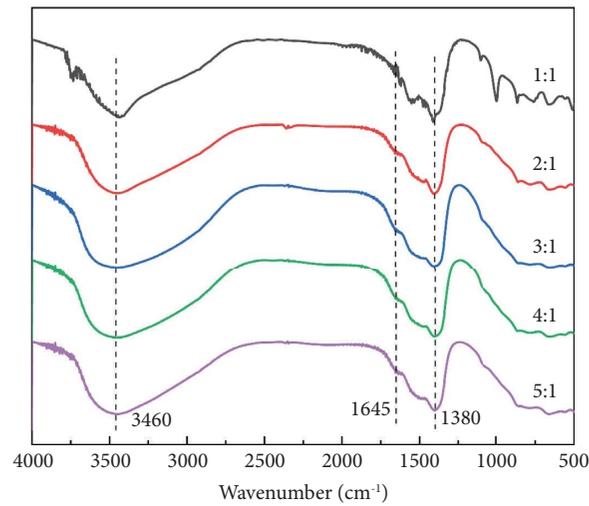


FIGURE 3: FT-IR spectra of different load ratios of KF/Mg-Ca-Al HTLCs (Ca/Mg = 1 : 1, hydrothermal time: 24 h, and Mg-Ca-Al HTLCs calcined at 773 K).

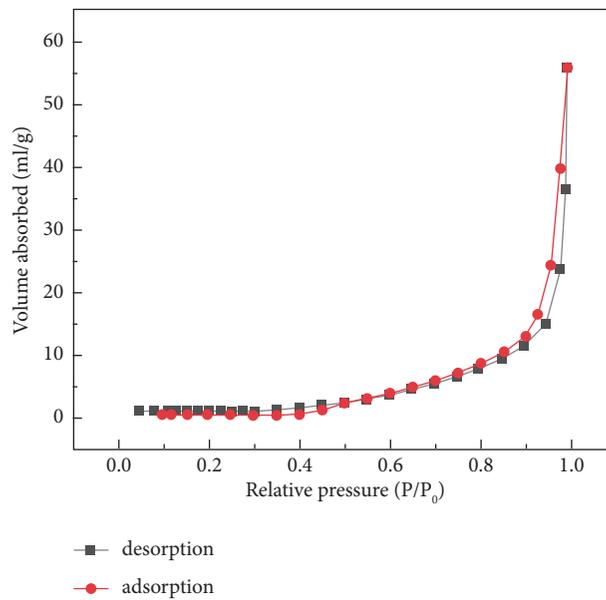


FIGURE 4: N₂adsorption-desorption isotherms of KF/Mg-Ca-Al HTLCs MS (Ca/Mg = 1 : 1, hydrothermal time: 24 h, Mg-Ca-Al HTLCs calcined at 773 K, and KF load ratio of 1 : 1).

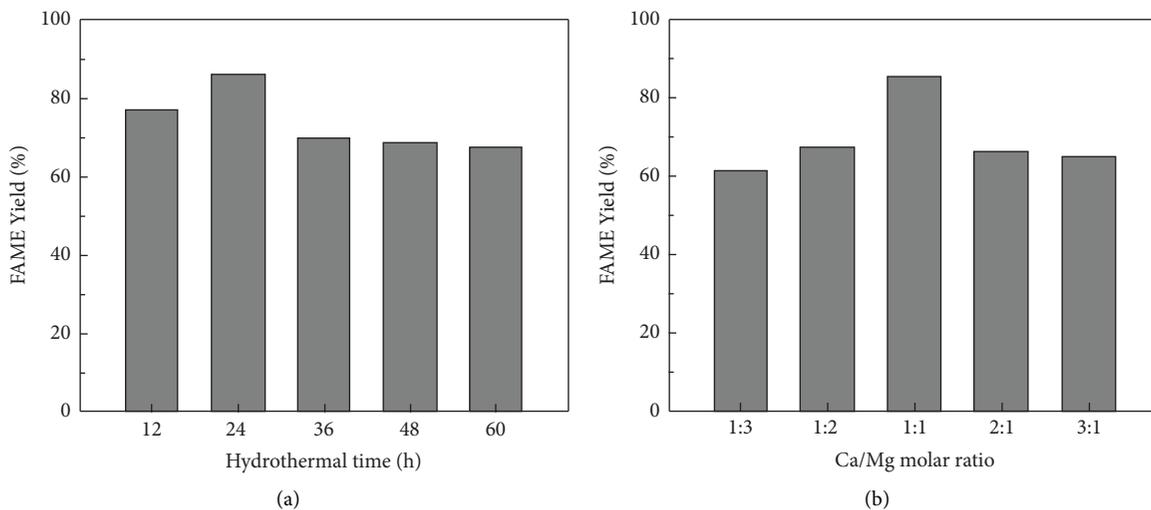


FIGURE 5: Continued.

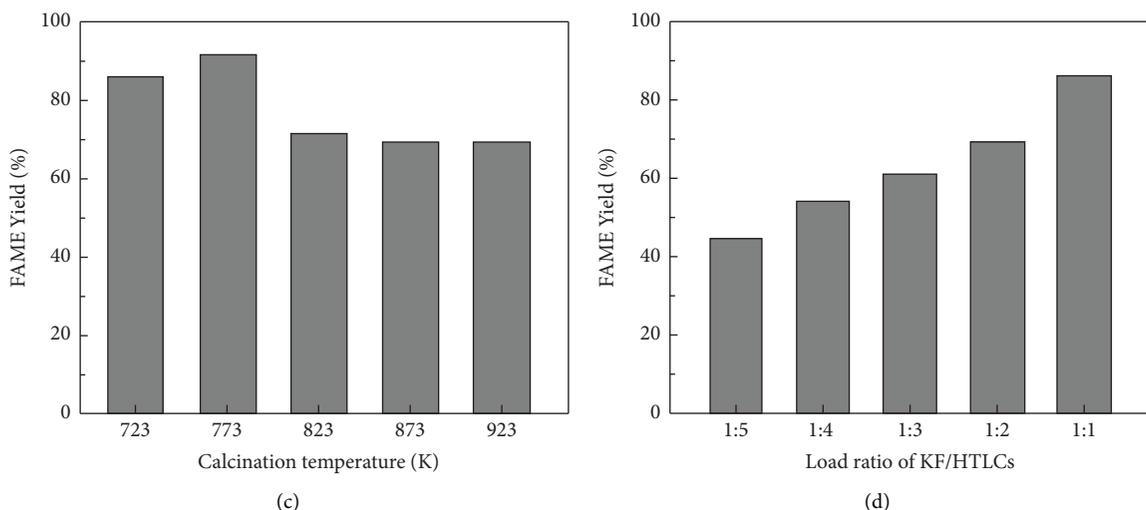


FIGURE 5: Effect of different catalyst preparation conditions on FAME yield: (a) hydrothermal time, (b) molar ratios of Ca/Mg addition, (c) calcination temperature, and (d) different load ratios of KF/HTLCs. Reaction conditions: 338 K 30 min, catalyst (2%), and alcohol/oil molar ratio 12:1.

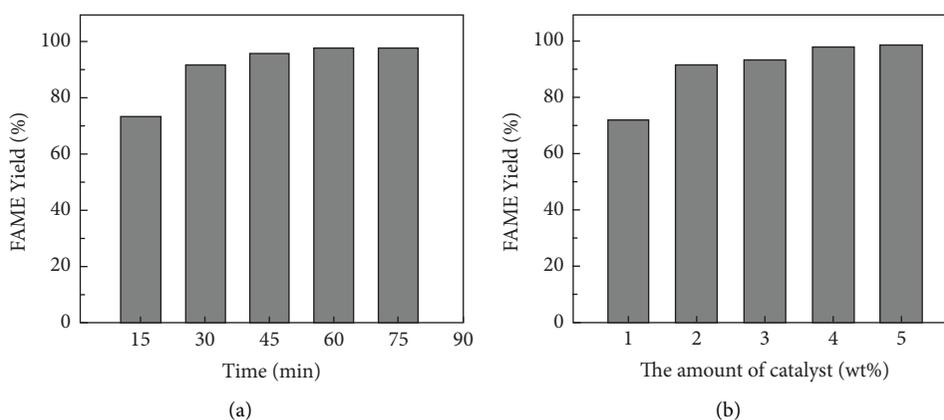
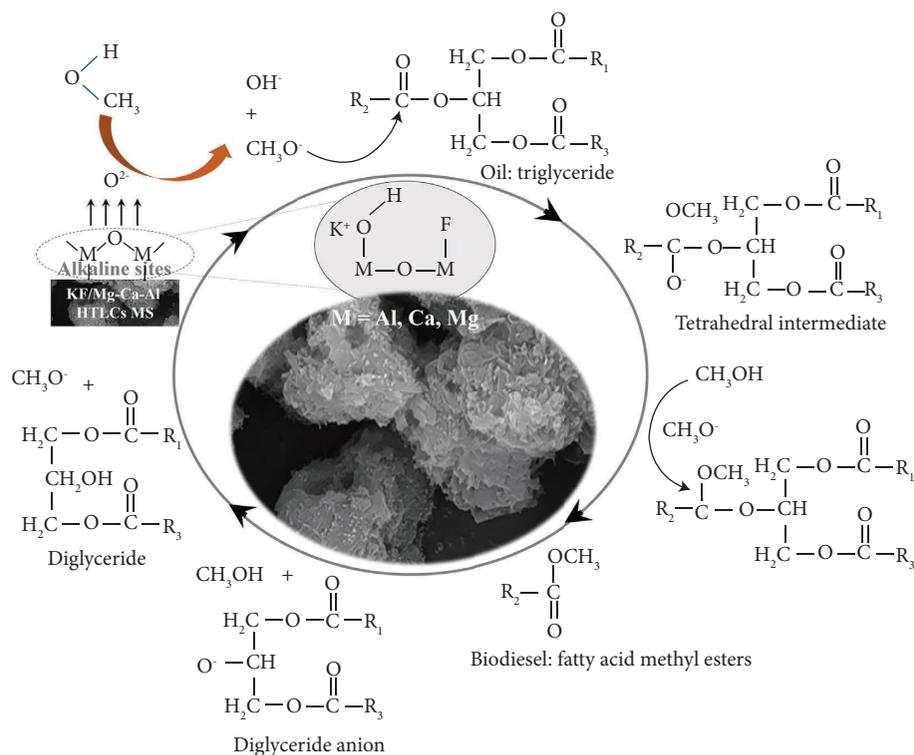


FIGURE 6: Effect of different catalyst preparation conditions on FAME yield: (a) reaction time and (b) the amount of catalyst. Reaction conditions: 338 K and alcohol-oil ratio 12:1.

A plausible reaction pathway for the reaction between methanol and oil (fatty acid triglyceride) was proposed (Scheme 1). The K^+ and F^- ions might embed into the vacancies associated with the loading of KF on the surface of Mg-Ca-Al HTLCs [37] and thus led to the formation of some new species [35], which played the role of alkaline active sites. First, the O^{2-} and the strong alkaline sites formed in the surface of the catalyst extracted H^+ from CH_3OH and formed CH_3O^- [38]. Then, the CH_3O^- attacked the carbonyl carbon atoms of triglyceride, forming a tetrahedral intermediate, which would decompose into FAME and a diglyceride anion. Finally, the diglyceride anion then reacted with methanol to form diglyceride and CH_3O^- , among which the diglyceride would convert to monoglyceride and

glycerol successively follows the same reaction path of triglyceride, while the CH_3O^- recycled to the next reaction cycle [39].

3.2.3. Reusability of KF/Mg-Ca-Al HTLCs MS. In order to investigate the reusability of the prepared catalysts, recycle experiments were performed. The used catalyst was separated from the reaction system, washed with methanol to remove impurities, and dried and calcined at $500^\circ C$ for 3 h for the next experiment. The yield of biodiesel obtained by fresh and reused catalysts is shown in Table 1. The catalyst exhibited considerable stability; the relevant FAME yield maintained 72.3% after three cycles. The decrease in



SCHEME 1: Plausible reaction pathway for the biodiesel production over KF/Mg-Ca-Al HTLCs MS catalyst.

TABLE 1: Catalyst reusability of KF/Mg-Ca-Al HTLCs MS.

Entry	Fresh	1st	2nd	3rd
Yield of biodiesel (%)	92.2	86.9	81.6	72.3

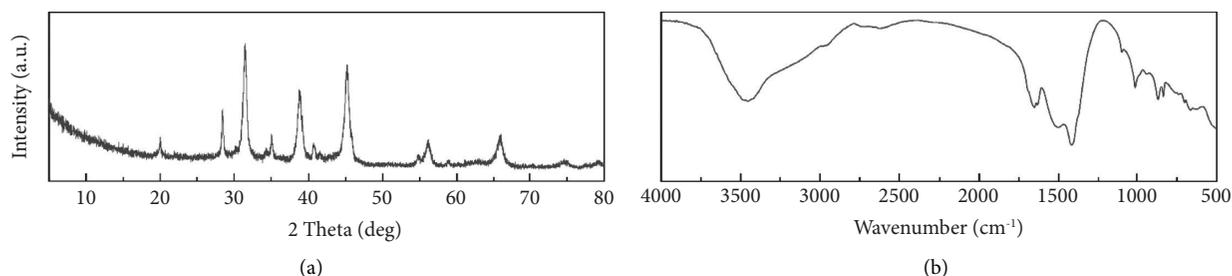


FIGURE 7: XRD pattern and FT-IR curve for the catalyst after 3 reused cycles.

catalytic efficiency might be due to the destruction of the lamellar structure of hydrotalcite after several reactions [35], which is proved by the XRD and FT-IR characterizations shown in Figure 7. In addition, the active sites might be lost during washing process or be covered by glycerol.

4. Conclusions

In conclusion, hollow Mg-Ca-Al HTLCs microsphere was synthesized in one step by a high-temperature solvothermal method and then modified with KF·2H₂O. The results showed that the optimal catalyst preparation conditions were hydrothermal time of 24 h, Ca/Mg

addition ratio of 1:1, calcination temperature of 773 K, and loading ratio of 1:1 (KF/HTLCs). Under the optimal reaction conditions, the yield of biodiesel was as high as 92% in 30 min with a considerable stability when the content of catalyst was only 2% of weight of oil.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This research work was supported by National Key R&D Program of China (no. 2019YFB1504003) and Natural Science Research Projects of Universities in Jiangsu Province (no. 20KJB530005). The authors also appreciated the support from the Talents Introduction Foundation of Nanjing Institute of Technology (YKJ201936) and Science Foundation of Nanjing Institute of Technology (no. CXY201926).

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