

Article

Preparation of ILe@Cu@MOF Catalyst and Its Application in Biodiesel Catalysis

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Abstract: Heterogeneous catalysts play a dual role in transesterification due to their advantages of being separable and reusable. In recent years, heterogeneous catalysts derived from renewable resources have received more attention. In this paper, the production of biodiesel from *Xanthoceras sorbifolia* bunge oil via transesterification was studied under the action of an ILe@Cu@MOF catalyst. Fourier-Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, scanning electron microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDS), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), Thermogravimetric (TG) and other characterization methods were used to characterize the microstructure and thermal stability of the catalyst and further study the ILe@Cu@MOF catalyst for the preparation of biodiesel from *Xanthoceras sorbifolia* bunge oil. The results show that the surface of the ILe@Cu@MOF catalyst is attached with a sheet-like structure of isoleucine (ILe), which mainly contains Cu, O, C and N elements. The specific surface area is 19.687 m²/g, and the average pore size is 31.74 nm, which belongs to mesoporous material. The pyrolysis temperature of ILe@Cu@MOF reached 360 °C, indicating that the grafting of ILe had a protective effect on Cu@MOF and increased the pyrolysis temperature of Cu@MOF. At the same time, the water contact angle increased from 86° to 121°, and the material was hydrophobic. The optimum conditions for the preparation of biodiesel were as follows: the amount of catalyst was 3 wt%, the molar ratio of methanol to oil was 35:1, the reaction temperature was 50 °C, and the reaction time was 4 h. At this time, the biodiesel yield was up to 82.85%. Moreover, after five cycles of ILe@Cu@MOF, the yield still reached 73.4%. GC–MS and MNR studies showed that the quality of biodiesel after catalysis was higher. The prepared catalyst can make biodiesel products more sustainable, environmentally friendly and economical, and can provide future prospects for the energy utilization of renewable resources.

Keywords: biodiesel; *Xanthoceras sorbifolia* bunge oil; ILe@Cu@MOF catalyst; yield; stability



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1. Introduction

As the global economy and industry continue to grow, coupled with rapid population urbanization, people rely heavily on energy from non-renewable resources such as fossil fuels [1–3]. Environmental pollution and climate change caused by the production and use of fossil fuels have prompted people to look for alternative fuels for oil [4–8]. Based on this, biodiesel is recognized as a promising liquid diesel biofuel due to its renewability and environmental friendliness. As a substitute for petroleum fuel oil, biodiesel has the advantages of non-toxicity and biodegradability. Therefore, a biodiesel made from renewable resources is needed [9–14].

At present, the production of biodiesel mainly adopts the transesterification method, which mainly includes acid catalysis and alkali catalysis. The acid catalytic reaction can ignore the influence of free fatty acids, which is more feasible and simple in the process flow. However, there are some problems such as long reaction times, difficult product separation and serious environmental pollution [15–18]. In contrast, due to the fast rate of the alkali-catalyzed reaction, it is widely used in actual industrial production. The alkali catalytic method can be divided into the homogeneous alkali catalytic method and the heterogeneous solid alkali catalytic method. Catalysts commonly used in homogeneous base catalysis include NaOH, sodium methoxide, etc., which have the advantages of fast reaction speeds and high conversion rates. However, homogeneous base catalysts are difficult to recycle, complex post-treatment, and will cause secondary pollution to the environment [19]. In order to solve these problems, solid base catalysts have emerged as the times require. Their reaction conditions are simple, their catalyst life is long, continuous and automated production can be achieved and environmental pollution can be effectively avoided. The commonly used types of alkali catalysts are alkali metals, hydrotalcites, alkaline earth metal oxides, hydrotalcite-like solid bases, supported solid bases, etc. At present, many kinds of solid bases have been applied to the preparation of biodiesel under laboratory conditions, which has become a new hot spot in the preparation of biodiesel [20–22].

To improve biodiesel yield and ensure a sustainable process, various biodiesel catalyst systems such as homogenous and heterogeneous catalysts have been practiced [23,24]. The transesterification for biodiesel reaction requires a catalyst, such as an alkaline catalyst or an acid catalyst. Reports indicate that reactions with an alkaline catalyst are faster than reactions with an acid catalyst, and that acid catalytic reactions require a high molar ratio of alcohol to oil to perform the reaction with good efficiency in a reasonable time. Alkaline metal carbonates, alkaline earth metal carbonates, alkaline earth metal oxides, transition metal oxides and a mixture of metal oxides have been used as alkaline heterogeneous catalysts in the transesterification method [6]. To date, homogenous catalysts such as KOH, NaOH and CH_3ONa are relatively moderate in activity due to soap formation during the purification process, which contributes to the inability to recover the glycerol [25]. For raw materials with a high FFA content, strong acidic catalysts are preferable because of their ability to inhibit soap formation, which results in high biodiesel yield. A heterogeneous catalyst is a more suitable option for easy separation and reusability, with better catalytic activity and stability being reported. Various heterogeneous catalyst systems have been employed, i.e., alkali-doped materials, transition metal oxides, hydrotalcite and silica-based materials. Heterogeneous catalysts offer several advantages, including their reusability, higher reaction rate and selectivity, simplification of crude biodiesel purification, eliminating the formation of soap, short process time, relatively lower operating temperature, recyclability, eco-friendliness and low cost. Metal–organic frameworks (MOFs) are emerging heterogeneous materials with a moderate surface area and more sites for the catalytic application, making them a promising alternative for stable biodiesel production.

Metal–organic frameworks (MOFs) are emerging heterogeneous materials which have been widely used in energy storage, catalytic activity, electrochemical magnetism and other scientific research fields [26]. MOFs are porous solids assembled by coordination bonds between metal ions and organic ligands [27]. MOFs have a moderate specific surface area and more catalytic application sites, making them a promising alternative for the stable production of biodiesel [28]. As a heterogeneous catalyst, copper-based MOFs can efficiently oxidize alcohols and convert them into corresponding products, which can be used as a promising catalyst for strengthening and stabilizing biodiesel production [29]. The synthesis of ILe@Cu@MOF catalysts with the general precursor as isoleucine is beneficial to the processability and optimization of the transesterification process [30].

In this study, the synthesis of a structured catalyst (ILe@Cu@MOF) for the preparation of biodiesel from *Xanthoceras sorbifolia* bunge oil was introduced. The structure and related properties of the synthetic catalyst were studied. The specific process of catalytic

biodiesel was further studied. The prepared biodiesel has good quality and provides a new way for biomass energy in the future.

2. Materials and Methods

2.1. Materials

Xanthoceras sorbifolia bunge oil came from Oriental Biofuel Group Co., Ltd. (Baotou, China) Copper sulfate pentahydrate, terephthalic acid, N, N-dimethylformamide, anhydrous sodium sulfate, methanol, L-isoleucine and anhydrous ethanol were purchased from Tianjin Xin Platte Chemical Co., Ltd., Tianjin, China. The chemical reagents were all analytically pure and used directly as acceptors without any further purification.

2.2. Synthesis of Catalysts

The synthesis of the Cu@MOF was performed by using a modified co-precipitation method. In total, 10% concentration of copper sulfate (CuSO_4) and 10% concentration of phthalic acid (H_2BDC) were dispersed in 100 mL water and 100 mL DMF, respectively. Then, the solution was mixed and stirred evenly and mixed into a round-bottom flask, then stirred in a water bath at a temperature of 85 °C for 24 h. After the stirring was completed, the filtration was carried out; the deionized water was repeatedly washed, the excess solvent was washed away, the temperature was 110 °C in the drying oven for 7 h and finally the Cu@MOF catalyst was prepared. The preparation flow chart is shown in Figure 1a.

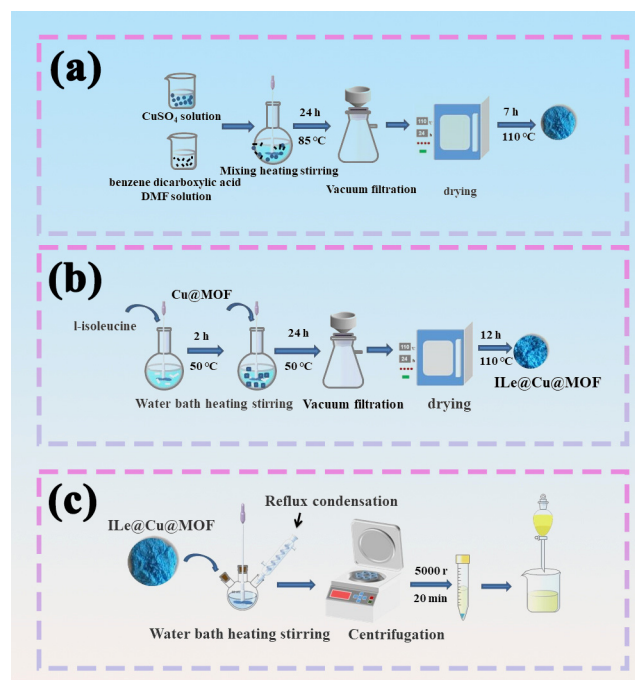


Figure 1. (a) The synthesis process of Cu@MOF catalyst, (b) the synthesis process of IL@Cu@MOF catalyst, (c) the process and determination of biodiesel preparation from Xanthoceras sorbifolia bunge oil by catalyst.

A certain mass fraction of L-isoleucine (IL: Cu@MOF = 15%, 25%, 30%, 45%, 55%) crystals were ground into fine powder and placed in a three-port flask with 100 mL ethanol. Stir at 50 °C for 2 h until dissolved. Add 2 g of Cu@MOF, heat and stir at 50 °C for 24 h, then pour it out, rinse with 100 mL of anhydrous ethanol and dry in a drying oven at 110 °C for 12 h, and finally the IL@Cu@MOF catalyst is prepared. The preparation flow chart is shown in Figure 1b.

2.3. Preparation and Determination of Biodiesel

Ten grams of *Xanthoceras sorbifolia bunge* oil and ILe@Cu@MOF catalysts with mass ratios of 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt% were added to three flasks, inserted into a condenser tube and stirred in a water bath at a certain temperature. When the oil phase temperature reached a certain value (50, 60, 70, 80, and 90 °C), a certain amount of methanol (methanol/oil molar ratio: 15:1, 20:1, 25:1, 30:1, 35:1) was added. After cooling and centrifugation, the catalyst was separated, and the liquid was poured into the separation funnel to stand for stratification. The upper liquid was heated to 80 °C, and the residual methanol was evaporated. Then, anhydrous sodium sulfate was added to remove water and weighed. The yield of biodiesel was measured via weighing method. The test process is shown in Figure 1c.

2.4. Catalyst Characterization

Hitachi S-4800 scanning electron microscope (SEM, Hitachi, Tokyo, Japan) was used to observe the surface structure and morphology of the catalyst. ICPOES 730 inductively coupled plasma spectrometer (Agilent, Palo Alto, CA, USA) was used to determine the element distribution in the catalyst. SOR-27 Fourier-transform infrared spectrometer (Bruker Optics, Billerica, MA, Germany) was used to determine the functional groups of the catalyst. The scanning range was from 4000 to 400 cm^{-1} . The phase structure of the single-crystal catalyst was analyzed using X-ray diffraction (XRD, Empyrean, Almelo, The Netherlands). A Cu-K α ray with a wavelength of $\lambda = 0.15418 \text{ nm}$ was used to analyze the samples in the range of 5–80° with a scanning speed of 10°/min. The specific surface area, pore volume and pore size distribution of the catalyst were obtained by using the specific surface area and pore size analyzer of BSD-PSI model produced by Beijing Beaud Electronic Technology Co., Ltd., Beijing, China. Using STA2500 synchronous thermal analyzer (Nechi, Selb, Germany), under the test conditions—the carrier gas was N₂, the temperature rose from room temperature to 800 °C, the heating rate was 10 °C/min and the flow rate was 50 mL/min—the mass change of the thermal decomposition catalyst was accurately measured to judge the thermal stability of the catalyst. The material was analyzed by using Renishaw's inVia confocal micro-Raman spectrometer (Hitachi, Tokyo, Japan) with laser wavelength of 523 nm, laser power of 50 mW, scanning time of 15 s and cumulative measurement of 2. The JY-PHa interfacial tension tester produced by Chengde Youte Testing Instrument Manufacturing Co., Ltd., Beijing, China, was used for testing, and the test was carried out at room temperature. The composition and content of biodiesel were determined using Agilent 8860-5977 B gas chromatography–mass spectrometry (Agilent, Palo Alto, CA, USA). The nuclear magnetic resonance (NMR) spectra of biodiesel samples were recorded at 2930 K using a BRUKER AVANCE III HD NMR spectrometer from Bruker Optics, Ettlingen, Germany. The chemical shift was based on the residual peak (ppm) of CHCl₃ in CDCl₃.

3. Results and Discussions

3.1. Characterization of Physicochemical Properties of Cu@MOF and ILe@Cu@MOF

Figure 2a,b show the FTIR spectra of Cu@MOF and ILe@Cu@MOF and the Raman spectra of ILe@Cu@MOF. The single peak at 1108 cm^{-1} and the double peaks at 738 cm^{-1} correspond to the in-plane and out-of-plane (C-H) bending modes of the benzene ring, respectively. The spectral region from 1150 to 1700 cm^{-1} represents the characteristic peak of carboxylate. The weak peak at 1286 cm^{-1} is attributed to the CO stretching vibration mode. The strong bands at 1385 and 1603 cm^{-1} are assigned to the asymmetric and symmetric stretching of carboxylate, respectively. The vibration associated with the metal bond exists below 600 cm^{-1} , and the bonding between Cu and O appears at 578 cm^{-1} . The FTIR spectra of amino-acid-modified Cu@MOF show all the characteristic peaks of Cu@MOF and an additional peak at 3247 cm^{-1} due to the stretching vibration mode in the N-H group [31]. The corresponding peaks can be found in the Raman spectra, which further confirm the results of FTIR; FTIR confirmed that Cu@MOF was successfully functionalized

by amino acids. The XRD patterns of Cu@MOF, ILe and ILe@Cu MOF are shown in Figure 2c. The characteristic peaks of isoleucine can be observed at 6.2° and 19° [32]. After functionalization, the main diffraction-peak intensity of Cu@MOF decreased, and some diffraction angles also shifted, which was caused by the pore filling effect of channels in porous materials. The existence of the XRD peak of ILe and the peak of Cu@MOF corresponding to ILe@Cu@MOF is consistent with the results of FTIR and Raman analysis.

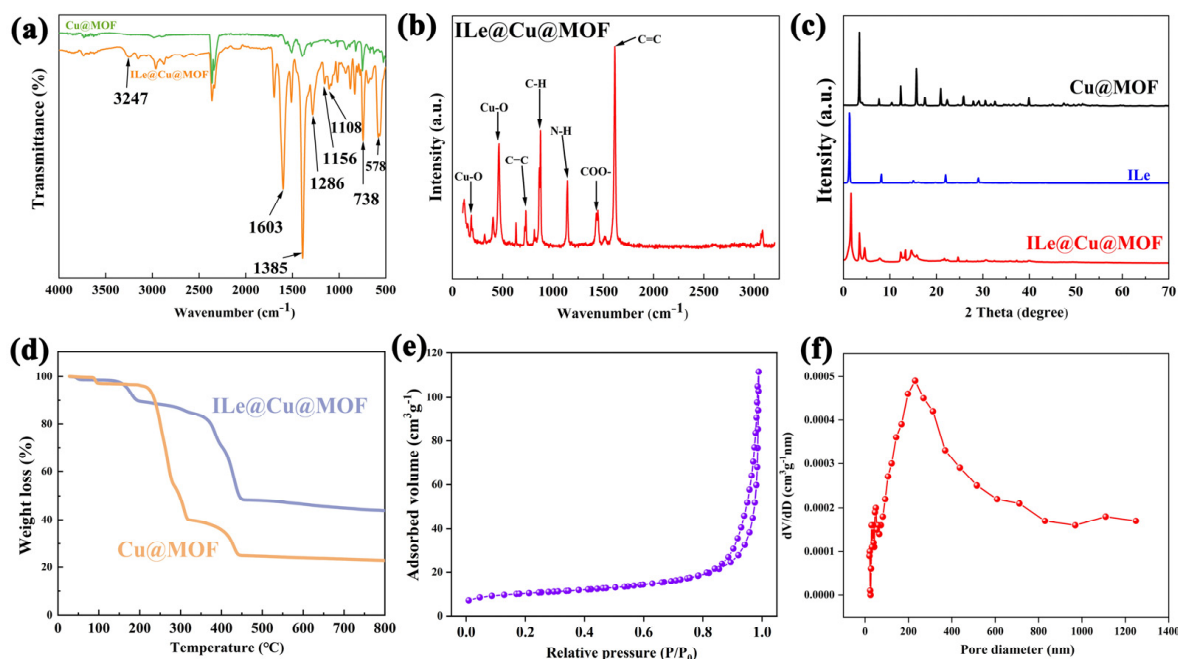


Figure 2. (a) FTIR spectrum of Cu@MOF and ILe@Cu@MOF; (b) Raman spectra of ILe@Cu@MOF; (c) XRD pattern of Cu@MOF, ILe and ILe@Cu@MOF; (d) TG of Cu@MOF and ILe@Cu@MOF; (e) N_2 —physisorption isotherms of ILe@Cu@MOF; and (f) pore size distribution of ILe@Cu@MOF.

Thermogravimetric analysis of ILe@Cu@MOF was performed. As shown in Figure 2d, two stages of weight loss can be observed from the ILe@Cu@MOF curve. The first stage of weight loss is between 135 and 200 °C, which was caused by the removal of water and DMF from Cu@MOF. The second stage of weight loss is from 360 to 450 °C, which is due to the degradation of the organic connector, resulting in weight loss. Comparing the thermal stability of ILe@Cu@MOF and Cu@MOF, the first weight loss caused by water in ILe@Cu@MOF is much lower than that of the parent. It can be concluded that amino acids replace the water molecules that are basically responsible for the catalytic degradation of Cu@MOF, resulting in the enhanced hydrophobicity of Cu@MOF [33]. Therefore, the grafting of ILe enhances the hydrothermal stability of Cu@MOF, and the use temperature of ILe@Cu@MOF should not exceed 360 °C. The specific surface area and pore size of ILe@Cu@MOF were analyzed by analyzing the N_2 adsorption–desorption isotherms. As shown in Figure 2e,f, there is no obvious inflection point in the downward concave of the isotherm. This is because the interaction between ILe@Cu@MOF is stronger than the interaction between ILe@Cu@MOF and N_2 , which leads to the difficulty of ILe@Cu@MOF adsorbing N_2 in the initial stage of adsorption. After that, the relative pressure increases and the adsorption capacity rises rapidly. Therefore, it can be judged that the curve is a type III isotherm. After amino acid modification, the specific surface area of Cu@MOF increased to $19.687 \text{ m}^2/\text{g}$, and the average pore size was 31.74 nm. Therefore, ILe@Cu@MOF is a mesoporous material.

3.2. Micromorphology of Cu@MOF and ILe@Cu@MOF

Figure 3a shows the surface morphology of Cu@MOF and ILe@Cu@MOF catalysts and the elemental composition of ILe@Cu@MOF catalysts. The left image in Figure 3a

shows the rectangular block structure of the parent Cu@MOF. The right figure shows the Ile-functionalized Cu@MOF image. It can be seen from the figure that many flaky forms of Ile are attached to the surface of Cu@MOF, which confirms that Cu@MOF is successfully functionalized with Ile. In order to further confirm the elements and contents in Ile@Cu MOFs, EDS analysis was performed on Ile@Cu@MOF. As shown in Figure 3b, there are Cu, O, C and N elements on the surface of the Ile@Cu@MOF catalyst. In addition, the uniform distribution of Cu, O, C and N elements in the material can be clearly seen in the EDS diagram. It can be seen from Table 1 that after Ile grafting, the content of the N element increased from 0.4 wt% to 3.6 wt%, which initially indicated the successful grafting of Ile, which was consistent with the results of previous analyses.

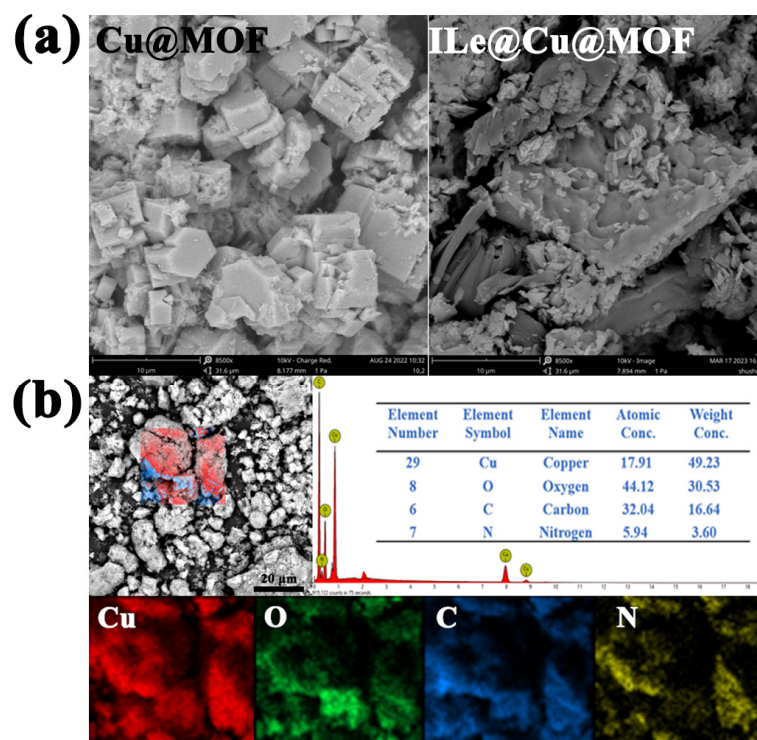


Figure 3. (a) SEM photos of Cu@MOF and Ile@Cu@MOF; (b) EDS spectrum of Ile@Cu@MOF.

Table 1. Element content of Cu@MOF and Ile@Cu@MOF.

Element Type	Ile@Cu@MOF Element Content (%)	Cu@MOF Element Content (%)
O	30.53	52.9
Cu	49.23	36.51
C	16.64	10.19
N	3.6	0.4

3.3. Analysis of Cu@MOF's and Ile@Cu@MOF's Hydrophobic Performance

Contact angle measurement is usually used to check the wettability of various materials, and is mainly used to study the effect of chemical functionalization on the wettability of materials. Figure 4a is the water contact angle image of Cu @MOF, and Figure 4b is the water contact angle image of Ile@Cu@MOF. The contact angle of Ile@Cu@MOF was 86°, showing a hydrophilic behavior, but after functionalization with amino acids, the contact angle of Ile@Cu MOF increased to 121°. Ile@Cu@MOF had a larger water contact angle than Cu@MOF, indicating that the hydrophobicity of Cu@MOF is enhanced after functionalization [34].

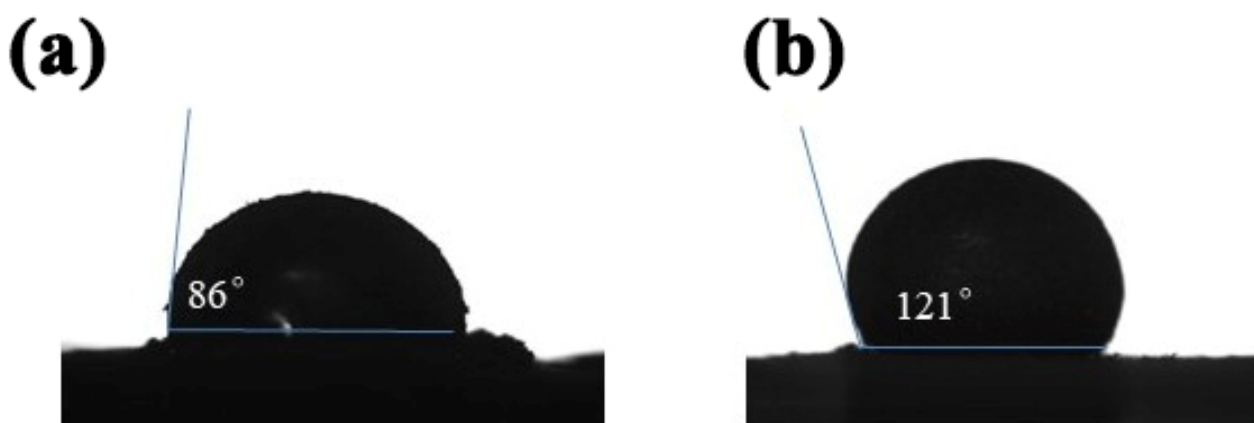


Figure 4. (a) Contact angles of Cu@MOF, (b) Contact angles of ILe@Cu@MOF.

3.4. Effect of the Production Process Parameters on the Yield of Biodiesel

Different amounts of ILe were grafted onto Cu@MOF to prepare the ILe@Cu@MOF catalyst and used to catalyze the preparation of biodiesel. As shown in Figure 5a, with the increase in ILe addition, the biodiesel yield showed a trend of increasing first and then leveling off. When the amount of ILe added to 45 wt%, the biodiesel yield reached the maximum. At this time, the solubility of ILe in the solution reached saturation, and then when we increased the amount of ILe added, the biodiesel yield did not increase. Therefore, the optimum addition amount of ILe was 45%. At this time, the biodiesel yield was 71.99%. The effect of the amount of catalyst on the yield was investigated under the experimental conditions of molar ratio of alcohol to oil of 20:1, reaction temperature of 60 °C and reaction time of 2 h. As shown in Figure 5b, with the increase in the amount of ILe@Cu@MOF catalyst, the biodiesel yield showed a trend of increasing first and then decreasing. This was due to the increase in the catalyst, with which the reactive sites also increased. After the addition of 3 wt% catalyst, the amount of catalyst continued to increase, the reaction system became thicker, the mass transfer capacity was weakened and the biodiesel yield was reduced. Therefore, the amount of ILe@Cu@MOF catalyst should be 3 wt%. Under the experimental conditions of an ILe@Cu@MOF catalyst addition of 3 wt%, reaction temperature of 60 °C and reaction time of 2 h, the effect of the molar ratio of alcohol to oil on biodiesel yield was analyzed. As shown in Figure 5c, with the increase in the molar ratio of alcohol to oil, the trend of biodiesel yield increased gradually and then tended to be gentle. This is because increasing methanol promotes the reaction in the direction of producing fatty acid methyl ester. When the molar ratio of methanol to oil was 30:1 to 35:1, the curve gradually flattened out. This is because the gradual increase in methanol dilutes the reaction solution and reduces the contact between the reactants. Therefore, the molar ratio of alcohol to oil was 35:1. The experimental conditions of an ILe@Cu@MOF addition amount of 3 wt%, molar ratio of methanol to oil of 35:1 and reaction time of 2 h were selected to explore the effect of reaction temperature on biodiesel yield. As shown in Figure 5d, with the increase in reaction temperature, the yield of biodiesel showed a trend of gradually decreasing. This is because increasing the temperature makes methanol enter a gasification state, reducing the contact of methanol with the catalyst and *Xanthoceras sorbifolia* bunge oil, so the biodiesel yield is reduced. Esterification transesterification is an endothermic process, and a too-low reaction temperature is not conducive to improving the yield of biodiesel. Considering the experiment comprehensively, the most suitable reaction temperature for this reaction is 50 °C. The effect of reaction time on the yield of biodiesel was discussed under the experimental conditions of 3 wt% ILe@Cu@MOF, 35:1 molar ratio of alcohol to oil and 50 °C reaction temperature. As shown in Figure 5e, with the increase in reaction time, the yield of biodiesel increased gradually. When the reaction time was 4 h to 5 h, the yield curve of biodiesel tended to be flat. This is because the longer the reaction time, the grafted ILe on the ILe@Cu@MOF catalyst gradually leached, exposing

the active sites of ILe@Cu@MOF, increasing the catalytic activity and increasing the yield. Therefore, the best reaction time is 4 h. Combined with the above test results, the optimum reaction conditions can be obtained: the amount of catalyst added is 3 wt%, the molar ratio of alcohol to oil is 35:1, the reaction temperature is 50 °C and the reaction time is 4 h. Under these reaction conditions, the biodiesel yield reached 82.85%.

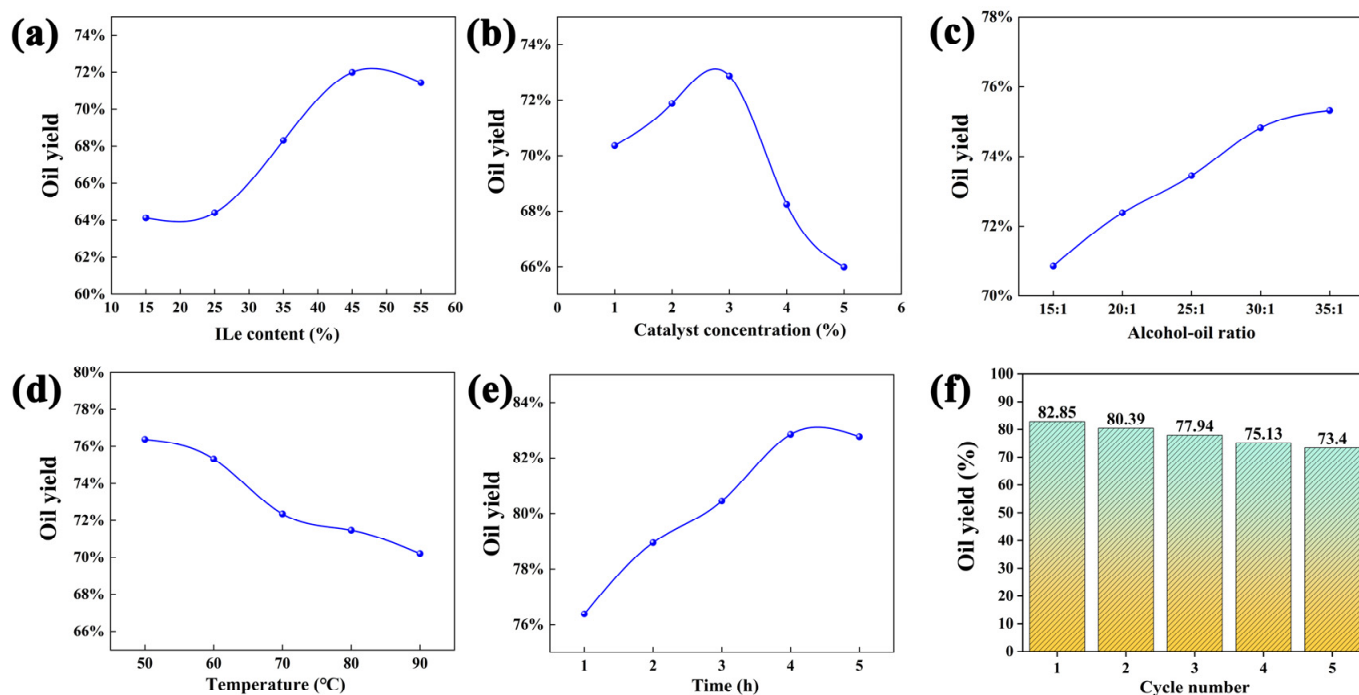


Figure 5. (a) Effect of ILe addition on the yield of biodiesel. (b) Effect of the amount of catalyst on yield of biodiesel. (c) Effect of molar ratio of methanol to oil on yield of biodiesel. (d) Effect of reaction temperature on yield of biodiesel. (e) Effect of reaction time on yield of biodiesel. (f) Biodiesel yield using the regenerated catalyst for various cycles.

ILe@Cu@MOF was used as a catalyst to react under the best experimental conditions. After the reaction, the catalyst was extracted via centrifugation and put into *Xanthoceras sorbifolia bunge* oil again for reaction, repeated five times and the biodiesel yield after each catalysis was calculated. As shown in Figure 5f, the yield of the ILe@Cu@MOF catalyst still reached 73.4% after five cycles. This proves that ILe@Cu@MOF is a catalyst with high catalytic efficiency and good reusability. The yield of ILe@Cu@MOF biodiesel can reach 73.4% after five times of use.

The specific surface area and pore size of Cu@MOF were analyzed by analyzing the N₂ adsorption–desorption isotherms. As shown in Figure 6a, there is no obvious inflection point in the downward concave of the isotherm. This is because the interaction between Cu@MOF was stronger than the interaction between ILe@Cu@MOF and N₂, which led to the difficulty of Cu@MOF adsorbing N₂ in the initial stage of adsorption. After that, the relative pressure increased and the adsorption capacity rose rapidly. Therefore, it can be judged that the curve is a type III isotherm. After amino acid modification, the specific surface area of Cu@MOF increased to 5.07 m²/g, and the average pore size was 23.64 nm. Therefore, Cu@MOF is a mesoporous material.

As shown in Figure 6b–f, a maximum yield of biodiesel of 82.85% was achieved at an ILe@Cu@MOF catalyst weight percentage of 3%, a methanol/oil molar ratio of 35:1, reaction temperature of 50 °C and reaction time of 4 h. The yield of biodiesel still reached 73.40% after the catalyst was reused in five cycles. In contrast, the yield of ILe@Cu@MOF biodiesel can reach a higher level.

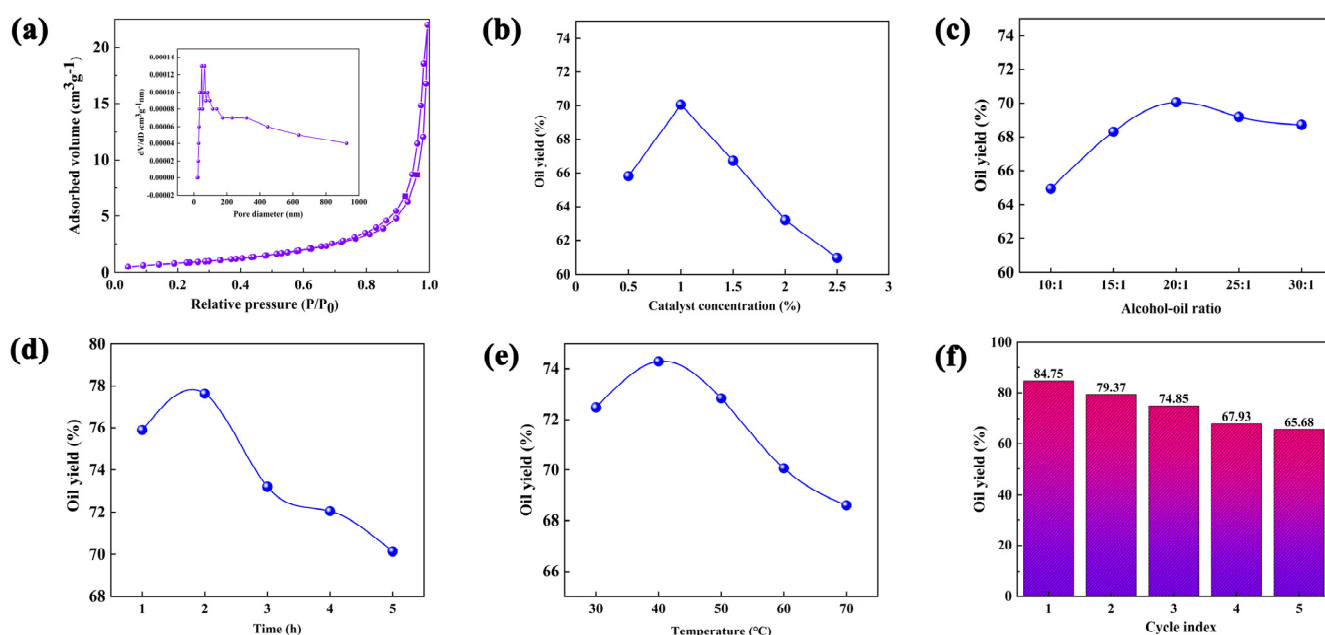


Figure 6. (a) N_2 -physorption isotherms of Cu@MOF and pore size distribution of IL@Cu@MOF. (b) Effect of the amount of Cu@MOF catalyst on yield of biodiesel. (c) Effect of molar ratio of methanol to oil on yield of biodiesel. (d) Effect of reaction time on yield of biodiesel. (e) Effect of reaction temperature on yield of biodiesel. (f) Biodiesel yield using the regenerated catalyst for various cycles.

3.5. FTIR and Raman Characterization of Biodiesel

Figure 7a is the FTIR spectrum of biodiesel. The bending-vibration absorption peak of long-chain methylene was at 723 cm^{-1} , the asymmetric stretching vibration peak of C-O-C was at 1168 cm^{-1} , the symmetric stretching vibration peak of C-O-C was at 1097 cm^{-1} and the stretching vibration absorption peak of ester carbonyl was at 1745 cm^{-1} . The above characteristic absorption peaks are all characteristic peaks of higher fatty acid methyl esters. The asymmetric bending vibration absorption peak of methoxy $-\text{OCH}_3$ was at 1463 cm^{-1} , the stretching vibration absorption peaks of the saturated C-H bond were at 2925 and 2854 cm^{-1} , and the stretching vibration absorption peak of the unsaturated C-H bond was at 3008 cm^{-1} [35]. Figure 7b is the Raman spectrum of biodiesel. It can be seen that the vibration of C-H corresponds to 1304 and 1450 cm^{-1} ; the vibration of C-H corresponds to 2855 , 2929 and 3012 cm^{-1} ; and the stretching vibration of C=C corresponds to 1666 cm^{-1} . There are obvious lipid characteristic peaks at 1450 cm^{-1} and 1666 cm^{-1} . Therefore, it can be determined that the product synthesized from *Xanthoceras sorbifolia bunge* oil is a mixture of multiple fatty acid methyl esters [36].

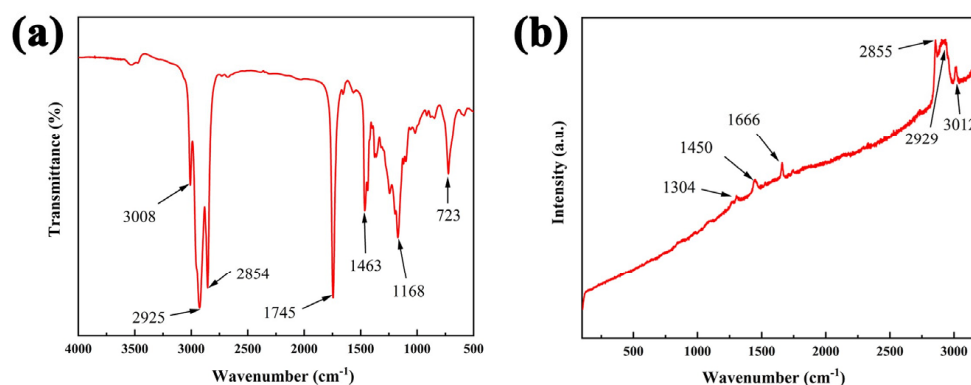


Figure 7. (a) FTIR spectrum of biodiesel, (b) Raman spectra of biodiesel.

3.6. GC–MS Analysis of Biodiesel

Gas chromatography (GC) coupled with mass spectroscopy (MS) is a viable analytical method used for the analysis of fatty acid methyl esters. In order to further determine the type and content of methyl esters in biodiesel, the products were analyzed using GC–MS. As shown in Figure 8, the products were mainly fatty acid methyl esters from C₁₉ to C₂₃, including methyl palmitate (4.65%), linoleic acid methyl ester (38.64%), methyl oleate (45.41%), methyl stearate (2.21%) and methyl erucate (4.17%). Fatty acid methyl esters accounted for 95.08% of the product, indicating that the quality of biodiesel was high [37,38].

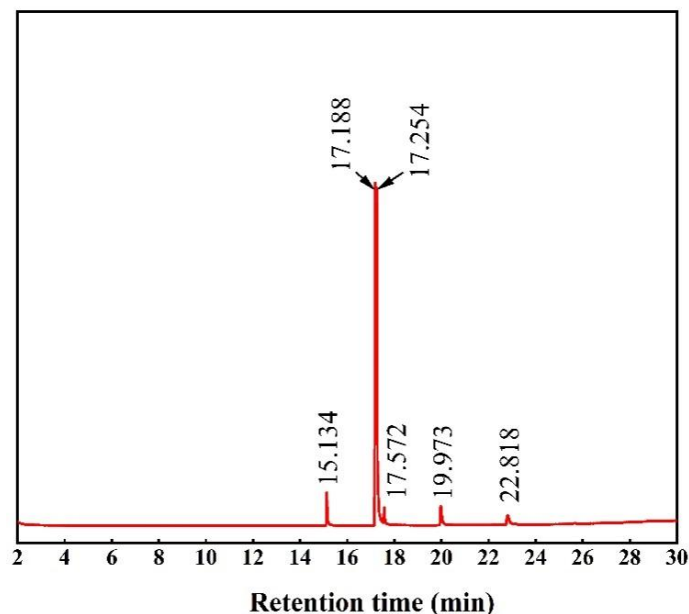


Figure 8. The GC–MS chromatogram of biodiesel was formed by optimizing the parameters in the presence of IL@Cu@MOF catalyst.

3.7. Comparison of NMR Analysis between Biodiesel and *Xanthoceras Sorbifolia*

We supplemented the NMR spectra of *Xanthoceras sorbifolia* bunge oil and biodiesel. The peak at 1.28 ppm was caused by the hydrogen in $-\text{CH}_2-$, the peak at 1.64 ppm was caused by β -methylene, the peak at 2.00 ppm was caused by the methylene on the double peak, the peak at 0.88 ppm was caused by $-\text{CH}_3$ and the peak at 5.32 ppm was caused by the hydrogen atom on the double bond. By comparing and analyzing Figure 9b,d, it can be found that in Figure 9d, two double peaks of $(-\text{CH}_2)$ at 4.32 ppm and $(-\text{CH}_2\text{CH}_3)$ at 4.15 ppm related to *Xanthoceras sorbifolia* bunge oil molecules appear, which are almost disappeared in the map of biodiesel in Figure 9b, and a single peak of the methoxy protons as a singlet ($-\text{OCH}_3$) is added at 3.61 ppm to assure the conversion of *Xanthoceras sorbifolia* bunge oil into biodiesel. The peak of *Xanthoceras sorbifolia* bunge oil at 0.90–2.80 ppm is shifted to 0.8–2.72 ppm in diesel, which proves that *Xanthoceras sorbifolia* bunge oil can be converted into biodiesel.

Comparing Figure 9a,c, it can be found that in the *Xanthoceras sorbifolia* bunge oil map, the single peak of $(-\text{CH}_3)$ at -82.15 ppm becomes a multiple peak of $(-\text{OCH}_3)$ at -85.96 ppm in the biodiesel map; the multiple peaks at -66.46 to -73.65 ppm shift to -67.73 to -77.16 ppm in biodiesel. A single peak of -46.00 ppm is added to biodiesel; the peaks of -18.84 to -19.48 ppm in *Xanthoceras sorbifolia* bunge oil move to -19.91 to -20.55 ppm, and 31.65 – 33.95 ppm moves to 31.67 ppm [39,40]. In addition, there are almost no miscellaneous peaks in the carbon spectrum of biodiesel, indicating that the purity is high and the reaction is thorough [41].

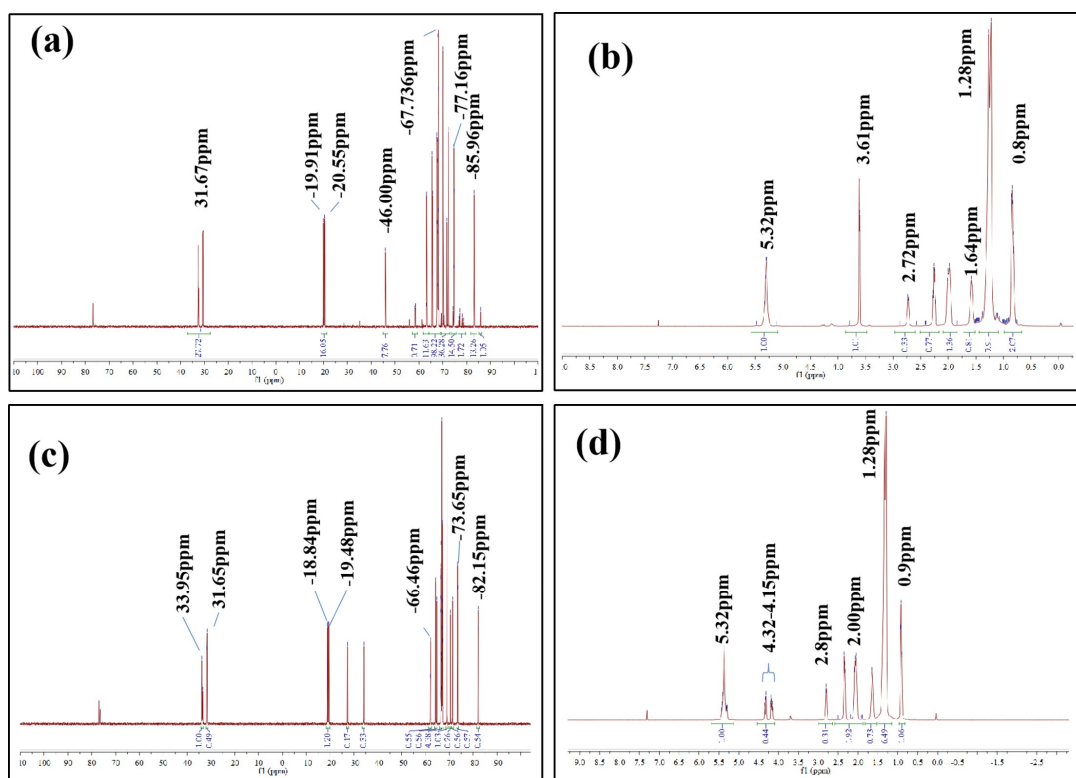


Figure 9. (a) ^{13}C NMR spectra of biodiesel, (b) ^1H NMR spectra of biodiesel, (c) ^{13}C NMR spectra of sorbifolia oil, (d) ^1H NMR spectra of sorbifolia oil.

3.8. Catalytic Mechanism Analysis

The *Xanthoceras sorbifolia bunge* oil contains about 6% water. Water will cause the deactivation of the Cu@MOF catalyst and reduce the catalytic efficiency. The new synthesized ILe@Cu@MOF in this work showed superior performance, especially regarding hydrophobicity and pyrolysis temperature, as compared with the other heterogeneous catalysts. The contact angle of water increased from 86° to 121° , indicating that the ILe@Cu@MOF catalyst was hydrophobic. The pyrolysis temperature of ILe@Cu@MOF reached 360°C , indicating that grafting ILe had a protective effect on Cu@MOF and increased the pyrolysis temperature of Cu@MOF. The maximum yields of biodiesel were 82.85% and 72.36% using ILe@Cu@MOF and Cu@MOF, respectively. Cu@MOF catalysts are porous solids with a well-structured assembly of coordinated bonds between metal ions and organic ligands. Cu@MOF catalysts have a moderate surface area and more sites for catalytic applications, making them a promising alternative for stable biodiesel production. Therefore, in this work, the Cu@MOF component in the ILe@Cu@MOF catalyst played a catalytic role in transforming *Xanthoceras sorbifolia bunge* oil into biodiesel. As shown in Figure 10, Cu@MOF efficiently oxidizes alcohols as heterogeneous catalysts, converting them into corresponding products which can be promising catalysts for enhanced and stable biodiesel production. As a Lewis acid catalyst, the reaction mechanism of ILe@Cu@MOF is as follows: ILe@Cu@MOF provides unsaturated open sites, and methanol molecules coordinate with the central Cu atoms of ILe@Cu@MOF particles. Methanol is adsorbed on the Lewis base (B) of the catalyst to form oxygen anions. The positions of methanol and triglyceride are close to each other, so their interaction is easy to occur. The nucleophilic oxygen atom from the hydroxyl group of methanol then attacks the electrophilic carbon at the triacylglycerol ester group, resulting in transesterification to produce a tetrahedral intermediate. The hydroxyl group is then broken to form two esters, producing glycerol by-products. The generated alkoxy anion obtains the H atom, and the generated Lewis base continues to catalyze the next reaction [42,43].

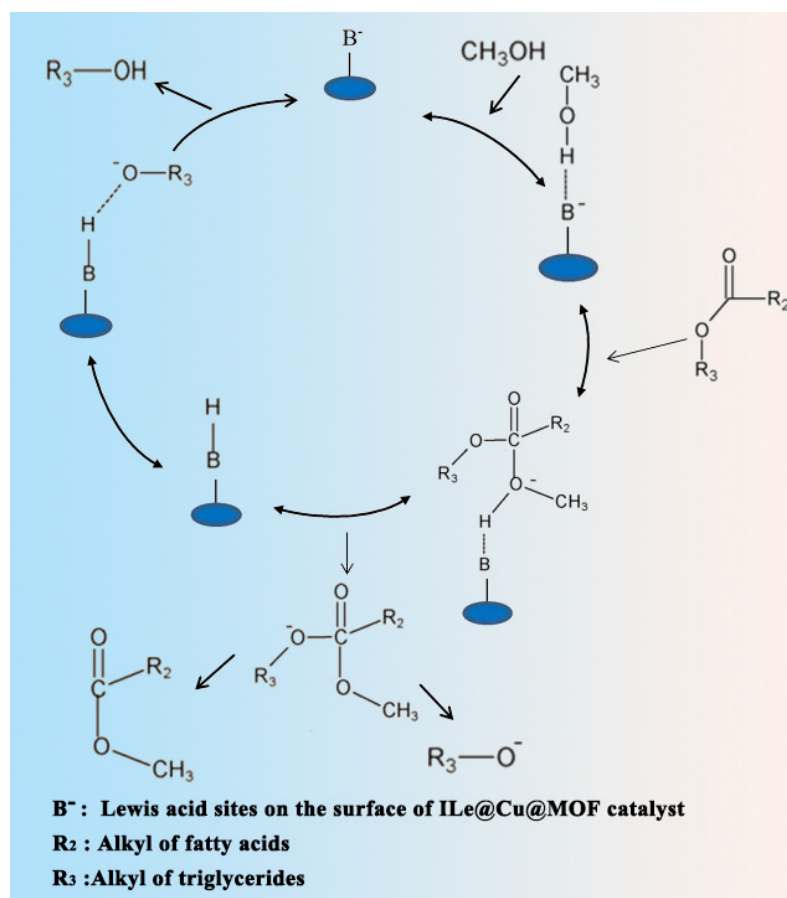


Figure 10. Schematic representation of ILe@Cu@MOF catalyst transesterification mechanism.

4. Conclusions

Although various plant resources have been used to produce biofuels, due to the huge demand for oil resources around the world, it is more necessary to use renewable plant resources to develop diesel fuel. In this work, an eco-friendly transesterification biodiesel production process using *Xanthoceras sorbifolia* bunge oil was developed. The new synthesized ILe@Cu@MOF in this work showed superior performance as compared with the other heterogeneous catalysts. SEM images exhibited that many flaky forms of ILe are attached to the surface of Cu@MOF, which is successfully functionalized with ILe. EDS depicts that the content of the N element from ILe increased from 0.4 wt% to 3.6 wt%. FTIR and Raman both confirmed that Cu@MOF was successfully functionalized by amino acids, especially with an additional peak at 3247 cm^{-1} due to the stretching vibration mode in the N-H group. TG depicted that the temperature of ILe@Cu@MOF should not exceed $360\text{ }^{\circ}\text{C}$, otherwise it will lead to the collapse of the Cu@MOF structure. XRD results indicated the formation ILe@Cu@MOF, while the main diffraction peak intensity of Cu@MOF decreased, and some diffraction angles also shifted, respectively. The specific surface area and pore size of ILe@Cu@MOF were $19.687\text{ m}^2/\text{g}$ and 31.74 nm , respectively. The water contact angle of Cu@MOF after grafting the ILe increased from 86° to 121° ; the hydrophobicity was visibly improved. According to the results obtained from the experimental design, the maximum yield of biodiesel of 82.85% was achieved at the catalyst weight percentage of 3%, methanol/oil molar ratio of 35:1, reaction temperature of $50\text{ }^{\circ}\text{C}$ and reaction time of 4 h. The yield of biodiesel still reached 73.40% after the catalyst was reused in five cycles. ^{13}C NMR and ^1H NMR spectroscopy affirmed the transformation of the *Xanthoceras sorbifolia* bunge oil to biodiesel with excellent quality and purity. GC-MS confirmed the biodiesel was composed of five fatty acid methyl esters.

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