Preparation of Copper (II) Containing Phosphomolybdic Acid Salt as Catalyst for the Synthesis of Biodiesel by Esterification

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Abstract: Copper (II) containing phosphomolybdic acid (PMA) catalysts were synthesized by ion exchange method and characterization using various physico-chemical techniques such as X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), thermogravimetric (TG) and scanning electron microscopy (SEM). The characterization results showed that the Keggin ions were retained in the catalysts and possessed well thermal stability. The catalytic esterification of lauric acid with methanol could be easily achieved about 78.7% conversion under optimum condition, the catalyst also contributed to the stability of the catalyst in which it can be reused for a certain time. This study demonstrated an alternative approach to biodiesel production with high efficiency by Cu (II) ion exchanged phosphomolybdic acid catalyst in the esterification catalytic.

Key words: phosphomolybdic acid, doped, lauric acid, esterification

1 Introduction

One of the main issues confronting human with creation to date and having taken much of man’s attention is energy security. From time immemorial, searching for effective energy sources is an urgent need. Some years ago, the discovery of fossil materials such as petroleum and coal seems to have solved the crisis, and brought the industrial revolution, which lead to an improvement of living standards. The demand for energy also increased following the growth of world population. Meanwhile, the environment turns to be a major concern with the concepts of sustainable development. Biodiesel is considered to be an alternative liquid fuel owing to the various advantages such as renewable, non-flammable, non-toxic, biodegradability and less emission of harmful gases such as sulphur dioxide, carbon monoxide, etc.

The common method for biodiesel production in industry is esterification or transesterification of vegetable oils and animal fats with short-chain alcohols, such as methanol or ethanol, in the presence of homogeneous basic catalysts. However, these catalysts can mainly be used for reacting with low free fatty acid (FFAs) pure refined oil owing to its basic nature. In addition, more than 95% of feedstock used for biodiesel production is from edible agricultural crops, which lead to the improvement of production cost. With that, a number of low-cost, non-agricultural, inedible and sustainable feedstocks such as Jatropha crude oil and Koelreuteria integrifoliola oil were proposed in order to solve this problem. Unfortunately, the reaction of cheap non-edible oils with high FFAs that exceeds the acceptable value for direct transesterification into biodiesel with FFA to form soap that eventually leads to difficulty in product separation. Therefore, a process acid-catalyzed esterification of FFAs into biodiesel is an economically attractive route.

In the esterification of fatty acids, it was generally carried out using homogeneous acid such as HCl, H₃PO₄ and H₂SO₄ acted as catalysts, and those acids are difficult to be separated and recuperated. Currently, the design and use of various solid acid catalysts for esterification have been widely developed to overcome these drawbacks. However, most of them have low thermal stability, the
preparation steps are rigorous and complicated, and more intensive reaction conditions were required\textsuperscript{10}, thus all of these factors resulted in a more complicated and higher cost of biodiesel production.

Heteropoly acids (HPAs) are typical strong Børnssted acids and catalyze a wide variety of reactions in both homogeneous and heterogeneous phases under more efficient and cleaner processes\textsuperscript{11}. However, they are difficult to recovered in polar solvents because of high miscibility, and this limit its application\textsuperscript{12}. To address these issues, partial substitution of hydrogen ion in HPAs with large monovalent ions have considered as an appropriate technique to create major effects on solubility of HPAs. Abdullah et al. reported a series of different Cs heteropolyacid catalysts, and the \( \text{Cs}_1.5\text{H}_{1.5}\text{PW}_{12}\text{O}_{40} \) catalyst showed the highest FAME (fatty acid methyl ester) yield of 81.3\%\textsuperscript{13}. Using Cs substituted silicotungstic acid as catalyst, Lingaiah et al. found that this catalyst was the robust, highest acidity, easily recyclable and showed better catalytic properties for the synthesis of 5-ethoxymethylfurural (EMF)\textsuperscript{14}. Lately, copper (II) has received much attention and was used in a variety of catalyst formulations. In previous studies, we reported a copper (II)-alginate acid for the synthesis of methyl oleate and the conversion with 71.8\% were obtained\textsuperscript{15}. As far as we know, there is no report about copper (II) containing phosphomolybdic acid (PMA) were studied for the esterification reaction.

In the present studies, a thermal stability copper (II) containing PMA catalyst was prepared and used as catalyst in the esterification of lauric acid and methanol for biodiesel production, and the catalyst was characterized by X-ray diffraction (XRD), fourier transform infrared (FT-IR) spectroscopy, thermogravimetric (TG) and scanning electron microscopy (SEM). The influence of various reaction parameters (reaction temperature and time, lauric acid-to-methanol molar ratio and catalyst dosage) on catalytic performance was studied. Moreover, the durability of the resulted copper (II) containing PMA catalyst was also studied in the study.

2 Experimental

2.1 Materials

Phosphomolybdic acid (AR), copper (II) chloride dihydrate (\( \text{CuCl}_2\cdot2\text{H}_2\text{O} \), AR), lauric acid (AR, 98\%) and methanol (AR, >99\%) were purchased from Sinopharm Chemical Regent Co., Ltd. All other chemicals were of analytical grade and used as received, unless otherwise noted.

2.2 Synthesis of copper (II) containing PMA solid acid catalyst (Cu-PMo)

Copper (II) containing phosphomolybdic acid catalyst was prepared according to the previous literatures\textsuperscript{51, 16} with slight modifications. In a typical procedure, phosphomolybdic acid (PMA, 0.17 g) was dissolved in deionized water with vigorous stirring at room temperature, copper (II) chloride aqueous solution (0.2 mol/L) was added dropwise into the PMA aqueous solution, and kept stirring for over 1 h at room temperature, the obtained mixture was heated at 70°C for 3 h, finally dried under vacuum at 110°C for 12 h to obtain the final copper (II) containing PMA (\( \text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40} \)) catalyst denoted as Cu-PMo.

2.3 Catalyst characterization

The XRD patterns of the catalysts were obtained using a Rigaku D/max 2000 ultima plus diffractometer (monochromatic nickel filter, Cu Ka radiation). The FT-IR spectra were scanned on a PerkinElmer spectrum100 using the KBr disc technique (4000-400 cm\textsuperscript{-1}). Thermo gravimetric analysis (TGA) was performed on NETZSCH/STA 409 PC Luxx simultaneous thermal analyzer with a heating rate of 5°C/min under an air flow rate of 20 mL/min. Scanning electron microscopy (SEM) images were obtained on JEOL-6701F scanning electron microscope at 10.0 kV.

2.4 Catalytic activity of esterification

Catalytic activity of Cu-PMo solid acid catalyst was determined by esterification of lauric acid with methanol. The esterification was conducted by adding certain dosage Cu-PMo (based on weight of lauric acid) catalyst into methanol (lauric acid-to-methanol molar ratio of 1:6) at reaction time (20, 40, 60, 80 and 100 min) and at temperature of 20, 30, 40, 50, 60 and 70°C with a mechanical stirrer. After the reaction, the mixture was cooled down to room temperature, and the catalyst was isolated from the liquid by filtration, the excess methanol with water was removed under reduced pressure to purify the product. The conversion of lauric acid was determined via a titration method and could be calculated depending on the equation (1). All data presented are averages of at least duplicate experiments.

\[
\text{Conversion (\%) } = \frac{AV_1 - AV_2}{AV_1} \times 100\% \quad (1)
\]

Notes: \( AV_1 \) –represents initial acid value of lauric acid; \( AV_2 \) –represents final acid value after esterification.

3 Results and discussion

3.1 Characterization of catalyst

3.1.1 XRD analysis of catalyst

The XRD analysis of samples was carried out to ascertain the crystal structure of the pristine PMA and Cu-PMo catalyst are shown in Fig. 1. The pristine PMA exhibited a series of sharp characteristic diffraction peaks at 7.6°, 8.8°, 25.9°, 26.7°, 28.0°, 32.2° and 35.0°, respectively, and were assigned to the characteristic diffraction peaks of Keggin
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The resultant copper(II) doped PMA catalyst also showed the characteristic diffraction peaks of Keggin ion at 7.8°, 8.8°, 26.3°, 27.8°, 28.8° and 33.8°. Even though characteristic peaks of Cu-PMo is very similar to Keggin ion of PMA, the slight shift were happened, especially at 25.9° and 32.2°, there also exhibited some strong peaks corresponding to Cu(II) ion appeared at 18.4°, 18.5°, 19.3°, 20.6° and 22.3°, indicating that the metal salt was formed for the exchange of protons with copper(II) ions. Accordingly, the XRD results corroborate the presence of Keggin ions of copper(II) containing PMA.

3.1.2 FT-IR analysis of the catalyst

The experimental procedure for the FT-IR measurements was described in previous studied using infrared spectroscopy. The majority of the characteristic infrared active bands of the Keggin anion can be found in the fingerprint region of the spectrum which lies between 2000 cm⁻¹ and 500 cm⁻¹. So, FT-IR spectra of pristine PMA and the Cu-PMo catalyst were exhibited in Fig. 2. Four featured peaks of PMA Keggin ion at 1064, 968, 874 and 787 cm⁻¹ could be observed, which might be attributed to P–O, Mo=O, Mo–O–Mo and Mo–Oe–Mo, respectively. Moreover, from the FT-IR spectrum of Cu-PMo, Keggin structure of Cu-PMo catalysts was found to remain unchanged, despite slight intensify in some peak strengths, which may be ascribed to the copper(II) ion was successfully exchanged with hydrogen from the PMA, this is similar to the result obtained by XRD.

3.1.3 TG analysis of the catalyst

The thermal stability of Cu-PMo was investigated by TG (Fig. 3). The TG analysis of the Cu-PMo catalyst shows that there are two weight loss steps: the first weight loss of the catalyst is about 3.4% from 50°C to 200°C, which is due to the loss of adsorbed water; The further weight loss (4.8%) from 200°C to 600°C is due to the thermal decomposition of constitutional water(H₂O⁻) from Cu-PMo. However, no other obvious weight loss is observed at the temperature >600°C. Based on the above discussion, this shows that the Cu-PMo catalyst has a very high thermal stability.

3.1.4 SEM analysis of the catalyst

SEM analysis was performed to evaluate the surface morphology of the synthesized metal salt catalysts, as shown in Fig. 4. With accuracy in figures, the pristine PMA (Fig. 4a) showed some aggregates and agglomerates with undefined shapes and mixture of larger. However, when copper(II) doped PMA (Fig. 4b), it showed the aggregation of small massive in irregular shapes and this catalyst surfaces were densely packed. From the results, it can be concluded the change morphology of the catalyst surface was highly correlated with the exchange of protons with copper(II) ions.
3.2 Catalytic activity of Cu-PMo for esterification of lauric acid

Obviously, the most important advantage of single factor is adaptable. In order to get the optimal reaction conditions, single factor design was thus applied to evaluate the effect of catalyst dosage, lauric acid-to-methanol molar ratio, reaction temperature and time in the esterification of lauric acid. The results were illustrated in Fig. 5.

3.2.1 Effect of lauric acid-to-methanol molar ratio

As we know, the esterification reaction between lauric acid and methanol generally requires a large excess of methanol to shift the equilibrium favorably, so the effect of lauric acid to methanol ratio on the conversion was investigated at different molar ratios of 1:2, 1:4, 1:6, 1:10, 1:14 and 1:18. Each reaction was carried out with 3 wt. % of the Cu-PMo catalyst at 70°C for 60 min. The experimental results are given in Fig. 5a. It was noticed that the conversion increased on varying the lauric acid to methanol ratio from 1:2 to 1:6, the methyl laurate conversion of biodiesel at the molar ratios of 1:2, 1:4 and 1:6 were 54.1%, 60.0% and 78.7%, respectively. However, the conversion was almost unchanged with the increase of methanol. Considering cost savings, the optimum molar ratio of lauric acid to methanol for the esterification reaction was considered to be 1:6.

3.2.2 Effect of catalyst dosage

In order to investigate the efficiency of the Cu-PMo cata-

![Fig. 4](image1)
![Fig. 5](image2)
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3.2.3 Effect of reaction time

The reaction time was varied as 20, 40, 60, 80 and 100 min at 70°C and a lauric acid to methanol molar ratio of 1:6 to determine the optimum reaction time for esterification. The effect of the reaction time on conversion is shown in Fig. 5c. It was demonstrated that the conversion of biodiesel was gradually increased with varying of the reaction time from 20 to 60 min, the conversion raised from 52.2% to 78.7%. Further increase in the reaction time show a slight decrease in the biodiesel conversion. This phenomenon may be due to the reaction reached near-equilibrium. The results of the study conclude that, the optimum reaction time was 60 min.

3.2.4 Effect of reaction temperature

In order to estimate the effect of temperature on methyl laurate conversion, the reaction was conducted at 20, 30, 40, 50, 60 and 70°C in the presence of 3 wt. % Cu-PMo catalyst with lauric acid to methanol molar ratio of 1:6 for 60 min (see Fig. 5d). It was observed that the conversion of lauric acid into methyl laurate increased with varying temperature from 20 to 70°C. At 20°C, only 28.7% of the conversion was obtained. Similarly, the conversion of methyl laurate at 30, 40, 50 and 60°C were about 54.8%, 55.6%, 56.0% and 65.1%, respectively. At the reaction temperature of 70°C, the conversion was 78.7%. Generally, high temperature exacerbated the methanol vaporization, which was unfavorable to esterification. Based on the above results, the reaction time of 70°C was chosen for subsequent optimization.

3.3 Catalyst reusability

To assess the recyclability feature of Cu-PMo in esterification of lauric acid, the solid catalyst was separated by centrifugation after each recycling test and was used directly for the next cycle. Each reaction was carried out with 3 wt. % of the Cu-PMo catalyst, 1:6 of lauric acid to methanol molar ratio at 70°C for 60 min. Under optimal conditions, the lauric acid conversion was 78.7%, 62.8%, 48.8%, 41.5% and 32.3% after the first to fifth reaction cycles, it could be speculated that the Cu-PMo catalyst is not stable enough in the lauric acid esterification. Furthermore, FT-IR was carried out to fully understand the reasons of catalyst deactivation (see Fig. 2). Both fresh and reused catalyst was determined with FT-IR spectra, and the result suggested that there was noticeable change in the Keggin structure of the catalyst during the esterification. From these results, we can concluded that it could be speculated that the active sites of the catalyst partially covered by organic matter so that the Keggin structure was destroyed.

4 Conclusion

In summary, a thermal stability Cu-PMo catalyst was prepared using copper (II) ion containing phosphomolybdic acid and its catalytic activities for esterification of lauric acid with methanol was investigated. The result showed that Cu-PMo exhibited good catalytic performance with 78.7% conversion of lauric acid under the optimum esterification reaction conditions (lauric acid-to-methanol molar ratio of 1:6, 3 wt. % catalyst dosage at 70°C for 60 min). Moreover, this catalyst could be reused and stabilized for a certain time. The good chemical activity and thermal stability of this Cu-PMo solid acid catalyst may enable them for another application in catalytic field.

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