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Biodiesel Production from Low-Quality Oils Using Heterogeneous Cesium Salts of Vanadium-Substituted Polyoxometalate Acid Catalyst

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Abstract: This research aims at developing an efficient and reusable catalyst to improve biodiesel production processes. To achieve this, a vanadium-substituted polyoxometalate (POM) acid, namely $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$, was firstly prepared, and then the heterogenization of the homogeneous Keggin-type heteropoly acids was performed by the partial proton substitution by monovalent large cesium cations with the formation of solid $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalysts. Several techniques, such as X-ray diffractometer, Fourier transform infrared, coupled plasma–atomic emission spectrometry, Diffuse reflectance ultraviolet–visible spectrum, thermal gravimetric analysis and N_2 adsorption–desorption techniques, were employed to characterize the as-prepared solid catalyst. The solid acid catalyst had the capacity to catalyze both the transesterification of soybean oil and esterification of free fatty acids (FFAs) simultaneously, providing an efficient production process for the production of biodiesel from low-quality oils. Under the operational conditions of a methanol/oil molar ratio of 30:1, a catalyst dosage of 5 wt.%, a reaction temperature of 140 °C, and a reaction duration of 8 h, an oil conversion of 92.2% was attained with the total FFA transformation to biodiesel. Furthermore, the catalyst could be reutilized for several cycles with no significant drop in its activity, thus having great potential for application with a bright perspective in the production of biodiesel, especially from low-quality oil feedstocks.

Keywords: biodiesel; heterogeneous catalyst; heteropoly acid; low-quality oil; acid catalyst

1. Introduction

In recent decades, the exploration of alternative sustainable fuels has become a significant research hotspot due to the depletion of fossil fuel reserves and aggravated environmental pollution [1]. Biodiesel, generally derived by the catalytic transesterification of plant oils or non-edible oils with methanol, appeared as a state-of-the-art sustainable biofuel to replace traditional petroleum-based fuels thanks to its renewability, local availability as well as its significant reduction in greenhouse gas emissions when it is combusted [2]. Traditionally, homogeneous alkali catalysts, such as KOH, NaOH and NaOCH_3 , are used in the transesterification reaction under mild reaction conditions. However, for the alkali-catalyzed transesterification reaction, the sensitivity of alkaline catalysts to moisture and free fatty acids (FFAs) in the oil feedstocks remains problematic, and therefore the oil feedstocks with the FFA content less than 0.5% and anhydrous methanol are generally necessitated [3,4].

On the other hand, the economics of biodiesel is chiefly affected by the feedstock cost. In general, the oil feedstocks for biodiesel make up approximately 75% of the total estimated cost of biodiesel production [5]. Currently, the common feedstocks, refined vegetable oils, are not entirely competitive, because of their limited supply and higher cost, thereby causing a major hurdle to the biodiesel

commercialization [6]. Low-quality oils such as waste cooking oils and non-edible oils have been identified as an economical oil feedstock to reduce the production cost and also to improve the practical feasibility of biodiesel production [5–7]. However, the main disadvantage of these low-cost oils usually is their high content of FFAs and water. As previously mentioned, the water and FFAs present in the oil feedstocks, as an alkali catalyst poison, could result in the severe deactivation of alkali catalysts and serious separation problems simultaneously. Therefore, in such cases, prior to the transesterification reaction, an acid-catalyzed pre-esterification step to eliminate the FFAs is commonly needed by initially converting the FFAs into biodiesel [8]. Unfortunately, for this method, the costly separation and neutralization procedures are required after the esterification reaction, thus leading to the raised production cost and environmental issues [9]. Alternatively, in view of the technological and economic feasibility, the acid-catalyzed biodiesel production is a promising methodology for the low-quality oils, since the transesterification of oils and esterification of FFAs are achieved simultaneously by one-pot process with an acid catalyst, being conducive to reduce the overall production cost of biodiesel [8–10].

Homogeneous Brönsted acid catalysts, such as sulfuric or hydrochloric acids, can be used for the acid-catalyzed transesterification processes [5]. However, the use of these homogeneous catalysts involves serious problems, such as the difficult catalyst separation and the corrosion of reactors, and additional neutralization and separation steps are mandatory after the reaction [8]. Heterogeneous acid catalysts, instead of the homogeneous ones to improve the biodiesel production efficiency, have significant merits in the catalytic transesterification, such as easy separation for recycles and simple purification steps without neutralization. Therefore, numerous solid acid catalysts, including $\text{SO}_4^{2-}/\text{ZrO}_2$, modified Amberlyst 15, sulphated zirconia, sulfated niobium ($\text{Nb}_2\text{O}_5/\text{SO}_4$), novel ionic liquid-supported composite, and sulfonated carbon-based solid acid catalysts have been proposed for the heterogeneous biodiesel production [8–17]. However, the transesterification conditions over these solid acid catalysts sometimes appear to be harsh (e.g., 200–220 °C reaction temperature) and energy and time consuming [15–17]. More significantly, the leaching issue of active components and the resultant poor recyclability are always encountered in the general heterogeneous biodiesel production [11,18]. In view of such problems, the more efficient and stable solid acid catalysts are expected to be further exploited so as to enhance the technical and economic feasibility for the biodiesel production from the low-quality oil feedstocks.

Recently, heteropolyoxometalate acids (HPAs) with Keggin anion structure, comprising early transition metal polyoxoanions generated from transition metals such as molybdenum, tungsten and vanadium, have particularly aroused great attentions in catalysis due to their simple preparation and strong Brönsted acidity [18]. Most HPAs employed for catalytic reactions mainly are $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{PW}_{11}\text{VO}_{40}$, and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$. The main hindrance of HPAs as used as a catalyst lies in their high solubility and lower surface area. Such a weakness for the HPAs can be solved by the formation of their insoluble solid salts with large monovalent metal cations [19]. For instance, doping cesium ions into HPAs can greatly enhance their insolubility in polar reaction mixture, thereby yielding heterogeneous catalysis feature [20,21]. Moreover, the vanadium-containing HPAs with a Keggin anion unit is shown to be a promising HPA catalyst, in which the molybdenum is partially substituted by vanadium [22–24]. The redox and acidic properties for the vanadium-containing HPAs can be tuned by the substitution of the vanadium metal in the primary Keggin structure unit. The inclusion of vanadium metal into the HPAs can improve the catalytic performance to some extents (redox and acid catalysts) [25–27]. Accordingly, the vanadium-substituted HPAs have been utilized as acidic catalysts for the organic transformations [28,29]. So far, to our knowledge, the vanadium-substituted HPAs and their metal salts are not appeared for the transesterification reaction in the literature.

In view of the above considerations, the fabrication of an efficient and recyclable solid catalyst for the biodiesel production is still a research hotspot and also has a high research value for the production of biodiesel, especially from the low-quality oils. Cs-doped tungstophosphoric salts, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$, with a greater surface area of 130–140 m^2/g , have already been reported to possess high catalytic activities to the transesterification reaction for the biodiesel production [30,31]. In this

current work, in an attempt to further develop alternative Keggin heteropolyoxometalate cesium salts as a heterogeneous catalyst, the vanadium-substituted HPA, namely $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$, was first prepared, and then the partial proton substitution by cesium cations was carried out so as to synthesize the solid acid catalyst. The so-prepared acid catalysts were systematically characterized by X-ray diffractometer (XRD), coupled plasma–atomic emission spectrometry (ICP-AES), Fourier transform infrared (FT-IR), inductively Diffuse reflectance ultraviolet–visible spectrum (UV-Vis), thermal gravimetric (TG) analysis and N_2 adsorption–desorption techniques. The catalytic performance of the catalyst was evaluated by the transesterification of soybean oil and esterification of FFAs for the production of biodiesel from the low-quality oils. Furthermore, the recycling experiments were performed to investigate the reusability of the solid acid catalysts.

2. Results and Discussion

2.1. Catalytic Activities of the Solid Acid Catalyst

Even though the HPAs have proved to be potential catalysts for different organic transformations, they are readily dissolved in polar reaction mixture, generating a homogeneous catalysis characteristic. This issue could be overcome by varying these HPAs into their salts, which generally show insoluble in the reaction mixture.

In this research, the vanadium-substituted HPA, $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$, was first prepared by adding the requisite of Na_2VO_3 , Na_2WO_4 , Na_2MoO_4 and NaH_2PO_4 to distilled water and adjusted the pH of the resulting solution to 2.6 with sulphuric acid. Alkali-exchanged HPAs display profound changes in the solubility over the parent HPAs, for instance, the salts of large monovalent Cs^+ ion. Therefore, the proton exchange of $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ acid with cesium carbonate was conducted to afford the solid acid catalyst. The other similar cesium salts of HPAs as used for comparative purpose, were also prepared according to the procedure described in the literature [30,31].

In the present work, the catalytic performances were first evaluated in the transesterification of soybean oil, and screening experiments were performed to identify the optimal solid acid catalyst. Over the $\text{Cs}_2\text{HSiW}_{12}\text{O}_{40}$, $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$, and $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ solid polyoxometalate catalysts, 72.4%, 85.6% and 92.2% oil conversions to biodiesel were achieved under the used transesterification conditions (methanol/oil molar ratio, 30:1; catalyst loading, 3 wt.%; reaction time, 8 h; reaction temperature, 140 °C). Based on the catalyst screening results, the $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalyst exhibited higher catalytic transesterification activities and was therefore chosen for the further catalyst characterization. However, the main disadvantage for the developed solid catalyst lies in the inclusion of toxic vanadium in the catalyst in terms of green chemistry.

It should be noted that the solubility and acidity for the solid polyoxometalate catalyst could be affected by the exchange extent of protons with larger cesium cations. As the cesium substitute number was 1, 2, 3, 4, and 5, the oil conversions of 92.6%, 92.2%, 76.4%, 58.7%, 32.6%, and 25.1% were attained by using the corresponding cesium salt catalysts. Obviously, for the polyoxometalate cesium salt catalyst, the catalytic activity was decreased with increasing the cesium substitute number probably owing to their decreased Brönsted acidities. However, when one cesium cation was doped in the $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ acid, the formed solid acid catalyst could be partially soluble in the reaction mixture, which therefore yielded some homogeneous catalytic activity. Based on our preliminary studies, it was shown that the partially substituted $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ salt was an efficient and stable catalyst and thus was selected for the further investigations. The elemental compositions for the $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalysts could be determined by ICP-AES techniques, and the obtained results are listed in Table 1. It was indicated that the $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalyst was successfully prepared by the ion-exchange method. By using the prepared solid catalyst, the heterogeneous transesterification of soybean oil was achieved with a good oil conversion of 92.2%.

Table 1. Elemental compositions for the $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalysts determined by plasma–atomic emission spectrometry techniques.

$\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$	P	V:P	Mo:P	W:P	Cs:P
Found	1.0	2.876:1	0.992:1	7.926:1	2.012:1
Calculated	1.0	3:1	1:1	8:1	2:1

2.2. Characterization of the Solid Acid Catalyst

The XRD patterns of the $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ acid and its cesium salts are presented in Figure 1. For the $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ acid, the main XRD diffraction peaks were shown at 2θ of 10.6° , 18.2° , 23.5° , 26.2° , 30.4° , 35.5° , and 38.7° , successively arising from the typical reflections of (110), (211), (310), (222), (400), and (322) crystallographic planes of the cubic phase, respectively, which were consistent with the characteristic XRD peaks of Keggin-type structure of HPAs [32,33]. After doping cesium ions into the HPAs, the typical XRD peaks were nearly remained except some differences in the Bragg intensity, manifesting that the Keggin structure was retained for the formed solid catalyst after the cesium substitution.

Figure 1. X-ray diffractometer patterns of the $\text{Cs}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ (a); $\text{Cs}_4\text{H}_2\text{PV}_3\text{MoW}_8\text{O}_{40}$ (b); $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ (c); and $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ (d).

Figure 2 illustrates the Fourier transform infrared (FT-IR) spectra for the $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ acid and its cesium salts. The Keggin-type polyoxoanions consist of a PO_4 tetrahedron surrounded by MO_6 ($\text{M} = \text{W}$, Mo or V) octahedral, which share edges in M_3O_{13} triads and corners with other triads through bridging oxygen [31]. As illustrated by curve a in Figure 2, $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ acid showed four characteristic IR bands at 1070 , 980 , 877 and 789 cm^{-1} , which were ascribed to $\nu_{\text{as}}(\text{P}-\text{O}_a)$, $\nu_{\text{as}}(\text{M}-\text{O}_d)$, $\nu_{\text{as}}(\text{M}-\text{O}_b-\text{M})$ and $\nu_{\text{as}}(\text{M}-\text{O}_c-\text{M})$ vibration modes (O_a , inner oxygen; O_b , bridging oxygen; O_c , corner sharing oxygen; O_d , edge sharing oxygen), respectively, corresponding to the primary Keggin-type HPA structure [33,34]. Besides, the IR spectral band at 596 cm^{-1} could be responsible for the O-P-O bending vibration, and the 524 cm^{-1} band was attributed to the M-O-M skeleton symmetrical stretching vibration of the polyoxometalate acids [21,35]. There were two IR bands around 1620 and 3455 cm^{-1} for the $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ acid to be detected, largely accounting for the H-O-H bending vibration and O-H stretching vibration modes of adsorbed water molecules [36]. More importantly, as shown in Figure 2, after the substitute of protons with the cesium ions, the characteristic IR bands arising from the Keggin polyoxoanion structure of HPAs were absolutely preserved for the prepared solid acid catalyst as expected, except a slight change in their position due to the incorporated cesium ions into the vanadium-substituted HPAs. By these observations, we can confirm that the primary featured structure for HPAs is essentially existed in the $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ acid and its cesium salts.

Figure 2. Fourier transform infrared spectra of $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ (a); $\text{CsH}_5\text{PV}_3\text{MoW}_8\text{O}_{40}$ (b); $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ (c); and $\text{Cs}_3\text{H}_3\text{PV}_3\text{MoW}_8\text{O}_{40}$ (d).

The N_2 adsorption–desorption isotherm was carried out over the $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalyst and the typical isotherm is presented in Figure 3. According to the International Union of Pure and Applied Chemistry (IUPAC) classifications, the nitrogen adsorption isotherm for the solid catalyst could be categorized as type I/IV isotherm with a H3-type hysteresis loop, which was characteristic of mesoporous and micro-porous catalyst [21]. From the nitrogen adsorption–desorption isotherm, the Brunauer-Emmett-Teller (BET) surface area, Brunauer-Emmett-Teller (BJH) pore volume and mean pore size were calculated to be $10.98 \text{ m}^2/\text{g}$, $0.025 \text{ cm}^3/\text{g}$, and 10.14 nm , respectively.

Figure 3. N_2 adsorption–desorption isotherm of the $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalyst.

The electronic properties of the $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalyst were investigated by UV–Vis spectroscopy. Generally, HPAs with Keggin polyoxoanion structure were reported to have two characteristic UV absorption peaks situated at about 190 nm and 255 nm [37]. As for the prepared $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalyst, there were two UV absorption peaks to be observed in Figure 4a as expected. The 203 nm UV peak could be originated from the charge transfer of edge sharing oxygen to metal ($\text{O}_d \rightarrow \text{M}$), meanwhile the UV absorption peak at 268 nm was attributable to the charge transfer between bridged oxygen and metal ($\text{O}_{b,c} \rightarrow \text{M}$) present in the heteropolyanion cages [38,39]. Such results further corroborated that this developed cesium salt catalyst has Keggin-type structure.

Figure 4. Diffuse reflectance ultraviolet–visible spectra (a) and thermal gravimetric curves (b) for the $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalyst.

Figure 4b gives the TG curve of the solid catalyst as heated at air atmosphere from room temperature to 700 °C. As shown in this figure, there were two main mass loss stages in the TG curve. An initial mass loss of approximately 2.25% up to 200 °C was observed, which was due to the loss of physically trapped water from the solid catalyst. Thereafter, the loss of the crystal water (structural water) present in the solid catalyst occurred in the temperature range between 200 and 500 °C with a mass loss of approximately 1.1%. In the third temperature range of 500–700 °C, no obvious further mass loss was found in the TG curve. Accordingly, the TG results unraveled that the prepared catalyst was thermally stable at the reaction temperature of 140 °C.

2.3. Transesterification Reaction Studies

The catalytic activity of the solid catalyst toward the transesterification reaction was investigated, and the main influencing reaction parameters on the oil conversion are the oil/methanol molar ratio, catalyst dosage, reaction temperature and reaction time.

Theoretically, three moles of methanol could be consumed for the transesterification reaction of each mole of triglycerides to its corresponding fatty acid methyl esters. However, in order to shift the reaction equilibrium to biodiesel production side, the methanol loading should be much higher than the stoichiometric ratio. The influence of methanol to oil molar ratio on the oil conversion was explored by using this solid catalyst. As observed in Figure 5a, the oil conversion was steadily enhanced from 32.5% to 92.2% upon raising the substrate molar ratio from 10:1 to 30:1. Thereafter, there was no significant change in the oil conversion to be shown beyond the substrate molar ratio of 30:1. Based on the obtained results, the methanol/oil molar ratio of 30:1 is selected for the transesterification reaction.

The effect of catalyst dosage from 1 to 10 wt.% was investigated for the transesterification reaction, and the obtained results are shown in Figure 5b. At a catalyst dosage of 1 wt.%, only 36.7% of oil conversion was attained owing to insufficient active site involved in the reaction. As observed, the oil conversion was increased as the catalyst dosage increased to 3 wt.%. However, beyond 3 wt.% of the catalyst loading, the conversion was not increased over this solid acid catalyst. In light of the results, one can conclude that the suitable catalyst dosage is 3 wt.%.

Another influential parameter is the reaction time, which affects the transesterification reaction. Figure 5c shows the evolution of the reaction with the reaction time ranging from 2 to 10 h, while keeping other transesterification parameters unchangeable. As seen, the conversion to biodiesel was increased from 65.1% to 92.2% with prolonging the reaction time from 2 to 8 h. However, the further increase in the reaction time to 10 h did not obviously alter the oil conversion, as a consequence of the transesterification equilibrium. Based on the results, the favorable reaction time of 8 h is suitable for the transesterification reaction.

Figure 5. Influence of methanol/oil molar ratio (a), catalyst dosage (b), reaction time (c) and reaction temperature (d) on the oil conversion over the $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalyst.

The influence of transesterification temperature was investigated by carrying out the reaction at different temperatures, and the plot for the oil conversion versus reaction temperature is given in Figure 5d. It was clearly observed that the oil conversion was increased with the rise in the reaction temperature, reaching the maximum value of 92.2% at a reaction temperature of 140 $^{\circ}\text{C}$; thereafter, no significant increment in the oil conversion was observed as the temperature exceeded 140 $^{\circ}\text{C}$. In general, the higher temperature not only could favor the transesterification reaction due to the shift of thermodynamic equilibrium, but also would increase the reactant and product transfer on the catalyst surface, both leading to the increased oil conversion. Thus, the transesterification temperature of 140 $^{\circ}\text{C}$ can be chosen for the reaction.

2.4. Influence of FFAs and Water Present in the Oils

The high cost of the oil feedstocks can greatly raise the cost of biodiesel production. However, as previously mentioned, the cheaper oils such as non-edible or waste cooking oils usually contain high amounts of FFAs and water, which could result in great deactivation of the solid catalyst. Accordingly, to determine the impact of FFAs and water on the catalytic activity, various amounts of water and oleic acid were deliberately introduced to the oil feedstock, then the transesterification reactions were performed under the optimized reaction conditions with this solid catalyst.

From Figure 6a, it was observed that the oil conversion was decreased with the increment of water content, and the conversion of 75% was still reached with a water content of 4%. However, the oil conversion was greatly decreased to 39.3% as the water content was 10%. Seemingly, the water can be adsorbed on the surface of the solid catalysts, and the adsorbed water deactivates the acidic sites, causing the significant decrease in the catalytic activity. As indicated in Figure 6b, the degree of oil conversion was decreased by increasing the FFA content, exhibiting a detrimental impact of FFAs on the catalytic activity. However, the solid catalyst still retained high activity with the oil conversion of 81.7% even with the FFA content of 8 wt.%. By these observations, it can be inferred that the detrimental impact of water was higher than that of FFAs for this prepared solid catalyst. In spite of this, the FFA and water impurities still posed an unimportant effect on the catalytic activity of the

solid catalyst as compared to the solid base catalyst, having potential to be utilized for the biodiesel production especially from low-quality oils.

Figure 6. Influence of water (a) and free fatty acids (FFAs) (b) on the oil conversion over the $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalyst.

2.5. Catalytic Activities of the Solid Catalyst to the Esterification of FFAs

By applying the solid acid catalyst, the simultaneous transesterification of triglycerides and esterification of FFAs would be achieved with the aims to conduct one-pot biodiesel production from low-quality oils. With this respect, the esterification activity of the developed catalyst was also assessed with the simulated low-quality oils (20% of oleic acid) as feedstocks. Under the optimized conditions (methanol/oil molar ratio, 30:1; reaction time, 8 h; reaction temperature, 140 °C; catalyst dosage, 3 wt.%), it was found that almost all the FFAs were converted to the biodiesel, since no FFA was remained in the reaction mixture after 8h of reaction by an acid-base titration method, implying that the solid catalyst possessed the capacity to esterify the FFAs with methanol to biodiesel.

In order to further ascertain the esterification activity of the solid catalyst, the reactions were also carried out at methanol reflux temperature under atmospheric pressure with the simulated low-quality oils, while keeping the other reaction parameters (methanol/oil molar ratio, 30:1; catalyst dosage, 3 wt.%) unalterable. As displayed in Figure 7, the FFA conversion level was enhanced to 95.2% as the reaction time prolonged up to 4 h. After 4 h of reaction, the FFA conversion remained nearly constant. Therefore, such results suggested that the solid acid catalyst could catalyze the esterification of FFAs and transesterification of oils simultaneously by one-pot process, therefore improving the biodiesel production especially from low-quality oils.

Figure 7. Influence of reaction time on the free fatty acid conversion over the $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalyst.

2.6. Reusability of the Catalyst

The reusability of the solid catalyst was also tested by performing repeated transesterification reactions. The activity of the recovered catalyst was examined under the optimized transesterification reactions, and the obtained results are presented in Figure 8. As can be seen, the catalytic activity was decreased slightly for the solid catalyst as it was reused up to five times, revealing a satisfactory reusability of the catalyst. Specifically, 76.4% of oil conversion was still retained after five cycles of reuse for the solid catalyst. The slight decrease in the catalytic activity was probably owing to the accumulation of organic or carbonaceous compounds on the catalyst surface that could block the active sites. Additionally, the main characteristic IR absorption bands of the recovered catalyst were almost unaltered in comparison with that of the fresh catalyst (figure not shown here). These recycling tests implied that the solid catalyst had long-term catalytic stability. In this scenario, the good stability of the catalyst was mainly owing to the strong interactions between the cesium ion and the Keggin heteropolyanions.

Figure 8. Recycling test results of the $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalyst for the transesterification of soybean oil. Reaction conditions: methanol/oil molar ratio, 30:1; catalyst amount, 3 wt.%, reaction time, 8 h; reaction temperature, 140 °C.

To further verify the heterogeneous behavior of the catalyst, a hot filtration experiment was conducted. The solid catalyst was filtered off after 4 h of the reaction, and then the liquid filtrate was subjected to further react for another 5 h under the same reaction conditions. To our satisfaction, the obtained results showed that the oil conversion in the liquid filtrate did not obviously increase. This observation proved that no active species was leached into the filtrate and the catalytic activity was indeed arose from the heterogeneous catalyst. Besides, ICP-AES analysis was employed for the detection of the biodiesel product, and the data suggested that no metal leached into the biodiesel product, thus providing another piece of evidence for the heterogeneity during the transesterification reaction. Overall, the recycling tests showed that the developed catalyst was stable and recyclable, and no obvious loss in the catalytic efficiency occurred after five cycles, highlighting its potential use in the biodiesel production in particular from low-quality oils.

3. Materials and Methods

3.1. Materials

Soybean oil procured from a local food store (Zhengzhou, China) possessed the fatty acid compositions: stearic acid (5.8%), palmitic acid (12.3%), oleic acid (26.5%), linoleic acid (49.3%), linolenic acid (5.9%) and traces of other fatty acids. The average molecular weight was measured

to be 874 g/mol and the acid value was less than 0.1 mg KOH/g. Sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$), sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$), sodium metavanadate dihydrate ($\text{Na}_2\text{VO}_3 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$), and cesium carbonate (Cs_2CO_3 , $\geq 99\%$) were supplied commercially by Sinopharm Chemical Reagent Company (Shanghai, China). All other chemicals were of analytical grade and used as received.

3.2. Catalyst Preparation

The $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ acid was initially synthesized from sodium vanadate, sodium tungstate and sodium molybdate precursors referring to the method reported in the literature [40]. In brief, 20 mL of $\text{Na}_2\text{VO}_3 \cdot 2\text{H}_2\text{O}$ (0.03 mol) aqueous solution, 20 mL of NaH_2PO_4 (0.01 mol) solution and 70 mL of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.08 mol) solution were first mixed with magnetic stirring, and then sulphuric acid solution (50%, *v/v*) was dropped slowly to adjust the pH to 2.6. Thereafter, 10 mL of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (0.01 mol) solution was added to the resultant mixture, and the pH was again adjusted to 2.6 using sulphuric acid solution (50%, *v/v*). Following this, the mixture was allowed to stir at a temperature of 75 °C. After being cooled naturally to room temperature, the solution was taken in a separatory funnel, and diethyl ether was added as an extractant, followed by vigorously mixing at room temperature. The heavy phase was collected and then diethyl ether was evaporated under reduced pressure, affording the $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ acid.

Heterogeneous $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ catalyst was prepared by partial cesium ion-exchange with heteropolyoxometalate acids. In a typical run, a required amount of Cs_2CO_3 aqueous solution (0.1 mol/L) was dropped slowly to an aqueous solution of $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ acid (0.1 mol/L) with a Cs/P ratio of 2 with vigorous stirring at room temperature. The formed colloidal mixture was stirred for 8 h and then aged for 12 h at room temperature. Afterward, the mixture was dried at 50 °C overnight. By the partial proton exchange with cesium ions, $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$ salt catalyst was thus obtained for the biodiesel production.

3.3. Catalyst Characterization

The crystallinity and phase of the samples were analyzed by a Rigaku D/MAX-3B powder X-ray diffractometer (Rigaku, Tokyo, Japan) with nickel-filtered Cu K α radiation (40 kV, 20 mA). Diffuse reflectance UV–Vis spectrum (UV–Vis DRS) of the solid catalyst was gained using a UV-22450 PC Shimadzu spectrometer (Shimadzu, Kyoto, Japan) in the range of 200–800 nm. The thermal gravimetric (TG) analysis was conducted under air atmosphere with a TA Instrument TG 2050 thermogravimetric analysis apparatus (TA Instruments Inc., New Castle, DE, U.S.A.). The N_2 adsorption–desorption isotherms were taken on a Quantachrome NOVA 1000e instrument (Boynton Beach, FL, U.S.A.) at -196 °C. To determine the surface area of different samples, the multipoint Brunauer–Emmett–Teller (BET) equation was applied, while the pore volume and pore size distribution were assessed by the Barrett–Joyner–Halenda (BJH) method. Fourier transform infrared (FT-IR) spectra were acquired by a Shimadzu IR-Prestige-21 spectrometer (Shimadzu, Kyoto, Japan) using a KBr matrix technique in the spectral region of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} . The elemental contents of the solid catalysts were determined by means of inductively coupled plasma–atomic emission spectrometry (ICP-AES; Thermo iCAP 6000 series).

3.4. Transesterification Process

The catalytic transesterification of soybean oil for biodiesel production was performed in a high-pressure stainless steel reactor fitted with a thermocouple. In a general procedure, the desired amounts of soybean oil, methanol (methanol/oil molar ratio, 20:1–40:1) and solid acid catalyst (referred to oil mass, 5–10 wt.%) were charged into the pressured reactor. Subsequently, the formulated mixture was heated to the temperature of 140 °C and then allowed to react for 8 h with stirring (about 600 rpm) under auto-genetic pressure. After completion of the reaction, the pressure reactor was cooled to room temperature. The solid catalyst was separated by filtration, and superfluous methanol was

recovered by a simple vacuum distillation. The transesterified products were analyzed with a 6890 N gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) fitted with a flame ionization detector (Agilent Technologies, Santa Clara, CA, U.S.A) and a fused silica capillary column (60 m × 0.25 mm). For the gas chromatography (GC) analysis, the oven temperature was initially held at 110 °C for 4 min, followed by temperature programming to 240 °C, and then kept at 240 °C for 15 min. The temperatures of injector and detector were set at 260 and 300 °C, respectively. The oil conversion to biodiesel was quantitatively evaluated by the obtained GC results as previously described in the literature [41]. All reactions were carried out in triplicate and the results were expressed as average values.

With the aims to investigate the reusability of the solid acid catalyst, the catalyst was separated by filtration after the transesterification reactions, washed with cyclohexane and methanol, and finally vacuum dried at 60 °C overnight. Thereafter, five transesterification runs were carried out under the optimized reaction conditions.

In order to evaluate the influence of FFAs and water on the catalytic activity, various amounts of oleic acid (as an model FFA) and water were introduced into the oil feedstock as simulated low-quality oils.

3.5. Esterification of FFAs to Biodiesel

The esterification activity of the developed catalyst was also evaluated by using simulated low-quality oils (with 20 wt.% of oleic acid). For this aim, 3 wt.% of solid catalyst was charged into a mixture of the simulated low-quality oil and methanol (methanol/oil molar ratio, 30:1). Thereafter, the reaction mixture was refluxed under atmospheric pressure with magnetic stirring. After the esterification reaction, the catalyst was filtered off, and then excessive methanol was completely eliminated by a vacuum distillation. To determine the acid value (AV) of the reaction mixture, samples were taken periodically and then titrated by 0.1 mol/L NaOH aqueous solution. The FFA conversion to biodiesel was assessed by the AVs of reaction mixture before and after the esterification reaction.

4. Conclusions

In this study, an efficient and recyclable solid acid catalyst, namely $\text{Cs}_2\text{H}_4\text{PV}_3\text{MoW}_8\text{O}_{40}$, was readily prepared by an ion-exchange of the $\text{H}_6\text{PV}_3\text{MoW}_8\text{O}_{40}$ acid with monovalent large cesium ion and was then used in the production of biodiesel from the low-quality oils in a heterogeneous manner. By using this solid acid catalyst, the biodiesel production by a simple one-pot process from the low-quality oils could be achieved through the simultaneous transesterification of oils and esterification of FFAs in a solvent-free system. More importantly, the solid catalyst showed good reusability with minimal loss of catalytic activity over several cycles, thus providing an efficient process for the production of biodiesel from the low-quality oils.

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