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ORIGINAL PAPER

Fatty Acid Methyl Ester Synthesis over Fe^{3+}-Vanadyl Phosphate Catalysts

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Abstract A heterogeneous acid catalyst, Fe^{3+}-vanadyl phosphate, prepared by the isomorphous substitution of some VO^{3+} groups in vanadyl phosphate with trivalent metal Fe^{3+}, was found to be active for the transesterification of soybean oil with methanol. When the transesterification reaction was carried out with a molar ratio of methanol to oil of 30:1, a reaction temperature of 473 K, a reaction time of 3 h and a catalyst amount of 5 wt%, the maximum conversion of soybean oil was 61.3%. Moreover, the catalytic activity of this catalyst was not significantly affected by the presence of free fatty acids and water in the reactants, and it also exhibits catalytic activity towards the esterification of free fatty acids with methanol. Further, it was shown that the spent catalyst could be easily reactivated by calcination at 773 K in air. There was very little change in the catalytic activity of the regenerated catalyst, even after five cycles.

Keywords Transesterification · Biodiesel · Heterogeneous catalyst · Vanadyl phosphate

Introduction

Decreasing fossil fuel reserves and the atmospheric pollution created by petroleum-based fuels have prompted major initiatives to find new renewable and sustainable energy sources to replace fossil fuels. Recently, biodiesel has emerged as a widely accepted alternative fuel due to its high cetane number, high flashpoint, excellent lubricity and lower environmental impact as compared to petroleum-based fuels. Additionally, biodiesel has the appeal of being derived from renewable resources, and it is biodegradable and nontoxic [1].

Currently, biodiesel is usually produced using transesterification reactions, which refer to a catalyzed chemical reaction involving vegetable oils and a primary alcohol (most commonly methanol) to yield fatty acid alkyl esters and glycerol. The transesterification of vegetable oils is usually performed using a basic or an acidic catalyst in a homogeneous manner. Common basic catalysts, including potassium hydroxide, sodium hydroxide as well as potassium and sodium alkoxides [1, 2], are well-known in industrial biodiesel production. The rates of base-catalyzed transesterification reactions are fast, and the reaction conditions are moderate. It is reported that the conversion of vegetable oils to methyl esters using these strong homogeneous basic catalysts can reach 99% within 1 h [3]. However, the application of the base catalysts to biodiesel production is somewhat limited, because they are sensitive to the presence of free fatty acids (FFAs) and water in the reactants. Therefore, the commonly practiced technology based on the use of homogeneous alkaline catalysts for biodiesel production requires refined vegetable oils that contain no more than 0.5% of FFAs and anhydrous conditions. Otherwise, FFAs can react with the base catalyst to form soaps, and these soaps results in the formation of emulsions during the transesterification process, which prevents the separation of biodiesel from the glycerol. In addition to this, the removal of these base catalysts after the reaction is technically difficult, and a large amount of wastewater is produced during the separation and cleaning of the catalysts and products. An acid catalyst would be

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useful for the saponification reaction during the transesterification process because it can catalyze both the transesterification and the esterification reactions simultaneously. In particular, deriving biodiesel from the transesterification of low-cost waste oils which contain large amounts of FFAs and water using an acid catalyst could allow it to be more competitive than petroleum-based diesel fuels. The acid-catalyzed transesterification process often uses sulfuric acid and hydrochloric acid as catalysts. Although acid catalysts have notable advantages, they are not preferred in the transesterification reaction due to their lower activities compared to conventional alkaline catalysts. A higher reaction temperature, a higher molar ratio of methanol to oil, and a longer reaction time are generally required [4, 5]. Besides, the corrosion and environmental problems associated with acid-catalyzed processes should also be considered in this case.

Recently, heterogeneous solid acid catalysts have become desirable for the development of environmentally benign processes and for simplifying the existing processes associated with homogeneous catalysts, since they do not produce corrosion and can be used in the transesterification reaction in the presence of FFAs and water. At the laboratory scale, several solid acid catalysts have been found to be efficient for catalyzing the transesterification reaction, such as sulfated zirconia [6], tungstated zirconia (WZ) [7], $ZnO\text{-}TiO_2/Al_2O_3$ [8] and TiO_2/SiO_2 [9].

Vanadyl phosphate, $VOPO_4{\cdot}2H_2O$ (VOP), which is a layered material, is usually used in catalytic reactions involving Bronsted and Lewis acid sites, such as dehydration [10] and hydrocarbon oxidation [11]. It was also recently shown to be a promising catalyst in vegetable oil transesterification with methanol [12]. Moreover, it has been previously reported that the acidity of VOP can be modified through the isomorphous substitution of some VO^{3+} groups with trivalent metal ions such as Fe^{3+}, Cr^{3+}, Ga^{3+}, Mn^{3+} and Al^{3+}. These vanadyl phosphate derivatives of general formula $[M(H_2O)]_x(VO)_{1-x}PO_4{\cdot}nH_2O$ ($x =$ 0.18–0.25) are characterized by stronger Lewis acidity than VOP itself [13], and they exhibit improved catalytic performance [10, 11]. Very recently, the catalytic performances of some M^{3+}-vanadyl phosphates in the transesterification reaction were tested and the preliminary results were published in the literature [14]. In the present work, more detailed investigations of the M^{3+}-vanadyl phosphate compounds were performed in relation to their use as catalysts in the transesterification of soybean oil with methanol. It was shown that the Fe^{3+}-vanadyl phosphate catalyst was very active in the transesterification reaction, despite its slow deactivation process; however, the spent catalyst could be regenerated by calcination in air. The transesterification conditions, such as the amount of catalyst, the molar ratio of methanol to oil and the reaction time, were also optimized for the catalyst. Furthermore, the effect of the presence of FFAs and water in the reactants on the catalytic activity was also investigated.

Experimental

Catalyst Preparation

$VOPO_4{\cdot}2H_2O$ (hereafter termed "VOP") was prepared by refluxing 10 g of V_2O_5 in 300 mL of 3.3 mol/L H_3PO_4 solution for 16 h and then calcined at 773 K for 2 h according to Ladwig's method [15].

The M^{3+}-substituted compounds $[M(H_2O)]_x(VO)_{1-x}PO_4{\cdot}nH_2O$ (M = Fe, Al, Cr and Mn; $x = 0.18$–0.25) were prepared by adding the appropriate amount of trivalent metal salt to the previous V_2O_5 and H_3PO_4 mixed suspension, and are denoted in the text as "MVOP" [16]. After 16 h of reflux time, the suspensions were hot-filtered, and then the precipitates were washed with cold water, except the chromium derivative, which was washed with an acetone–water mixture. The obtained compound was dried afterwards in air. The preparations of various compounds and their chemical analysis have been reported in detail previously. The chemical compositions of these compounds, prepared in this way and determined by chemical analysis [16, 17], are listed in Table 1. All of the substituted compounds have a layered tetragonal structure and are isomorphous with VOP [13, 17]. Prior to any catalytic test, the catalyst was calcined at desired temperatures (typically at 773 K) in air for 2 h.

The catalysts were characterized using X-ray powder diffraction (XRD). The X-ray powder diffraction patterns were recorded on a Rigaku (Tokyo, Japan) D/MAX-3B diffractometer employing Cu Kα radiation ($\lambda =$ 0.1548 nm) over the 2θ range between 10° and 70° at a scanning speed of 6°/min at 40 kV and 30 mA.

Transesterification Reaction

Commercial edible-grade soybean oil was obtained from market and used as received. According to GC (DC-9A, Shimadzu, Kyoto, Japan) analysis, the fatty acid

Table 1 Chemical compositions of the obtained compounds with their abbreviations

Compound	Abbreviations
$VOPO_4{\cdot}2H_2O$	VOP
$[Fe(H_2O)]_{0.20}(VO)_{0.80}PO_4{\cdot}2H_2O$	FeVOP
$[Al(H_2O)]_{0.15}(VO)_{0.85}PO_4{\cdot}2H_2O$	AlVOP
$[Cr(H_2O)]_{0.17}(VO)_{0.83}PO_4{\cdot}2H_2O$	CrVOP
$[Mn(H_2O)]_{0.25}(VO)_{0.75}PO_4{\cdot}2H_2O$	MnVOP

compositions of the used soybean oil are as follows: palmitic acid, 12.3%; stearic acid, 5.8%; oleic acid, 26.5%; linoleic acid, 49.4%; and linolenic acid, 5.9%. The acid value was less than 0.1 mg KOH/g, and the average molecular weight was 874 g/mol, as calculated from the saponification index ($S_V = 192.6$ mg KOH/g).

All of the transesterification reactions were conducted in a 250 mL stainless high-pressure autoclave reactor with different molar ratios of methanol to soybean oil and varied amounts of the catalysts. Pressure vessels are required to contain the transesterification reaction at higher reaction temperature. To minimize mass transfer limitations, the reactants were stirred at 350 rpm. The reactor temperature was raised to a fixed value for the desired reaction time in a ventilated oven, and then the reactor was cooled to room temperature. After cooling, the reaction mixture was carefully filtered and the residual methanol was separated with the help of a rotary evaporator under reduced pressure prior to the subsequent analysis.

The conversion of soybean oil to methyl esters was determined using a ^{1}H NMR technique (Bruker, 400 MHz). Normally, the reaction mixture, after methanol was removed completely, was washed three times with a saturated aqueous NaCl solution for removal of the formed glycerin. The organic phase was separated by decantation, dried with anhydrous sodium sulfate and then submitted to ^{1}H NMR analysis (DPX-400, Bruker, Ettlingen, Germany) in $CDCl_3$ using TMS as internal standard. The soybean oil conversions were estimated by measuring the area of the ^{1}H NMR signal relative to the methoxy (A_1) and α-carbon CH_2 groups (A_2) respectively, according to [18]

$$\text{The conversion to methyl esters} = \frac{A_1/3}{A_2/2}.$$

In order to study the influence of FFA and water on the activity of the catalysts, additional experiments were performed by deliberately adding water or oleic acid to the reactants. Further, the esterfication of oleic acid present in the reactants with methanol over the catalyst was also performed in a stainless high-pressure vessel using 5 wt% of catalyst in the presence of 10 wt% FFA.

Results and Discussion

Screening experiments were performed to evaluate the catalytic activities of different catalysts for the soybean oil transesterification, and the results obtained are summarized in Table 2. In order to identify the most active catalyst for the reaction, the same preliminary reaction conditions were used for each catalyst in all experiments. As can be seen from Table 2, when there was no catalyst, the conversion of soybean oil was relatively low (12.6%), even when the reaction was conducted at high temperature (473 K) for a long reaction time (3 h). A contribution to the uncatalyzed reaction could be due to the internal stainless steel surfaces of the vials, which may catalyze the transesterification reaction [19]. When the selected catalysts were added to the reaction system, the conversion to methyl esters increased significantly. This indicated that vanadyl phosphate (VOP) and M^{3+}-vanadyl phosphate (MVOP) may exhibit catalytic activity towards the transesterification reaction. Using the VOP catalyst, a soybean oil conversion of 50.7% was achieved (entry 2 in Table 2). The MVOP catalysts showed even better catalytic activities. Among these catalysts, FeVOP had the best catalytic activity, giving the highest conversion of 61.3% (entry 4 in Table 2), probably due to its more strong acid sites. In the previous work, the acidity of the catalysts was measured using NH_3 thermodesorption (NH_3-TPD) techniques. A wide distribution of acid strengths was observed; the FeVOP catalyst possesses a higher surface concentration of acid sites than the VOP catalyst [17]. The other MVOP catalysts, such as AlVOP, CrVOP and MnVOP, were also found to show some catalytic activity towards the transesterification reaction, although relatively low conversions of 58.5, 55.9 and 52.0%, respectively, were achieved (entries 3, 5 and 6 in Table 2). Conversion data obtained here with our catalysts can be compared with literature data. Serio et al. [12, 14] reported a soybean oil conversion of 78% over VOP and 69.4% over FeVOP, respectively. It can be seen that the soybean oil conversions obtained here were lower than the literature data, probably because of the different reaction conditions employed. Based on the aforementioned results, the FeVOP catalyst shows the potential to be used as a heterogeneous catalyst for the transesterification reaction, and it was therefore chosen for subsequent studies.

Table 2 Catalytic activities of different heterogeneous catalysts

Entry	Catalyst	T_p (K)	Conversion (%)
1	–	–	12.6
2	VOP	773	50.7
3	AlVOP	773	58.5
4	FeVOP	773	61.3
5	CrVOP	773	55.9
6	MnVOP	773	52.0

Reaction conditions: methanol/oil molar ratio 30:1, catalyst amount 5 wt%, reaction temperature 473 K, reaction time 3 h

T_p, temperature of calcination

The XRD pattern of FeVOP is reported in Fig. 1, together with that of VOP for comparison. All of the considered compounds exhibited XRD patterns that were in accordance with the literature [17], thus suggesting that the

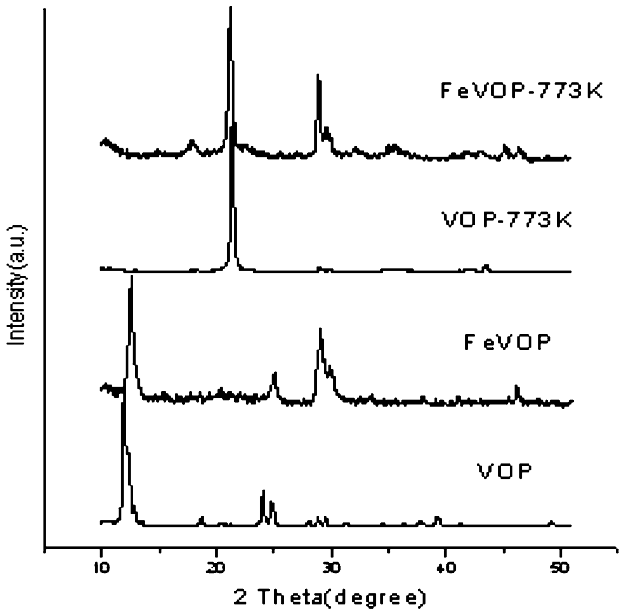

Fig. 1 XRD patterns of the catalysts

Fe was actually introduced into the layered structure of VOP. In the layered tetragonal structure, each vanadium atom is pentacoordinated with oxygen atoms and acts as a Lewis acid site. When Fe atoms are introduced, the FeVOP material can show improved acidity. As shown in Fig. 1, the FeVOP sample retained the layered structure and had a degree of crystallinity comparable with that of VOP. Similarly to VOP, after calcination at 773 K, the FeVOP sample yielded a different XRD pattern to that obtained using the as-prepared compound, and had a similar layered structure. This effect has also been observed by other authors [17].

The catalytic activity of the FeVOP catalyst at various calcination temperatures is plotted in Fig. 2. As shown in this figure, in the absence of calcination, the as-prepared FeVOP catalyst presented lower catalytic activity, probably due to a lack of strong acid sites on which the transesterification reaction could occur. However, after being calcined at a temperature of >673 K, the catalysts exhibited significant catalytic activity, suggesting that high-temperature pretreatment is required for the catalyst to exhibit high catalytic activity during the reaction. Moreover, the conversion increased as the calcination temperature increased from 673 to 773 K, as indicated in Fig. 2. The optimal calcination temperature for the reaction was found to be 773 K. At this calcination temperature, the highest conversion of 61.3% was obtained. However, when the calcination temperature increased beyond 773 K, the conversion of soybean oil decreased. This is probably because the FeVOP starts to decompose, and so the Lewis acidity of the solid decreases.

The molar ratio of methanol to soybean oil is one of the important variables affecting the conversion to methyl esters. Chemically, the transesterification of soybean oils consists of three consecutive and reversible reactions. In the reaction sequence, triglycerides are converted stepwise to diglyceride, monoglyceride and finally to glycerol, and a fatty acid ester is liberated from each acylglycerol at each step. Stoichiometrically, the transesterification reaction requires three moles of methanol for each mole of triglyceride. However, in practice the methanol loading needs to be high enough to shift the equilibrium favorably. In general, acid-catalyzed transesterification needs high molar ratios of methanol to oil (30–150:1) due to its relatively slow reaction rates [4], while a molar ratio of methanol to oil of 6–15:1 is usually used in base-catalyzed processes [1, 2]. The influence of the methanol/oil molar ratio on the conversion of soybean oil was tested and the results obtained are illustrated in Fig. 3. Clearly, the conversion

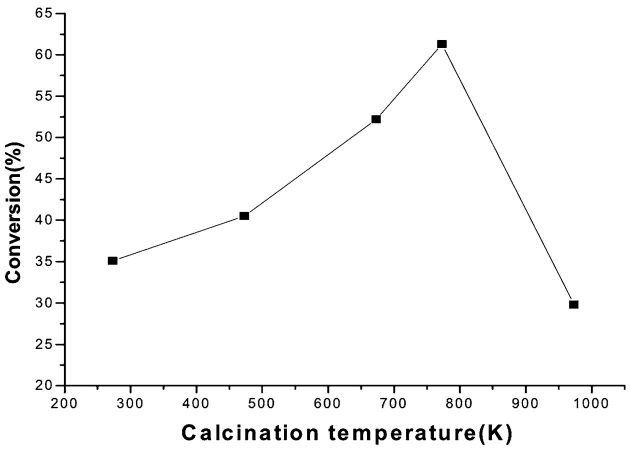

Fig. 2 Influence of calcination temperature on the conversion to methyl esters. Reaction conditions: methanol/oil molar ratio 30:1, catalyst amount 5 wt%, reaction time 3 h, reaction temperature 473 K

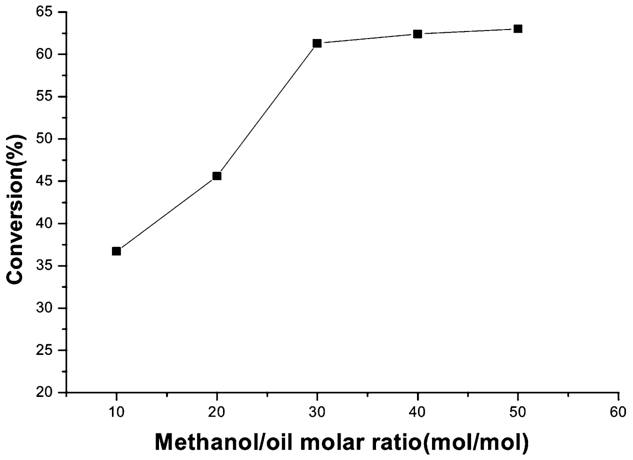

Fig. 3 Conversions of soybean oil as a function of methanol/oil molar ratio. Reaction conditions: catalyst amount 5 wt%, reaction time 3 h, reaction temperature 473 K

increased with increasing methanol. When the molar ratio was very close to 30:1, maximum conversion was obtained. However, beyond the molar ratio of 30:1, the excess menthanol had no significant effect on the conversion. Therefore, the optimum molar ratio of methanol/oil needed to produce methyl esters is approximately 30:1, which produces a conversion of 61.3%. The excess methanol used in the reaction can be recovered by simple distillation.

The influence of the amount of FeVOP catalyst on the conversion to methyl esters was investigated at a 30:1 molar ratio of methanol to oil at 473 K for 3 h. The experiments were carried out with various amounts of catalyst (1–9 wt% in relation to the amount of oil). The conversion levels are plotted against the amount of catalyst in Fig. 4. From this figure, it can be seen that the transesterification reaction was strongly dependent upon the catalyst applied. Without the addition of a catalyst, the transesterification procedure gives only a low conversion; the presence of the catalyst dramatically increases the reaction rate. As is evident in Fig. 4, when the amount of catalyst is increased from 1 to 5 wt%, the corresponding conversion increases gradually from 25.6% to the maximum value of 61.3%. The increase in conversion that occurs as the amount of catalyst increases is probably due to an increase in the number of acidic sites in the transesterification reaction. However, when the amount of catalyst is increased further, decreased conversion was observed, most likely due to a mixing problem involving reactants and the solid catalyst. Accordingly, in this reaction, the optimum amount of catalyst is considered to be 5 wt%.

In order to study the influence of the reaction temperature on the conversion of soybean oil, experiments using the FeVOP catalyst were conducted at different temperatures, ranging from 393 to 523 K. As can be seen from Fig. 5, the oil conversion was low at 393 K, and increased as the reaction temperature rose, reaching its maximum value of 61.3% at 473 K. This indicates that a higher temperature can increase the reaction rate, especially when using the solid acid catalyst. However, above the reaction temperature of 473 K, there was no significant increase in the conversion of soybean oil. In the presence of heterogeneous catalysts, the transesterification reaction initially constitutes a three-phase system, oil/methanol/catalyst, which inhibits the reaction for mass transfer reasons. Obviously, the solubility of methanol in soybean oil can be enhanced by increasing the temperature. Nevertheless, it is worth noting that the higher temperature can also enhance the solubility of the byproduct glycerol in the fatty phase, thus promoting the glycerolysis of methyl esters and lessening the effect of increasing the reaction temperature on the conversion. Therefore, a suitable reaction temperature for this transesterification reaction is 473 K.

Studies were also carried out at different reaction times with 5 wt% FeVOP used as catalyst and a methanol/oil molar ratio of 30:1. Figure 6 shows that when the reaction time was less than 3 h, increasing the reaction time resulted in a significant increase in the conversion from 32.4 to 61.3%. However, increasing the reaction time still further, from 3 to 8 h, resulted in an almost constant conversion of about 61%, as a consequence of catalyst deactivation during the run. Thus, 3 h was chosen as a suitable reaction time.

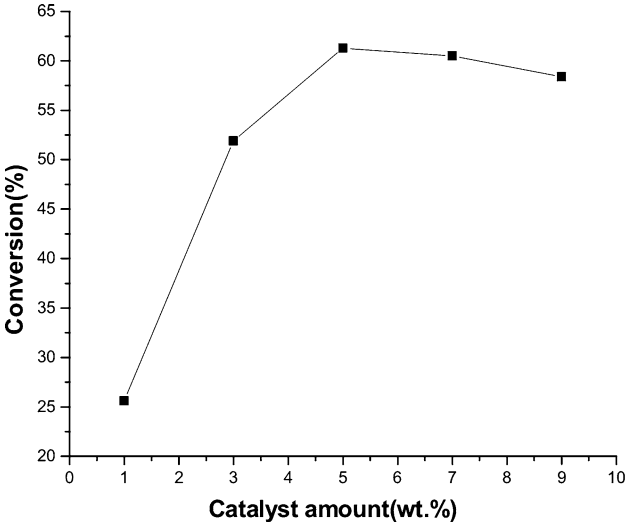

Fig. 4 Conversions of soybean oil as a function of amount of catalyst. Reaction conditions: methanol/oil molar ratio 30:1, reaction time 3 h, reaction temperature 473 K

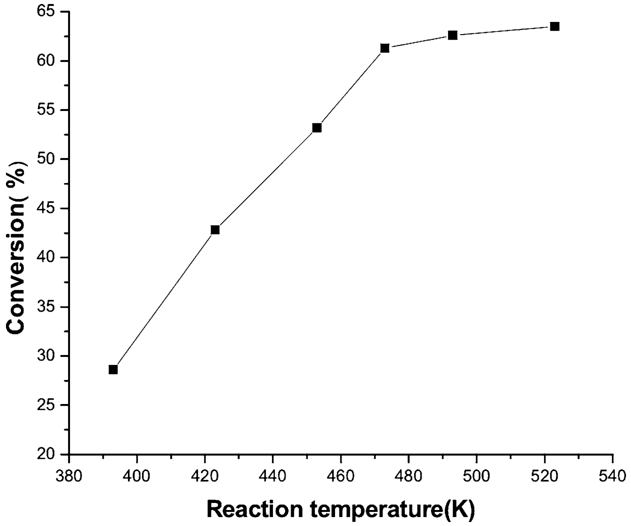

Fig. 5 Conversion of soybean oil as a function of reaction temperature. Reaction conditions: methanol/oil molar ratio 30:1, catalyst amount 5 wt%, reaction time 3 h

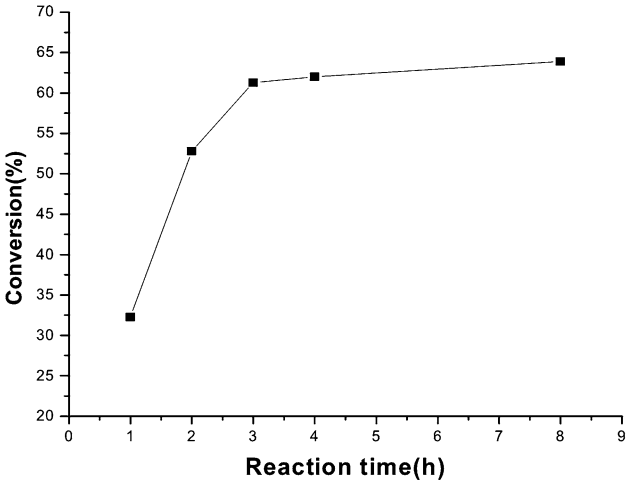

Fig. 6 Conversion of soybean oil as a function of reaction time. Reaction conditions: methanol/oil molar ratio 30:1, catalyst amount 5 wt%, reaction temperature 473 K

It is known that the alkali-catalyzed transesterification of vegetable oils is inhibited by the presence of FFA and water in the reactants. Therefore, dehydrated vegetable oil with less than 1 mg KOH/g FFAs and anhydrous alcohol are necessary for commercially viable alkali-catalyzed systems. For alkaline catalysts, vegetable oils containing high FFA contents suffer from soap formation, leading to a reduction in the amount of product obtained, and problems with product separation and purification. Canakci and Gerpan [20] reported that when using alkaline catalysts the FFA concentration should be less than 0.5%. This is likely to be a significant limitation on the use of waste cooking oil as a low-cost feedstock in a base-catalyzed system. However, methodologies based on acid-catalyzed reactions have the potential to achieve this since acid catalysts do not show measurable susceptibility to FFAs and water. Moreover, acid catalysts can simultaneously catalyze both the transesterification and the esterification reactions. It is desirable, for economic reasons, to find solid catalysts that can handle unrefined and waste oils. Thus, the effects of soybean oils with different FFAs and water contents on the catalytic activity of FeVOP were also investigated. Experimental runs were made with the addition of oleic acid and water to the reactants. The results obtained are included in Fig. 7 and Table 3. From Fig. 7, it can be seen that the effect of water on the soybean oil conversion is related to its content. When the added water was increased to 1%, the conversion decreased from 61.3 to 52.3%. As indicated in Table 3, the soybean oil conversion was still 56.5% even when 10% FFAs was added to the reactants. While the results suggest that the conversion of soybean oil decreased as the amount of FFAs and water added increased; the FFA concentration and water content of the feedstock did not have a great effect on the conversion, even when their levels were high, such as 10 and 1.0%. Many other investigators have noted that the presence of more than 0.3% water or more than 0.5% FFAs in this system significantly reduces the conversion in base-catalyzed processes [20, 21]. As a result, this catalyst can be used for transesterification reactions when the feedstock does not meet the requirements of the base-catalyzed process.

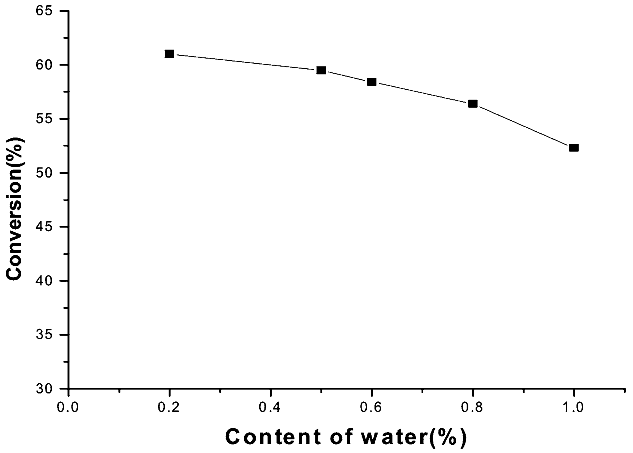

Fig. 7 Effect of water content on the conversion of soybean oil. Reaction conditions: methanol/oil molar ratio 30:1, catalyst amount 5 wt%, reaction time 3 h, reaction temperature 473 K

In order to confirm that the FeVOP and VOP catalysts are active in the esterification of FFAs, the esterification of oleic acid present in the reactants with methanol over the catalysts was performed in a stainless high-pressure vessel, using 5 wt% of catalyst at a methanol/oil molar ratio 30:1 and a reaction temperature of 473 K. The acid values of the reaction mixtures were estimated by titration methods with an alkali solution. The FFA conversions can be determined from the equation:

FFA conversion (%) = (initial acid value
– final acid value)/initial acid value.

The evolution with reaction time of the FFA conversion is plotted in Fig. 8. It can be seen that, when the reaction temperature reached 1 h, the FFA conversion (72.4%) over the VOP catalyst was more than that of the FeVOP catalyst (69.3%). However, after 1 h of reaction, the conversion of FFAs over the VOP catalyst remained almost constant

Table 3 Influence of FFA content on the conversion of soybean oil

	FFA(%)			
	1.0	3.0	5.0	10.0
Conversion(%)	61.3	60.0	58.3	56.5

Reaction conditions: methanol/oil molar ratio 30:1, catalyst amount 5 wt%, reaction temperature 473 K, reaction time 3 h

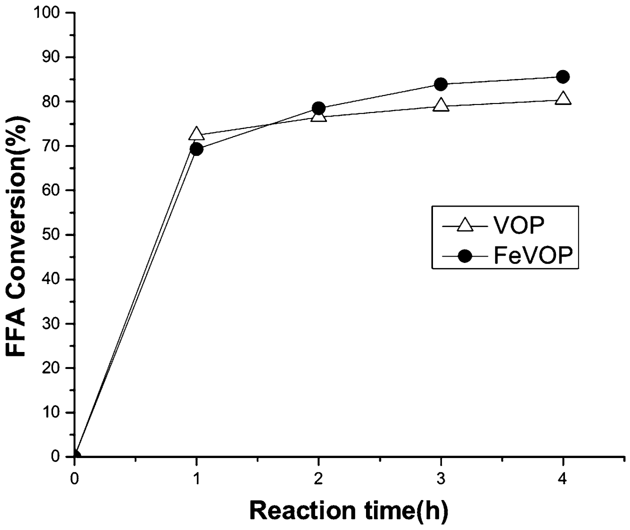

Fig. 8 FFA conversions over VOP and FeVOP catalysts as a function of reaction time. Reaction conditions: methanol/oil molar ratio 30:1, catalyst amount 5 wt%, reaction temperature 473 K, FFA amount 10 wt%

(78.9%), while the conversion over the FeVOP catalyst increased to 85.6%, probably due to the slower deactivation of the FeVOP catalyst compared to that of the VOP catalyst in the reaction conditions. Based on the results, it is clear that the catalysts for the transesterification reactions also show activity toward the esterification of FFAs.

The catalyst reusability was examined by carrying out subsequent reaction cycles under the same reaction conditions as described above. The catalyst used was separated from the reaction mixture by filtration, washed thoroughly with cyclohexane, and then heated at 398 K overnight before it was reused in a second reaction cycle. The reaction catalyzed by the recovered catalyst provided only 30.8% conversion, which was much lower than the conversion of 61.3% over the original catalyst. This indicated that the FeVOP catalyst was significantly deactivated and could not be directly reused for the transesterification reaction. Mostly likely, deactivation of the catalysts is due to the progressive reduction of the surface vanadium species by methanol [12]. However, the used catalyst can easily be regenerated by calcination in air. The experimental results showed that the regenerated catalyst could give a soybean oil conversion of 60.2%—almost as high as the conversion provided by the fresh sample (Fig. 9). In addition, the experiments were repeated five times in the same transesterification procedure where the catalyst was regenerated by calcination in air before each run. The conversions obtained in this series of reaction cycles are presented in Fig. 9. It can be seen that the conversion of soybean oil barely changes, remaining at 50.6% even after five cycles.

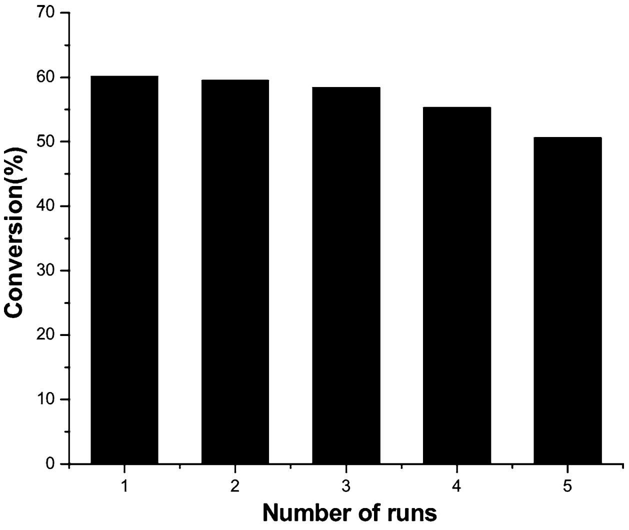

Fig. 9 Catalyst activity over five reaction cycles. Reaction conditions: methanol/oil molar ratio 30:1, catalyst amount 5 wt%, reaction time 3 h, reaction temperature 473 K

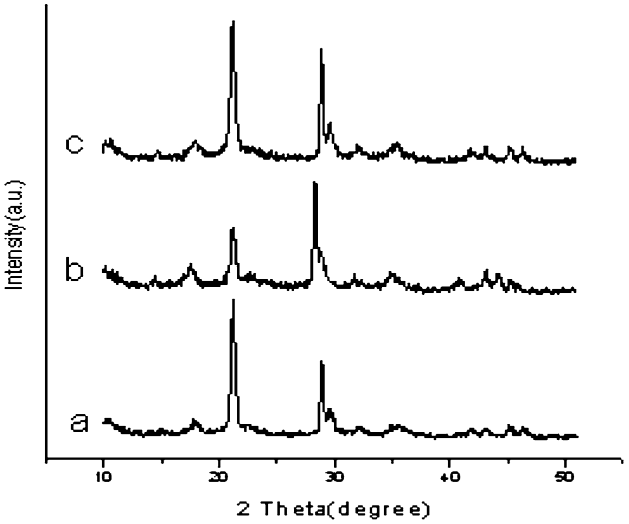

Fig. 10 XRD patterns of (*a*) FeVOP calcined at 773 K, (*b*) the used FeVOP catalyst, and (*c*) the regenerated FeVOP catalyst

Figure 10 reports the XRD patterns of (a) the FeVOP calcined at 773 K, (b) the used FeVOP catalyst, and (c) the regenerated FeVOP catalyst calcined at 773 K. As can be seen, a decrease in the intensity of the diffraction peaks in the used FeVOP catalyst with regard to the FeVOP calcined at 773 K is observed. This decrease is not due to the destruction of the crystalline structure, but to some loss of the catalytically active species, which probably results in a drop in the activity of the used FeVOP catalyst. However, after calcination at 773 K, the diffraction intensity of the regenerated FeVOP catalyst increased because the crystalline phases were restored, and thus the activity of the used FeVOP catalyst was also restored, in agreement with the experimental results mentioned above.

It is evident that the conversion to methyl esters over the FeVOP catalyst is not sufficient for industrial biodiesel production, and therefore the activity of the catalyst needs to be improved considerably to achieve satisfactory conversions. Alternatively, for industrial applications, another transesterification stage after the application of the catalyst and glycerol separation is needed to complete the reaction when the FeVOP catalyst is used for biodiesel synthesis.

Several other heterogeneous acid catalysts have also been reported in the literature. For example, Jitputti et al. [6] studied the tranesterification of crude palm kernel oil in the presence of SO_4^{2-}/ZrO_2 catalyst. Despite the fact that this catalyst showed a good conversion reaction yield (up to 95%) at 473 K, the leaching of the catalytic active species caused rapid deactivation of the catalyst. Delfort et al. [8] patented the use of a $ZnO–TiO_2/Al_2O_3$ catalyst to obtain a yield of about 68% at 473 K and for 2 h reaction time. Also, over a TiO_2/SiO_2 catalyst [9] a lower yield of 60% was achieved at reaction conditions similar to those reported here (a reaction temperature of 473 K and a reaction time of 3 h).

In the present work, the transesterification of soybean oil with methanol was performed using FeVOP as a heterogeneous catalyst. Under the reaction conditions of a temperature of 473 K and a methanol/oil molar ratio of 30:1, FeVOP calcined at 773 K gave a conversion of 61.3% of the oil within 3 h. The catalytic activity of this catalyst was not significantly affected by the FFA and water present in soybean oil, and it was also suitable for FFA esterification. The catalysts used could be regenerated by calcination in air without any appreciable loss in activity.

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