We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



17

Heterogeneous Catalysts Based on $H_3PW_{12}O_{40}$ Heteropolyacid for Free Fatty Acids Esterification

Marcio Jose da Silva[1], Abiney Lemos Cardoso[1], Fernanda de Lima Menezes[1], Aline Mendes de Andrade[1] and Manuel Gonzalo Hernandez Terrones[2]
[1]*Federal University of Viçosa/Chemistry Department,*
[2]*Federal University of Uberlândia/Chemistry Institute,*
Brazil

1. Introduction

1.1 Biodiesel chemical background

The inevitable exhaustion of the fossil diesel reserves, besides the environmental impact generated by the green-house effect gas emission by these fuels has provoked the search by renewable feedstokes for energy production (Srivastava & Prasad, 2000; Sakay et al., 2009). Due to this crescent demand, the industry chemistry in all parts of world has search to develop environment friendly technologies for the production of alternative fuels (Di Serio et al., 2008; Marchetti et al., 2007). Biodiesel is a "green" alternative fuel that has arisen as an attractive option, mainly because it is less pollutant than its counterpart fossil and can be obtained from renewable sources (Maa & Hanna, 1999).

Although it is undeniable that biodiesel is a more environmentally benign fuel, its actual production process cannot be classified as "green chemistry process" (Kulkarni et al., 2006). The major of the biodiesel manufacture processes are carry out under alkaline or acid homogeneous catalysis conditions, where is not possible the recycling catalyst, resulting in a greater generation of effluents and salts from neutralization steps of the products and wastes (Kawashima et al., 2008). Moreover, there are some important points related to raw materials commonly used, such as high costs, besides to crescent requirements of large land reserves for its cultivation.

1.2 Production of biodiesel from triglycerides transesterification reactions

Currently, the biodiesel is manufactured from alkaline transesterification of edible or non-edible vegetable oils via a well-established industrial process (Maa & Hanna, 1999). The transesterification reaction proceeds well in the presence of some homogeneous catalysts such as alkaline metal hydroxides and Brønsted acids (Demirbas, 2003). Traditionally, sulfuric acid, hydrochloric acid, and sulfonic acid are usually preferred as acid catalysts. (Haas, 2005). The catalyst is dissolved into alcohol (methanol or ethanol) by vigorous stirring in a reactor. The vegetal oil is transferred into the biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil (Demirbas, 2003). However, the use them usually require drastic reaction conditions, i.e., high temperature and elevated pressure

(Lotero et al., 2005). In addition, serious drawbacks related to its conventional production have aroused a special attention to biodiesel industry. Some of the natural oils or animal fats contain considerable amounts of free fatty acids (FFA), which are undesirable for the transesterification processes. These important features have hardly affected the final cost to biodiesel production (Haas, 2005).

1.3 Production of biodiesel from FFA esterification reactions

An attractive alternative for lower biodiesel price is produce it directly from domestic reject such as used cocking oil and waterwastes generated by food industry (Lou et al., 2008). Nevertheless, since these low cost lipidic feedstokes are rich in FFA, it's conversion into biodiesel is not compatible with alkaline catalysts. Nevertheless, different approaches have been proposed to get rid of this problem, and frequently, two alternative pathways have been employed for produces biodiesel from these kinds of resources. At first, a two-stage process that requires an initial acid-catalyzed esterification of the FFA followed by a base-catalyzed transesterification of the triglycerides; and secondly, a single-process that makes exclusive use of acid catalysts that promote both reactions simultaneously (Dussadee et al., 2010; Zullaikah et al., 2005).

Nowadays, the catalysts conventionally used in the FFA esterification reactions are Brønsted acids and work in a homogeneous phase (Lotero et al., 2005). Acids can catalyze the reaction by donating a proton to the FFA carbonyl group, thus making it more reactive. It should be mentioned that even though traditional mineral acids catalysts are an inexpensive catalysts able to those processes, they are highly corrosive, are not reusable, and results in a large generation of acid effluents which should be neutralized leaving greater amount of salts and residues to be disposed off into environment (Di Serio, 2007). Indeed, the reduction of environmentally unacceptable wastes is a key factor for developing less pollutants and advanced catalytic processes (Haas, 2005).

Thus, to develop alternative catalysts for the direct conversion into biodiesel of lipid wastes which are basically constituted of FFA, or yet for the pre-esterification of feedstokes that has high acidity seem be also a challenge to be overcome (Demirbas, 2008). Lewis acids can be interesting alternative catalysts for biodiesel production (Corma & Garcia, 2003). Nevertheless, their high cost, the manipulation difficult and the intolerance to water of compounds traditionally used such as BF_3 and others common reagents of organic synthesis, also does not favor the use of these later in FFA esterification at industrial scale (Di Serio et al., 2005).

For all these reasons, to develop recyclable alternative catalysts for FFA esterification presents on inexpensive raw materials and food industry rejects can be an option strategically important, and undoubtedly can make the biodiesel with more competitive price using a cleaner technology (Lotero at al., 2005).

1.4 Lewis or Brønsted acids heterogeneous catalysts for biodiesel production

Recent advance in heterogeneous catalysis for biodiesel production has the potential to offer some relief to the biodiesel industry by improving its ability to process alternative cheaper raw material, and to use a shortened and low cost manufacture process. Even though many alkaline heterogeneous catalysts have been reported as highly active for biodiesel synthesis, they still cannot tolerate acidic oils with FFA content 3.5%, which are frequently used as raw material (DiMaggio et al., 2010). Contrarily, solid acids catalysts are more tolerant to FFA and are potentially less corrosive for the reactors. Consequently, these catalysts have been increasingly used in biodiesel production processes (Hattori, 2010).

A plethora of works have described the development of heterogeneous catalysts based on acids solids, which appear to offer an attractive perspective to turn the biodiesel production more environment friendly (Kiss et al., 2006; Jothiramalingam & Wang, 2009; Refaat, 2011). These solid catalysts, which normally present Lewis acidity, are easily separated from the reaction medium and are potentially less corrosive for the reactors. Normally, these processes focus on transesterification reactions of the triglycerides presents in the vegetable oils, which after react with methanol are converted into biodiesel. However, serious technological drawbacks such as drastic conditions reaction, the strict control of raw material quality in relation to water content, beyond of the leaching catalyst provoked by presence of alcohol besides water generated into reaction medium seems suggest that those process yet are hard to become effective (Kozhevnikov, 2009).

Particularly, the authors have concentrating efforts in developing alternative processes of esterification based on two recyclable catalysts linked to both acid types:

i. heteropolyacids, with a special highlighted for the dodecatungstophosphoric acid ($H_3PW_{12}O_{40}12H_2O$) (Silva et al., 2010; Cardoso et al., 2008);
ii. tin chloride, an simple, easily handling, water tolerant and inexpensive Lewis acid (Cardoso et al., 2009; da Silva et al., 2010).

On the hand, catalysis by heteropolyacids of the Keggin's structure such as $H_3PW_{12}O_{40}$ is one of the most important and growing areas of research in recent years (Timofeeva, 2003). They have been extensively used in both homogeneous and heterogeneous catalysis (Misono et al, 2000; Sharma et al., 2011).

On the other hand, the use $SnCl_2$ catalyst is also most attractive, because it is solid, commercially available, and easy to handle. Moreover, its display remarkably tolerance to water, has an economically cost effective, and can be used in recyclable processes (Cardoso et al., 2008). Herein, the authors investigate the catalytic activity of heterogeneous catalysts based on acid solids composites (e.g. $H_3PW_{12}O_{40}$ supported on silicon, niobium and zirconium oxides) towards the esterification of oleic acid with ethanol.

1.5 Keggin heteropolyacid catalysts: a brief introduction

Tungtstophosphoric acid ($H_3PW_{12}O_{40}$) is a heteropolyacid largely used, in special under heterogeneous catalysis conditions. As a homogeneous catalyst the $H_3PW_{12}O_{40}$ has showed higher activity, selectivity and safety in handling in comparison to conventional mineral acids (Cardoso et al., 2008). Recent works have shown that the Keggin-type $H_3PW_{12}O_{40}$, for which the physicochemical and catalytic properties have been fully described, is an efficient super-acid that can be used in homogeneous or heterogeneous phase (Kozhevnikov, 1998). Moreover, in the heterogeneous phase, supported on several solid matrixes, heteropolyacid composites also have showed highly efficient as catalysts in several types of reactions (Pizzio et al., 1998; Timofeeva et al., 2003; Sepulveda et al., 2005).

The activity of $H_3PW_{12}O_{40}$ catalyst supported on zirconia was assessed in transesterification reactions with methanol (Sunita et al., 2008); high yields FAMEs were achieved in reactions performed at temperatures of 200 °C. On the other hand, impregnated $H_3PW_{12}O_{40}$ heteropolyacid on four different supports (i.e. hydrous zirconia, silica, alumina, and activated carbon) also were investigated and converting low quality canola oil containing to biodiesel at 200 °C temperature (Kulkarni et al., 2006). Recently, the use of an impregnation route to support $H_3PW_{12}O_{40}$ on zirconia in acidic aqueous solution and further applied in the oleic acid esterification with ethanol was described (Oliveira et al., 2010). Those authors verified that 20% w/w $H_3PW_{12}O_{40}/ZrO_2$ was the most active catalyst (*ca*. 88% conversion,

4 h reaction, with 1:6 FA:ethanol molar ratio and 10% w/w of the catalyst in relation to FA. However, a minor leaching of catalyst (*ca*. 8% w/w related to the initial loading), affected drastically its efficiency, resulting in decreases yielding obtained from its reuse.

2. Results and discussion

2.1 General aspects

Herein the $H_3PW_{12}O_{40}$ catalyst were supported on three different solid matrixes (i.e. silicon, niobium, and zirconium oxides) by impregnation in ethanol solutions under different loads (*ca*. 10, 30 and 50% w/w). The solids were characterized by FTIR spectroscopy and the $H_3PW_{12}O_{40}$ catalyst content was determined by UV-Vis and AAS spectroscopy analysis.

2.2 Syntheses of the $H_3PW_{12}O_{40}$ catalysts

Differently than others supports, which were used as received, zirconium oxide was obtained from thermal treatment of $ZrOCl_2.8H_2O$ salt at 300 °C during 4 hours. Composites of $H_3PW_{12}O_{40}$ supported on silicon, niobium and zirconium oxides were prepared via impregnation method (Pizzio et al., 1998). During preparation, ethanol solutions of $H_3PW_{12}O_{40}$ in hydrochloric acid 0.01 mol L^{-1} were used to avoid any hydrolysis. All composites were prepared with concentrations depending upon the loading required to the support (e.g. 10, 30 and 50% w/w $H_3PW_{12}O_{40}$) using 10 ml of the solution per gram of support. The addition of the support to the solution formed a suspension, which after stirred, was evaporated at 80 °C until dryness. All samples of supported heteropolyacid were dried at 100 °C for 12 h and then thermally treated for 4 h at 200 or 300 °C in air.

2.3 FTIR spectra of the supported heteropolyacid catalysts: $H_3PW_{12}O_{40}/SiO_2$, $H_3PW_{12}O_{40}/Nb_2O_5$ and $H_3PW_{12}O_{40}/ZrO_2$

The supported $H_3PW_{12}O_{40}$ composites were analyzed by FTIR aims to confirm the presence of the Keggin anion structure on support employed. The $PW_{12}O_{40}^{3-}$ Keggin ion structure is well known, and consists of a PO_4 tetrahedron surround by four W_3O_{13} groups formed by edge-sharing octahedral (Pope, 1983). These groups are bonded each other by corner-sharing oxygens. This structure gives rise to four types of oxygen atoms, being responsible for the fingerprint bands of the $PW_{12}O_{40}^{3-}$ Keggin ion (*ca*. 1200 - 700 cm^{-1}). FTIR spectra were obtained from all samples with different content of HPW (*ca*. 10, 30 and 50% w/w). However, the typical bands of the Keggin ions were more evident for samples with HPW contents of 30 and 50 % w/w. Herein, only the FTIR spectra of the composites with 30 % w/w $H_3PW_{12}O_{40}$, which were thermally treated at temperature of 100, 200 and 300 °C are shown. Figures 1-3 shows the characteristic bands for absorptions of ν (P–O) and ν (W-O) bonds existent on $H_3PW_{12}O_{40}$ composites. All FTIR spectra of both supported $H_3PW_{12}O_{40}$ catalyst or pure are displayed in Figures 1-3.

When niobium oxide was the support, only a stronger band at 1080 cm^{-1} relative to ν (P–O) bond was easily observed (Figure 1). All others bands were overlapping by support bands. Conversely, when the support employed was the SiO_2, all the bands related to others oxygen atoms were observed ν (W = $O_{tethraedric}$) bond at 985 cm^{-1}; ν (W–O_{cubic}–W) bond, at 895 cm^{-1}, and ν (W–O–W) bond, at 795 cm^{-1}; only the band of ν (P–O) bond was not visible.

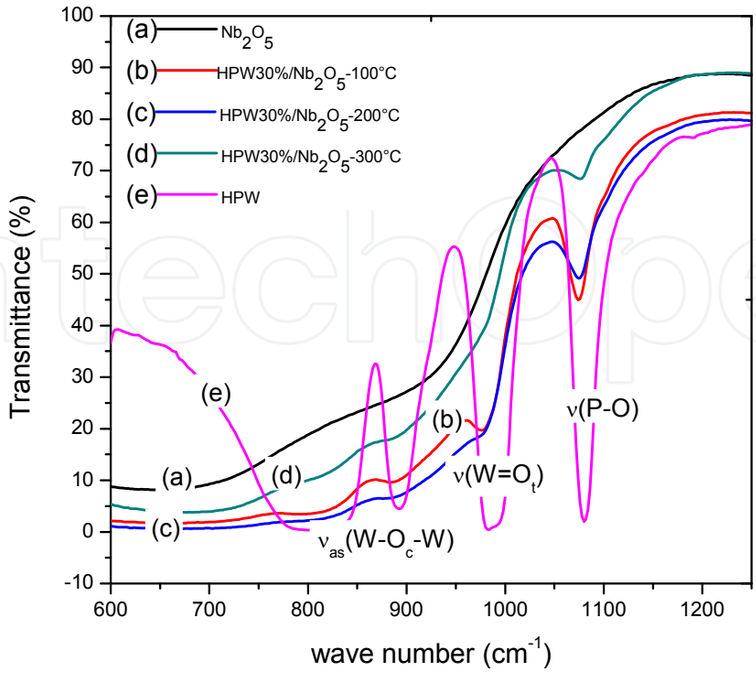


Fig. 1. FTIR spectra of (30% w/w HPW) $H_3PW_{12}O_{40}$ composites (a) Nb_2O_5; (b) HPW 30%/ Nb_2O_5-100°C; (c) HPW 30% Nb_2O_5-200°C; (d) HPW 30%/ Nb_2O_5-300°C; (e) HPW

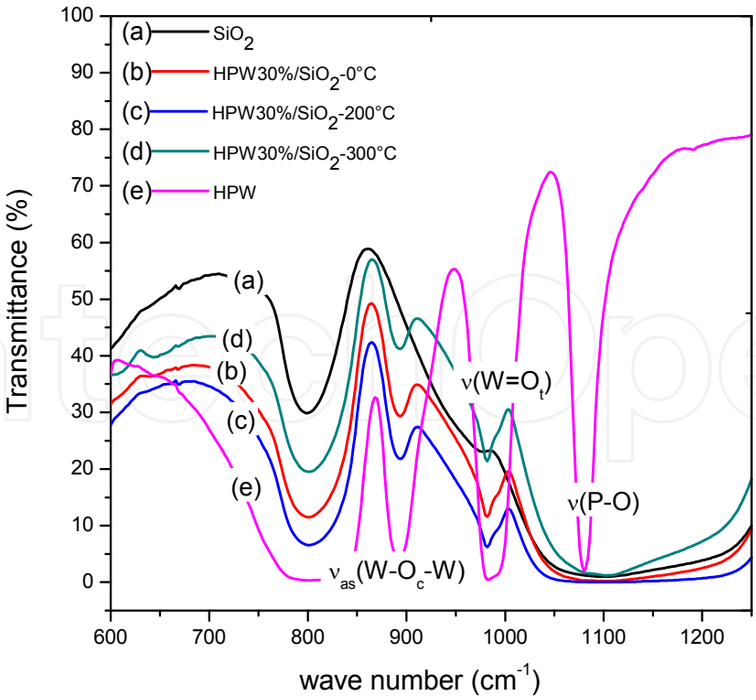


Fig. 2. FTIR spectra of (30 %w/w HPW) $H_3PW_{12}O_{40}$ composites (a)- SiO_2; (b)- HPW 30%/SiO_2-100°C; (c) HPW 30%/SiO_2-200°C; (d) HPW 30%/SiO_2-300°C; (e)- HPW.

These bands are preserved on the silicon-supported catalyst samples, but they are slightly broadened and partly obscured because of the strong absorptions of silica at 1100 and 800 cm^{-1} region.

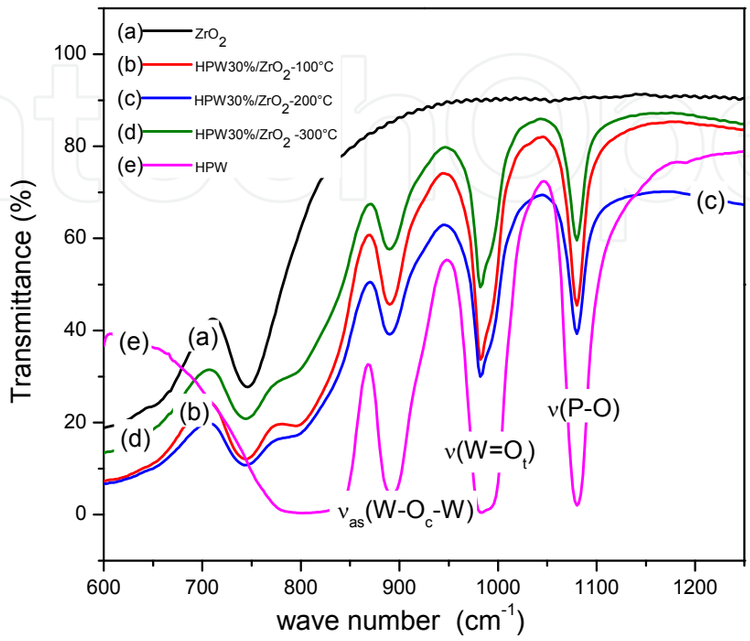


Fig. 3. FTIR spectra of $H_3PW_{12}O_{40}$ (30% HPW) composites (a)- ZrO_2; (b)- HPW/ZrO_2-100 °C (c) HPW 30%/ZrO_2-200°C; (d) HPW 30%/ZrO_2-300°C; (e)- HPW.

In Figure 3, where FTIR spectra obtained from HPW composites supported on ZrO_2 are shown, all characteristics bands of the Keggin anion are present.
In general, FTIR spectra of the HPW composites on different supports were not affected by temperature of thermal treatment. On the temperature range studied herein, all they have shown similar characteristics. However, a measured of interaction strength of HPW with support may be obtained from shift of more well defined bands to a region of lower wave number in comparison with the same band present on HPW pure (Figures 1-3).

2.4 UV-Vis spectra of the supported heteropolyacid catalysts: $H_3PW_{12}O_{40}/SiO_2$, $H_3PW_{12}O_{40}/Nb_2O_5$ and $H_3PW_{12}O_{40}/ZrO_2$

Beckman DU-650 UV-Vis spectrophotometer and quartz cells of 1.0 and 0.1 cm pathlength were employed for the adsorption experiment and measurements of $H_3PW_{12}O_{40}$ spectra, respectively (Oliveira et al., 2010). The concentration of $H_3PW_{12}O_{40}$ on catalysts was measured by UV-Vis spectroscopy before and after 6 hours of adsorption. The content of HPW in the solid was determined by AAS. In all composites yielding upper of 95% of impregnation were achieved.

2.5 Catalytic tests

2.5.1 Reaction conditions

The reactions conditions used were based on typical heterogeneous process (Figure 4). The catalyst is recovered from solution from simples filtration; the ethanol used in excess is

dried and reused in other catalytic run, similarly to solid catalyst. As will show on next section, ethanol in excess not favors the ester formation under these reaction conditions.
The load catalyst used when the composites have 50% w/w HPW is corresponding to *ca.* 1 mol % in relation to oleic acid; in all reactions 1 mmol of oleic acid is used against 0.0087 mmols of HPW present in 50 mg of catalyst.

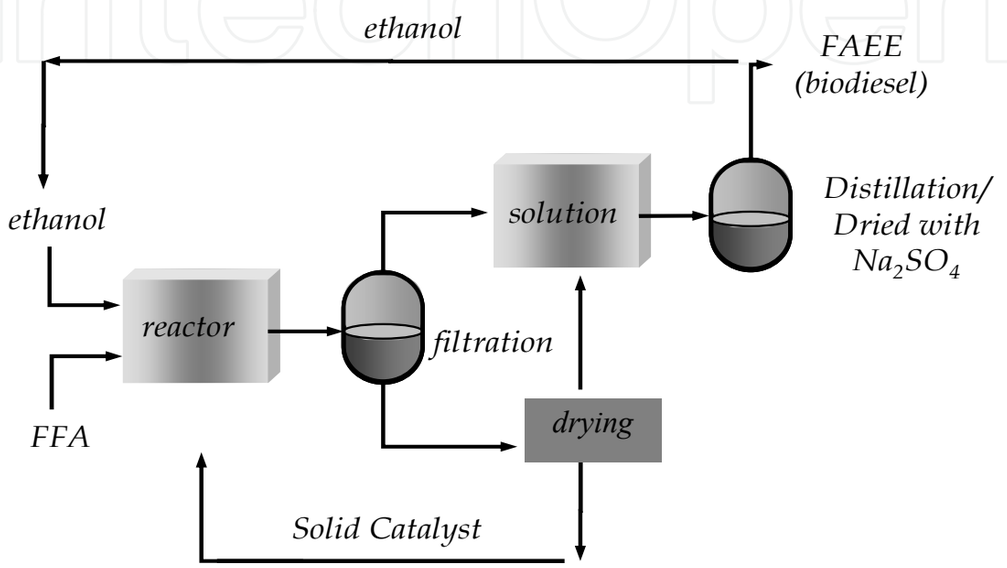
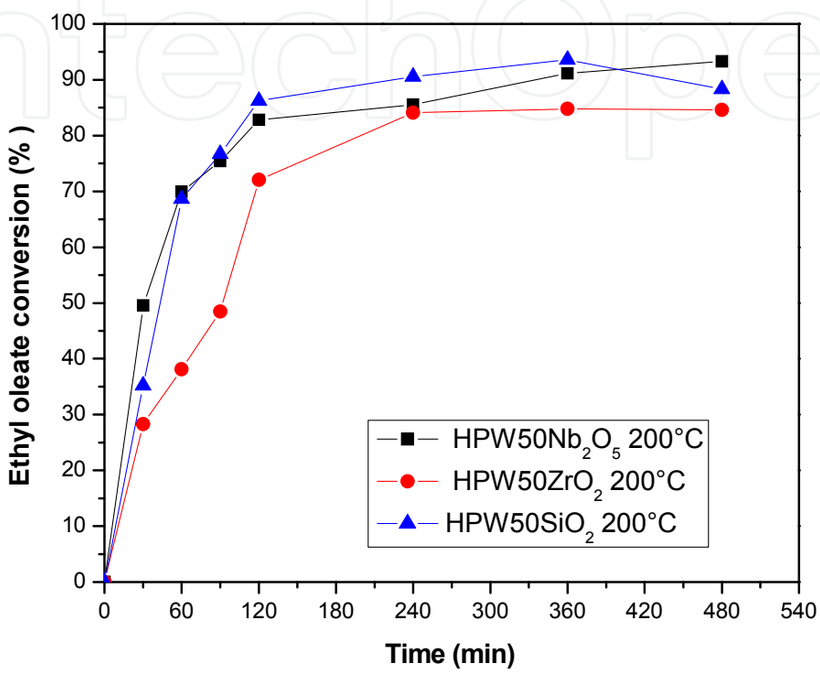


Fig. 4. Scheme of a typical acid solid-catalyzed process of FFA esterification in liquid phase

2.5.2 The effect of support on catalytic activity of HPW composites

The low surface area of solid $H_3PW_{12}O_{40}$, which implies a small amount of H^+ ions available on the surface; for circumvent these problems, three supports with a higher surface area were selected on this study. When solid supported heterogeneous catalyst are prepared, important aspects such as temperature of the thermal treatment, method of synthesis, type and precursor nature and also of the support, besides catalyst loading can affect drastically the efficiency of catalyst (Hattori, 2010).
Herein the temperature of thermal treatment was the parameter selected for an adequate comparison between the catalytic activities of different HPW composites. High temperatures may favor the reduction of support surface area (300 °C) and lower temperatures (100 °C) may favor catalyst leaching when impregnation is synthesis method; for these reasons, the authors selected results obtained with catalyst treated at 200 °C as displayed in Figure 5.
However, another important aspect that can be affected by thermal treatment is the water content on both support and HPW catalyst. All solid supports were completely dried (*ca.* 120 °C) before of the HPW composite synthesis. Conversely, termogravimetry analysis results described in literature (Essayem et al., 1999) revealed that for the zirconium containing HPW, the loss of crystallization water upon the thermal treatment at 120 °C

which retains six water mols per mols Keggin ion. After activation at 200 °C, HPW still retains some crystallization water molecules. (Morim et al., 2007).
The thermal treatment herein employed was the same for all supported-composite; so is reasonable conclude that although not quantitatively determined, water effect act equally onto both composites.



Reaction conditions: oleic acid (1.0 mmol); ethanol (155.0 mmols); catalyst (50.0 mg); 60 °C

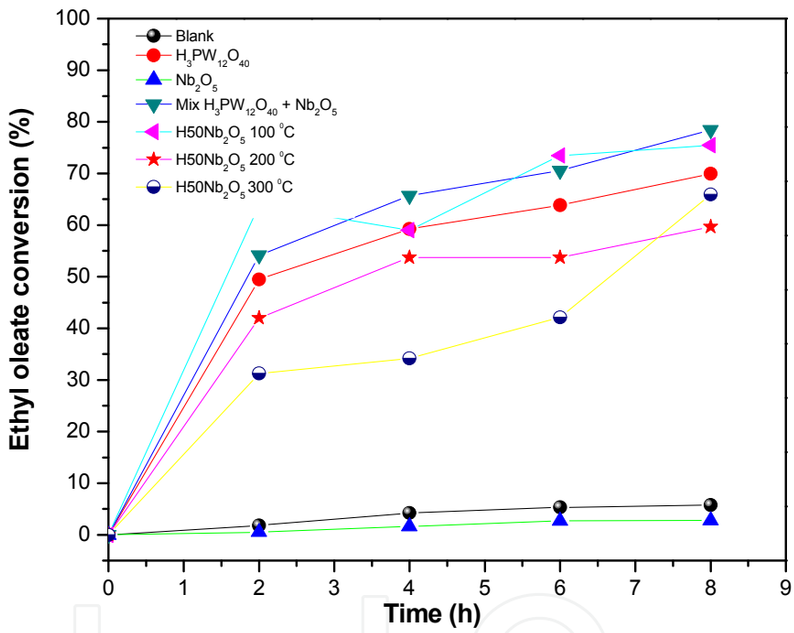
Fig. 5. Oleic acid esterification with ethanol catalyzed by HPW 50% w/w composites supported on niobium, zirconium and silicon treated at 200 °C temperature

The HPW 50% w/w/niobium composite is strongest Lewis acid support; nevertheless, Figure 5 reveals the all catalyst have a very close behavior. The HPW/Nb_2O_5 composite was the catalyst selected to assess the effects of others reaction parameters because there are scarce data on literature; moreover, as will showed it was the catalyst more efficient and less leached in reactions. All results obtained on HPW/niobium-catalyzed oleic acid esterification with ethanol are highlighted in next sections.

2.5.3 Temperature effects of the thermal treatment on catalytic activity of the HPW/niobium composites

The esterification of oleic acid with ethanol conducted in the absence of the acidic catalysts (HPW) produced no significance yields of the corresponding ethyl oleate in spite of the high molar ratio of ethanol/oleic acid used. For instance, only a very low oleic acid to ethyl oleate conversion (*ca*. 10%) was achieved even after a reaction time as long as 8 h (Figure 6). Moreover, despite Lewis acidity of the support, when in presence only of niobium, a poor conversion of oleic acid into ethyl oleate was also reached (Figure 6).

Conversely, in the presence of $H_3PW_{12}O_{40}$ pure or niobium-supported and after a reaction time of 8 h much greater yields (*ca*. 86%) were attained, as concisely displayed in Figure 5. In all reactions, a high selectivity for the ethyl oleate greater than 90 % (analysis) was achieved, determined by GC analyses (no showed herein). Investigating the performance of supported HPW can be observed that the best and worst results were obtained when the HPW/niobium composites were treated at 100 and 300 °C temperatures. A possible leaching of catalyst (see next section) and the reduction of surface area provoked by high temperature of thermal treatment may be reasonable explanations.
On the other hand, the highest conversion was obtained when a mechanic mixture of niobium and $H_3PW_{12}O_{40}$ was used, probably due the simultaneous presence of the first and second catalyst; this later soluble and consequently more reactive (Lewis and Brønsted acids respectively).

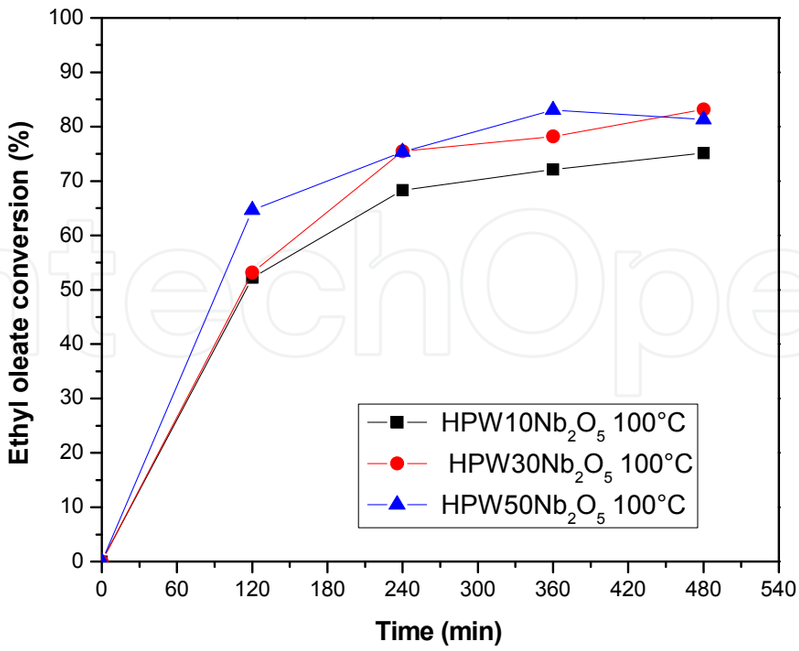


Reaction conditions: catalyst (50.0 mg); oleic acid (1.0 mmol); ethanol (155.0 mmols); 60°C.

Fig. 6. $H_3PW_{12}O_{40}/Nb_2O_5$-catalyzed oleic acid esterification with ethanol

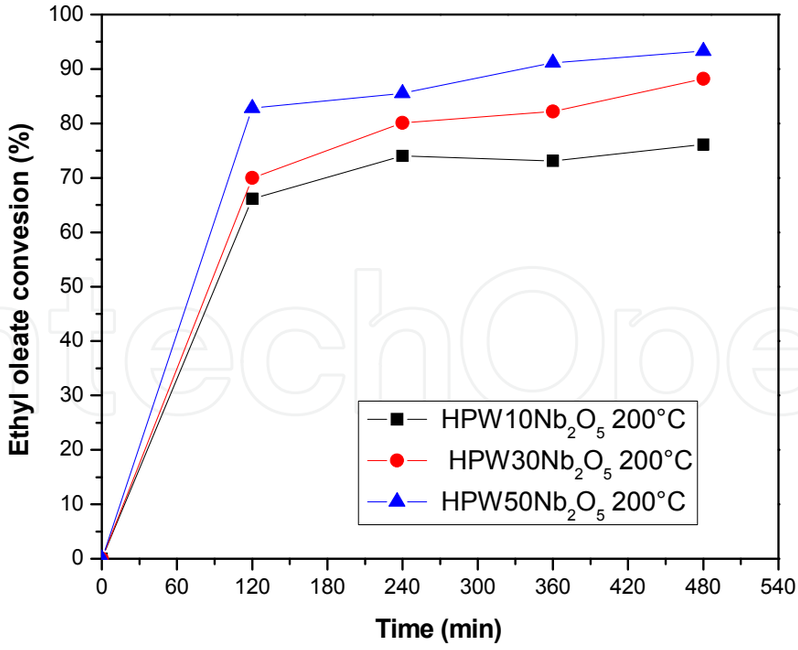
2.5.4 The effect of HPW loading on catalytic activity of the HPW/niobium composites

In many cases, there are obvious approaches to improving and optimizing the yielding of catalytic reactions. Among the mains, is highlighted an increase on amount of reactants and of the catalyst. Recognized, the catalyst load can affect remarkably the efficiency of catalyst. Kinetic curves obtained from HPW/niobium-catalyzed esterification reactions with loads of HPW equal to 10, 30 and 50 % w/w respectively are shown in Figures 7-9. Because the temperature used on the thermal treatment may also affect both stability and activity of catalyst, three results obtained at three different temperatures are reported.



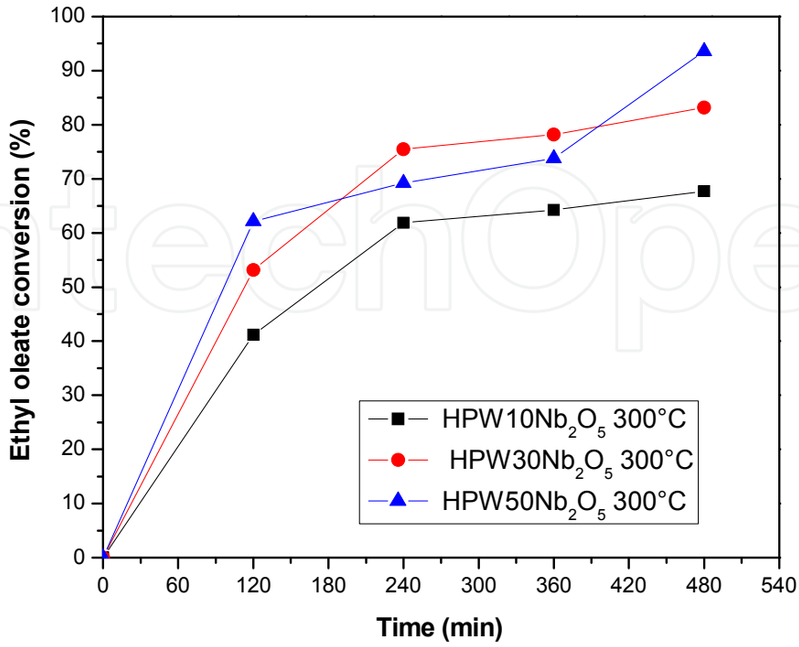
Reaction conditions: catalyst (50.0 mg); oleic acid (1.0 mmol); ethanol (155.0 mmols); 60°C.

Fig. 7. Effect of the HPW load on HPW/Nb_2O_5-100 °C-catalyzed oleic acid esterification with ethanol



Reaction conditions: catalyst (50.0 mg); oleic acid (1.0 mmol); ethanol (155.0 mmols); 60°C.

Fig. 8. Effect of the HPW load on HPW/Nb_2O_5-200 °C-catalyzed oleic acid esterification with ethanol



Reaction conditions: catalyst (50.0 mg); oleic acid (1.0 mmol); ethanol (155.0 mmols); 60°C.

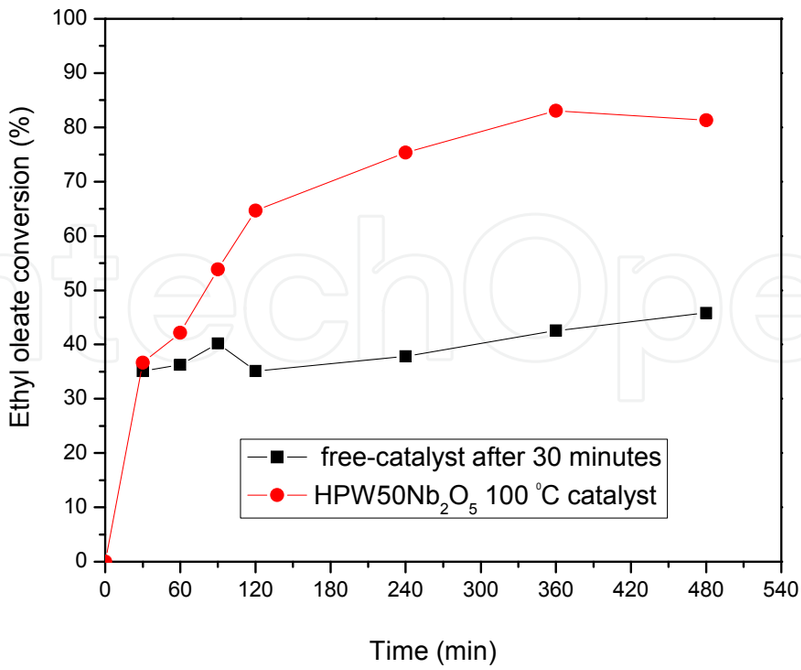
Fig. 9. Effect of the HPW load on HPW/Nb_2O_5-300 °C-catalyzed oleic acid esterification with ethanol

Although literature data described that occur a significance decreases on surface area with an increase of acid content, which may then reduce its catalytic activity (Dias et al., 2003), results displayed in Figures 6 to 8 suggest that a higher HPW load increases the efficiency of HPW/Nb_2O_5 catalyst. Interestingly, it's occurred independently of the thermal treatment employed on synthesis of these catalysts (Figures 7-9).

2.5.5 Evaluating catalyst leaching

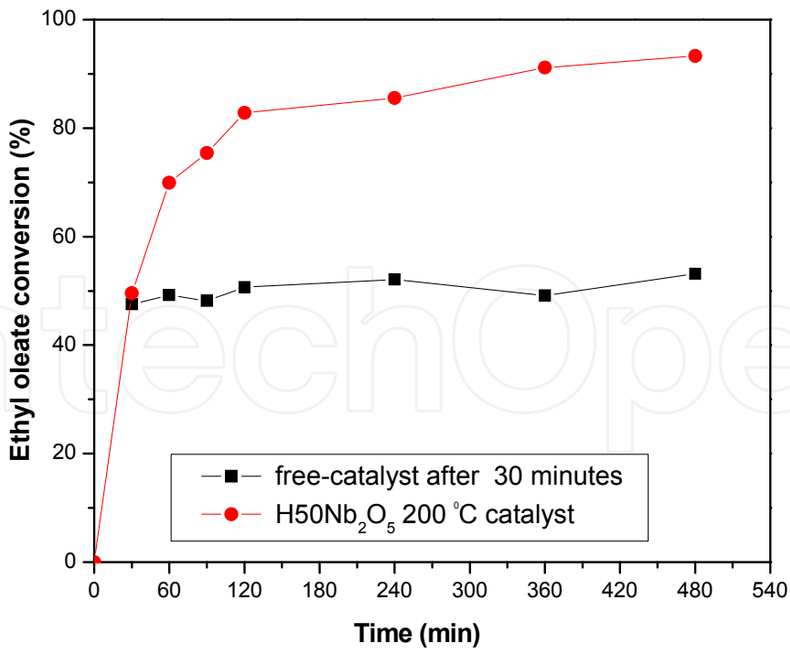
Leaching affects the industrial application as extensive leaching may threaten the reusability and the environmental sustainability of catalyst (Di Serio et al., 2010). Conceptually, catalyst leaching is usually associated with a phase boundary. For example, the active component of an insoluble acid solid catalyst might slowly leach into solution by some mechanism, perhaps involving bond breaking. When the catalyst has leached into a product phase, the sample should exhibit some catalytic activity. Thus, an efficient procedure that allows evaluates if there is any leaching is remove the catalyst out of the reaction and continue to run in your absence. Figures 10 to 12 displayed kinetic curves of reactions catalyzed by HPW/niobium composite before and after its remove.

It was found that the composites obtained at temperatures of 200 or 300 °C, seems be more stable under reactions conditions; noticeably, after catalyst remove the conversion of oleic acid into ethyl oleate remains constant. However, when the catalyst was synthesized at 100 °C, there was an increase in the conversion of oleic acid, suggesting that possibly a part of HPW can has been lixiviated to reaction solution. Interesting, the same occurred for the catalyst supported on zirconium and silicon (Figures 13 and 14).



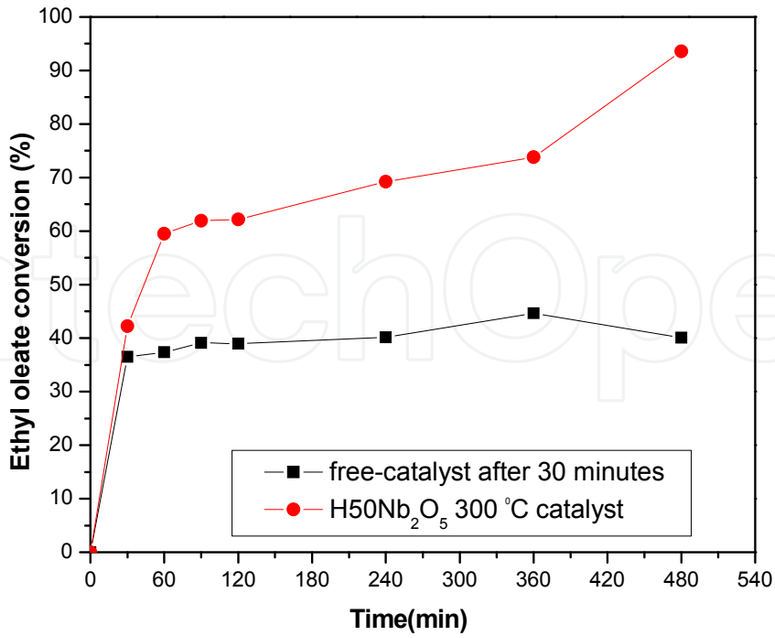
Reaction conditions: catalyst (50.0 mg); oleic acid (1.0 mmol); ethanol (155.0 mmols); 60°C.

Fig. 10. Effect of the HPW leaching on HPW/Nb_2O_5-100 °C-catalyzed oleic acid esterification with ethanol



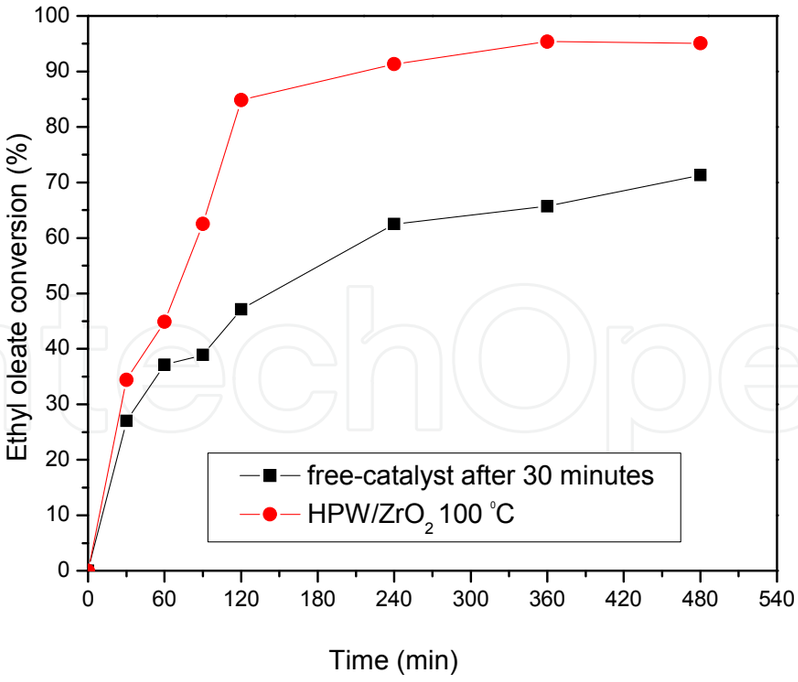
Reaction conditions: catalyst (50.0 mg); oleic acid (1.0 mmol); ethanol (155.0 mmols); 60°C.

Fig. 11. Effect of the HPW leaching on HPW/Nb_2O_5-200 °C-catalyzed oleic acid esterification with ethanol



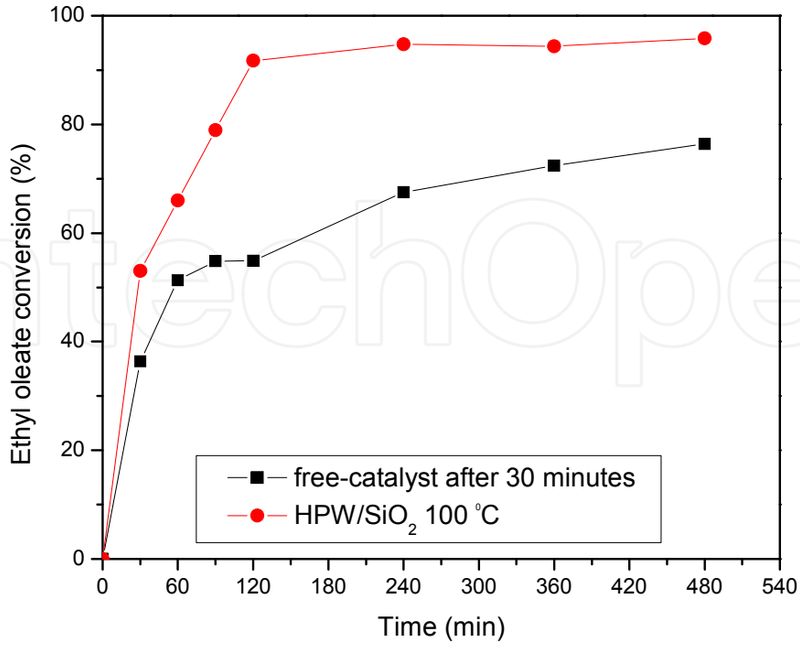
Reaction conditions: catalyst (50.0 mg); oleic acid (1.0 mmol); ethanol (155.0 mmols); 60 °C.

Fig. 12. Effect of the HPW leaching on HPW/Nb_2O_5-300 °C-catalyzed oleic acid esterification with ethanol



Reaction conditions: catalyst (50.0 mg); oleic acid (1.0 mmol); ethanol (155.0 mmols); 60 °C

Fig. 13. Effect of the HPW leaching on HPW/ZrO_2-100 °C-catalyzed oleic acid esterification with ethanol



Reaction conditions: catalyst (50.0 mg); oleic acid (1.0 mmol); ethanol (155.0 mmols); 60 °C

Fig. 14. Effect of the HPW leaching on HPW/SiO_2-100 °C-catalyzed oleic acid esterification with ethanol

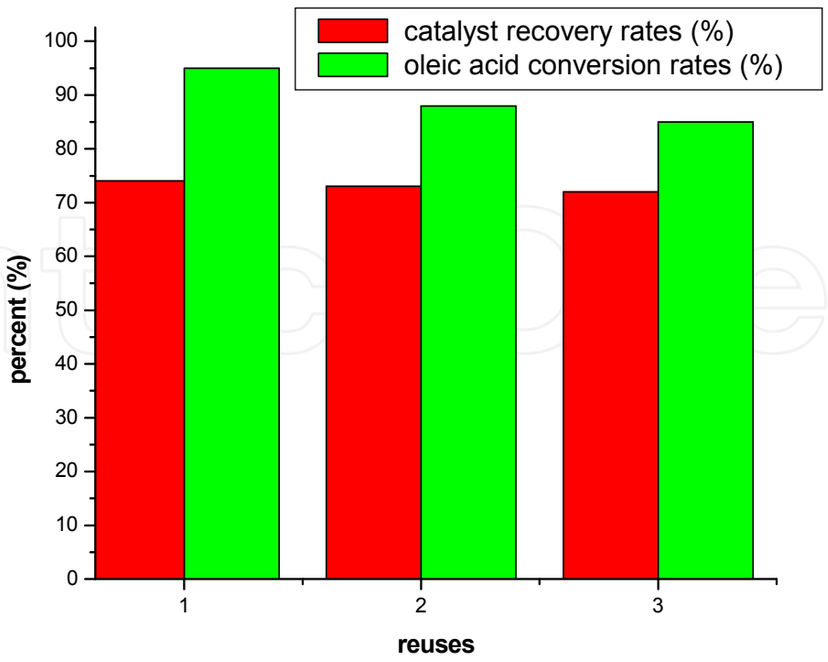
Various measures of catalyst leaching must be interpreted based in others contexts. For example, atomic absorption spectroscopy and ICP–MS are very sensitive analytical methods. However, a simple qualitative procedure can be used based only on visual observation; the addition of ascorbic acid to a solution containing HPW soluble assume blue color. Herein, its procedure allows easily confirm the catalyst leaching treated at 100 °C temperature; contrarily, in the runs with HPW/niobium-200 °C catalyst the solution remained with color unaltered (pale yellow).

2.5.6 Recovery and reuse of catalyst

The greatest advantage of the heterogeneous goal of this study over the homogeneous catalyst is the prolonged lifetime of the solid catalyst for ethyl esters production. However, leaching of catalyst components can cause its deactivation quickly. Herein, the stability of HPW 50 % w/w/niobium-200 °C after successive protocols of recovery/reuse was assessed (Figure 15). The recovery yields of solid catalyst isolated from procedure of filtration are most commonly determined gravimetrically.

A remarkable result was observed as the HPW/niobium catalytic activity stayed almost unaltered even after three recovery/reutilization cycles. However, it should be noted that a weights of catalyst fresh (ca. 20% in relation to started weight).

It was found that although recovery rate has been kept constant (*ca.* 72-75 %) in all catalytic runs, its suggest that the catalyst leach to solution; however, in Figures 10 to 12 it was demonstrated that oleic acid conversion remains unaltered after catalyst remove. This observation suggests an absence of leaching of catalyst. Probably, the procedure used is not efficient as desired.



[a]Reaction conditions: catalyst (50.0 mg); oleic acid (1.0 mmol); ethanol (155.0 mmols); 60 °C
[b]Rates recovery calculated from initial catalyst mass
[c]In all runs fresh catalyst was added to reaches 50.0 mg mass

Fig. 15. Recovery Yields of HPW 50% w/w/niobium catalyst obtained by the filtration[a,b,c] procedures and oleic acid conversion rates obtained from its esterification with ethanol

The procedure employed for catalyst recovery involves its separation from reaction by filtration, washed with ethyl ether and drying at 100 °C; then the catalyst has its mass determined. Losses of mass through of these several steps may be occurring. A more detailed treatment of the recovery procedure of catalyst may lead to efficient methods, which can reaches higher recovery rates. The authors are developing studies on this direction.

2.5.7 Mechanistic insights

Tunstophosphoric acid ($H_3PW_{12}O_{40}$) is strongest heteropolyacid of Keggin series being completely ionizable in water. Measurements of pKa in organic solvents showed that it is 100 units of pka more acid than sulfuric acid (Kozhevnikov, 1998); therefore is almost probably that its ionization in ethanol occur in greater extension. Thus, is possible that HPW/niobium catalyst undergoes at least a partial ionization along oleic acid esterification reaction in ethanol as described on equilibrium displayed in Figure 16.

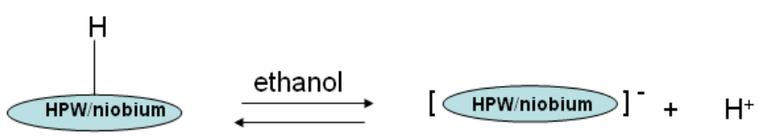


Fig. 16. Partial ionization equilibrium of HPW/niobium catalyst in ethanol solution

Consequently, if this part of the reaction pathway is similar to homogeneous systems, the others steps commonly involved in esterification reactions (e.g. protonation carbonyl group FA, attack of the alcohol molecule on protonated FA, water elimination, etc) may then proceed as described in Figure 16.

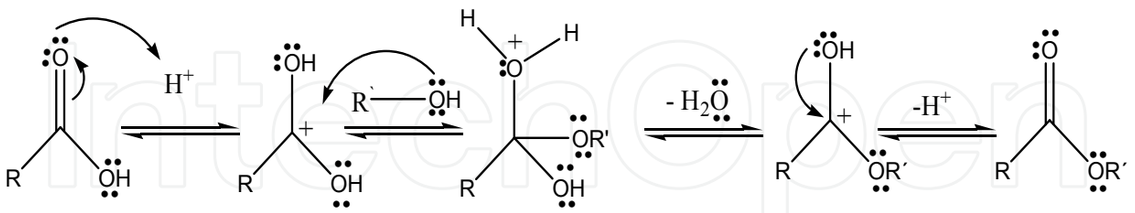


Fig. 17. Mechanism of formation ester catalyzed by free H^+ ion in solution

Conversely, is also possible that other FA molecules can be activated via protonation on surface of supported-catalyst. Thus, an alternative proposal is displayed in Figure 18.

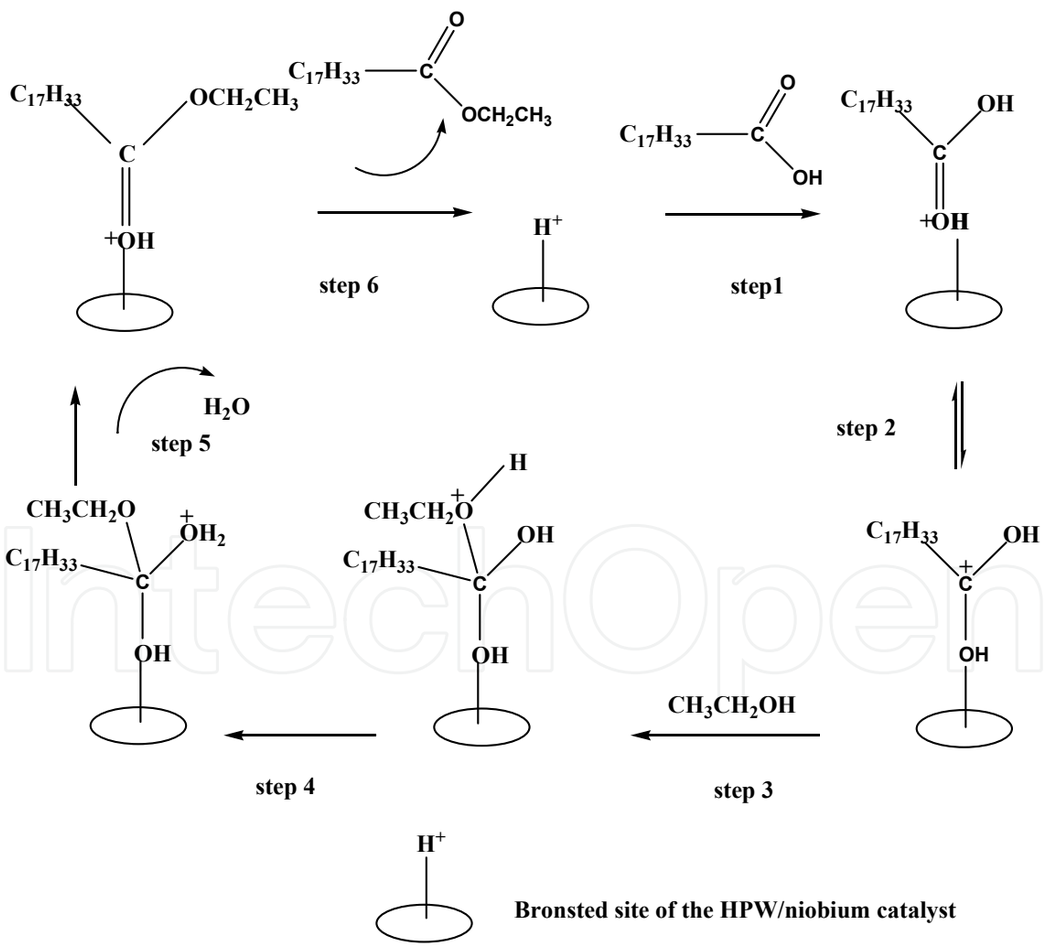


Fig. 18. Proposal of an alternative mechanism of formation ester catalyzed by free H^+ ion in the solution

In according with this mechanism (Figure 18), all steps of oleic acid esterification reaction with ethanol occur on surface of HPW/niobium catalyst. Nevertheless, is also possible that ethyl oleate formation may occur by both pathways of reaction Although both proposal are plausible, is important to note that studies in situ are require for a better and more detailed description of these mechanism of this reaction.

3. Conclusion

The efficiency of tungstophosphoric acid ($H_3PW_{12}O_{40}$) immobilized by impregnation method on silicon, zirconium and niobium oxides was assessed in the esterification of oleic acid with ethanol, at 60 °C temperature. As a general tendency, it was observed that the catalytic activity decreases in the series HPW/Nb_2O_5 > HPW/ZrO_2> HPW/SiO_2 with all catalyst being treated on temperature range 100 to 300 °C. Moreover, good yielding of recovery of HPW 50% w/w/Nb_2O_5 catalyst (*ca*. 75 %) and high conversions of acid oleic were obtained in recycle experiments. From leaching tests and of the rates of recovery may be concluded that the HPW/Nb_2O_5 catalysts are stable under reaction conditions used; however the recovery procedure employed it should be enhanced. Thus, it can be concluded that although yet non-finished, present methodology offers several advantages such as high yields, simple procedure for recovery and reuse of catalyst and mild reaction conditions.
The authors hope that with this work a significant advance on the field of recoverable catalysts can has been proved.

4. Acknowledgment

The Federal University of Viçosa, Federal University of Uberlândia and Arthur Bernardes Foundation are warmly thanked for financial support. Moreover, CAPES, CNPq and FAPEMIG deserves our special thanks.

5. References

Anton, A. K.; Alexandre, C. D.; & Gadi, R. (2006) Solid Acid Catalysts for Biodiesel Production - Towards Sustainable Energy. *Advances Synthesis Catalysis,* Vol.348, pp. 75 – 81

Ayhan D.; Biodiesel A Realistic Fuel Alternative for Diesel Engines; ISBN-13: 9781846289941 2008 Springer-Verlag London Limited

Ayhan, D. (2003). Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey. *Energy Conversion and Management,* Vol.44, (September 2007), pp. 2093–2109, ISSN 0196-8904

Cardoso, A.L.; Neves, S.C.G.; & da Silva, M.J. (2009). Kinetic Study of Alcoholysis of the Fatty Acids Catalyzed by Tin Chloride(II): An Alternative Catalyst for Biodiesel Production. *Energy Fuels,* Vol.23 (January 2009), No. 3, pp. 1718–1722, ISNN 0887-0624

Chongkhong, S.; Tongurai, C.; Chetpattananondh, P. (2009). Continuous esterification for biodiesel production from palm fatty acid distillate using economical process. *Renewable Energies,* Vol.34, (April 2009), pp.1059– 1063, ISSN 0960-1481

Di Serio, M.; M. Cozzolino, M. Giordano, R. Tesser, P. Patrono, & E. Santacesaria. (2007). From Homogeneous to Heterogeneous Catalysts in Biodiesel Production. *Industrial Engineering Chemistry Researches* Vol.46, (August de 2007), pp 6379–6384, ISNN 0088-5885

Di Serio, M.; Tesser, R.; Casale, L.; D'Angelo, A.; Trifuoggi, M. & Santacesaria, E., (2010). Heterogeneous catalysis in biodiesel production: The influence of leaching. *Topics in Cataysis,* Vol.53 (July 2010), pp.811-819 ISNN 1022-5528

Di Serio, M.; Tesser, R.; Pengmei, L.; & Santacesaria, E. (2008) Heterogeneous Catalysts for Biodiesel Production. *Energy and Fuels,* Vol.22, (December 2007), pp. 207–217, ISSN 0887-0624

Essayem, N.; Coudurier, G.; Vedrine, J.C.; Habermarcher, D.; Sommer, J. (1999). Activation of Small Alkanes by Heteropolyacids, a H/D Exchange Study: The Key Role of Hydration Water. *Journal of Cataysis,* Vol.183, (April 1999), pp. 292-299, ISSN 00219517

Haas, M. J . (2005). Improving the economics of biodiesel production through the use of low value lipids as feedstocks: vegetable oil soapstock. *Fuel Processing Technologies,* Vol.86, (June 2005), pp. 1087–1096, ISNN: 0378-3820

Hideshi H. (2010). Solid Acid Catalysts: Roles in Chemical Industries and New Concepts. *Topics in Catalysis,* Vol.53, (June 2010), pp.432–438, ISNN 1022-5528

Kawashima, A.; Matsubara, K.; Honda, K. (2008). Development of heterogeneous basecatalysts for biodiesel production. *Bioresource Technology,* Vol.99, pp. 3439–3443, ISNN 0960-8524

Kozhevnikov I.V. (1998). Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions. *Chemical Reviews,* Vol.98, (February 1998), No.1, pp.171–198

Kozhevnikov, I.V. J. (2009) Heterogeneous acid catalysis by heteropoly acids: approaches to catalyst deactivation. *Journal of Molecular Catalysis A,* Vol.305, (june 2009), pp. 104–111, ISNN 1381-1169

Kulkarni, M. G.; Gopinath, R.; Meher, L.C.; & Dalai, A. K. (2006). Solid Acid Catalyzed Biodiesel Production by Simultaneous Esterification and Transesterification. *Green Chemistry,* Vol.8, (September 2006), pp. 1056–1062, ISSN 1463-9262

Lotero E.; Liu, Y.; Lopez, D. E.; Suwannakarn, K.; Bruce, D. A. & Goodwin, J. G. (2005) Synthesis of biodiesel via acid catalysis. *Industrial Engineering Chemistry Researches,* Vol.44, (January 2005), pp. 5353–5363, ISNN 0088-5885

Lou, W. Y.; Zong, M. H.; & Duan ,Z. Q. (2008). Efficient production of biodiesel from high free fatty acid-containing waste oils using various carbohydrate-derived solid acid catalysts. *Bioresource Technology* Vol.99, (December 2008), pp. 8752–8758, ISNN: 0960-8524

Maa, F.; & Hanna, M.A. (1999). Biodiesel production—a review. *Bioresource Technology,* Vol.70, (February 2007), pp. 1–15, ISSN 0960-8524

Makoto M.; Izumi O.; Gaku K.; & Atsushi A. (2000). Heteropolyacids. Versatile green catalysts usable in a variety of reaction media. *Pure Applied Chemistry,* Vol. 72, No. 7, pp. 1305-1311, ISSN 0033-4545

Marchetti, J. M.; Miguel, V. U.; & Errazu A. F. (2007). Possible methods for biodiesel productions. *Renewable Sustainable Energies Reviews,* Vol.11, pp.1300- 1311, ISSN 1364-0321

Morin, P. B.; Hamad, G.; Sapaly, M. G.; Carneiro, R.; Pries, P.G. O.; Gonzalez, W. A.; Sales, A. E.; Essayem, N. (2007). Transesterification of rapeseed oil with ethanol I. Catalysis with homogeneous Keggin heteropolyacids. *Applied Catalysis A: General,* Vol. 330, (October 2007), pp. 69–76, ISSN: 0926-860X

Oliveira, C. F, Dezaneti, L. M.; Garcia, F. A. C.; Macedo, J. L.; Dias, J. A.; Dias, S. C. L.; Alvim, K. S. P. (2010). Esterification of oleic acid with ethanol by 12-tungstophosphoric acid supported on zirconia. *Applied Catalysis A: General,* Vol.372, (January 2010), pp. 153–161, ISSN: 0926-860X

Patil, P.D.; & Deng. (2009) Optimization of biodiesel production from edible and non-edible vegetable oils. *Fuel,* Vol.88, pp. 1302–1306. ISSN 00162361

Pizzio, L. R.; Caceres, C. V.; Blanco, M. N. (1998). Acid catalysts prepared by impregnation of tungstophosphoric acid solutions on different supports. *Applied Catalysis A: General,* Vol.167, (February 1998,) pp.283-294, ISSN: 0926-860X

Pope, M.T. *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, 1983. ISBN 3-540-11889-6

Prasad, R; & Srivastava, A. (2000). Triglycerides-based diesel fuels. Renewable and Sustainable *Energy Reviews,* Vol.4, (July 1999), pp. 111-133, ISSN 1364-0321

Rajabathar, J.; & Ming K. W. (2009). Review of Recent Developments in Solid Acid, Base, and Enzyme Catalysts (Heterogeneous) for Biodiesel Production via Transesterification. *Industrial Engineering Chemistry Researches,* Vol.*48,* No.13, pp. 6162–6172, ISNN 0088-5885

Rattanaphra, D.; Harvey, A. & Srinophakun, P. (2010). Simultaneous Conversion of Triglyceride/Free Fatty Acid Mixtures into Biodiesel Using Sulfated Zirconia. *Topics in Catalysis,* Vol.53, (March 2010), pp.773–782, ISNN 1022-5528

Sakai, T.; Kawashima, A.; & Koshikawa, T. (2009). Economic assessment of batch biodiesel production processes using homogeneous and heterogeneous alkali catalysts. *Bioresource Technology* Vol.100, (July 2009), pp.3268–3276, ISSN 0960-8524

Sepulveda, J.H.; Yori, J.C.; Vera, C.R. (2005). Repeated use of supported $H_3PW_{12}O_{40}$ catalysts in the liquid phase esterification of acetic acid with butanol. *Applied Catalysis A: General,* Vol.288, (July 2005), pp.18–24, ISNN: 0926-860X

Shuli Y. C. D.; Siddharth, M.; Manhoe K.; Steven O. S.; & Simon, K. Y. N. (2010). Advancements in Heterogeneous Catalysis for Biodiesel Synthesis. *Topics in Catalysis,* Vol.53, (July 2010), pp.721–736, ISNN 1022-5528

Silva, G. W. V.; Lair, O. L.;, da Silva, J. M. (2011). Novel $H_3PW_{12}O_{40}$ Catalysed Esterification Reactions of Fatty Acids at Room Temperature for Biodiesel Production. *Catalysis Letters*, Vol.135 (January 2010), pp.207-211, ISSN: 1011-372X

Silva, M. L.; Figueiredo A. P.; Cardoso, A. L.; Natalino, R.; da Silva, M. J. (2011) Effect of Water on the Ethanolysis of Waste Cooking Soybean Oil Using a Tin(II) Chloride Catalyst. *Journal American Oil Chemisty Society*, Vol. 88, (march 2011), pp.1431-1437, ISSN 0003-021X

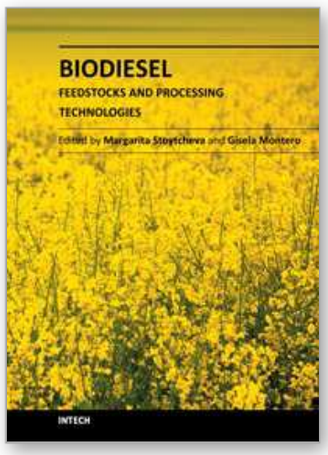
Sunita, G; Devassy, B.M.; Vinu, A.; Sawant, D.P.; Balasubramanian, V.V.; & Halligudi, S.B. (2008). Synthesis of biodiesel over zirconia-supported isopoly and heteropoly tungstate catalysts. *Catalysis Communications,* Vol.9, (March 2008), pp.696-702, ISSN: 1566-7367

Timofeeva, M.N. (2003). Acid catalysis by heteropoly acids. *Applied Catalysis A: General,* Vol.256, (December 2003), pp.19–35, ISNN 0926-860X

Timofeeva, M.N.; Matrosova M.M.; Ilinich, G.N.; Reshetenko, T.V.; Avdeeva, L.B.; Kvon R.I,.; Chuvilin A.L.; Budneva,. A.A.; Paukshtis, E.A.; Likholobov, V.A . (2003). Esterification of n-butanol with acetic acid in the presence of $H_3PW_{12}O_{40}$ supported on mesoporous carbon materials. *Kinetic Catalysis* Vol.44, (November 2003) No.3, pp.778–787, ISSN 0023-1584

Yogesh C. S.; & Bhaskar S. (2011). Advancements in solid acid catalysts for ecofriendly and economically viable synthesis of biodiesel. *Biofuels, Bioproduts Biorefinerie,* Vol.5, (September 2010), pp. 69–92, ISSN 1932-104X

Zullaikah, S.; Lai C, C.; Vali, S. R. & Ju, Y.H. (2005). A two-step acid-catalyzed process for the production of biodiesel from rice bran oil. *Bioresource Technology,* Vol.96, (November 2005), pp. 1889–1896, ISNN: 0960-8524



Biodiesel - Feedstocks and Processing Technologies

Edited by Dr. Margarita Stoytcheva

ISBN 978-953-307-713-0
Hard cover, 458 pages
Publisher InTech
Published online 09, November, 2011
Published in print edition November, 2011

The book "Biodiesel: Feedstocks and Processing Technologies" is intended to provide a professional look on the recent achievements and emerging trends in biodiesel production. It includes 22 chapters, organized in two sections. The first book section: "Feedstocks for Biodiesel Production" covers issues associated with the utilization of cost effective non-edible raw materials and wastes, and the development of biomass feedstock with physical and chemical properties that facilitate it processing to biodiesel. These include Brassicaceae spp., cooking oils, animal fat wastes, oleaginous fungi, and algae. The second book section: "Biodiesel Production Methods" is devoted to the advanced techniques for biodiesel synthesis: supercritical transesterification, microwaves, radio frequency and ultrasound techniques, reactive distillation, and optimized transesterification processes making use of solid catalysts and immobilized enzymes. The adequate and up-to-date information provided in this book should be of interest for research scientist, students, and technologists, involved in biodiesel production.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Marcio Jose da Silva, Abiney Lemos Cardoso, Fernanda de Lima Menezes, Aline Mendes de Andrade and Manuel Gonzalo Hernandez Terrones (2011). Heterogeneous Catalysts Based on H3PW12O40 Heteropolyacid for Free Fatty Acids Esterification, Biodiesel - Feedstocks and Processing Technologies, Dr. Margarita Stoytcheva (Ed.), ISBN: 978-953-307-713-0, InTech, Available from: http://www.intechopen.com/books/biodiesel-feedstocks-and-processing-technologies/heterogeneous-catalysts-based-on-h3pw12o40-heteropolyacid-for-free-fatty-acids-esterification

INTECH
open science | open minds

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the Creative Commons Attribution 3.0 License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen