Esterification of oleic acid using 12-tungstophosphoric supported in *flint* kaolin of the Amazonia ☆

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HIGHLIGHTS

▶ Efficient impregnation of supported HPW on kaolin *flint* were in acetonitrile.
▶ Esterification using catalyst with 60 wt% HPW showed better conversion.
▶ Effect of time and temperature were studied for catalyst with 20 wt% HPW.
▶ Esterification of oleic acid reactor was adjusted to apparent first order kinetics.
▶ Assays were performed in a batch reactor whose contact time is the reaction time.

GRAPHICAL ABSTRACT
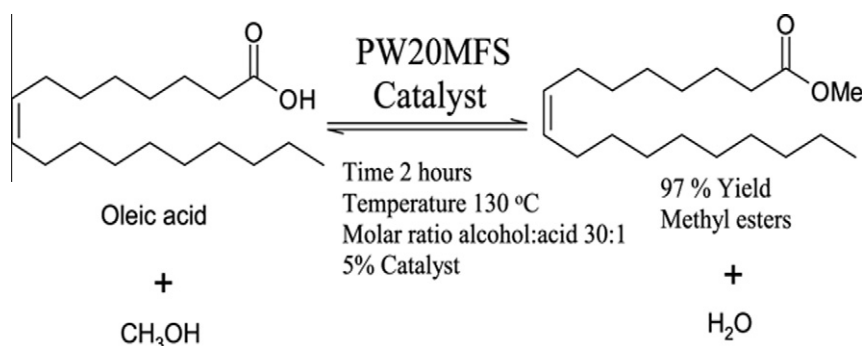
ARTICLE INFO

ABSTRACT

In this study, 12-tungstophosphoric acid was supported in different proportions, 20, 40 and 60 wt%, using as a matrix of the Amazon kaolin *flint* and century (commercial kaolin) via impregnation in aqueous solution (HCl 0.1 and 0.5 mol L^{-1}) and acetonitrile. Before the impregnation, kaolin were subjected to a leaching acid in order to increase surface area and acidity. For characterization of the catalysts, FT-IR, XRD and XRF were employed. The FT-IR analysis showed that there was no decomposition of the HPW Keggin structure during material preparation. However, in the presence of HCl 0.1 mol L^{-1}, it was not possible to conclude that the impregnation was due to the low intensity of the absorptions for the HPW; for the spectra with acetonitrile and HCl 0.5 it was possible to observe them. The XRF and XRD data confirmed these results. The catalysts were tested in the esterification reaction using molar ratio alcohol: acid equal to 30 at 100 °C for 2 h in a PARR 4348 reactor in the presence of different alcohols. Best conversions were obtained with the use of methanol, reaching 97.21% yield, independent of HPW support. A study of reaction parameters, temperature and time with the catalyst PW(20)MFS and 20 wt% concentration of HPW in metakaolin *flint* (with and without acid treatment) was also conducted. It was observed that the catalyst deactivation occurred by coke formation, since leaching was about 2%.

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1. Introduction

Esterification reactions appear to be attractive in the production of biodiesel, especially in use with raw materials containing high levels of free fatty acids (e.g. industrial sludge and waste oil) [1]. Catalysts commonly used are mineral acids, which act in the homogeneous phase [2]. A great alternative to reduce the environmental impact of these acids is heterogeneous catalysis, which can make the production process more viable [2]. The solid type heteropolyacids Keggin series (HPW) offers high thermal stability, high strength and low acid corrosive power. However, pure HPW has a low surface area (1–10 m^2/g), which restricts its use as a solid catalyst in liquid phase reactions [3].

Catalyst support impregnation by HPW in solid matrices with high surface areas has been used to increase the surface area of the solid, making it accessible to a larger number of reactant molecules and, consequently, a more efficient catalyst [3,4]. Examples of such arrays are zeolites [5], zirconia [1], titanium [6], and polymers [7], with silica (SiO_2) as the most widely used. In this case, through interaction of the support with the heteropolyacid, there is the formation of the species ($\equiv SiOH^{2+}$) ($H_2PW_{12}O_{40}^-$) [8], which provides greater strength to the HPW acid than in its pure form [9]. Several studies have shown the impregnation of HPW on media with silica, silica gel [8,10], MCM41 [11] and MCM48 [12]; however, these arrays have high costs, increasing production of the catalyst. Following this line, in the present study HPW was supported on *flint* kaolin, an industry waste kaolin, and in kaolin century, the commercial form of kaolin, as sources of silica [13].

Kaolin *flint* is an aluminosilicate containing source of silica (SiO_2) and alumina (Al_2O_3), small fractions of iron (Fe_2O_3) and titanium (TiO_2) [13]. The high content of octahedral aluminum makes the kaolin resistant to acid attacks; however, the transformation of kaolin into metakaolin between 550 and 960 °C leads to dehydroxylation of the aluminum, iron and magnesium phase octahedral crystalline clay, which makes it more vulnerable to attacks [14–16]. The acid treatment of metakaolin leads to leaching of aluminum, magnesium and iron cations from the layer of tetra and penta coordinated metakaolin, making it more acidic and more superficial [17,18].

In this study, we evaluated the effect of solvent (HCl 0.1 and 0.5 mol L^{-1} and acetonitrile) in the impregnation of HPW in support of metakaolin century and *flint.* We also observe the catalytic activity of the compounds prepared in the esterification of oleic acid.

2. Experimental

2.1. Materials and reagents

Kaolin *flint* was obtained in the region around the Grass River (Pará-Brazil). Century commercial kaolin was used for comparison. Acetonitrile (PA) and HPW were obtained from TEDIA BRAZIL. The hydrochloric acid (HCl, PA) and sulfuric (H_2SO_4, 90%) were purchased from Vetec.

2.2. Preparation of catalysts

The 12-tungstophosphoric acid (HPW) was subjected to heat treatment at 200 °C for 4 h before the impregnation procedure. It was supported on kaolin and *flint* century with levels of 20, 40 and 60% w/w and then investigated in hydrochloric acid solutions and in the organic solvent, acetonitrile. For this purpose, HPW was dissolved in aqueous solutions of HCl 0.1, 0.5 mol L^{-1} and CH_3CN at a ratio of 1 gram of kaolin for every 10 mL of solution. The system

was heated to 80 °C under constant agitation until total evaporation of the solution according to the method of Caliman et al. [19]. The resulting composite was pulverized and dried at 100 °C in an oven for 2 h followed by calcination at 200 °C for 4 h.

2.3. Heat treatment and acid activation of kaolin

Samples of kaolin *flint* (KF) and century (KC) were prepared according to the procedured of Lenard et al. [17] and Nascimento et al. [13]. The samples were subjected to calcination at 960 °C for 2 h, followed by acid treatment with 2 mol L^{-1} H_2SO_4 for 2 h and dried at 400 °C for 2 h.

2.4. Catalytic tests

The esterification reactions were performed using oleic acid in a PARR 4843 reactor. Oleic acid was mixed with different alcohols (methanol, ethanol or propanol) plus 5% of the catalyst (w/w), which was previously activated at 130 °C in a muffle furnace for 2 h. The system was kept under constant agitation at 750 rpm, sufficient for avoiding any external diffusion, with temperatures ranging from 70 to 160 °C and reaction times from 5 to 120 min.

At the end of the reaction, the catalyst was separated by filtration. The percentage conversion of oleic acid in the corresponding ester was estimated by calculating the product of an acid by titration with sodium hydroxide 0.1 mol L^{-1}, according to the following equation [13,24]:

$$X_{ffa} = (a_f - a_i/a_f) \times 100 \tag{1}$$

where a_i and a_f correspond to initial and final acidity of the mixture, respectively, and X_{ffa} is the percentage conversion of oleic acid ester.

2.5. Reuse and leaching of the catalyst

At the end of the esterification, the catalyst PW(20)MFS was collected by filtration and washed with excess methanol. Then, it was dried at 100 °C for 2 h and calcined at 200 °C for 4 h to be further applied in assay esterification. The test concentration of the active phase of the catalyst leaching was conducted by a spectrophotometer in the region UV/VIS equipment in a Shimadzu Model UV-1650PC with scanning 200–800 nm and resolution of 1 nm.

2.6. Analysis of infrared (FT-IR)

The FT-IR spectra of the catalysts were obtained in a Fourier transform spectrometer (Pelkin Elmer FT-IR Spectrum Espectrometer 2000) in the region of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. The samples were analyzed under tablet form containing 1% of the sample with respect to the KBr.

2.7. X-ray diffraction (XRD)

The spectra of X-ray diffraction (XRD) were obtained in the device model Shimadzu XRD-6000. Using the Kα line of copper [Cu (Kα)] (30 kV and 30 mA). The acquisition was made in the range $2\theta = 5–60°$ at a scan rate of 2° min^{-1}.

2.8. Chemical analysis via XRF

The analysis of the oxide content present in the samples was obtained b Spectrometer X-ray Fluorescence (XRF), model RAYNY EDX-700, Shimadzu, voltage 15 kV, current of 320 μA, scan time of 100 min, in atmosphere of air and liquid mode.

2.9. Scanning electron microscopy (SEM)

Scanning electron micrographs were obtained using a microscope FEI-COMPANY, QUANTA 250 model, rated at 20 kV. To improve the conductivity of the samples, they were coated with a thin layer of gold.

3. Results and discussion

3.1. Characterization

Fig. 1 shows the X-ray spectra of kaolin *flint* (KF) not calcined, *flint* kaolin calcined at 960 °C (MF) and metakaolin *flint* treated with 2 mol L^{-1} H$_2$SO$_4$ (MFS). For comparison, the patterns also show samples of the century kaolin (KC) and non-calcined metakaolin century with acid treatment (MCS).

The sample of kaolin *flint* (KF) presented mainly the mineral kaolinite (Al$_2$Si$_2$O$_5$ (OH)$_4$), whose main reflections are located at $2\theta = 12.43°$ and $24.8°$ (Fig. 1a) [13]. The reflections at $2\theta = 26.26°$ and $36.77°$ in the sample are characteristic of the century kaolin minerals quartz and mica, respectively [17,18] (Fig. 1b). The reflection $2\theta = 21.61°$ is indicative of the existence of the mineral goethite, FeO(OH), which was only observed in the sample of kaolin *flint* [13] (Fig. 1). After heat treatment at 960 °C, the spectra of both specimens of kaolin (*flint* and century) (Fig. 1c and d) had low crystallinity and highlighted a small contribution of reflection $2\theta = 25.3°$, which is characteristic of the mineral anatase (TiO$_2$). This is commonly found as an accessory in the region Amazônica [20], confirming the findings of Nascimento et al. [13].

3.2. Effect of solvent on the impregnation of HPW on metakaolins century

The stability of HPW catalysts impregnated into metakaolin *flint* (PW(x)MFS) and metakaolin century steeped in HPW (PW(x)MCS) in the presence of aqueous and organic solvents was evaluated using FT-IR, XRD and FRX. Fig. 2 shows the FT-IR analysis of catalysts impregnated with 20 wt% metakaolin century in HPW prepared in HCl 0.1 and 0.5 mol L^{-1} and in CH$_3$CN: PW(20)MCS. We included the spectra of HPW and metakaolin century (MCS) isolated for confirmation of the Keggin ion in support. In turn, Fig. 3 shows the XRD patterns of the respective samples.

The metakaolin century (MCS) presents absorption around 1100–806 cm^{-1}, which is characteristic of silica absorptions. The absorptions at 974 cm^{-1} may be related to surface OH groups of

Fig. 2. FT-IR spectra of HPW supported on metakaolin century with acid treatment (a) pure HPW, (b) 20 wt% HPW supported on metakaolin with acetonitrile (b) with aqueous acid HCl 0.5 mol L^{-1}, (d) with aqueous acid HCl 0.1 mol L^{-1} and (e) metakaolin century-MCS.
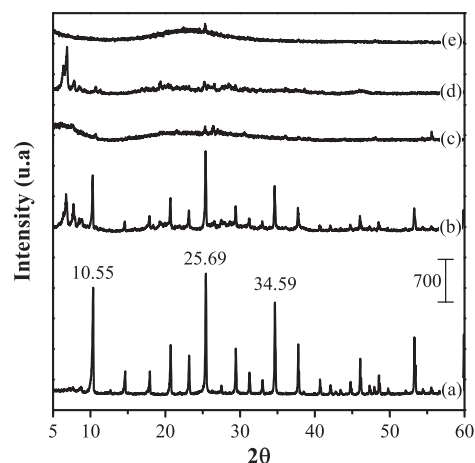
Fig. 3. XRD patterns of HPW supported on metakaolin century with acid treatment (PW(x)MCS): (a) pure HPW, (b) supported HPW with aqueous acid HCl 0.1 mol L^{-1} (c) with acetonitrile; (d) with aqueous acid HCl 0.5 mol L^{-1} and (e) MCS metakaolin century.

silica [21]. For HPW, three typical absorptions appear at 1072 cm^{-1} (P—O), 961 cm^{-1} (W=O) and 884 cm^{-1} (W-Oc-W) [1,8,19].

For HPW supported by 20 wt% metakaolin century with different solvents (Fig. 2a) of the HPW, two absorptions were observed at 961 and 884 cm^{-1}, while the absorption around 1072 cm^{-1} overlapped with the strong absorption of silica (SiO$_2$) of kaolin around 1100 cm^{-1}. These results are consistent with those reported by Kuang et al. [21]. However, when the primers used acetonitrile and aqueous solution with HCl 0.5 mol L^{-1}, the absorptions are typical of those corresponding to the structure of the Keggin ion. Furthermore, in aqueous solution with HCl 0.1 mol L^{-1}, the characteristic bands of HPW are not well visualized, and its spectrum is similar to the spectrum of kaolin.

Fig. 3 shows the XRD patterns of 20 wt% HPW supported with metakaolin century in different solvents. The position and intensity of the main peaks characteristic of HPW are observed in the $2\theta = 10.55, 25.69$ and $34.59°$ [1,8]. The purpose of the XRD analysis was to confirm that the HPW presented in the crystalline form or dispersed when supported. The results demonstrate the HPW in crystalline form with HCl 0.1 mol L^{-1} and low intensity using
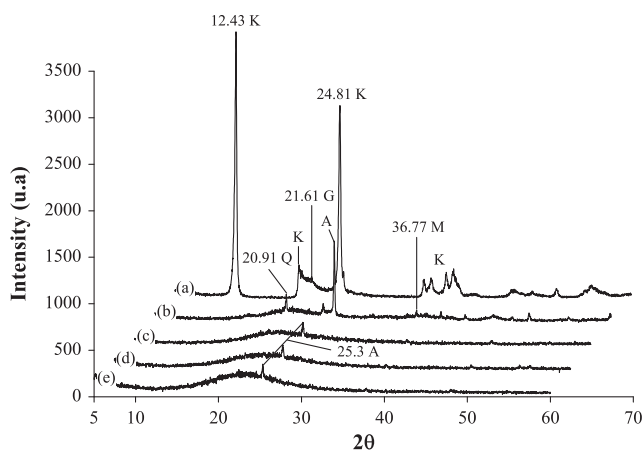

Fig. 1. X-ray patterns: (a) non-calcined kaolin *flint*-KF (b) non-calcined kaolin-century KC (c) calcined metakaolin *flint*-MF, (d) acid-treated metakaolin *flint*-MFS and (e) metakaolin century acid treated-MCS.
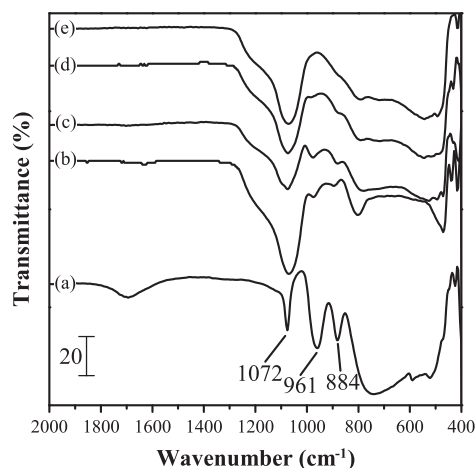
Table 1
XRF chemical composition of the HPW, metakaolins century media (MC) and *flint* (MF), with acid treatment (MCS,) (MFS), respectively, and the catalysts supported HPW on metakaolin century with aqueous HCl 0.1 mol L^{-1} (PW(20)MCS0.1); supported HPW on metakaolin century with aqueous HCl 0.5 mol L^{-1}(PW(20)MCS0.5); supported HPW on metakaolin century with acetonitrile (PW(20)MCSA), supported HPW on metakaolin *flint* with aqueous HCl 0.1 mol L^{-1} (PW(20)MFS0.1) and supported HPW on metakaolin *flint* with acetonitrile solution (PW(20)MFSA).

Catalisadores	SiO$_2$	Al$_2$O$_3$	WO$_3$	P$_2$O$_5$	TiO$_2$	Fe$_2$O$_3$	SO$_3$	ZrO$_2$	Si/Al
HPW	–	–	98.31	1.413	–	–	–	–	–
MC	48.18	49.57	–	–	1.089	0.913	–	0.036	1.21
MCS	93.62	4.173	–	–	2.036	0.134	–	0.033	
MF	47.87	49.33			2.333	10.33			1.23
MFS	84.53	8.118	–	–	6.091	0.529	0.379	0.336	12.58
PW(20)MCS0.1	35.10	41.41	20.33	–	1.014	0.779	0.296	0.075	1.06
PW(20)MCS0.5	25.66	46.594	15.57		1.071	0.870	0.195	0.045	0.901
PW(20)MCSA	39.28	39.27	17.45	0.204	2.343	1.373	0.001	–	1.69
PW(20)MFS0.1	36.14	8.092	20.83	–	6.868	0.700	0.471	0.899	5.57
PW(20)MFSA	54.45	5.750	22.34	–	6.079	–	0.362	0.714	11.58

solutions with acetonitrile or aqueous HCl 0.5 mol L^{-1}, indicating a qualitatively good dispersion in the support for the metakaolin century.

Table 1 presents the results of the chemical composition by XRF in the HPW metakaolin (century or *flint*) with and without acid treatment, impregnated in the presence of aqueous solutions (HCl 0.1 and 0.5 mol L^{-1}) and acetonitrile (CH$_3$CN).

The metakaolin century without acid treatment (MC) showed alumina 49.57% and silica 48.18%. The composition of *flint* kaolin (MF) is similar to that of the century, with 41.34% and 44.35%, respectively [13,20]. In both metakaolins (century and *flint*), there is an increased percentage of silica relative to alumina, the treatment with acid (H$_2$SO$_4$ 2 mol L^{-1}), justified by the aluminum leaching process as tetra and pentacoordinated [13].

According to several literatures [13,17,18,20], the process makes them more acidic media, increasing their acid sites with a ratio of silica/alumina in a ratio close to 12 [17]. In impregnation metakaolin century and *flint* (MCS and MFS) both with aqueous acid (HCl 0.1 and 0.5 mol L^{-1}) was significantly lower in the ratio Si/Al support, from 12.58 to 1.06, which makes media sites with lower acid, unlike the situation where the HPW was impregnated with acetonitrile, where the grounds Si/Al media were kept almost. Based on analysis of the solvent effect, the kaolin was impregnated with HPW in levels of 20, 40 and 60 wt% acetonitrile solution; with support for the kaolin *flint*, impregnation was evaluated without acid treatment (MF) and treatment acid (MFS).

With levels of 20, 40 and 60 wt% of HPW in the media using acetonitrile as solvent, Fig. 4 shows the XRD patterns of HPW supported on acid-treated metakaolin century PW(x)MCS; Fig. 5, on
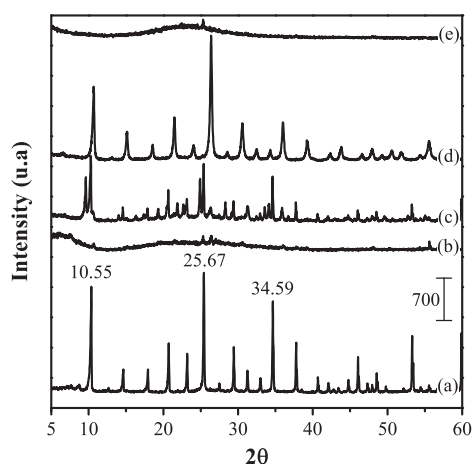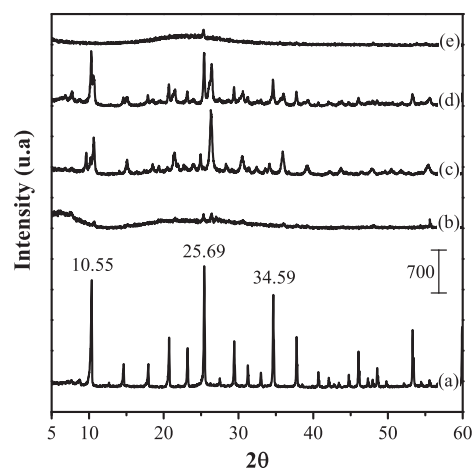

Fig. 5. XRD patterns of HPW supported on metakaolin *flint* with acid treatment PW(x)MFS: (a) PW, (b) PW(20)MFS, (c) PW(40)MFS, (d) PW(60)MFS and (e) MFS.
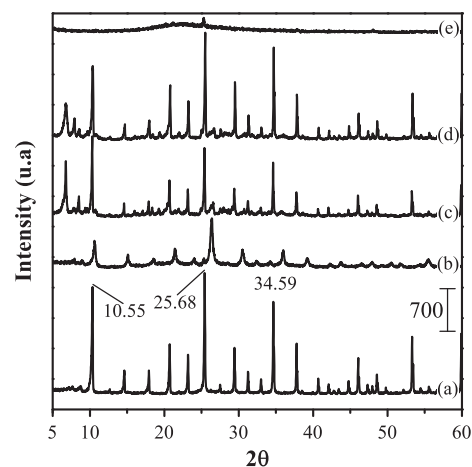

Fig. 6. XRD patterns of HPW supported on metakaolin *flint* without with acid treatment PW(x)MF: (a) HPW, (b) PW(20)MF, (c)PW(40)MF, (d) PW(60)MF and (e) MF.

Fig. 4. XRD patterns of HPW impregnated by kaolin century PW(x)MCS: (a) PW, (b) PW(20)MCS, (c) PW(40)MCS, (d) PW(60) and MCS (e) MCS.

acid-treated metakaolin *flint* PW(x)MFS; and Fig. 6, on metakaolin *flint* PW(x)MF without acid treatment.

The reflections at 2θ = 10.55, 25.67 and 34.59° indicate the presence of the crystalline phase of HPW [1,8,20]. The sample PW(20)MCS (Fig. 4b) shows signs with very low intensity of the HPW indicating a possible spread on the support, however, as the HPW content increases to 40% (Fig. 4c) and 60% (Fig. 4d), reflections

$2\theta = 10.3°$ and $25.3°$ are identified, respectively, indicating the presence of crystalline phase in support of HPW. Similar results were obtained when the HPW impregnated on kaolin *flint* in acid treatment (Fig. 5). However, the HPW presented in the same crystalline form from the content of 20 wt% impregnated in the support (Fig. 6b); this result may be related to the low surface area of metakaolin *flint* without acid treatment (MF) near 24 m^2/g [17]. Blasco et al. came to similar conclusions, investigating the impregnation of HPW supported on molecular sieves MCM41 type with surface area (1024 m^2/g) and silica SiO$_2$ with surface area (137 m^2/g) [11].

3.3. Scanning electron microscopy (SEM)

To verify the crystalline formation or spread of HPW, Fig. 7 shows the images obtained by scanning electron microscopy (SEM) sample of kaolin *flint* (Fig. 7a), the metakaolin *flint* with acid treatment (Fig. 7b), the HPW (Fig. 7c) and related catalysts prepared with HPW in acetonitrile, PW(x)MFS, x = 20 wt% (Fig. 7d), 40 wt% (Fig. 7e) and 60 wt% (Fig. 7f).

The micrograph of kaolin *flint* (KF) (Fig. 7a) was formed mainly by stacking particles without shape using a pseudo-hexagonal morphology. The general appearance of the flint metakaolin (MFS) (Fig. 7b) is a cluster of particles with rough surfaces, without shape and porosity related to the spaces between these agglomerates [13]. For the HPW, the micrograph shows a rough surface with clusters of particles and glans forms of balls with some cracks and voids between the particles.

Moreover, all concentrations (20, 40 and 60 wt%) of HPW are well dispersed on the surface of metakaolin *flint*. There is a greater tendency for clusters of crystals above 20 wt% [19]. In PW(20)MFS (Fig. 7d), a greater surface roughness of the support (MFS), a distribution of crystals with different sizes and the presence of empty
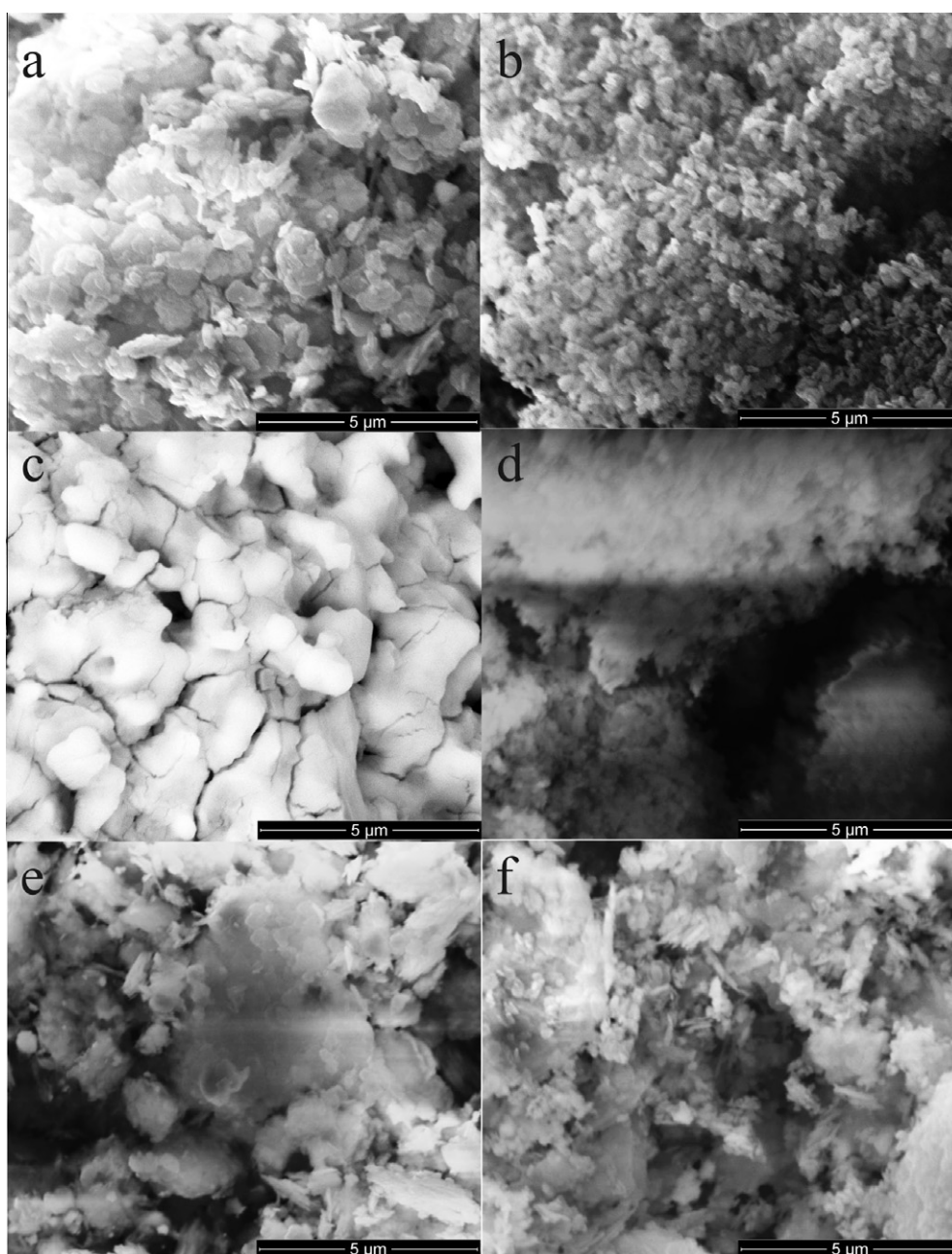

Fig. 7. SEM: (a) KF, (b) MCS, (c) HPW, (d) PW(20)MFS, (e) PW(40)MFS the (f) PW(60)MFS.

spaces between them can be observed. As for PW(40)MFS (Fig. 7e) a smooth surface was associated with some crystals flattened and few empty spaces when compared with the sample PW(20)MFS. The sample PW(60)MFS (Fig. 7d), in turn, shows a greater amount of clusters of crystals that are more elongated and more uniform than in PW(20)MFS and with more clusters of fine crystals than in PW(40)MFS.

3.4. Catalytic test

Testing of catalytic composites in acetonitrile was performed in the esterification of oleic acid using ethanol in the molar ratio alcohol: acid equal to 30 under heating to 100 °C for 2 h. The yield of ester was determined from the acid value of the final product. Figs. 8 and 9 show the results of the conversion of oleic acid into ethyl oleate in the presence of HPW supported on metakaolins century and *flint*.

A low yield of 5.01% was observed without catalyst in the esterification, which confirms that this type of reaction develops very slowly in the absence of an acid catalyst [22]. Similar behavior was observed with the use of MC support (metakaolin century), where the conversion reached only 11.13%. However, the use of metakaolin promoted HPW supported on a good conversion (>63%); this conversion was enhanced with a gradual increase in support of HPW. The catalyst with PW(60)MCS showed the highest activity, which is very close to that presented by HPW in pure form. However, the advantage of the PW(60)MCS in relation to HPW is that it can be removed from the reaction medium more easily.

Similar results were observed for the esterification of oleic acid with catalysts HPW impregnated with kaolin *flint* (Fig. 9). After acid treatment, there was not much difference in the yield of esters, and there was a gradual increase in conversion to oleic acid ethyl ester upon increasing the content of HPW on the support.

3.5. Effect of chain length of alcohol in the esterification

The effect chain length alcohol was studied with catalysts PW(x)MFS after acid treatment as illustrated in Fig. 10.

Higher conversion was achieved using methanol, especially the composite metakaolin *flint* with 20 wt% HPW (PW(20)MFS). This presented up 35% (from 55.51% for 90.01%) income regarding alcohol greater jail propanol. This increase is justified by the greater nucleophilicity of methanol, since a greater number of carbon atoms in propanol reduces its nucleophilicity [13,23]. Indeed,
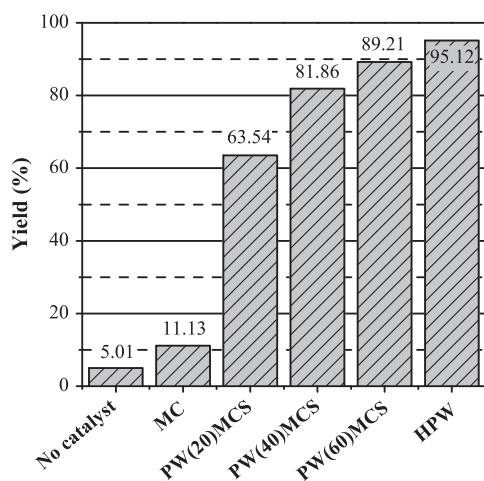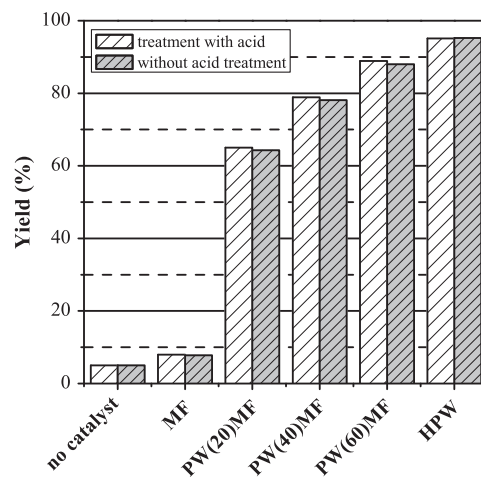
Fig. 9. Conversion of oleic acid catalysts using MFS, MF, HPW and composites, with and without acid treatment PW(x)MF; PW(x)MFS, respectively, with x = 20, 40 and 60 wt% HPW.
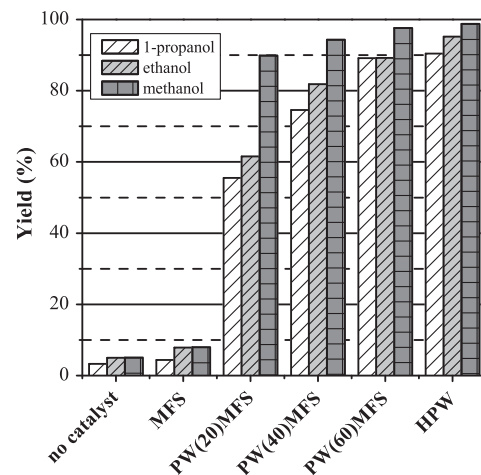
Fig. 10. Effect of alcohol chain length on the conversion of oleic acid in the presence of catalysts, MF, HPW and HPW impregnated into metakaolin *flint* after acid treatment (MFS) at a ratio of 20, 40 and 60 wt%.
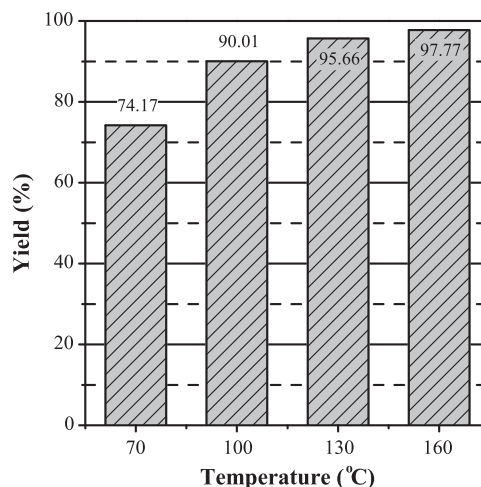
Fig. 8. Conversion of oleic acid catalysts using the MC, and HPW composite PW(x)MCS with x = 20, 40 and 60 wt% HPW on metakaolin century.

Fig. 11. Temperature effect in esterification acid oleic with methanol due molar 1:30 using catalyst PW(20)MFS in 2 h.
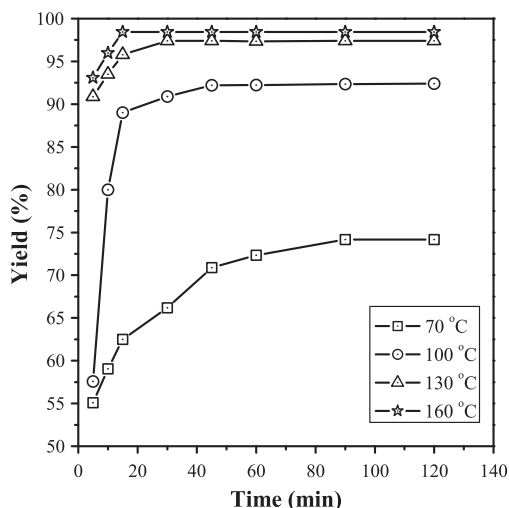
Fig. 12. Esterification acid oleic in different temperature (70, 100 130 and 160 °C) using methanol and molar ratio 1:30 with catalyst PW(20)MFS.

Fig. 13. Chart Arrhenius ln (k) versus 1/T.

Fig. 10 shows that the highest conversion rates were observed using catalysts in the presence of a shorter alcohol chain. This trend is valid for all types of catalysts.

3.6. Effect of temperature on esterification

For the temperature effect, was prioritized catalyst PW(20)MFS in methanol. Thus, reactions with esterification acid oleic were performed using one molar ratio 1:30 at 70, 100 130 and 160 °C. The esterification reaction was monitored every 15 min, by 70 °C to 100 °C there was a considerable increase in conversion with increasing temperature, 74.17% and 90.01%, respectively, in the next intervals of temperature, 100–130 °C and 130–160 °C, the increase in conversion was slight (Fig. 11). This behavior supports the work of Palani and Pandurangan [23], who found that increasing temperature promoted water removal in byproducts. This acts as a poison adsorption on heterogeneous acid catalysts, so removing it improves the catalytic activity of the material [23].

3.7. Effect reaction time using catalyst PW(20)MFS

Studies of the effect of reaction time were assessed using esterification reactions in periods of 5, 10, 15, 30, 45, 60, 90 and 120 min under the same conditions as the temperature effect study.

The results (Fig. 12) indicate that the reaction reached the steady state and probably the end of reaction within 90 min at a temperature of 70 °C, reaching a conversion of 74.17%. Conversions of 90.21% and 97.21% were achieved at 100 °C and 130 °C, respectively, in just 30 min. In an even shorter period (15 min), a 97.77% conversion was achieved at 160 °C. In addition, there was little difference in conversion between 130 and 160 °C.

Nascimento et al. [13], Gokulakrishnan et al. [22], Carmo et al. [24], and Kirumakki et al. [25] recommend first-order kinetics for esterification reaction with excess alcohol. Thus, we adjusted the linear results for the first-order equation according to the equation $-\ln(1 - income) = kt$ for 70 °C reaction. From these results, we obtained activation energy Ea and factor frequency reaction esterifying the oleic with methanol by applying Arrhenius settings in first-order kinetic constants.

The Arrhenius Equation relates rate constant reaction k with temperature [26] being calculated by following equation: $k = Ae^{(-Ea/RT)}$ where k is the kinetic constant first order gases (L/mol min) the factor frequency, Ea is the activation energy (J/mol) R to constant gases and T is the absolute temperature.
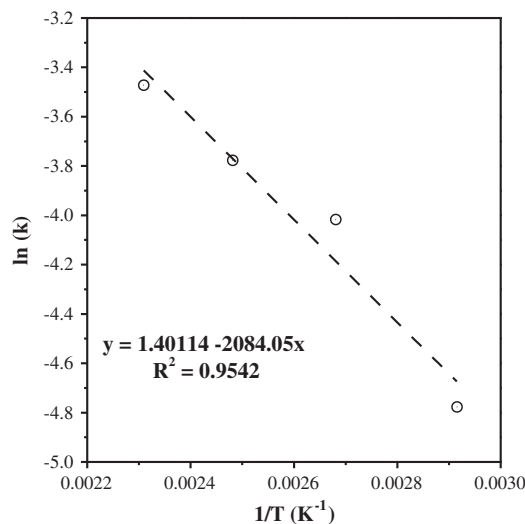
The kinetic constants obtained by linear fitting of the first order kinetic model were 0.00863 to 70 °C, 0.14748 to 100 °C, 0.19671 to 130 °C and 0.26011 to 160 °C. From these data, we created a graph $\ln(k)$ versus $1/T$ (Fig. 13) and obtained the activation energy Ea and frequency factor A, with values of 44.75 kJ/mol and 1.06×10^{-5} L/mol min, respectively.

3.8. Study of reuse and leaching of the active phase of the catalyst

Fig. 14 shows the first esterification reaction of oleic acid with the catalyst PW(20)MFS had a better performance than the second esterification with the same catalyst under the same reaction conditions, namely 130 °C for 2 h. After the first reuse of the catalyst, a significant loss of conversion (63.95%) was observed. The reduction of the catalytic activity could be related to three factors: (i) mass loss of the catalyst (close to 14%) during the filtration process, (ii) coke formation inside the pores of the catalyst and (iii) leaching of the active phase [27].

While monitoring the presence of HPW by UV–VIS based on the absorption at 220 nm and 265 nm, assigned to the charge transfer ligand–metal ($O^{2-} \rightarrow P$) and charge transfer lingate metal
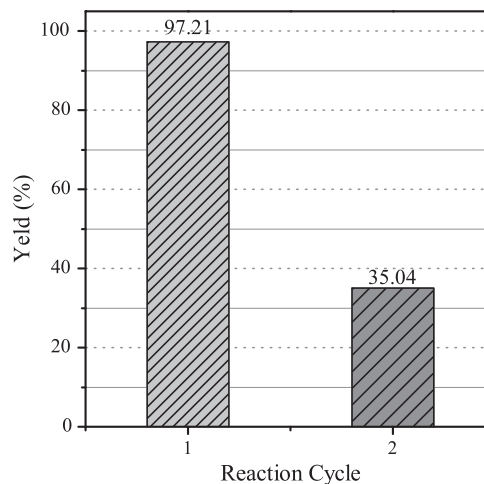

Fig. 14. Conversion of oleic acid using the catalyst PW(20)MFS with first and second cycles under the temperature of 130 °C/2 h and 1:30 M ratio oleic acid: methanol.
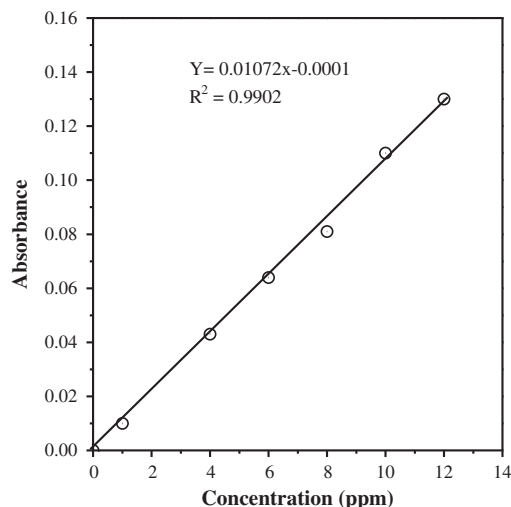
Y= 0.01072x-0.0001
R^2 = 0.9902

Fig. 15. Calibration curve for determining the leaching of the catalyst PW(20)MFS.

($O^{2-} \rightarrow W^{6+}$) respectively [28]. For the leaching test of the active phase of the catalyst in the presence of methanol, a calibration curve was constructed taking into account the wavelength of 270 nm (λ_{max}) and concentrations of HPW standard solutions in methanol of 1, 4, 8, 10 and 12 ppm (Fig. 15). The concentrations of the catalyst PW(20)MFS newly synthesized and after reaction were determined from the curve obtained, which also determined leaching of the catalyst during reuse.

The results showed a 2% leaching of the active phase of the catalyst. In this case, it is believed that the reaction occurred in the predominantly heterogeneous step, supported by Kozhevnikov, who argues that the leaching of the active phase of the catalyst should not exceed 2.7% [9].

4. Conclusions

The XRD and FTIR analysis indicated that the preparation of catalysts, solvents with higher efficiency in the impregnation of kaolin *flint* and century, were the solution of HCl 0.5 mol L^{-1} and acetonitrile, although analysis by XRF only indicated the acetonitrile solvent. Acid leaching leads to a reduction of alumina, leaving them in the amorphous form. The catalytic results with ethanol at 100 °C for 2 h showed that HPW supported on metakaolins with acid treatment promoted good conversion of more than 63%, followed by a gradual increase with added support in HPW. Compared to HPW alone, PW(*x*) MFS showed slightly lower yields, but the composites could be recovered after the reaction, while HPW could not. In contrast with propanol, a higher conversion was achieved when using alcohol methanol in the esterification, especially with the use of PW(20)MFS, showing an increase of 35%. Evaluating the effect of temperature and time parameters, better conversion occurred at 130 °C, achieving 97.21% conversion in 30 min. The kinetic parameters activation energy (Ea) and

frequency factor (A) obtained were 44.75 kJ/mol and 1.06×10^{-5} L/mol min, respectively. As for the reuse of the catalyst, some deactivation was observed, possibly caused by coke deposits within the pores and lack of leaching during the active phase. Thus, PW(20)MFS can be considered an efficient catalyst for the esterification of raw material with high acidity, providing an alternative route to sustainable production of biofuel.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2013.01.008.

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