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# Esterification of free fatty acids to biodiesel over heteropolyacids immobilized on mesoporous silica

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#### ABSTRACT

Tungstophosphoric acid (PW), molybdophosphoric acid (PMo) and tungstosilicic acid (SiW) immobilized on SBA-15 were used, as catalysts, in the esterification of palmitic acid with methanol, at 60 °C. Catalysts were characterized by  $N_2$  adsorption, FTIR, X-ray diffraction, ICP-AES and TEM.

All catalysts exhibited high catalytic activity in palmitic acid esterification with methanol. It was observed that the catalytic activity decreases in the follow series: PW1-SBA-15>SiW-SBA-15>PMo-SBA-15.

A series of PW immobilized on SBA-15 with different PW loadings from 2.7 wt% to 8.3 wt% were prepared. It was observed high catalytic activity with low amount of tungstophosphoric acid immobilized on SBA-15.

In order to optimize the reaction conditions, the effect of different parameters, such as catalyst loading, carbon length of the alcohol and temperature, molar ratio of fatty acid to methanol in the presence of PW3-SBA-15 were studied.

PW3-SBA-15 catalyst can be separated from reaction system for re-use. It was observed a small leaching of the PW from SBA-15 to liquid phase.

PW3-SBA-15 catalyst was also used in the esterification of stearic and oleic acid with methanol. High catalytic activity was observed.

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#### 1. Introduction

Biodiesel, an alternative fuel for diesel engines, is biodegradable, nontoxic and renewable. Generally, biodiesel is produced via the transesterification of vegetable oils or animal fats with shortchain alcohols (e.g., methanol), which is carried out by acid or base catalysis, to form alkyl esters that have properties similar to those of fossil-derived diesel [1–13]. Biodiesel can also be prepared by the esterification of free fatty acid present in animal fats (ex. lard or tallow), with methanol over acid catalysts [1,2].

Traditionally, esterification reactions are carried out using homogeneous catalysts, such as sulfuric acid. However, in order to become a "green process", the homogenous catalysts need to replace by heterogeneous ones. The solid acid catalysts are preferable, offering easy separation from the reactants and products by filtration, allowing continuous operation of reactors.

Heteropolyacids (HPAs) have been extensively studied as acid catalysts for a wide range of reactions [14,15]. The low specific areas and solubility in polar media have been reported as the major disadvantages of Keggin-type HPA. In order to overcome this problem, different supports, like silica [16–21], activated carbons [22–25], zeolites [26–29] and polymers [30–33] have been used to immobilize HPAs.

The esterification of fatty acids has been carried out over acid clays [34] heteropolyacids [35] and heteropolyacids supported in zirconium oxide [36], activated carbon, silica [37,38] and tantalum pentoxide [39].

New kinds of acid solids have emerged in the last years based on heteropolyacids immobilized in mesostructured MCM-41 [40,41] and SBA-15 materials [42,43]. These catalysts lead to materials with high surface area, narrow pore size distribution with high accessibility of acid centres and relative high acid strength.

SBA-15 mesoporous silica (prepared using neutral block copolymer), with well ordered hexagonal arrays of cylindrical channels, narrow pore size distributions, remarkable thermal stability, high surface area ( $600-1000 \text{ m}^2/\text{g}$ ) [44,45], and a large number of silanol groups at the surface of its channels [46], serves as an interesting support for the purpose. Furthermore, SBA-15 mesopores are interconnected by micropores [47,48], enabling the pore surfaces to be accessed in three dimensions in catalytic reactions.

In this work we report the esterification of palmitic, oleic and stearic acid with methanol over tungstophosphoric acid

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(PW), tungstosilicic acid (SiW) and molybdophosphoric acid (PMo) immobilized on SBA-15.

#### 2. Experimental

#### 2.1. Preparation of catalyst

Mesoporous silica SBA-15 was prepared according to the literature [49] by using an ethylene oxide (EO)/propylene oxide (PO) triblock copolymer (P123) with composition  $EO_{20}PO_{70}EO_{20}$  and with an average molecular weight of 5800, as the template. In a typical synthesis, 2.0 g of triblock P123 was dissolved in 60 cm<sup>3</sup> of 2 M aqueous HCl and 15 cm<sup>3</sup> of distilled water under stirring, and then 4.4 g of tetraethyl orthosilicate (TEOS) was added dropwise to the solution at room temperature. The mixture was stirred for 24 h at 313 K, and then the temperature was raised to 373 K and kept at 373 K for another 24 h in a Teflon-lined autoclave. Finally the resulting precipitate was filtered, washed carefully with distilled water, air-dried, and calcined at 773 K in air for 5 h to remove the template and to obtain the final product SBA-15.

The catalysts were prepared by shaking 1 g of SBA-15 in  $30 \text{ cm}^3$  of methanol, with an appropriate amount of HPA, during 24 h, at room temperature. Evaporation of the suspensions was carried out below  $60 \,^\circ$ C using a rotary vacuum evaporator. The catalyst samples were calcined at  $130 \,^\circ$ C for 1.5 h.

#### 2.2. Characterization of the catalyst

The textural characterization of the catalysts was based on the nitrogen adsorption isotherm, determined at 77 K with a Micromeritics ASAP 2010 apparatus.

The amount of Mo and W in silica catalysts was measured by dissolving the catalyst in  $H_2SO_4/HF$  1:1 (v/v) and analysing the obtained solution using inductively coupled plasma analysis (ICP), which was carried out in a Jobin-Yvon ULTIMA instrument. The FTIR spectra were recorded with a Bio-Rad FTS 155 instrument.

The X-ray diffraction (XRD) patterns of the heteropolyacid, silica and catalysts were obtained by using a Bruker powder diffractometer with built-in recorder, using Cu K $\alpha$  radiation, nickel filter, 30 mA and 40 kV in the high voltage source, and scanning angle between  $0.7^{\circ}$  and 55° of  $2\theta$  at a scanning rate of 1°/min.

Transmission electron microscopy (TEM) analyses were performed on a Hitachi S-2400 scanning electron microscope, at a current voltage of 25 kV.

Catalyst acidity was measured by means of potentiometric titration, according to Pizzio et al. [17]. A small quantity of *n*-butylamine solution (0.05 N) in acetonitrile was added to a known mass (0.05 g) of solid suspended in acetonitrile (90 cm<sup>3</sup>), and shaken for 3 h. The suspension was then potentiometrically titrated with the same solution of *n*-butylamine in acetonitrile. The electrode potential variation was measured with a Crison micropH 2001 instrument.

#### 2.3. Catalytic experiments

The catalytic experiments were carried out in a stirred batch reactor at 60 °C. In a typical experiment, the reactor was loaded with  $30 \text{ cm}^3$  of methanol and 0.2 g of catalyst. Reactions were started by adding 8 mmol of free fatty acid.

In order to study the reusability, the PW3-SBA-15 catalyst was filtered from the reaction mixture. After this operation, it was soaked in hexane overnight and it was dried overnight.

A posterior catalytic experiment was also conducted where the PW3-SBA-15 (0.2 g) was put in contact with methanol  $(30 \text{ cm}^3)$  during 48 h, at 60 °C under stirring, without palmitic acid. After this period, the catalyst was separated from methanol by centrifugation, and the substrate (palmitic acid) was added to the reaction mixture.



**Fig. 1.**  $N_2$  adsorption–desorption isotherm of the SBA-15 and SBA-15 with heteropolyacid. ( $\blacktriangle$ ) SBA-15; ( $\bigcirc$ ) PW4-SBA-15; ( $\bigcirc$ ) SiW-SBA-15; ( $\times$ ) PMo-SBA-15.

Samples were taken periodically and analysed by GC, using a KONIC HRGC-3000C instrument equipped with a  $30 \, m \times 0.25 \, mm$  DB-1 column.

#### 3. Results and discussion

#### 3.1. Catalyst characterization

Fig. 1 shows the nitrogen adsorption-desorption isotherms at 77 K of the samples. A typical IV adsorption isotherm with H1 hysteresis loop as defined by IUPAC is observed. The hysteresis loop shows typical capillary condensation within uniform pores and considerable adsorption amounts for all materials, indicating that the samples have considerable volumes of nanospaces even after the introduction of heteropolyacids. All the materials have large surface areas, while the impregnation of HPAs decreases the specific surface area and total pore volume of SBA-15 (Table 1). Similar results were also observed by Luo et al. [50].

The Keggin-anion density of the catalysts (HPA nm<sup>-2</sup>) expressed as the number of Keggin anions per square nanometre was calculated according to the actual HPA loading and catalyst surface area (Table 1). The surface coverage of catalyst was calculated according to a literature method using the following equation [51]:

Keggin-anion density (HPA nm<sup>-2</sup>)

=

$$\frac{\left[\text{HPA loading }(wt\%)/100\right] \times 6.02 \times 10^{5}}{\text{BET surface area of catalyst }(m^{2}\,g^{-1}) \times MM(\text{HPA})}$$

where MM(HPA) is the molecular weight of the heteropolyacids.

It was observed that all catalysts showed low Keggin-anion density and when the heteropolyacid amount immobilized on SBA-15 increases the density increases as well. Similar results were also observed by Atia et al. [52] and Chai et al. [51].

The FTIR spectrum of immobilized HPA on SBA-15 catalysts is shown in Fig. 2. There are four different kinds of oxygen atoms, in Keggin anion structure  $[XM_{12}O_{40}]^{n-}$ , according to the location they take in that unit: oxygen atoms bound to three M atoms and to the X heteroatom (O<sub>a</sub>), bridging oxygen atoms (O<sub>b</sub> and O<sub>c</sub>), and terminal oxygen atoms (O<sub>d</sub>). The symmetric and asymmetric vibrations of different M–O bonds are observed in the following regions of the vibration spectra: M–O<sub>d</sub> bonds (1000–960 cm<sup>-1</sup>); M–O<sub>b</sub>–M bonds (890–850 cm<sup>-1</sup>); and M–O<sub>c</sub>–M bonds (800–760 cm<sup>-1</sup>) [53]. However, some bands typical of the Keggin-type HPA structures are overlapped or partially overlapped with the bands of the SBA-15 matrix framework.

The X-ray diffraction patterns of the samples are shown in Fig. 3. The hexagonal structure of SBA-15 is confirmed by a sharp peak

#### Table 1

Physicochemical characterization of HPAs immobilized on SBA-15.

Sample	HPA load <sup>a</sup> (wt%)	Surface area <sup>b</sup> (m <sup>2</sup> /g)	Total pore volume <sup>c</sup> (cm <sup>3</sup> /g)	Keggin-anion density (HPA nm <sup>-2</sup> )
SBA-15	-	1020	1.32	-
PW1-SBA-15	2.7	880	1.19	0.006
PW2-SBA-15	6.7	761	1.12	0.018
PW3-SBA-15	7.3	754	0.94	0.020
PW4-SBA15	8.3	672	0.84	0.026
SiW-SBA-15	2.8	812	0.99	0.007
PMo-SBA-15	3.3	844	1.06	0.013

<sup>a</sup> HPA load determined by ICP analysis.

<sup>b</sup> BET.

<sup>c</sup> p/po = 0.98.



Fig. 2. FT-IR spectra of catalysts: (A) SBA-15; (B) SiW-SBA-15; (C) PW3-SBA-15; (D) PMo-SBA-15.



**Fig. 3.** X-ray diffractograms of catalysts (A): (a) SBA-15; (b) PW1-SBA-15; (c) PW2-SBA-15; (d) PW3-SBA-15; (e) PW4-SBA-15; (f) SiW-SBA-15; (g) PM0-SBA-15; (B) (a) PW; (b) SiW; (c) PM0; (a) SBA-15; (b) PW1-SBA-15; (c) PW2-SBA-15; (d) PW3-SBA-15; (e) PW4-SBA-15; (f) SiW-SBA-15; (g) PM0-SBA-15.

along with two weak peaks at lower  $2\theta$  region of  $0.7-2^{\circ}$  and the (100), (110) and (200) reflections corresponding to basal spacing of the mesoporous silica (Fig. 3A). The presence of the small angle diffraction peaks for HPA-SBA-15 suggests that the mesostructures are reserved after heteropolyacid immobilization [54]. SBA-15 supported samples did not present the characteristic XRD pattern of crystalline PW, PMo and SiW (Fig. 3B).

TEM images of the SBA-15 exhibit the existence of well-ordered nanochannels, and the nanochannels are arranged on 2D hexagonal structure and appear to be continuous over very large scales (Fig. 4). According to SEM images (Fig. 4A and B), morphology of SBA-15 supports have remained intact after immobilization of the heteropolyacid. A similar result was also observed by Luo et al. [50].

The potentiometric titration curves, with *n*-butylamine, obtained for the silica and the catalysts are presented in Fig. 5. The initial electrode potential ( $E_i$ ) indicates the maximum acid strength of the surface sites [15]. The acidic strength of surface sites can



Fig. 4. Transmission electron microscopy (TEM) images of (A) SBA-15 and (B) PW3-SBA-15.



**Fig. 5.** Potentiometric titration of catalysts. (○) SBA-15; (□) PW1-SBA-15; (×) PW2-SBA-15; (■) PW3-SBA-15; (▲) PW4-SBA-15; (④) SiW-SBA-15; (◊) PMo-SBA-15.

be assigned according to the following ranges: very strong site,  $E_i > 100 \text{ mV}$ ; strong site,  $0 < E_i < 100 \text{ mV}$ ; weak site,  $-100 < E_i < 0 \text{ mV}$  and very weak site,  $E_i < -100 \text{ mV}$  [17]. Table 2 shows the maximum strength of the catalysts. PW-SBA-15 samples show higher maximum strength that the PMo-SBA-15 and SiW-SBA-15 catalysts. It can be also observed that the  $E_i$  of PW-SBA-15 samples increases with the amount of PW immobilized on SBA-15 (Table 1). This behaviour can be explained due to the increases of protons amount with PW loading. Similar results were also observed by Díez et al. [55] and Gagea et al. [56].

#### 3.2. Catalytic experiments

Esterification of palmitic acid with methanol was carried out, on homogenous phase, with PW,  $H_2SO_4$ , as catalysts. Turnover frequency (TOF) of sulphuric acid, PW and PW3-SBA-15 are 8, 30 and 243 h<sup>-1</sup>, respectively. Similar results were obtained by Alsalme et al. [21], in esterification of hexanoic acid with methanol over PW,  $H_2SO_4$  and PW supported on Nb<sub>2</sub>O<sub>5</sub>. However, after 4 h of reaction, a high palmitic acid conversion was obtained (Table 3).

Esterification of palmitic acid with methanol was also carried out over heteropolyacids immobilized on SBA-15. Fig. 6A shows the initial activities (mol/h g<sub>HPA</sub>) of the catalysts in the esterification of palmitic acid with methanol, calculated from the maximum slopes of the methyl palmitate kinetic curve. It was observed that the catalytic activity decreases in the series: PW1-SBA-15 > SiW-SBA-15 > PMo-SBA-15. This behaviour can be explained due to the PW1-SBA-15 catalyst possessing the highest acid strength of heteropolyacids (Table 2). After 6 h of reaction, it was observed that the palmitic acid conversion (%) is 92%, 57% and 45% for the PW1-SBA-15, SiW-SBA-15, PMo-SBA-15 catalyst, respectively (Fig. 6B).

Fig. 7A compares the initial activity  $(mol/h\,g_{PW})$  of PW-SBA-15 catalysts loaded with different PW amounts on the esterification of

Table	2
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Sample	E <sub>i</sub> (mV)	
SBA-15	118	
PW1-SBA-15	675	
PW2-SBA-15	694	
PW3-SBA-15	710	
PW4-SBA15	714	
SiW-SBA-15	565	
PMo-SBA-15	475	

Table 3

Esterification of palmitic acid with methanol (60  $^\circ\text{C},$  1:98 substrate:methanol molar ratio).

Catalyst	Conversion (%) <sup>d</sup>
PW <sup>a,b</sup>	98
H <sub>2</sub> SO <sub>4</sub> <sup>a,b</sup>	99
PW3-SBA-15 <sup>c</sup>	96

<sup>a</sup> Homogeneous reaction.

<sup>b</sup> 0.015 g catalyst.

<sup>c</sup> 0.2 g catalyst (7.3 wt%).

<sup>d</sup> After 4 h of reaction.

palmitic acid with methanol. It was observed that the initial catalytic activity increases with the PW content, from PW1-SBA-15 to PW2-SBA-15. These results can be explained due to the increases of acid strength of catalysts with the amount of PW immobilized on SBA-15 (Table 2). However, with higher PW loading on SBA-15, it was observed that the catalytic activity decreases from PW2-SBA-15 to PW3-SBA-15 and it seems to be kept from PW3-SBA15 to PW4-SBA-15. This behaviour can be explained, probably, due to some hindrance inside the porous system, once the maximum acid strength of PW3-SBA-15 and PW4-SBA-15 samples is similar (Table 2). A decrease of S<sub>BET</sub> and total porous volume with the amount of PW on SBA-15 was observed (Table 1). Probably, the accessibility to acid sites decrease as well. However, all catalysts exhibited high palmitic acid conversion (%), after 6h of reaction (Fig. 7B).

In order to optimize the reaction conditions, the effect of different parameters (catalyst loading, molar ratio alcohol to fatty acid



**Fig. 6.** Esterification of palmitic acid with methanol over heteropolyacids immobilized on SBA-15. (A) Initial activities taken as the maximum observed reaction rate, calculated from the maximum slope of the methyl palmitate kinetic curve. (B) Palmitic acid conversion (%) versus time on stream (h). ( $\bigcirc$ ) PW1-SBA-15; ( $\blacktriangle$ ) SiW-SBA-15; ( $\bigcirc$ ) PM0-SBA-15. Reaction conditions: temperature = 60 °C; catalyst loading = 0.2 g.



**Fig. 7.** Esterification of palmitic acid with methanol over PW immobilized on SBA-15. (A) Initial activities taken as the maximum observed reaction rate, calculated from the maximum slope of the methyl palmitate kinetic curve. (B) Palmitic acid conversion (%) versus time on stream (h). (**○**) PW1-SBA-15; (**□**) PW2-SBA-15; (**▲**) PW3-SBA-15; (**×**) PW4-SBA-15. Reaction conditions: temperature = 60 °C; catalyst loading = 0.2 g.

and carbon length of the alcohol and temperature) on the esterification of palmitic acid over PW3-SBA-15 catalyst was studied.

#### 3.2.1. Effect of catalyst loading

The effect of PW3-SBA-15 loading on esterification of palmitic acid with methanol was studied at 60 °C. The results are shown in Fig. 8. It was observed that the increase in catalyst loading from 0.05 g to 0.2 g showed an increase on the palmitic acid conversion. These results can be attributed to an increase in the availability and number of catalytically active sites [57]. The esterification of



**Fig. 8.** Esterification of palmitic acid with methanol over PW3-SBA-15. Effect of catalyst loading. Palmitic acid conversion (%) versus time on stream (h). ( $\Box$ ) Without catalyst; ( $\blacktriangle$ ) *m* = 0.5 g; ( $\bigcirc$ ) *m* = 0.2 g.



**Fig. 9.** Esterification of palmitic acid with methanol or ethanol over PW3-SBA-15. Effect of temperature. Palmitic acid conversion (%) versus time on stream (h). ( $\bigcirc$ ) reaction with methanol, at 60 °C; ( $\square$ ) reaction with ethanol, at 60 °C; ( $\blacktriangle$ ) reaction with ethanol, at 80 °C.

palmitic acid with methanol was studied over PW catalyst [58]. The catalyst amount was varied in the range of 0.03–0.12 mmol. It was observed that the conversion was increased firstly with the increase of catalyst amount (55% at 0.03 mmol of catalyst and 87% at 0.06 mmol of catalyst, after 12 h of reaction). However, the conversion was increased slowly, with further increase in the catalyst amount (95% at 0.09 mmol of catalyst and 95% at 0.12 mmol of catalyst, after 12 h of reaction). This behaviour was attributed to the increase in the number of catalytically active site [58].

#### 3.2.2. Effect of the carbon length of the alcohol and temperature

The most frequently alcohols used in the biodiesel production are methanol and ethanol. Due to the low cost of methanol, this alcohol is the first choice for the esterification/transesterification reactions. However, ethanol is the ideal candidate for the synthesis of a fully biogenerated biodiesel [11].

The type alcohol influence (methanol and ethanol) on esterification of palmitic acid over PW3-SBA-15, at  $60 \,^{\circ}$ C, is shown in Fig. 9. The reaction of palmitic acid with ethanol over PW3-SBA-15 at  $80 \,^{\circ}$ C is also shown in Fig. 9. It can be seen that the esterification of palmitic acid with ethanol led to lower conversion, when compared with methanol, at  $60 \,^{\circ}$ C. These results can be explained due to the reaction rate with ethanol is slower than with methanol, once the ethyl nucleophile is less reactive than the methyl nucleophile. Similar results were also observed by Aranda et al. [8]. An increase of the palmitic acid conversion was observed using ethanol, when the temperature was increased from  $60 \,^{\circ}$ C to  $80 \,^{\circ}$ C.

#### 3.2.3. Effect of molar ratio alcohol to fatty acid

The esterification of palmitic acid with methanol is a reversible reaction. High conversion can only be obtained if the backward reaction is minimized. There are two ways to reduce the rate of backward reaction: (1) to remove the product water simultaneously or (2) to use excess of one of the reactants (methanol). In this system, it is not easy to remove water, as the boiling point of methanol (65  $^{\circ}$ C) is lower than the boiling point of water (100  $^{\circ}$ C). Thus, the second option was applied in the present work. However, the excess of methanol used in the reaction can be collected and reused. In order to study the effect of molar ratio palmitic acid to methanol on esterification reaction, different experiments were carried out using 1:6, 1:32, 1:63 and 1:95 at 60 °C. Total volume of reaction mixture was the same. The amount of catalyst, as concentration of catalyst expressed in  $g/dm^3$ , is 6.67  $g_{cat}/dm^3$ . Fig. 10A shows the effect molar ratio palmitic acid to methanol on palmitic acid conversion (%). The equilibrium conversion of palmitic



**Fig. 10.** Esterification of palmitic acid with methanol over PW3-SBA-15. Effect of the molar ratio of palmitic acid to methanol. (A) Palmitic acid conversion (%) versus time on stream (h). (**D**) 1:95; (**A**) 1:63; (**D**) 1:31; ( $\times$ ) 1:6. (B) Conversion (%) after 5 h versus molar ratio. Reaction conditions: temperature = 60 °C; catalyst loading = 0.2 g.

acid increased from about 88% to 96% at molar ratio palmitic acid to methanol 1:6 and 1:95, respectively. Similar results were also observed by Teo and Saha [59]. After 5 h, the conversion increased with the increases of molar ratio (Fig. 10B).

#### 3.2.4. Catalyst stability and reusability

In order to study the reusability, the PW3-SBA-15 catalyst was filtered from the reaction mixture and then was soaked in hexane overnight to remove the esters present on the surface. Finally, the catalyst was dried overnight (80 °C) and used for esterification. Fig. 11 shows the palmitic acid conversion (%) obtained using fresh and spent catalyst. The loss of activity can be explained not only due



**Fig. 11.** Esterification of palmitic acid with methanol over PW3-SBA-15, at 60 °C. Palmitic acid conversion (%) versus time on stream (h). ( $\blacktriangle$ ) SBA-15; ( $\bigcirc$ ) PW3-SBA-15 (fresh); ( $\times$ ) PW3-SBA-15 (used, dry overnight at 80 °C); (+) PW3-SBA-15 (used, dry overnight at 110 °C); ( $\Box$ ) PW3-SBA-15 after catalyst removal.



**Fig. 12.** Esterification of free fatty acid with methanol over PW3-SBA-15. Initial activities taken as the maximum observed reaction rate, calculated from the maximum slope of the methyl palmitate, methyl stearate and methyl oleate kinetic curve. Reaction conditions: temperature =  $60 \,^{\circ}$ C; catalyst loading = 0.2 g.

to the leaching and a loss of the catalyst (fine powder) in separation, but also due to some water (product of esterification) present on catalyst. When the PW3-SBA-15 was dried overnight at 110 °C, it was observed similar activity of fresh and spent catalyst (Fig. 11).

In order to study the catalytic stability of PW3-SBA-15, an experiment, similar to the "hot-filtration experiment", was carried out. The PW3-SBA-15 catalyst was put in contact with the methanol during 48 h, at 60 °C under stirring, without palmitic acid. After this period, the catalyst was separated from methanol by centrifugation, and the palmitic acid was added to the reaction mixture. The reaction was carried out during 6 h. Fig. 11 compares the conversion of palmitic acid obtained with SBA-15 and with and without catalyst. It was observed that the heteropolyacid leaching from SBA-15 to reaccional mixture seem to be small.

#### 3.2.5. Esterification of oleic and stearic acid with methanol

The PW3-SBA-15 catalyst was also used in esterification of others fatty acids: oleic and stearic acid. Fig. 12 compares the initial catalytic activities of the PW3-SBA-15 in esterification of palmitic, stearic and oleic acid, calculated from the maximum slopes of ester kinetic curves. It was observed that the catalytic activity of PW3-SBA-15 decreases, when the carbon numbers of fatty acid increases. This behaviour can be explained not only due to some hindrance inside the porous system of the SBA-15 but also due to the structure of FFA. According to Warabi et al. [60], the conversion of fatty acids decreases with an increase of carbon number in the chain of FFA. After 5 h, the conversion of palmitic, oleic and stearic acid was 96, 85 and 78% respectively.

#### 4. Conclusions

Tungstophosphoric acid (PW), molybdophosphoric acid (PMo) and silicotungstic acid (SiW) immobilized on SBA-15 were successfully employed in the esterification of palmitic acid with methanol. It was observed that the catalytic activity decreases in the series: PW1-SBA-15 > SiW-SBA-15 > PMo-SBA-15.

SBA-15 with different PW amount, which varied from 2.7 to 8.3 wt%, were also prepared and used in the esterification of palmitic acid. High catalytic activity was observed.

In order to study and optimize the reaction conditions, the effect of various parameters, such as catalyst loading, molar ratio of palmitic acid to methanol and carbon length of the alcohol and temperature of PW3-SBA-15 were carried out.

PW3-SBA-15 catalyst was re-used. A small leaching of the heteropolyacid from SBA-15 to liquid phase was observed. Due to the high catalytic activity of PW3-SBA-15 on the esterification of palmitic acid with methanol, the catalyst was also used in esterification of stearic and oleic acid with methanol. It was observed that the catalytic activity decreases with the increases of the number of carbon atoms.

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