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Biodiesel production by acid catalysis with heteropolyacids supported on activated carbon fibers



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ABSTRACT

Different catalysts, based on heteropolyacids supported on activated carbon fibers, have been prepared for palmitic acid esterification reaction. The influence of the catalyst (heteropolyacid) and the support on the catalytic activity have been analyzed. The results prove that an adequate combination of both is required to achieve the most suitable catalysts. Regarding to the heteropolyacid, phosphomolybdic acid seems to be the most suitable appropriate taking into account its lowest leaching. About the support, it must show an optimum microporosity, which must be wide enough to allow the entrance and exit of the reagents and products but not too wide in order to avoid the leaching of the catalyst. In addition, both decreasing of the catalytic activity and its recovery over several cycles have been analyzed.

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1. Introduction

Biodiesel is a liquid fuel which is considered as an alternative to petroleum diesel. This fuel is obtained by transesterification and esterification reactions from renewable raw materials such as vegetable oils, animal fats or free fatty acids (FFA) derived from the above [1–3]. In order to achieve high conversions with the cited reactions at economically viable temperatures, the catalysts use is essential. In this sense, there exist a wide variety of catalysts, both in homogeneous and heterogeneous phase, which can be used to speed up the reaction. Among these, different catalysts can be found (e.g., basic, acid or even enzymatic catalysts). Nowadays, basic homogeneous catalysis is the most widely used, reaching at 80 °C conversions close to 100% and reaction times less than 3 h. However, it is essential to minimize the presence of water and FFA in the raw materials since secondary reactions can be produced between the catalysts and free fatty acids such as soap formation [4]. These reactions cause the catalysts deactivation, a conversion decrease and an increase of the purification costs [5,6]. For this reason, the use of vegetable oils or animal fats with FFA contents lower than 0.5 on weight percentage (wt%) is necessary. This implies the use of high purity raw materials such as virgin oils which increases the final cost of biodiesel. It is estimated that 60-75% of the final cost of biodiesel can be attributed to the refining process of the raw material used. Using recycled materials (i.e., waste cooking oils)

the cost would be reduced drastically. However, in these materials, FFA content is higher than 10 wt%. An alternative to solve this issue could be the design of a two-step process [7,8]: a first step where the FFA are esterified using an acid catalyst followed by a transesterification by means of a basic catalysis. Strong Brönsted acids, such as sulphuric acid, hydrochloric acid or ortophosphoric acid, are usually used as catalysts. These compounds do not present saponification problems but they show different drawbacks such as environmental problems, reactor corrosion, higher amounts of methanol and catalyst (i.e., 5-25 wt% H₂SO₄), they also require a washing phase and catalyst recovery stage, common in homogeneous catalysis. These problems can be overcome by the use of acidic solid catalysts [1-3,9]. For this reason, in the last years a large number of studies related to the use of acidic solid catalysts for the esterification of FFA have been performed. Thus, a wide variety of catalysts have been used such as acidic clays [10], tantalum oxide [11], modified zirconia [12], modified silica [13]. However, when hydrotalcites and modified zirconia are used, stronger conditions are necessary (>140 °C) to obtain similar conversions to those achieved using basic homogeneous catalysis [14].

Thus, to perform the reaction at similar temperature conditions to those employed in basic catalysis, the use of solid acids with high activity is required. In these sense, heteropolyacids (HPA) highlight among the solid acids. These compounds are oxygenated compounds based on polyoxometalates (POM) [15]. These compounds are extremely strong acids, close to super-acid region. The main advantage of HPA compared with H₂SO₄, HCl or HF is that they are environmentally friendly. However, almost all HPA show a high solubility in polar solvents [15]. Therefore, in order to use HPA as

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heterogeneous acidic catalysts, they should be supported on porous materials [16–18]. Different studies have been performed using immobilized HPA on a wide number of materials such as MCM-41 [19], zirconia [20], activated carbons, silica and alumina [21] for esterification reactions.

Previous works, carried out in our labs, demonstrated the suitability of using activated carbon fibers (ACF) to adsorb HPA showing high adsorption capacities. HPA were adsorbed mainly on the super-micropores, achieving a high dispersion [18]. The selection of ACF in liquid reactions is highly advantageous compared to conventional activated carbons since they show smaller hydrodynamic resistance, due to their fibrous shape, high mass transfer rates and their easy removal from the reaction medium [22]. Hence, the main aim of this work is to analyze the suitability of the use of supported HPA on an industrially and environmentally interesting reaction such as biodiesel synthesis through the study of free fatty acid esterification reaction.

2. Experimental

2.1. Materials

For this study, palmitic acid (Sigma Aldrich) was selected as fatty acid for the synthesis of the corresponding monoalkyl ester. Among all vegetables oils, the one obtained from African palm is the highest oil production per hectare and year, showing a lower and stable price compared to other vegetable oils for food use [23]. In addition, its methyl ester shows one of the highest cetane index (higher than petroleum diesel) which gives more value to biodiesel obtained from this compound [24]. However, the main disadvantage of the use of palm oil is its high FFA content (around 5–8 wt%, of which 44 wt% corresponds to palmitic and 38% to oleic acid-). This aspect makes its application in a single basic transesterification step process ineffective. For this reason, it would be more appropriate to subject the palm oil to a previous acidic esterification stage to eliminate the presence of FFA. Thus, the application of HPA supported on ACF will be used for this reaction.

For the pre-esterification stage, the following materials were selected: palmitic acid (Sigma Aldrich), methanol (Sigma Aldrich), three commercially available ACF from Osaka Gas Co. (samples A10, A15 and A20) and two HPA, phosphomolybdic acid (HPMo) and phosphotungstic acid (HPW).

2.2. Catalyst preparation

A series of different catalysts were prepared by an impregnation method using the above ACF and HPAs, which has been described in a previous work [18]. Among the prepared supported catalysts, the most used in this manuscript were a 44 wt% HPMo supported on A20 ACF (HPMo/A20) and a 52 wt% HPW supported on A20 ACF (HPW/A20) (the amount of supported HPA was determined by difference of the initial weight of ACF and the final weight of impregnated and dried sample). In order to analyze the support's pore size effect on the reaction, two catalysts were using the A10 and A15 supports, containing a 27 and 32 wt% of supported HPMo, respectively. Additionally, to analyze the influence of the HPA amount on the reaction yield, four different samples were studied: 12 and 24 wt% and 10 and 21 wt% for HPW/A20 and HPMo/A20, respectively.

2.3. Catalytic activity tests

Reaction was carried out in a glass flask reactor where 1 g of palmitic acid (3.8 mmol) and 15 cm^3 of methanol were added (molar ratio 1/97) [25]. The flask reactor was sealed to avoid evaporation and placed on a shaker at constant stirring speed

with a thermostatically controlled bath at different temperatures (between 30 and 60 °C). Once the palmitic acid was dissolved, the catalyst was added. The amount of catalyst varied from 3 to 80 mg for unsupported HPA studies and between 50 and 200 mg for supported HPA on ACF. These experimental conditions were maintained during 6 h, although additional experiments were performed up to 24 h. In addition, the used catalysts were reused in successive cycles.

To determine the progress of the reaction, three different aliquots were analyzed at 1, 3 and 6 h (also at 24 h for longer duration experiments). Reaction yield was determined by titration using a NaOH 0.1 M (Aldrich) standard pattern. Moreover, the nature of the reaction products was analyzed by gas chromatography coupled to mass spectrometry (Shimadzu, GCMS QP5050A with a polydimethylsiloxane column CBPI PONA-M50-042 from Shimadzu, 100 mm \times 0.25 mm \times 0.5 mm), so methyl palmitate was confirmed as the only reaction product.

In order to analyze the regeneration process, additional treatments were performed with the used catalysts. The treatments tested were (i) thermal treatment at 300–400 °C during 6 h; (ii) washing step with ethanol (25 ml, 40 °C and 30 min) and (iii) washing step with ethanol in acidic medium (25 ml ethanol/20 μ l H₂SO₄ 98 wt%, 40 °C and 30 min). In the last two processes, catalysts were dried at 110 °C for 12 h.

2.4. Characterization of the supports and catalysts

Additional characterization of the prepared catalysts was performed in a previous work, using gas adsorption, DRX and TEM [18].

2.4.1. Chemical analysis

The elemental analysis of HPA, ACF and the fresh and used catalysts (P, Mo, W) was determined by inductively coupled plasma spectrometry (ICP 7700x Agilent) and hydrogen, carbon and nitrogen contents were carried out by a Carlo Erba EA 1110 CHNS-O. For ICP–MS analysis the solid samples were dissolved in acidic mediun and digested under reflux for 6 h. Aliquots of the obtained solution were diluted to 50 cm³ using deionized water.

2.4.2. Temperature-programmed desorption (TPD)

The total amount of acid sites present on the catalysts was estimated by temperature-programmed desorption (TPD) of chemisorbed NH₃ recorded with a quadrupole mass spectrometer (Balzers QMS 100) connected to a quartz micro-reactor. 0.05 g of the catalyst sample were placed in the micro-reactor with a heating rate of 20 °C/min up to 200 °C under a He flow rate of 60 cm³/min, and then cooled down to room temperature. Then, a flow of 10 vol% NH₃ in He (60 cm³/min) was passed over the samples until no further uptake of ammonia was observed. Next, the gas flow was switch to a pure He flow and the sample was heated up to 120 °C. In this step, the physically adsorbed ammonia was desorbed. After that, the ammonia TPD profile was recorded upon heating the sample at a rate of $10 \circ C/min$ up to $350 \circ C$ under He atmosphere. The acid sites were evaluated assuming an interaction 1:1 between NH₃ and the acid site.

In order to obtain a better characterization of the ACFs support TPD experiments were carried out in a furnace coupled to a mass spectrometer (VG Quadrupoles). In these experiments, samples were heated up to 900 °C (heating rate 20 °C/min) under a helium flow rate of $60 \text{ cm}^3/\text{min}$. The quantification of gases that evolved as CO and CO₂ was analyzed in a mass spectrometer.

Table 1
Textural properties and TPD oxygenated groups.

Sample	VN_2^b (cm ³ /g)	VCO_2^c (cm ³ /g)	S BET (m ² /g)	CO (µmol/g)	CO ₂ (µmol/g)
A20 ^a	1.01	0.56	1990	2100	190
HPMo/A20 10	0.85	0.52	1752	-	-
HPMo/A20 21	0.64	0.43	1550	-	-
HPMo/A20 44	0.29	0.22	650	-	-
HPW/A20 12	0.82	0.51	1743	-	-
HPW/A20 24	0.61	0.41	1557		
HPW/A20 52	0.24	0.19	577		
A15 ^a	0.57	0.33	1290	1800	150
HPMo/A15 32	0.31	0.20	695	-	-
A10 ^a	0.53	0.40	1220	1580	170
HPMo/A10 27	0.31	0.24	677	-	-

^a ACFs of average fiber diameter from 13 to 15 µm (A20 to A10).

^b Total micropore volume (pore size <2 nm).

^c Narrow micropore volume (pore size <0.7 nm).

2.4.3. Thermogravimetry analysis of used catalyst

The catalysts, fresh and used were analyzed by Thermogravimetry (TA Instruments, SDT 2960). Experiments were carried out using 50 mg of sample, into a sapphire crucible, with a heating rate of $20 \,^{\circ}$ C/min up to $1000 \,^{\circ}$ C under He atmosphere (flow rate: $60 \,\text{cm}^3$ /min).

2.4.4. Analysis of leaching of catalysts by UV-visible

The leaching of the catalyst into the reaction mixture was investigated by UV–Vis spectroscopy (UV–vis/NIR Jasco V-670). Previous to the analysis, solutions were acidified up to pH 1 to ensure that all POM present in solution show Keggin structure. 264 and 220 nm were the main absorption bands analyzed, which correspond to $PW_{12}O_{40}^{-3}$ and $PMo_{12}O_{40}^{-3}$, respectively. These absorption bands were obtained by previous experiments for determining the absorbance dependence with the concentration (Bouguer–Lambert–Beer Law): $A = \varepsilon \times l \times C$, where A is the absorbance, C de concentration of dissolution, l the path length of cell (1 cm), and ε the molar absorption coefficient (37,100 l/mol/cm for anion $PW_{12}O_{40}^{-3}$; 5800 l/mol/cm for anion $PMo_{12}O_{40}^{-3}$).

2.4.5. Porous texture characterization

The porous texture of the ACF supports and the fresh and used catalysts samples were characterized by physical adsorption of gases (i.e., N_2 at $-196\,^\circ C$ and CO_2 at $0\,^\circ C)$ using volumetric equipments (Autosorb-6B and Autosorb-6, respectively, Quantachrome Instruments). Prior to the analysis, the samples were evacuated at 150 °C in vacuum for 4h. Additionally, for samples used 6 cycles, the effect of the degasification temperature was analyzed between 200 and 400 °C. Apparent surface area was determined by applying the Brunauer-Emmett-Teller (BET) equation. The Dubinin-Radushkevich (DR) equation was used to calculate the micropore volume. The different pore volumes used in our discussion have been calculated as follows: (a) The narrow micropore volume (pore size <0.7 nm), VCO₂, was estimated from CO₂ DRs plots (relative pressures <0.015); (b) The total micropore volume (pore size <2 nm), VN₂, was calculated from N₂ DRs plots (relative pressures <0.14).

3. Results and discussion

3.1. Support and catalyst characterization

Table 1 shows the porous texture characterization data of supports and catalysts obtained from the N_2 and CO_2 adsorption isotherms. It is important to remark that the comparison of both, VCO₂ and VN₂, gives us an idea about the micropores size. Regarding the supports, sample A20 shows VN₂ > VCO₂, which

denotes that there are wider micropores. It can also be seen that VN_2 of samples A10 and A15 are similar, showing the main differences in the VCO_2 , indicating that A15 contains a wider microporosity than A10. On the other hand, sample A20 has the highest specific micropore volume and surface area of all supports used in this work. As it was expected, HPA impregnation produces the reduction of the micropore volume. The higher the adsorbed amount, the higher the reduction. The study about where HPA are adsorbed and how their adsorption modifies the porous texture of ACF has been previously reported [18].

Regarding the surface chemistry, the analysis and quantification of the evolution of the surface oxygen groups, which evolve under thermal treatment to CO_2 and CO, provides information concerning the amount, the nature and the chemistry of oxygen groups present on the carbon surface. It is known that CO_2 evolves at low temperatures as a consequence of the decomposition of the acidic groups, whereas evolution of CO is originated by decomposition of basic, neutral or weakly acidic groups. From the TPD experiments it can be appreciated that all supports show similar acid surface groups, showing the main difference in their basic groups, being A20 the one that shows the highest amount of them.

Table 2 contains the elemental analysis and the quantification of acid sites of supports and the fresh and the used catalyst. The amounts of elements are closed to the expected values of HPA obtained from mass balance during their preparation by impregnation of support [18]. The experimental P/Mo and P/W ratios are in agreement with the exclusive presence of the Keggin compound on the support, which indicates that no HPA decomposition takes place during the impregnation process. Tables also contain the characterization of the reused catalyst after 1 and 3 catalytic cycles. As can be appreciated, the amount of HPA supported on the catalysts decreases with their use, which is indicative of a leaching process. This aspect will be analyzed on Section 3.3.2.

The most important property of prepared catalysts for the catalytic activity on this reaction is their acidity. The total amount of acid sites present on the catalysts was evaluated by TPD of NH₃, as it was used for the case of HPMo/TiO₂ catalysts [26], whose values are included in Table 2. As can be appreciated, initially the amount of acid sites increases with the HPA loaded up to 20-25 wt%, and then decreased at higher HPA loadings. This decrease in the surface acidity at high HPA contents has been reported by other authors, which can been explained by: (i) the remaining protons were inaccessible due to the pore blocking by HPA [18], (ii) these were neutralized by basic groups of support [27], or (iii) due the formation of a multilayer coverage of HPA on the support [28]. The main conclusion of this analysis is that, on the basis of similar acid sites values, in principle, all catalysts should show the same catalytic activity for the esterification reaction. This will be shown in the next section.



Fig. 1. Palmitic acid (1 g) conversion with 15 cm³ methanol as a function of time for HPMo and HPW (80 mg) using 30, 40 and 60 °C.

3.2. Catalytic activity tests

3.2.1. HPA catalytic activity tests

The experimental conditions used for the esterification of palmitic acid have been described in Section 2.2. It is important to indicate that HPA are soluble in the reaction medium (methanol) and, therefore, they act as homogeneous catalysts. In Fig. 1, the results obtained for the palmitic acid conversion versus time, for HPMo and HPW, carried out at temperatures between 30 and $60 \,^\circ$ C are shown.

Firstly, it can be observed that HPW shows a higher activity than HPMo which is in agreement with their strongest acidity [15]. Also it can be seen that final conversion is achieved almost completely during the first 6 h independently of the catalyst. It was observed that higher temperatures lead to higher conversion (the higher the temperature, the higher the conversion). This

Table 2

Elemental analysis and quantification of acid sites.



Fig. 2. Palmitic acid (1 g) conversion with 15 $\rm cm^3$ methanol versus amount of HPMo and HPW at 40 $^\circ C$ for 6 h.

increase of temperature is not homogeneous since increasing the temperature from 30 to 40 °C, higher conversions for similar time intervals and catalyst are reached. However for temperatures higher than 40 °C, a lower increase of conversion is detected. In addition, these conditions are less appropriated because they are close to methanol boiling point (63.7 °C).

From the above results, optimal experimental conditions were determined (i.e., 40 °C and 6 h). These experimental conditions were used to establish the optimal amount of catalyst. The obtained results are shown in Fig. 2. In this figure, it can be seen that, in the absence of catalyst and after 6 h at 40 °C, only a 5% of conversion is reached. In contrast, after the addition of around 3 mg of catalyst (approximately 2 μ mol HPMo and 1 μ mol HPW) a 25% of conversion is achieved. The same behavior can be observed for both catalysts, the higher the amount of catalyst, the higher the conversion. In fact, the conversion rises quickly up to values close to 40 mg (22 μ mol HPMo and 14 μ mol HPW). For higher amounts of catalyst, the increase is less significant. On the other hand, HPW

	-								
Sample	Mo (wt%)	P (wt%)	H (wt%)	C (wt%)	N (wt%)	O (wt%)	Mo/P ^c	HPMo ^d (wt%)	Acid sites ^e (µmol/g)
A20	0.00	0.00	0.03	95.10	0.42	4.45	-	-	37
HPMo	63.18	1.71	0.16	0.00	0.00	35.07	11.94	-	1511
HPMo/A20 10	6.51	0.17	0.04	85.11	0.37	7.80	12.38	10.3	213
HPMo/A20 21	13.10	0.36	0.06	75.30	0.34	10.84	11.76	20.7	325
HPMo/A20 44	29.12	0.77	0.09	51.02	0.23	18.77	12.22	46.1	288
1st cycle ^a	20.77	0.55	1.21	61.95	0.24	15.27	12.21	32.9	285
3th cycle ^a	16.95	0.45	1.98	65.95	0.24	14.43	12.18	26.8	215
A15	0.00	0.00	0.04	95.68	0.43	3.85	-	-	33
HPMo/A15 32	21.48	0.55	0.03	63.15	0.28	14.51	12.63	34.0	345
A10	0.00	0.00	0.04	96.12	0.44	3.40	-	-	35
HPMo/A10 27	18.76	0.49	0.03	67.76	0.31	12.64	12.28	29.7	351
Sample	W (wt%)	P(wt%)	H (wt%)	C (wt%)	N (wt%)	O (wt%)	W/P ^c	HPW ^d (wt%)	Acid sites ^e (µmol/g)
HPW	76.75	1.08	0.10	0.00	0.00	22.22	12.02	-	1120
HPW/A20 12	9.03	0.13	0.04	83.92	0.38	6.51	12.18	11.7	184
HPW/A20 24	19.10	0.27	0.05	71.85	0.31	8.43	11.93	24.9	296
HPW/A20 52	38.30	0.53	0.07	46.20	0.23	14.67	12.19	50.0	254
1st cycle ^b	26.47	0.37	0.93	61.34	0.24	10.64	12.06	34.5	261
3th cycle ^b	15.30	0.21	2.25	71.96	0.26	10.03	12.29	20.0	217

^a Used HPMo/A20 44 wt% at 40 °C.

^b Used HPW/A20 52 wt% at 40 °C.

^c Atomic ratio.

^d HPA loading in ACF.

^e Total acidity calculated by desorption NH₃ at temperatures higher than 120 °C.



Fig. 3. Palmitic acid (1 g) conversion with 15 cm^3 methanol carried out for 6 h at $40 \degree \text{C}$ using unsupported HPA and supported HPA as function of: (a) total amount of catalyst of HPMo/A20 44 wt% and HPW/A20 52 wt% and (b) HPA weight present in the reaction.

shows a higher catalytic activity than HPMo, being this difference more important for amounts above 25 mg.

3.2.2. Catalytic activity tests for HPA supported on activated carbon fiber A20.

Once the catalytic activity of HPA was determined and the reaction conditions were established, the next step was the analysis of the catalytic activity for the HPA supported on the carbon material. For this purpose, as in the previous study, firstly, the optimal amount of catalyst was studied using, as starting point, the same experimental conditions applied in Section 3.2.1 (i.e., 40 °C and 6 h).

For this study, two supported catalysts were selected: (i) HPMo/A20 (44 wt% of HPMo) and (ii) HPW/A20 (52 wt% of HPW). In Fig. 3a palmitic acid conversion results are plotted versus the total amount of supported catalyst (including both the weight of the catalyst and the A20 fiber). In the same figure, these results are compared with those obtained from the unsupported HPA. Additionally, palmitic acid conversion obtained for the activated carbon fiber A20 is included. As can be seen, A20 fiber shows a low catalytic

activity value, in agreement with their lower acid sites in comparison with HPA/A20 as lists Table 2. This activity can be explained by the presence of acidic surface oxygen groups, as shows Table 1, specifically the CO_2 groups related with carboxylic acids. So, clearly the catalytic activity shown by the HPA/A20 is related to the presence of HPA. According with the results in Fig. 3, it can be concluded that supported HPA keep their catalytic activity for the palmitic acid conversion. Tendencies of supported HPA on the carbon material are quite similar to the unsupported HPA. It can be observed that increasing the amount of catalyst, conversion increases quickly, reaching high values up to values of 100 mg. For higher amounts of catalyst, the increase of the activity is less significant. These results agree with those previously published by other authors [25].

Results in Fig. 3a seem to indicate that catalytic activity of the supported HPA is lower than the unsupported HPA. For a more appropriate comparison, conversion results, taking into account the amount of HPA present in the reaction medium (i.e., subtracting the weight of the support), are shown in Fig. 3b. In this figure it can be observed that supported HPA present a similar trend to that showed by unsupported HPA. Moreover, for low amounts of catalyst, supported HPA exhibit a lower activity than unsupported samples. However, increasing the amount of catalyst, catalytic activity is becoming more similar, reaching comparable values around 80–100 mg. This fact could indicate that, at these experimental conditions, the reaction is governed by the mass transfer of the reagents from the solution to the microporosity (where the HPA are anchored) and the subsequent product release. However, analyzing only the supported catalysts, the fact that, throughout the range, the reaction rate (estimated from the conversion/time ratio) increases proportionally with the catalyst weight, indicates (in agreement with Madon-Boudard [29]) that the reactions have been performed in absence of mass transfer control.

The similar catalytic activity shown by the supported-catalysts, beside the results obtained from the homogeneous reaction, indicates the high catalytic activity of the supported HPA. This behavior contrasts with the previous results published which show a decrease of the catalytic activity for supported HPA samples [30,31]. In our case, the results seem to indicate that the catalytic activity is even higher, taking into account that, being anchored on the surface of the carbon material, not all HPA molecules participate in the reaction. Thus, the amount of HPA that acts in the reaction would be less than in the homogenous reaction, which is in agreement with the lower acid sites (see Table 2) shown by HPMo/A20 44 wt% and HPW/A20 52 wt% regarding expected on the basis of the HPA loading. Additionally, it must be highlighted the easy accessibility of the palmitic acid to the active sites of HPA, which are located in the super-microporosity of A20 fiber. In principle, this fact did not seem to be feasible since the dimensions of the porosity, where the HPA are adsorbed, are lower than 2 nm (microporosity) and the size of HPA is \sim 1 nm. These results in a free space less than 1 nm and the dimensions of palmitic acid (linear chain of 16 carbon atoms with a carboxylic acid in one of the edges) are 1.9 nm of length and a diameter of 0.6 nm. In this sense, previous analysis carried out with different activated carbon fibers (A10 and A15), (see supplementary material, Fig. A.1) at the same experimental conditions, demonstrated that the catalytic activity of the latter samples was very low, even using a similar amount of HPA and with a higher amount of acid sites than those shown by HPMo/A20 (see Table 2). Considering that samples A10 and A15 show a narrower microporosity than A20 (Table 1), these results confirm the influence of the pore size on the kinetic control of the reaction, allowing or restricting the accessibility of the reagents [32].

The above comments are also reflected on the analysis of the results extracted from the study of temperature and time effect on the palmitic acid conversion using supported catalysts (Fig. 4). Thus, it can be observed that, for temperatures of 40 and 60 °C, the



Fig. 4. Palmitic acid (1 g) conversion with 15 cm³ methanol as a function of time for samples HPMo/A20 44 wt% and HPW/A20 52 wt% (80 mg of HPA) at 30, 40 and 60 °C.

behavior of the catalysts is similar, both the conversion reached and the kinetic, to those obtained for homogeneous phase experiments (Fig. 2). The conversion reached the maximum value after 6 h of reaction. For temperatures higher than 40 °C, no significant increase in the conversion is observed. By contrast, for temperatures of 30 °C, supported catalysts show a slower kinetics than for homogenous phase. This different behavior may be due to the lower diffusion of the palmitic acid at 30 °C. Finally, the kinetic analysis of data contained in Fig. 4 are in accordance with the expected first order chemical reaction (Fig. A.2 supplementary material), which is in agreement with the comments that the reaction takes place without mass transfer control.

3.3. Study of the reuse of the supported catalysts in several successive reactions

3.3.1. Reuse of the supported HPA.

The reuse of the catalysts in several successive reaction cycles is of great interest from an economical and operational point of view [33]. In many cases, supported catalysts are submitted to a regeneration step of the active phase, previous to their reuse. In this work, successive experiments were performed using the same HPA/A20 sample, which was added to a fresh solution without any intermediate regeneration step. Conversion results obtained in the first three cycles (for the three temperatures tested) are shown in Fig. 5.

In general, the catalytic activity decreases after each cycle. This decrease depends on the reaction temperature and on the nature of the HPA. Thus, although HPW/A20 shows a higher catalytic activity in its first cycle, this catalyst is less efficient than HPMo/A20 for successive cycles, in the senses that show a higher loss on their catalytic activity. On the other hand, independently of the HPA used, a minor decrease of the catalytic activity occurs at 40 °C.

3.3.2. Analysis of the catalytic activity decrease for the supported HPA after successive reaction cycles

3.3.2.1. Determination of the percentage of catalyst leached. In heterogeneous catalysis, decrease of the catalytic activity can be caused by different factors [32]: e.g., (i) loss of the supported catalyst to the bulk of solution (leaching), (ii) inaccessibility of the reagents to the active sites present in the microporosity (fouling)



Fig. 5. Palmitic acid (1 g) conversion with 15 cm^3 methanol after catalyst reuse for successive cycles using HPMo/A20 44 wt% and HPW/A20 52 wt% (80 mg of HPA) at 30, 40 and 60 °C during 6 h.

Table 3	
Leaching percentage based on the initial amount of fresh catalyst.	

Leaching (wt%)						
Temperature (°C)	Cycle number					
	1	2	3	1	2	3
60	54	15	11	30	12	10
40	48	10	9	24	8	8
30	37	10	8	20	7	7
	HPW/A20 HPMo/A20				20	

and (iii) deactivation of the active sites. In this particular reaction, leaching of a fraction of the supported HPA (at similar reaction conditions) has been observed by other authors [19,20]. In this study, yellow coloration of solution during reaction was observed for HPMo/A20 samples, indicative of catalyst leaching. With the aim of quantify the amount of catalyst which is being leached after successive cycles, solutions were analyzed by UV/Vis spectroscopy. Leaching percentages, taking into account the initial amount in the fresh catalyst (80 mg HPA), are summarized in Table 3. The obtained results show a clearly trend with the reduction in the catalytic activity (Fig. 5). HPW/A20 presents the higher amount of leached catalyst, which agrees with its lower activity. Similar tendencies have been observed by other authors [34] whom analyzed leaching of HPW and HPMo supported on SiMCM-41 in an ethanol/water medium. In the same way, the higher the reaction temperature, the higher the loss of catalyst, which would explain the higher decrease of the catalytic activity observed in the experiments performed at 60 °C. However, leaching of the supported catalyst cannot explain the results shown in Fig. 5. So, although the highest loss of catalyst occurs during the first cycle, this is not reflected in the catalytic activity decrease, which is more pronounced in the third cycle. On the other hand, the catalysts behavior at 30 °C can neither be justified with these leaching results since there is a higher reduction in the catalytic activity even when the loss of catalysts is lower.

A more detailed analysis of the Table 3 reveals two different conclusions. On one hand, with the exception of the first cycle, the amount of catalyst in the solution in each cycle varies from 8 to 9 mg for HPW/A20 and 6–7 mg for HPMo/A20. Taking into account these amounts of catalyst, reaction which would take place in homogenous phase only could reach conversions around 20–30% (Fig. 2). This fact would not explain the high conversions achieved in cycles 2 and 3. Therefore, these results confirm that esterification reaction occurs, mainly, in a heterogeneous phase. By other hand, the amount of catalyst, which remains supported after successive

cycles, fluctuates between 30 and 50 mg in the case of HPW/A20 and 50–60 mg for HPMo/A20 (see Table 2). In addition, the amount of acid sites (Table 2) is high enough to allow reaching conversions higher than 60%, in accordance with results showed in Fig. 3b. Therefore, the important reduction observed in the catalytic activity for experiments carried out at 30 °C and in the third cycle at 60 °C has to be consequence of other factors.

3.3.2.2. Determination of porosity blockage of the support. Palmitic acid is a white solid which melts at 63 °C and evaporates at 351 °C. It is insoluble in water, scarcely soluble in cold methanol and soluble in hot methanol. All these facts suggest that at the experimental conditions, below the melting point and in a medium where this compound is not soluble, palmitic acid may precipitate. For this reason, it is reasonable to think that this compound can be retained in the porosity of the support, not only taking into account its dimensions but also for solubility reasons. This fact may explain the fast deactivation of catalysts at 30 °C. So, after successive cycles, accumulation of palmitic acid (or its reaction product) is blocking the active sites, with the subsequent reduction of the catalytic activity. This phenomenon has been described by Liu et al. [35]. In order to prove this hypothesis, different thermogravimetric experiments were carried out with fresh catalysts and the catalysts recovered after cycle 1 and 3. These results are shown in Fig. 6.

As it can be observed from Fig. 6, after the use of the catalysts, TG curve shows a new loss weight stage between 200 and 400 °C. Neither the support nor the fresh catalysts present this new stage. So, this new weight loss may be attributed to the adsorbed compounds (palmitic acid or its reaction product, methyl palmitate) on the support porosity. For both catalysts, the adsorbed amount increases with the number of cycles, being this amount quite similar for both catalysts. Therefore, these results indicate that: (i) retention is caused mainly by the physical adsorption of these compounds on the microporosity of the support and (ii) these compounds are being accumulated after each cycle.

In order to elucidate if the adsorption of these compounds occurs inside the microporosity of the activated carbon fiber A20 or it is only on the surface of the support, porosity of the catalysts after three cycles was studied by physical adsorption of N₂ at -196 °C. These isotherms were compared with that obtained with the fresh catalyst. Isotherms are plotted in Fig. 7. Previous to the degasification stage, samples were washed with ethanol (5 min under agitation). The reason for this washing step was based on the fact that the analysis of the isotherms revealed no adsorption for the used unwashed samples. Comparing washed and unwashed isotherms, it can be observed that the unwashed ones hardly show N₂ adsorption. However, the washed samples show an adsorption capacity similar to the fresh catalyst. These results agree with the formation of a solid film on the external part of the fiber. Thus, once fibers are removed from the reaction medium, these are impregnated with the solution. After solvent (methanol) evaporation, components from solution (palmitic acid and palmitate) remain on the surface of the activated carbon fibers. Washing step with ethanol allows dissolving these compounds. Other authors have used a washing step with hexane for 12 h to remove of this film [32]. However, even the washing step with ethanol, the adsorption capacity of the catalysts is reduced after each reuse. This behavior cannot be attributed to the formation of such a film. This adsorption capacity reduction is related to the retention of species (palmitic acid and/or methyl palmitate) on the microporosity of the activated carbon fiber. In this sense, the obtained results agree with the trends observed in the TG curves. The higher the reuse, the higher the adsorption of these compounds, and, hence, a lower porosity is available after each cycle. However, the amounts of these retained species, obtained by TG analysis, do not correlate with the decrease in the N₂ adsorption capacity. Thus, for the first cycle, isotherms



Fig. 6. TG experiments corresponding to A20, fresh catalyst (a) HPW/A20 52 wt% and (b) HPMo/A20 44 wt% and after the first and the third reaction cycle ($40 \degree C$ and 6 h).

of the washed samples show an adsorption capacity similar to the one obtained for the fresh catalyst, even when *TG* shows a retained amount around 50% of that shown by the 3rd cycle sample. However, for the catalysts used in three cycles, their isotherms present an important reduction of the adsorption capacity, what is reasonable. All these results seem to indicate that retention of these species on the porosity takes place progressively. Firstly, on the external part of the fibers and subsequently towards the inner part. Finally, as it has been commented previously, sample HPW/A20 shows a larger reduction of porosity over the cycles, which may be attributed to a higher retention of the substances in the reaction medium.

With the aim of establishing a relation between the porosity reduction of the catalysts and the presence of reaction products that can be adsorbed; a catalysts (HPMo/A20 44 wt%) whose catalytic activity was reduced drastically up to 20% of conversion after 6 cycles was selected. The influence of the degasification temperature on the porosity was analyzed using this catalyst. Fig. 8 presents the N₂ adsorption isotherms of this sample using different degasification temperatures. As can be seen, even applying an outgassing temperature of 250 °C, catalyst shows a low porosity development



Fig. 7. N₂ adsorption isotherms at -196 °C of the fresh catalysts (a) HPW/A20 52 wt% and (b) HPMo/A20 44 wt% and the same catalyst used over 1, 2 y 3 cycles 40 °C at 6 h outgassed at 150 °C.

which would explain the low conversion observed. The increase in the outgassing temperature provokes an increase in the N_2 adsorption capacity which indicates a higher presence of accessible porosity. For temperatures of 400 °C, adsorption capacity is closed



Fig. 8. N₂ adsorption isotherms at -196 °C of the fresh catalysts HPMo/A20 44 wt% and the same catalyst used over 6 cycles (40 °C at 6 h) outgassed at different temperatures.

to the fresh catalyst values. These results agree with the weight evolution observed in Fig. 6, in which for temperatures of $400 \,^{\circ}$ C, the weight loss corresponding to the adsorbed compounds takes place almost completely, confirming the relation between porosity reduction of the catalysts and the adsorption of compounds present in the solution.

3.4. Process improvements for a higher reuse of the catalysts

Results analyzed in the latter section indicate: (i) leaching and (ii) fouling due to the porosity blockage are the main factors responsible of the reduction of the catalytic activity (especially for the HPW catalyst). Therefore, with the objective of maintaining a high catalytic activity during successive reaction cycles, these two factors must be reduced.

The results highlight that the main leaching takes place in the first cycle, while for the successive cycles, it is much lower. Therefore, these values suggest that a fraction of the supported catalyst is strongly anchored to the support and, hence, catalyst is not easily leached. Thus, different experiments were carried out using catalysts with similar amounts of supported HPA to those which exist in HPW/A20 catalysts (52 wt%) after the first and the third cycle (see Table 2). Specifically, two different samples of HPW/A20 with 24 and 12 wt% were analyzed, performing the experiments at 40 °C for 6 h with 80 mg of the supported catalyst (340 mg of HPW/A20 (24 wt%) and 650 mg of HPW/A20 (12 wt%)). Interestingly, low conversions were obtained with both, 45% and 14%, respectively, despite the higher acidity that shows these samples (see Table 2). Similar results were obtained using HPMo with amounts of 21 and 10 wt% (43% and 13%, respectively). These results highlight that not all the supported HPA shows the same catalytic activity. We have to take into account that, according to the highest adsorption potential, the filling of the porosity occurs, firstly, in pores of smaller size and then in pores with a larger size [18]. In other words, for initial amounts of HPA (around 10 wt%) its adsorption is produced preferably in the smallest porosity which presents the highest adsorption potential. When the adsorbed amount of HPA increases, the adsorption takes place on the microporosity that is becoming available, the higher the amount adsorbed, the larger the size of the porosity where the HPA is being adsorbed. Therefore, the degree of filling seems to be related to the decrease in the catalytic activity since HPA is adsorbed in a microporosity which is not accessible to the palmitic acid. This agrees with the low catalytic activity shown by other supports with a smaller pore size (A15 and A10). Another possibility would be that the fraction of HPA strongly anchored presents a lower catalytic activity [36,37]. So, for samples HPW/A20 (52 wt%) and HPMo/A20 (44 wt%) only half of the amount shows an acceptable catalytic activity which corresponds to the HPA located in the wider microporosity of the A20. This micropore size is suitable for the reaction, allowing the inlet and outlet of the reagents and products. On the other hand, when the sample is reused, this porosity has a disadvantage since catalyst adsorbed on these pores is more easily leached because of its adsorption is weaker. Thus, it is clear that there exists an optimum micropore size for HPA adsorption and its subsequent application on this reaction. In this sense, taking into account this hypothesis, in the particular case of HPMo, its lower leaching degree and its higher catalytic activity could be explained considering that, due to the size of this compound, a higher amount of catalyst is adsorbed on the optimum pore size range. Considering all the above arguments, leaching issue can be minimized using HPMo as catalyst. A more detailed study of this process would involve the optimization of the porosity.

The second reason of the decrease in the catalytic activity is the fouling caused by the porosity blockage. A possible solution for this issue is based on a thermal treatment of the catalysts after each cycle, which is a common practice for regenerating this kind



Fig. 9. Palmitic acid (1 g) conversion with 15 cm³ methanol using HPMo/A20 44 wt% for 6 h at 40 °C after successive reuse cycles without washing, washing with ethanol and, washed with ethanol acidified with H_2SO_4 .

of catalysts [20]. As it has been pointed out previously, removal of these compounds occurs at temperatures higher than 250°C, being necessary higher values (>350 °C) for the complete removal (Figs. 6 and 8). In this sense, HPMo/A20 was submitted to a thermal treatment at 300, 350 and 400 °C after its first reaction cycle (40 °C and 6 h). During this thermal procedure a weight loss between 11% and 17% is achieved. From the three different selected temperatures, the best results were obtained using 350 °C. In this particular case, the conversion was 44%, which is much lower than that obtained for the second cycle without regeneration (73%). These results are due to two processes which take place during the thermal treatment. An effective removal of the adsorbed compounds requires temperatures higher than 300 °C. However, from 350 °C a partial decomposition of the Keggin structure occurs and hence the reduction of its acidity [15]. This reduction provokes the deactivation for this reaction. Therefore, thermal treatment of the catalyst is not suitable for its regeneration.

An alternative to eliminate adsorbed compounds from the microporosity can be by using solvents. This process has been applied successfully by other authors for the extraction of products from Fries transposition reaction of phenyl acetate on SBA-15 [38] or the removal of by products from the biodiesel process using a first washing step with hexane in order to eliminate nonpolar compounds, following by methanol to extract polar products [32]. In our case, we tested that the use of ethanol was effective and necessary to dissolve compounds adsorbed on the external microporosity. Thereby, after each cycle, catalysts were washed with ethanol for 30 min at 40 °C. The obtained results are shown in Fig. 9. As it can be observed in this figure, the washing step with ethanol causes a rapid decrease in the catalytic activity. In fact, the higher the number of cycles, the lower the catalytic activity, being effective only for the first 3 cycles. In this sense, this procedure is not effective since produces worse results than for the unwashed catalysts. Textural characterization of the reused catalyst after the 4th washing step showed an N₂ adsorption capacity at $-196 \,^{\circ}\text{C}$ of $350 \,\text{cm}^3/\text{g}$ (STP) (Fig. A.3 supplementary material). This value is higher than that obtained with the fresh catalyst (Fig. 7b). This behavior can only be explained if the catalyst presents a lower amount of HPMo. This result indicates that the washing step with ethanol, even though is effective for the removal of organic by products adsorbed on the porosity, also causes the leaching of the HPMo. Thus, pH of the washing solution is around 5-6. At these conditions, decomposition of Keggin structure of HPMo is favored, which would explain the reduction of the catalytic activity after the 3rd cycle.

Taking into account these results and in order to avoid the HPMo decomposition, pH of the ethanol solution was adjusted to 3 by using H_2SO_4 . With this last regeneration option, the best results were obtained as it can be seen in Fig. 9.

These results, especially for the first three cycles where the catalytic activity remains unchanged, are a consequence of the role of the H⁺ coming from the H₂SO₄. In order to elucidate how H⁺ are affecting the activity, two different analyses were performed. On one hand, A20 was submitted to the same washing procedure and then it was tested in the reaction. The obtained results pointed out that the washing step introduced no improvement (8%), rejecting a possible adsorption of H⁺ on the porosity of the carbon material A20. On the other hand, titration of the washing solution after the process indicated that all H⁺ from the H₂SO₄ were in the solution. Despite of this result, it must be taking into account that the error of the titration is around 50 μ mol, which is on the same magnitude order than the amount of the catalytic sites (see Table 2).

One of the reasons of the reduction of the catalytic activity is the deactivation of the active sites, Brönsted acid sites. This can be due to the water cluster formation strongly bonded around the active sites [40] which is being formed during the esterification reaction. This process is critical in the case of catalysts that use zirconia as support since they are easily deactivated by water. In this particular case, a calcination step is necessary at temperatures higher than 300 °C for its regeneration [20,39]. In our case this effect is not very important because the carbon support presents a high hydrophobicity and HPA are water-tolerant acid catalysts. These results seem to indicate that activated carbon fibers are suitable for this application. Another cause may be the irreversible adsorption of palmitic acid on the acidic active sites [35]. Thus, the palmitic acid can pass into solution during the reaction or in the washing step, removing the H⁺ of the acid sites. This process would be the reason of the gradual decrease of the acid sites during the reuse of the catalysts. In this sense, during the washing step, H⁺ coming from the H₂SO₄ can regenerate these active sites and, hence, maintain the catalytic activity for a longer number of cycles.

4. Conclusion

Supported heteropolyacids on activated carbon fibers result suitable catalysts for esterification reaction of the palmitic acid. However, using ACF with a narrower pore size distribution, catalytic activity is not observed. This fact indicates an important influence of the micropore size of the support on the kinetic control of the reaction because it allows or restricts reagent accessibility.

Also, catalytic activity of HPA is closely related with the micropore size in which they are adsorbed. So, it seems that there is an optimum microporosity for the HPA adsorption, which must be wide enough to allow its entrance and exit of the reagents and products but not too wide in order to avoid the leaching of the catalyst since adsorption would be weaker.

HPW is more effective than HPMo because the first shows a higher acidity. Nevertheless, HPW results less effective than HPMo/A20 for successive cycles.

The main causes of the reduction of the catalytic activity of the supported HPA are: (i) leaching (especially for the HPW) and (ii) soiling caused by the porosity blockage. Leaching takes place mainly during the first cycle while the adsorption on the porosity of compounds present in the solution occurs progressively, starting from the external part of the fibers and progressing inward.

Thermal treatment of the catalysts is not a suitable process for the regeneration. Temperatures required for the recovery of the porosity produce the partial decomposition of catalysts. The use of ethanol to eliminate the by products adsorbed on the porosity is not effective since it increases the catalyst leaching. Washing step using ethanol and H_2SO_4 has been demonstrated to be the most effective treatment for the catalyst regeneration. H_2SO_4 has a dual role: (i) it provides an acidic medium which reduces HPA leaching and (ii) H⁺ coming from the H_2SO_4 regenerate the active sites and thereby maintains the catalytic activity a higher number of cycles.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.09. 006.

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