

Short Communication

Acetylation of glycerol over heteropolyacids supported on activated carbon

P. Ferreira^a, I.M. Fonseca^b, A.M. Ramos^b, J. Vital^b, J.E. Castanheiro^{a,*}^a Centro de Química de Évora, Departamento de Química, Universidade de Évora, 7000-671 Évora, Portugal^b REQUIMTE, CQFB, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

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ABSTRACT

The acetylation of glycerol was carried out over dodecatungstophosphoric acid (PW) supported on activated carbon, being the monoacetic, diacetic and triacetic the reaction products.

A series of catalysts, with different heteropolyacid loading (from 3.5 to 6.5 wt.%), were prepared. It was observed that the catalytic activity increases with the amount of PW immobilized on the activated carbon, being the PW2_AC (with 4.9 wt.%) the most active sample. However, at high loading of heteropolyacid on the activated carbon, a decrease on the catalytic activity was observed, which can be probably explained due to some hindrance in the activated carbon porous system.

All catalysts exhibited good values of selectivity to the diacetic.

Catalytic stability of the PW2_AC was also studied by performing consecutive batch runs with the same catalyst sample. After the third batch, it was observed that the catalytic activity stabilized.

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1. Introduction

Glycerol is a byproduct of biodiesel production. Glycerol is a very promising low-cost feedstock or platform molecule for producing a wide variety of value-added special and fine chemicals [1–3]. Acetylation of glycerol can be a good alternative to the glycerol produced by biodiesel. The products of glycerol acetylation, monoacetic, diacetic and triacetic (Scheme 1), have a great industrial applications. The triacetic has applications going from cosmetics to fuel additive, while the monoacetic and diacetic have applications in cryogenics and as raw material for production of biodegradable polyesters [1–3].

Traditionally, the esterification reactions have been carried out over strong homogeneous acid catalysts, e.g. sulphuric acid. However, in order to become the processes into “green processes”, the liquid acids have been replaced by solid acids.

Esterification of glycerol with acetic acid has been carried out in the presence of zeolites and ionic resin [4], mesoporous silica with sulfonic acid groups [5] and Starbon[®][6].

Heteropolyacids (HPAs) are widely used as acid catalysts, due to their very strong Brønsted acidity and their structural properties [7,8]. However, the HPAs have a low specific surface area (1–10 m²/g). In order to increase the specific surface area of HPAs or even better to increase the number of accessible acid sites of the HPAs, a variety of supports like activated carbon [9–12], silica [13–18], zeolite [19–21] and polymeric matrixes [22–24] have been used to immobilize HPAs.

Heteropolyacids have been used as catalysts in different reactions where the glycerol is involved, such as dehydration [25–28], esterification [29–31], acetalisation [32] and dichloropropanol synthesis [33].

In this work, we study the esterification of glycerol with acetic acid over dodecatungstophosphoric acid (H₃PW₁₂O₄₀) immobilized on activated carbon.

2. Experimental

2.1. Preparation of the catalysts

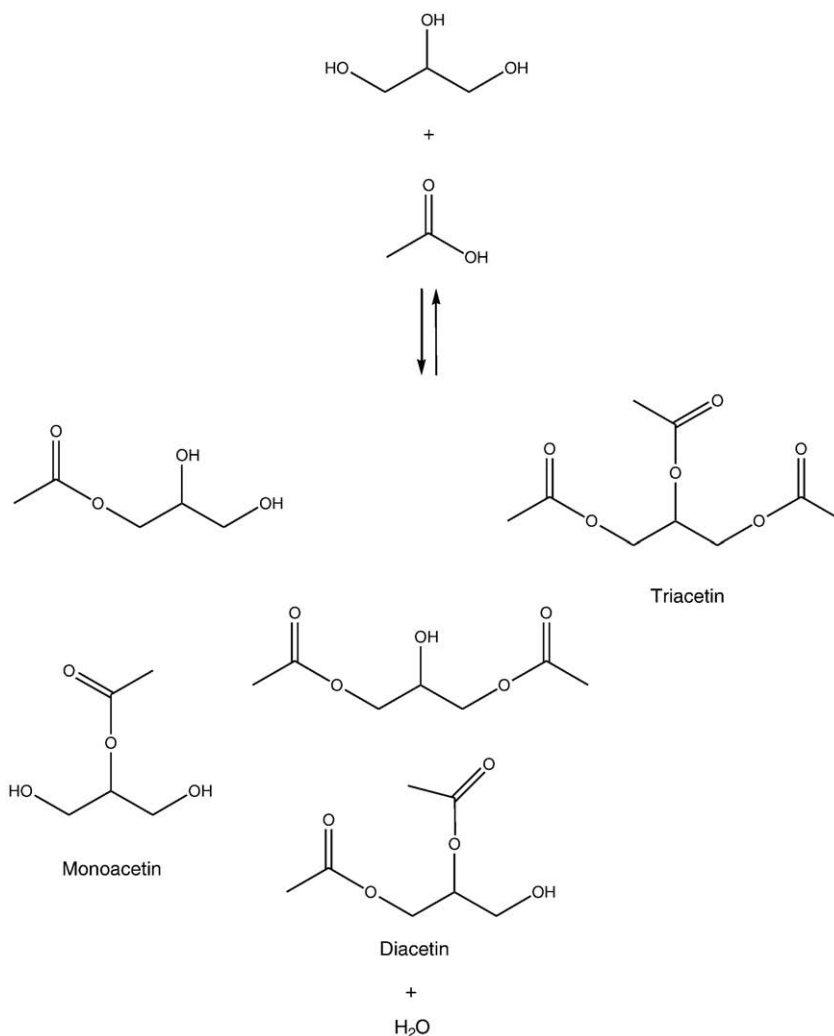
The immobilization of PW on activated carbon was carried out according to Chimienti et al. [13]. Before the impregnation experiments, the activated carbon (AC) was first washed in a solution of 0.1 M NaOH, then in 0.1 M HCl to eliminate the soluble acidic and alkaline impurities. After this treatment, the activated carbon particles were then treated with a 30 wt.% solution of HNO₃ and heated up to boiling in a reflux system for 2 h to make the carbon more acidic. HPW solutions with different concentrations were prepared by using a mixture of demineralized water and ethanol (96%) in a volumetric ratio of 1:1, as solvent. The pretreated activated carbon particles were then impregnated by the prepared HPW solutions. After drying overnight, these catalysts were calcined at 403 K by an air flow of 4 h. The catalysts were excessively washed in ethanol after the calcination step.

2.2. Characterization of the catalysts

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

* Corresponding author. Tel.: +351 266745311; fax: +351 266744971.

E-mail address: jefc@uevora.pt (J.E. Castanheiro).



Scheme 1. Esterification of glycerol with acetic acid.

ASAP 2010 apparatus. The amount of dodecatungstophosphoric acid immobilized on activated carbon was measured by dissolving the catalyst in $\text{H}_2\text{SO}_4/\text{HF}$ 1:1 (v/v) and analyzing the obtained solution by using inductively coupled plasma analysis (ICP), which was carried out in a Jobin-Yvon ULTIMA instrument. FT-IR spectra were recorded on a Bio-Rad FTS 155 FTIR spectrometer at room temperature in KBr pellets over a range of $400\text{--}4000\text{ cm}^{-1}$ under atmospheric conditions. The X-ray diffraction (XRD) patterns of the heteropolyacid, activated carbon and catalysts were obtained by using a Rigaku Miniflex powder diffractometer with built-in recorder, using $\text{Cu K}\alpha$ radiation, nickel filter, 30 mA and 40 kV in the high voltage source, and a scanning angle between 5 and 55° of 2θ at a scanning rate of $1^\circ/\text{min}$.

2.3. Catalytic experiments

The catalytic experiments were carried out in a stirred batch reactor at reflux conditions. In a typical experiment, the reactor was loaded with 20 cm^3 of acetic acid, 2 g of glycerol and 0.2 g of catalyst.

Stability tests of PW2_AC were carried out by running four consecutive experiments, in the same reaction conditions. Between each catalytic experiment, the catalyst was separated from the reaction mixture by centrifugation, washed with water and dried at 120°C overnight.

A posterior catalytic experiment was also conducted where the PW2_AC (0.2 g) was put in contact with acetic acid (20 cm^3) during 72 h, at 120°C under stirring, without glycerol. After this period, the

catalyst was separated from acetic acid by centrifugation, and the glycerol was added to the reaction mixture.

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

3. Results and discussion

3.1. Catalysts characterization

Table 1 shows the textural characterization (S_{BET} specific area (S_{BET}), microporous volume (V_{micro}) and total porous volume) of the

Table 1
Physicochemical characterisation of catalysts: amount of PW; microporous volume (V_{mic}); total porous volume (V_{total}); external surface area (S_{ext}); BET surface area (S_{BET}); Keggin-anion density.

Sample	Amount PW ^a (gPW/gsupport)	S_{BET}^b (m^2/g)	S_{ext}^c (m^2/g)	V_{mic}^c (cm^3/g)	V_{Total}^d (cm^3/g)	Keggin-anion density/HPA nm^{-2}
AC	–	836	81	0.34	0.49	–
PW1_AC	0.035	588	53	0.24	0.35	0.012
PW2_AC	0.049	389	35	0.15	0.22	0.026
PW3_AC	0.065	352	26	0.11	0.20	0.039

(a) ICP.

(b) BET.

(c) *t*-Method.

(d) $(p/p^*) = 0.98$.

catalysts. The specific surface area (S_{BET}) was determined by using the BET method while microporous volume (V_{micro}) and external surface area were determined by the t -method, using a standard isotherm proposed by Rodríguez-Reinoso et al. [34]. It was observed that the immobilization of dodecatungstophosphoric acid on activated carbon leads a decrease of the surface area, microporous volume and total porous volume. The reduction in surface area, microporous volume and total porous volume of catalysts may be due to the blockage of pores by active species. A similar result was also observed by Sepulveda et al. [12].

The Keggin-anion density of the catalysts (HPA nm^{-2}) expressed as the number of Keggin anions per square nanometre, was calculated according to the actual PW loading and catalyst surface area (Table 1). The surface coverage of catalyst was calculated according to a literature method using the following equation [26]:

$$\text{Keggin-anion density (HPA nm}^{-2}\text{)} \\ = \frac{[\text{HPA loading (wt\%)} \div 100] \times 6.02 \times 10^5}{\text{BET surface area of catalyst (m}^2\text{.g}^{-1}\text{)} \times 2880.2}$$

It was observed that all catalysts have showed low Keggin-anion density. It was also observed that when the amount of PW immobilized on activated carbon increases, the density increases as well. Atia et al. [25] and Chai et al. [26] also observed analogous results.

Fig. 1A shows the FTIR spectra of the PW (Fig. 1A), PW1_AC (Fig. 1B), PW2_AC (Fig. 1C) and PW3_AC (Fig. 1D). Pure PW exhibited typically four major IR bands located at 1080, 985, 890 and 839 cm^{-1} attributed to absorption modes of Keggin ion $[\text{PW}_{12}\text{O}_{40}]^{3-}$. The bands at 1080, 985, 890 and 839 cm^{-1} are assigned to the stretching modes

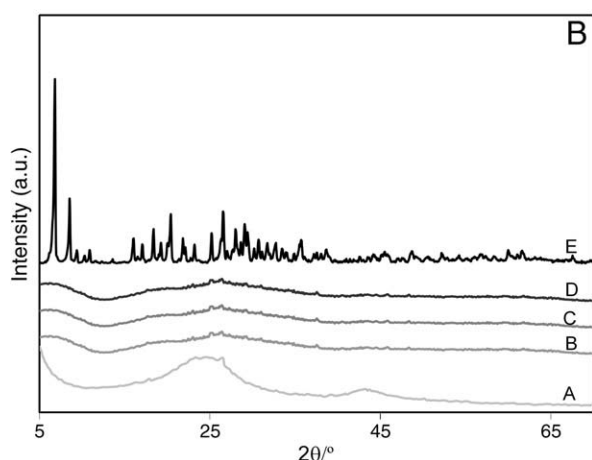
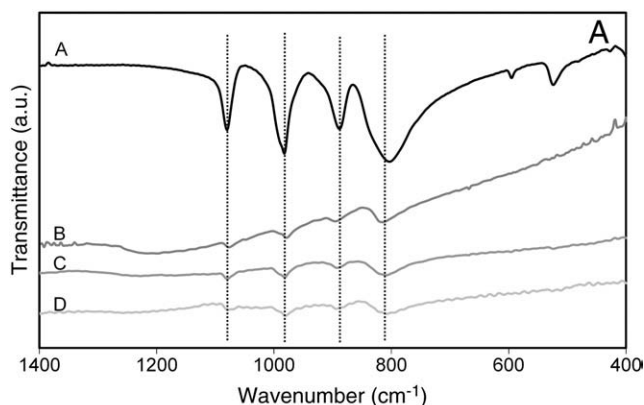


Fig. 1. A. FTIR spectra: (a) PW; (b) PW1_AC; (c) PW2_AC; (d) PW3_AC. B. XRD patterns of (a) AC; (b) PW1_AC; (c) PW2_AC; (d) PW3_AC; (e) PW.

of oxygen atom bond to tungsten and phosphorous, P–O, W=O, W–O–W in corner shared octahedral and W–O–W in edge shared octahedral, respectively [35]. In all catalysts, it was observed the characteristic bands of Keggin structure. Similar results were also observed by Chimienti et al. [13] and Kulkarni et al. [35].

XRD patterns of the heteropolyacid, activated carbon and catalysts are shown in the Fig. 1B. No diffraction peaks assigned to PW were detected on the catalysts. This result indicates that the particles are too small or well dispersed to be detected by XRD [35]. Another reason for no diffraction lines due to PW is the low loading of the heteropolyacid on activated carbon. The low value of surface density (Table 1) indicates high dispersion of HPA over the activated carbon, which could explain why XRD of the catalysts did not show any crystalline phases related to the heteropolyacid. Atia et al. [25] has also observed similar behaviour.

3.2. Catalytic experiments

Fig. 2 compares the initial activity of PW_AC catalysts loaded with different amounts of HPA on the esterification of glycerol with acetic acid. It was observed that the initial catalytic activity increases with the HPA content until a maximum value, which was obtained with PW2_AC catalyst. With higher heteropolyacid load on activated carbon, a decrease in the catalytic activity is observed. At low PW_AC loads, the increase of the heteropolyacid amount, leads to the increase of activity, probably by kinetic effect. However, with the higher amount of heteropolyacid on activated carbon, leads a decrease of catalytic activity. These results can be explained due to the internal diffusion limitations inside the porous catalysts. A decrease of S_{BET} , microporous volume and porous volume (Table 1) with the amount of heteropolyacid on activated carbon was observed. The accessibility to acid sites might decrease as well.

The catalytic activity of PW2_AC, in the esterification of glycerol with acetic acid, was compared with the activity of others catalysts used in this reaction, reported in the literature. The catalytic activity (expressed as $\text{mol/h mol}_{\text{H}^+}^{\text{cat}}$) of the different solid catalysts increases as follow: $2.46 \times 10^{-3} \text{ mol/h mol}_{\text{H}^+}^{\text{cat}}$ (obtained with HZSM-5, [4]) $< 6.01 \times 10^{-3} \text{ mol/h mol}_{\text{H}^+}^{\text{cat}}$ (obtained with PW_2O_5 , [31]) $< 2.13 \times 10^{-2} \text{ mol/h mol}_{\text{H}^+}^{\text{cat}}$ (obtained with ionic resin, [4]) $< 4.61 \times 10^1 \text{ mol/h mol}_{\text{H}^+}^{\text{cat}}$ (obtained with SBA-15- SO_3H , [6]) $< 1.72 \times 10^2 \text{ mol/h mol}_{\text{H}^+}^{\text{cat}}$ (obtained with PW-S, [32]) $< 2.21 \times 10^2 \text{ mol/h mol}_{\text{H}^+}^{\text{cat}}$ (obtained over PW2_AC) $< 1.81 \times 10^3 \text{ mol/h mol}_{\text{H}^+}^{\text{cat}}$ (obtained with carbon- SO_3H , through microwave technology, [5]).

Table 2 shows the glycerol conversion and selectivity to the products obtained by the esterification of glycerol with acetic acid over PW immobilized on the activated carbon, after 3 h of reaction. It

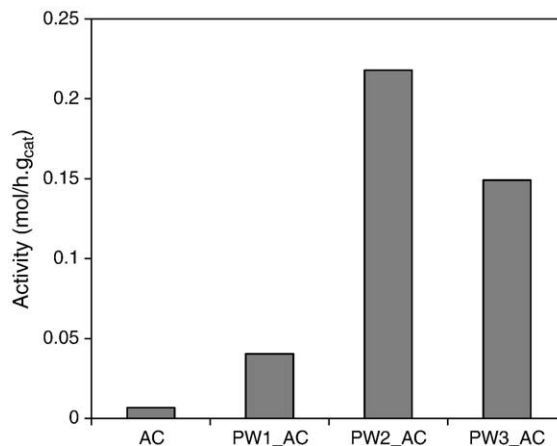


Fig. 2. Esterification of glycerol with acetic acid over PW immobilized on activated carbon. Initial activities were taken as the maximum observed reaction rate, divided by the catalyst amount.

Table 2

Conversion and selectivity to the products of the esterification of glycerol with acetic acid over PW_AC catalyst. Reaction conditions: molar ratio of glycerol to acetic acid = 1:16; Temperature = 120 °C; catalyst loading = 0.2 g.

Sample	Conversion ¹	Selectivity (%)			
	(%)	Monoacetin	Diacetin	Triacetin	Others
AC	15	42	54	3	1
PW1_AC	55	20	65	14	1
PW2_AC	86	25	63	11	1
PW3_AC	75	24	63	12	1

¹Glycerol conversion after 3 h of reaction.

Table 3

Catalytic stability of the PW2_AC sample in acetylation of glycerol. Reaction conditions: molar ratio of glycerol to acetic acid = 1:16; Temperature = 120 °C; catalyst loading = 0.2 g.

Experiments	Activity (mol/h.g _{cat})
First use	0.22
Second use	0.18
Third use	0.16
Forth use	0.15

can be seen that PW2_AC presents the highest conversion. After 3 h of reaction, the glycerol conversion was 86%, with a selectivity of 63% to diacetin, 25% to monoacetin and 11% to triacetin. The high selectivity to diacetin can be explained due to diacetin and triacetin products to be formed through consecutive esterification reactions. In fact, PW immobilized on activated carbon is an effective catalyst in the esterification of acetic acid with butanol [12].

In order to study the catalytic stability of the PW2_AC, consecutive batch runs with the same catalyst sample and in the same reaction conditions were carried out. A decrease of the catalytic activity from the first to the second use was observed (Table 3). This behaviour can be explained due to some leaching of heteropolyacid from the catalyst to the liquid phase. However, after the third use, it was observed a stabilization of the catalytic activity. The amount of heteropolyacid on PW2_AC catalyst, after the reactions, was measured by ICP. The catalyst only lost 10% of the PW from the activated carbon support. This behaviour can be explained due to the PW to be strongly adsorbed over activated carbon. Similar results were also observed by Sepúlveda et al. [12].

In order to study the catalytic stability of PW2_AC, an experiment, similar to the “hot-filtration experiment”, was carried out. The PW2_AC catalyst was put in contact with the acetic acid during 72 h, at 120 °C under stirring, without glycerol. After this period, the catalyst was separated from acetic acid by centrifugation, and the glycerol was added to the reaction mixture. The reaction was carried

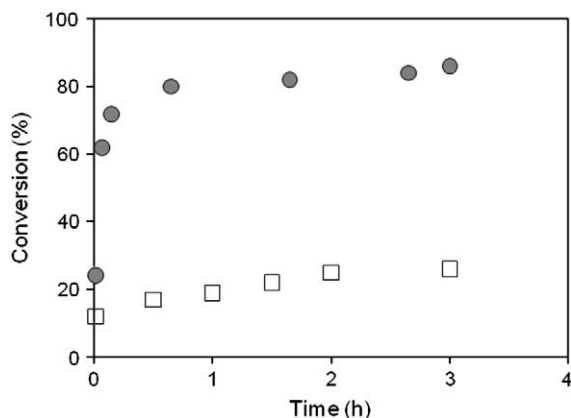


Fig. 3. Esterification of glycerol with acetic acid over PW2_AC catalyst. Conversion (%) versus time (h): (●) PW2_AC (fresh); (□) PW2_AC after catalyst removal.

out during 3 h. Fig. 3 compares the conversion of glycerol obtained with PW2_AC and without catalyst. It was observed that the heteropolyacid leaching from activated carbon to reaction mixture seem to be small.

4. Conclusions

The esterification of glycerol with acetic acid was carried out over a series of PW immobilized on activated carbon. Catalysts with different PW loading on activated carbon, which varied from 3.5 to 6.5 wt.%, were prepared. It was observed that the PW2_AC (with 4.9 wt.%) shows the highest catalytic activity. Good values of selectivity to diacetin were obtained with all catalyst. Catalytic stability of the PW2_AC was evaluated by performing consecutive batch runs. After the third batch, a stabilization of the catalytic activity was observed.

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