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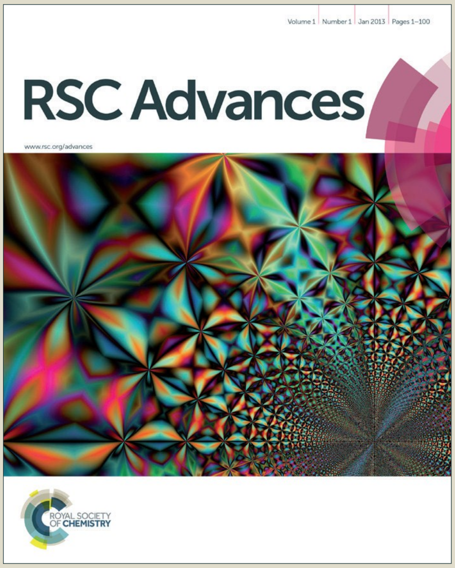

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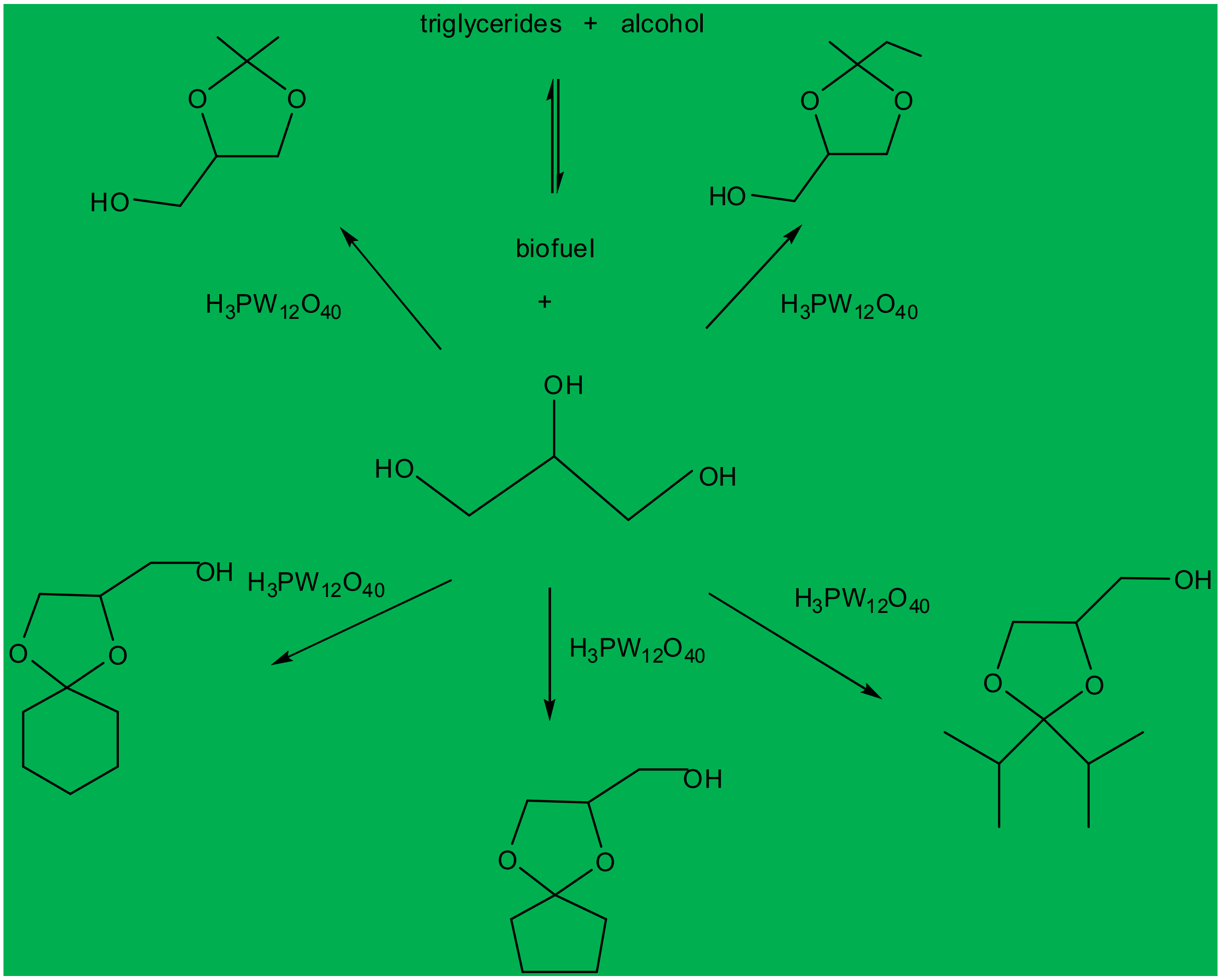
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ARTICLE

Solvent free heteropolyacid-catalyzed glycerol ketalization at room temperature

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Currently, the glycerol has been produced in large amounts as biodiesel co-product. Therefore, to develop processes to convert it to more valuable chemicals has attracted significance attention. Glycerol ketals are compounds useful as synthesis intermediates, and fragrances ingredient and mainly, bioadditives for diesel and gasoline, and have been produced trough reactions catalyzed by mineral acids. In this work, we assessed the activity of $H_3PW_{12}O_{40}$ heteropolyacid on glycerol ketalization with different ketones at room temperature and in the absence of an auxiliary solvent. The effects of the principal reactional parameters such as the reactants stoichiometry, catalyst concentration, reaction temperature, and type of carbonylic reactant were investigated. $H_3PW_{12}O_{40}$ heteropolyacid was much more active than other Brønsted acid catalysts evaluated (i.e. H_2SO_4, *p*-toluenesulfonic acid, $H_3PMo_{12}O_{40}$ or $H_4SiW_{12}O_{40}$) and exhibited high selectivity toward five-membered (1,3-dioxolane) cyclic ketals. Although homogeneous, heteropolyacid catalyst could be recovered and reused without loss activity.

Introduction

The biodiesel industry has growing around wide world, producing glycerol surplus, motivating then that new processes will be developed aiming valorize this strategic feedstock [1]. The glycerol is a platform-molecule of biorefineries and derivatives as 1,2-propanediol, acrolein, glyceric and tartronic acids have been produced at industrial scale since long time ago. However, the market of these products is enable to absorb the glycerol excess currently generated as biodiesel co-product [2]. Ketals, acetais, as well as glyceryl esters are valuable ingredients for diesel formulation and gasoline and may answer this demand [3,4]. Nowadays, all these reactions have been carried out via a homogeneous catalytic process using mineral acids (i.e. H_2SO_4, HCl), which are unfriendly to the environment because are no recyclable and corrosive liquid Brønsted acids [5]. Therefore, to develop alternative processes to synthesize glycerol ketals, using catalysts that are less impacting to the environment is one of the great challenge to be overcomes by industry.

Although laborious synthesis, solid acids are an attractive option to the homogenous catalysts. Molybdenum promoted solid catalysts (i.e. MoO_3/ ZrO_2 or TiO_2) were used in glycerol acetalization reactions with benzaldehyde carried out in different solvents (toluene, benzene, dichloromethane) at reflux temperature [6]. Other solid acids such as Amberlyst-15 resin, niobium, zeolite and niobium oxides has been successfully used on glycerol esters synthesis [7,8].

Among different solid catalysts, heteropolyacids incorporated to solid matrixes with high surface area has been also extensively explored to add value to the glycerol [9-12]. Heteropolyacids are a versatile class of catalysts that have been successfully used either in homogeneous or heterogeneous catalysis conditions [13-16]. In special, Keggin-type heteropolyacids deserves highlight because have acidity and redox properties, which becomes it useful catalysts for the different reactions [17,18]. Solid matrixes supported heteropolyacids such as niobium, zeolites, zirconium, silica or active carbon have been used in esterification, etherification, acetylation, dehydration or ketalization of glycerol [19-22].

Despite successful of the solid supported heteropolyacids catalysts, the synthesis procedures are sometimes laborious and required additional costs with thermal treatment which in general consumption long time. In addition, the solid-catalyzed glycerol ketalization reactions have been performed in the presence of auxiliary solvents at their respective reflux temperatures resulting in an increase on process cost [23].

On this regard, da Silva et al circumvented this difficulty proposing the use of commercial heteropolyacid without any previous treatment in homogeneous conditions to esterify free fatty acids or even glycerol [24,25]. On those processes, heteropolyacid catalyst could be recovered after reaction ends throughout the solvent distillation followed by the filtration of solid heteropolyacid remaining.

In general, glycerol ketalization has been carried out heating reactions to reflux temperature of the solvent, using liquid mineral acid catalysts as H_2SO_4, or organic such as *p*-toluenesulfonic acid, and ketone excess [26,27]. Alternatively, solid acids have successfully catalyzed these reactions [28]. However, besides laborious synthesis, sometimes water produced during reaction may result in the catalyst leaching [29].

In this paper, we investigate the $H_3PW_{12}O_{40}$-glycerol ketalization reactions with different ketones as carbonylic reactants in solvent free conditions and at room temperature. The effects of the ketones in the selectivity of the products, in addition to others reactional parameters such as the reactants stoichiometry, temperature, catalyst concentration were studied. The $H_3PW_{12}O_{40}$

activity has compared with other Brønsted acid catalysts. Noticeably, $H_3PW_{12}O_{40}$ was the most active catalyst and provided a highly regioselective conversion of glycerol toward the 1,3-dioxolane derivatives, regardless of ketone utilized.

Experimental

Chemicals

All chemicals were purchased from commercial sources. The three hydrate heteropolyacids (i.e. $H_3PW_{12}O_{40}$, 221856 sigma code; $H_3PMo_{12}O_{40}$, P4006 sigma-aldrich code, and $H_4SiW_{12}O_{40}$ n H_2O (n = 12 to 18), 95395 sigma-aldrich code) were acquired from Sigma-Aldrich. Glycerol (99 % w/w) and all the ketones (99 % w/w) were acquired from Sigma-Aldrich.

General ketalization procedure

The reactions were carried out in a stirred glass reactor in a 50-mL three-necked glass flask. Typically, glycerol and ketone at adequate molar ratio were magnetically stirred at room temperature and $H_3PW_{12}O_{40}$ catalyst (0.0923 mmol) was then added to solution (10.0 mL), being then started the reaction. Blank-reactions were carried out at the same conditions with ketone and glycerol but in the absence of catalyst at different ketone to glycerol molar ratio.

Reaction monitoring

The progress reaction was monitored analyzing aliquots taken off at periodic time intervals by gas chromatography (Shimadzu GC 17A instrument), equipped with a flame ionization detector (i.e. FID) and fitted with Carbowax capillary column (30 m length x 0.25 mm i.d. x 0.25 mm film thickness). Gas chromatographic conditions were as follows: 80 °C (3 min); temperature rate: 10 °C/ min; final temperature: 260 °C; injector temperature: 250 °C; detector temperature: 280 °C. The concentration of the products in the reaction mixture was calculated from the corresponding chromatographic peak areas. Toluene was internal standard. The reaction aliquots were kept at low temperatures (*ca*. < 253 K) before GC analysis to avoid reaction progress.

The conversion rate of reactions were calculated as shown in Equation 1;

$$\% \text{ conversion} = 100 - (C_i/C_0) \times 100 \quad \text{(Equation 1)}$$

where C_i = glycerol concentration calculated trough glycerol stander curve (i.e. glycerol concentration versus GC peak areas of glycerol) and C_0 = initial concentration of glycerol.

Product chromatographic separation and characterization

Reaction products were separated by column chromatography (silica) using mixtures of hexane, CH_2Cl_2 and methanol as eluents and then identified by GC-MS spectrometry (Shimadzu MS-QP 5050A mass spectrometer instrument operating at 70 eV coupled Shimadzu 17A GC).

The products were characterized through ^1H and ^{13}C NMR spectroscopy analyses. The NMRs spectra were taken in $CDCl_3$ solutions, using a Varian 300 spectrometer at 300.13 and 75.47 MHz, respectively. The chemical shifts were expressed as δ (ppm) relatively to tetramethylsilane (TMS) as internal stander. FT-IR spectroscopy analysis were performed in Varian spectrometer 660, in dichloromethane solutions.

Spectral data

The main spectral data of products obtained are displayed as follows in according with the structures shown in the Figures 1-5.

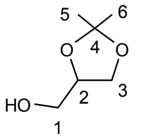


Figure 1. (2,2-dimethyl-1,3-dioxolan-4-yl)methanol

^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.68 (C-5); 25.24 (C-6); 62.93 (C-1); 65.64 (C-3); 76.08 (C-2); 109.39 (C-4).

FT-IR (CH_2Cl_2 - $\nu_{máx}$ /cm^{-1}): 3428; 2986; 2936; 2884; 1372; 1256; 1214; 1156; 1050; 844.

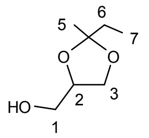


Figure 2. (2-ethyl-2-methyl-1,3-dioxolan-4-yl)methanol

^{13}C NMR (75 MHz, CD_3OD): δ = 7.30 and 7.00 (C-7); 23.09 and 22.01 (C-5); 31.22 and 32.14 (C-6); 62.47 (C-1); 66.22 and 66.03 (C-3); 76.79 and 76.03 (C-2); 110.60 and 110.82 (C-4).

IV (CH_2Cl_2 - $\nu_{máx}$ /cm^{-1}): 3436; 2987; 2978; 2936; 2882; 1376; 1248; 1192; 1138; 1080; 878.

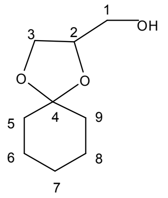


Figure 3. (1,4-dioxaspiro[4.5]decan-2-yl)methanol

^{13}C NMR (75 MHz, CD_3OD): δ = 23.68 (C-6); 23.84 (C-8); 25.11 (C-7); 34.70 (C-5); 36.35 (C-9), 62.87 (C-1); 65.84 (C-3); 76.18 (C-2); 109.72 (C-4);

FT-IR (CH_2Cl_2 - $\nu_{máx}$ /cm^{-1}): 3420; 2936; 2530; 1100.

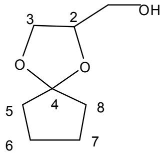


Figure 4. (1,4-dioxaspiro-[4.4]nonan-2-yl)methanol

^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.69 or 23.28 (C6 e C7); 36.51 or 35.99 (C5 e C8); 63.16 (C-1); 65.38 (C-3); 75.78 (C-2); 119.37 (C-4).

FT-IR (CH_2Cl_2 - $\nu_{máx}$ /cm^{-1}): 3430; 2958; 2874; 1336; 1206; 1106; 1042; 972; 860.

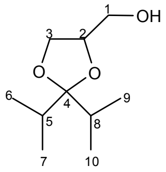


Figure 5. (2,2-diisopropil-1,3-dioxolan-4-yl)methanol

^{13}C NMR (75 MHz, CD_3OD): δ = 16.46 (C-6, C-7, C-9 or C-10); 33.51 or 34.54 (C-5 or C-8); 62.75 (C-1); 68.93 (C-3); 78.38 (C-2); 116.42 (C-4)

FT-IR (CH_2Cl_2 - $\nu_{máx}$ /cm^{-1}): 3394; 2967; 2937; 2159; 2046; 1471; 1380; 1218; 1118; 1079; 1025; 929.

Procedures to recovery and reuse of $H_3PW_{12}O_{40}$ catalyst

The reactions were carried out in a scale five times greater than that described in previous section, in order to facilitate the catalyst recovery. Additionally, $H_3PW_{12}O_{40}$ catalyst concentration was increased of 1 to 5 mol % aiming maximize the glycerol conversion. Typically, a solution of glycerol (*ca*. 31.6 mmol, 2.3 mL) and propanone (*ca*. 633.2 mmol, 45.9 mL) at 1:20 molar ratio was magnetically stirred at room temperature; toluene (1.8 ml) and $H_3PW_{12}O_{40}$ catalyst (5 mol %) were then added to solution (50.0 mL), being then started the reaction. The reaction solution was evaporated almost until dryness heating in oil bath and under reduced pressure by using rotatory evaporator. After removing the ketone and solketal, the solid $H_3PW_{12}O_{40}$ was filtered, washed with small portions of dichloromethane aiming eliminate the unreacted glycerol. Afterward, we dried $H_3PW_{12}O_{40}$ under vacuum and heating to 333 K, to be reutilized it in further catalytic runs. This overall procedure has repeated for three times.

Results and discussion

Effect of the glycerol ketone molar ratio on $H_3PW_{12}O_{40}$-catalyzed glycerol ketalization with propanone

The glycerol molecule is highly functionalized and consequently the selectivity control is always hard. On the other hand, the low polarity of some ketones sometimes compromises the glycerol solubility, requiring that an auxiliary solvent or heating source have be used. We investigate $H_3PW_{12}O_{40}$ catalytic activity on ketalization of glycerol with propanone ranging molar ratio glycerol to ketone of 1:1 to 1: 30. The main results are summarized in Table 1.

We find out that the presence of $H_3PW_{12}O_{40}$ in the solution drastically changes the solubility of glycerol in the ketone. In all catalytic runs, the system was completely homogeneous regardless amount ketone at room temperature. Conversely, in the blank-reactions using low molar ratio ketone to glycerol, the system became cloudy. This different behavior may be attributed to increase of ketone polarity provoked by dissolution of heteropolyacid, which favoring the glycerol solubility.

Table 1. Effect of glycerol ketone molar ratio on $H_3PW_{12}O_{40}$-catalyzed glycerol ketalization with propanone[a]

Run	Glycerol ketone molar ratio	Conversion[b] (%)	Products selectivity[b] (%)		Blank-reaction conversion[d] (%)
			Solketal	ni[c]	
1	1:1	38	98	2	0
2	1:4	44	97	3	<5
3	1:10	58	97	3	5
4	1:15	63	96	4	8
5	1:20	83	98	2	10
6	1:30	85	97	3	15

[a]Reaction conditions: $H_3PW_{12}O_{40}$ (1.0 mol %), room temperature, magnetic stir, 2 hours.
[b]Determined by GC analyses.
[c]ni: complex mixture of not identified minority products.
[d]Reactions-blank carried out in the absence of catalyst

When carrying out reactions in absence of catalyst, we have noted that even not significant, an increase on ketone amount resulted in an increase in the glycerol conversion. However, poor conversions (i.e. lower than *ca*. 5 %) were achieved regardless ketone excess (Table 1).

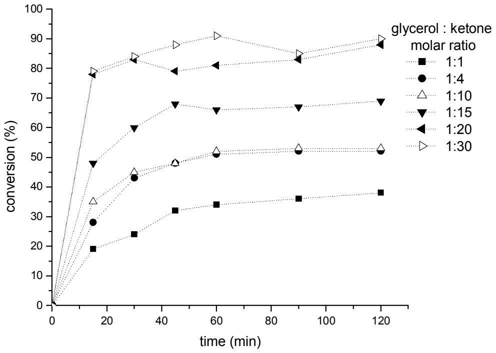


Figure 6. Kinetic curves of $H_3PW_{12}O_{40}$-catalyzed glycerol ketalization with propanone using different reactants stoichiometry[a]

[a]Reaction conditions: $H_3PW_{12}O_{40}$ (1.0 mol %); toluene (7.06 mmol); volume (15 mL); 298 K.

Therefore, we can neglect this minor effect herein. On the other hand, the reaction selectivity remained unchanged and did not affected by ketone excess. Unlikely, the addition the $H_3PW_{12}O_{40}$ catalyst to solution provoked a rapid conversion of glycerol to solketal (Figure 6).

Within the range of molar ratio studied, the highest conversion was obtained using 1:30 of glycerol to ketone. However, a very close conversion was reached using 1:20, consequently, it was the molar ratio selected to study the other reaction parameters.

Regardless of glycerol to ketone molar ratio, the selectivity of products remained almost constant during the whole reaction. Outstandingly, solketal was always the major product in all the reactions. For this reason, we omitted selectivity curves of products versus time.

The glycerol ketalization is an acid-catalyzed reversible reaction that may give two main products: (2,2-dimethyl-1,3-dioxolan-4-yl)-methanol (i.e. solketal, 1a) and 1,3-dioxane-5-methanol (1b). These products are resulting of the nucleophilic attack of the primary and secondary hydroxyl group of glycerol, respectively, on the carbonylic carbon of propanone (Figure 7).

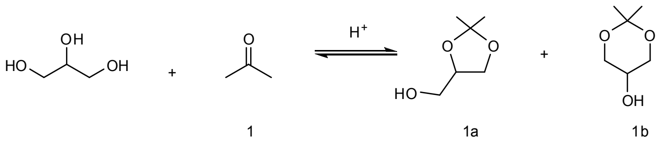


Figure 7. Glycerol ketals with propanone.

Products with 1,3-dioxolane-type carbon skeletal (i.e. 1a) are formed throughout reaction between neighboring hydroxyl groups present on glycerol (i.e. 1 and 2 positions) and the carbonyl group of the ketone. Otherwise, product 1b (i.e. 1,3-dioxane-type carbon skeletal) are formed via reaction of glycerol hydroxyl groups placed at 1 and 3 positions and carbonyl of the ketone. Different of the reactions of glycerol acetalization with aldehydes, which commonly result in an equimolar mixture of five and six-membered cyclic products, the glycerol ketalization provided preferentially 1,3-dixolane five-membered ring product (i.e. 1a).

The lower stability of six-membered (1,3-dioxane) compared to five-membered (1,3dioxolane) is attributed to repulsion between the methyl group in the axial position, and the two hydrogen atoms in the others axial positions of the six members ring. Conversely, when has a five-membered ring, this repulsion is significantly lower [26].

If we compare these results to ones achieved in solid supported heteropolyacid-catalyzed glycerol acetalization reactions, we may realize some positive points of this homogeneous process. Undoubtedly, the reusability of heterogeneous catalyst is an aspect relevant, because it makes the process lesser pollutant than homogeneous reactions in addition to be more attractive economically. However, sometimes it is require more drastic reaction conditions or longer reaction times. For instance, Castanheiro et al assessed the activity of supported silica Keggin heteropolyacids (i.e. $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$), and they found that the best result was attained heating the reaction to 343 K during 4 hours [9]. In that case, as observed herein, the $H_3PW_{12}O_{40}$ was also the most active catalyst. However, those authors verified that regardless heteropolyacid nature, the supported silica catalysts lost activity after successive cycles of reuse, provoked by high polarity of reaction medium. Herein, as will be described in the next section, although homogeneous, we recovered and reused the soluble heteropolyacid without activity loss.

The profile of kinetic curves shows that maximum conversion was attained within the first reaction hour. After this period, only slight increase on conversion is noted. Moreover, the higher initial rate of reaction were achieved when a higher amount of ketone was present at reaction beginning.

Recovery and reuse of $H_3PW_{12}O_{40}$ catalyst

The catalyst has retained its activity after three successive recycles (Figure 8). Even after recycling the catalyst three times, the conversion and reactions selectivity were practically identical to those observed when fresh catalyst was used (*ca*. 90%). However, the washing of catalyst with dichloromethane was inefficient to total removing of the unreacted glycerol. Consequently, we did not measuring the recovery rate of catalyst due to its increase of weight. To circumvent this problem, before recycle runs, we solubilize the recycled catalyst in propanone. After this procedure, a content of glycerol lower than 5 % was detected in all the reactions. Thus, we adjusted the initial amount of glycerol to be added discounting glycerol already present in solution. We believes that an inevitable loss of catalyst could occur during recovery steps; nevertheless, this did not compromises the catalytic activity.

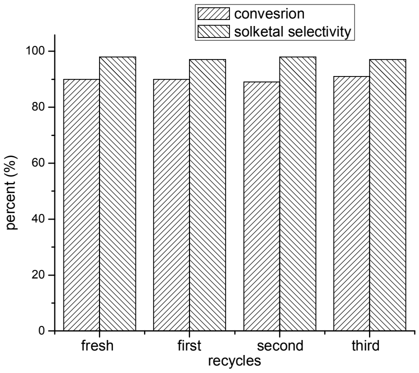


Figure 8. Conversion and selectivity achieved after recovery and reuse of $H_3PW_{12}O_{40}$ catalyst.[a]

[a]Reaction conditions: glycerol (31.6 mmol); propanone (633.2 mmol); catalyst concentration (5 mol %); toluene (1.8 mL); volume (50 mL).

Effect of the $H_3PW_{12}O_{40}$ concentration on glycerol ketalization with propanone

The effect of the catalyst concentration on conversion and reaction selectivity was investigate within the range of 0.10 to 1.00 mol % (Table 2). Indeed, the catalyst concentration do not affect the conversion reached in the reaction equilibrium. However, our intention herein was assess what the minimum concentration required to achieve maximum conversion within reaction time equal to 2 hour. To accurately determining the effect of catalyst concentration on reaction rate it is require carry out the measurements within initial period of the process, where a decreasing on reactant concentration should not affect the reaction rate. Nevertheless, as showed in the Figure 9, the glycerol ketalization is a fast reaction and within the first 30 minutes, a high conversion is achieved, regardless catalyst concentration employed. After this period, the reaction rate decrease due to glycerol consumption.

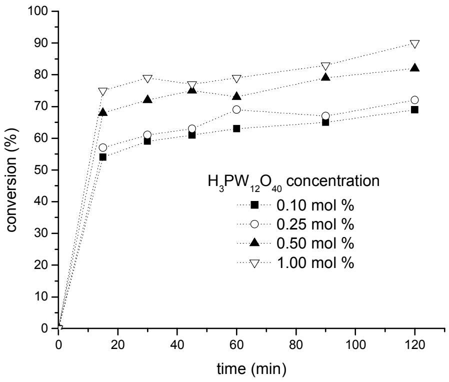


Figure 9. Kinetic curves of $H_3PW_{12}O_{40}$-catalyzed glycerol ketalization with propanone[a]

[a]Reaction conditions: glycerol (9.23 mmol); propanone (184.6 mmol); toluene (7.06 mmol); volume (15 mL); 298 K.

It is important to highlight that, although the kinetic curves of Figure 9 were achieved by using different initial concentration of catalyst in relation to the glycerol, this later not remained constant throughout the whole reaction. However, as glycerol is the limiting reactant and the ketone was used in large excess, the change in the proportion glycerol/ catalyst was higher than ketone/ catalyst. For these reasons, the profile of kinetic curves show that after the first 30 minutes reaction, the reaction rate becomes significantly lower than ones observed at initial period initial of process. We expected that a linear dependence of reaction rate, as described in heteropolyacid-catalyzed esterification reactions [30]. However, it is not clear in Figure 9.

Table 2. Effect of catalyst concentration on conversion and selectivity of glycerol ketalization with propanone[a]

Entry	$H_3PW_{12}O_{40}$ concentration (mol %)	Conversion (%)	Products selectivity (%)	
			Solketal	Others
1	0.10	65	98	2
2	0.25	68	97	3
3	0.50	75	98	2
4	1.00	90	97	3

[a]Reaction conditions: glycerol (9.23 mmol); propanone (184.6 mmol); toluene (7.06 mmol; 0.75 mL); volume (15 mL); room temperature (ca., 298 K); reaction time (2 h).

High regioselectivity toward 1,3-dioxolane product (i.e. solketal) was attained in all reactions, regardless catalyst concentration used. In addition, as displayed in the Fig. 9, highest reaction initial rate was obtained when 1.0 mol % of $H_3PW_{12}O_{40}$ was employed.

Effect of the catalyst nature on glycerol ketalization with propanone

To compare the activity of the $H_3PW_{12}O_{40}$ with other Brønsted acid catalysts, the reactions of glycerol ketalization with propanone were carried out using equal hydrogenionic concentration (*ca*. 3 mol % H^+) at glycerol to ketone molar proportion 1 to 20 at room temperature (Table 3).

Regardless of acid catalyst, a high solketal selectivity was obtained in all catalytic runs. Otherwise, the conversion achieved was highly dependent of kind of catalyst. The acid strength of heteropolyacid catalysts depends on their composition; to replace W(VI) by Mo(VI), or P(V) by Si(IV) result in a decrease of the acidity strength [13,14]. Therefore, it was expected that this aspect might affect the activity of these catalysts. On the other hand, it has known that species present in the reaction solution may affect the ionization of these acid catalysts. For instance, the water provokes a levelling effect on these catalysts that make them totally ionizable; however, their pKa values are drastically changed when other solvents are employed [31].

In general, notwithstanding Brønsted acid catalyst, the reactions rates obtained after the 60 minutes of reaction were significant lower than ones measured within initial period. This fact can be once more attributed to decreasing on glycerol concentration. Results showed in Table 3 and Figure 10 indicate that heteropolyacid catalysts activity follow the sequence: $H_3PW_{12}O_{40}$ > $H_3PMo_{12}O_{40}$ > $H_4SiW_{12}O_{40}$. This result is in according with acid strength reported in literature [13,14]. Isumi et al by using Pope's method reported that the acidity strength of these heteropolyacids accompany the same sequence [32]. They verified that when the heteropolyanion structure is unchanged (i.e. Keggin structure), a decreases on charge of the anion result on increases of acid strength of the catalyst. Thus, we initially think that heteropolyanion type may affect these reactions.

On the other hand, Misono et al discussed a possible formation of complexes between cationic organic intermediates and heteropolyanions [33]. They verified that in reactions involving alcohol substrate, the heteropolyanion softness that could have essential role on stabilization of the charged intermediates is insignificant. Consequently, only acid strength of heteropolyacids may explain their catalytic activity.

The mechanism of Brønsted acid-catalyzed glycerol ketalization involve an initial protonation of carbonyl group by acid catalyst. The attack of terminal hydroxyl group of glycerol on carbonylic carbon atom of protonate ketone, result in the formation of a hemicetal (i.e. protonate oxonium intermediate), which after a rearrangement produce a tertiary carbocation intermediate. The neighbor hydroxyl group attacks the tertiary carbocation giving a cyclic ketal and eliminating water. We believe that in glycerol ketalization, there are no complexes between heteropolyanions and these charged intermediates and that the catalyst efficiency depends on its acid strength.

Conversely, the low activity of sulfuric acid may be attributed to the use of an H_2SO_4 aqueous solution (i.e. 97-99 w/w), what resulted in the introduction of a water additional amount who might to shift the reaction equilibrium toward the reactants. Early, we have verified the high activity of *p*-toluenesulfonic acid in solketal synthesis [34].

Table 3. Effect of catalyst nature on conversion and selectivity of glycerol ketalization with propanone[a]

Entry	Catalyst	Conversion (%)	Products selectivity (%)	
			Solketal	Others
1	$H_3PW_{12}O_{40}$	83	98	2
2	$H_3PMo_{12}O_{40}$	41	98	2
3	$H_4SiW_{12}O_{40}$	40	98	2
4	H_2SO_4	31	98	2
5[b]	PTSA	76	98	2

[a] Reaction conditions: glycerol (9.23 mmol); propanone (184.6 mmol); catalyst concentration (3 mol % H^+); toluene (7.06 mmol); volume (15 mL); room temperature (*ca.* 298 K); reaction time (2 h).

[b] PTSA = *p*-tolenesulfonic acid

In organic solvents, the *p*-toluenesulfonic acid is weaker than sulfuric acid or Keggin heteropolyacids [14]. Nevertheless, it is possible that different of other reactions studied, in *p*-toluenesulfonic acid-catalyzed reactions may exist van der Walls strengths between the substrates (i.e. ketone, glycerol) and organic catalyst molecule favoring interactions that resulting in a high glycerol conversion.

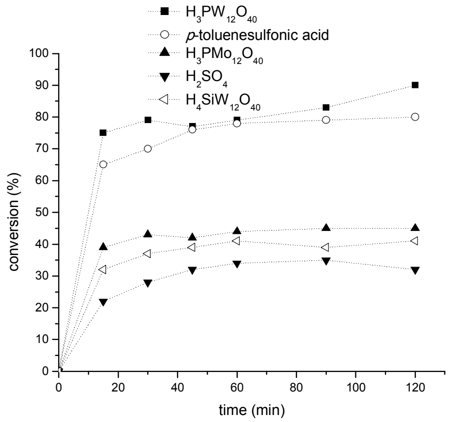


Figure 10. Kinetic curves of Brønsted acid-catalyzed glycerol ketalization with propanone[a]

[a] Reaction conditions: glycerol (9.23 mmol); propanone (184.6 mmol); catalyst concentration (3 mol % H^+); toluene (7.06 mmol); volume (15 mL); 298 K.

Effect of the temperature on $H_3PW_{12}O_{40}$-catalyzed glycerol ketalization with propanone

In general, we find out that these reactions are little sensible to temperature variation of 298 to 338 K (Figure 11). Although of low difference between final conversions obtained, it can be noted that a decrease on temperature seem to enhance efficiency of reaction, resulting in slightly superior conversions.

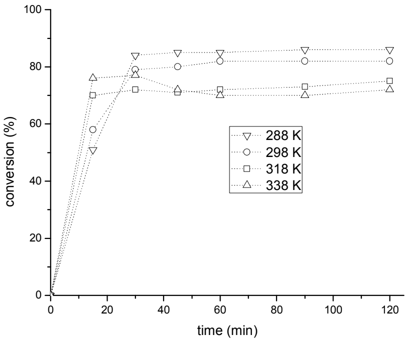


Figure 11. Kinetic curves of $H_3PW_{12}O_{40}$-catalyzed glycerol ketalization with propanone[a]

[a] Reaction conditions: glycerol (9.23 mmol); propanone (184.6 mmol); catalyst concentration (3 mol % H^+); toluene (7.06 mmol); vol. (15 mL).

To attempt verify if the reaction conversions may be increased with a decreasing on temperature, we carry out reactions at temperatures lower than room temperature (i.e. 288 K). Although the initial rate of reaction has been lower if compared the those obtained at higher temperatures, after two hours reaction carried out at 288 K was achieved the highest conversion. It is suggestive that the reaction has an exothermic character.

Effect of the ketone nature on solventless $H_3PW_{12}O_{40}$-catalyzed glycerol ketalization at room temperature

Acid-functionalised solid catalysts materials have been used in the solvent-free acetalisation of glycerol with propanone to produce 2,2-dimethyl-1,3-dioxolane-4-methanol (solketal), nevertheless, heating reaction to propanone reflux temperature [35,36]. Herein, this reaction has extended to other ketones. Unlike of cyclic ketones, aliphatic ketones with carbon chain containing more than five carbon atoms are immiscible with glycerol. Consequently it is difficult determine the reaction conversion and build the kinetic curves. For this reason, their results were omitted in the Figure 12.

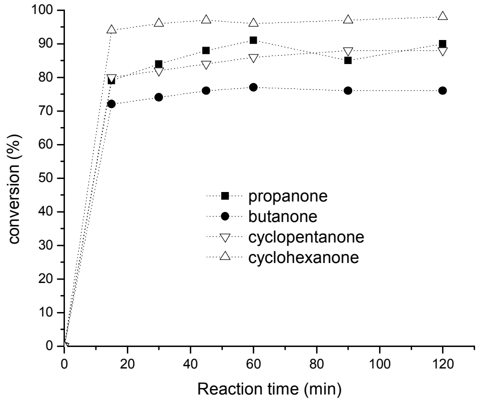


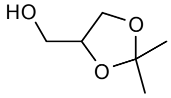
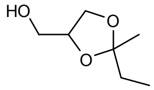
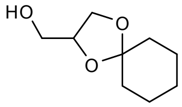
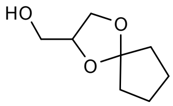
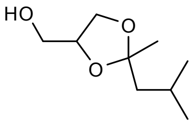
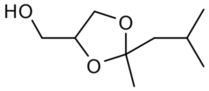
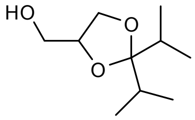
Figure 12. Kinetic curves of $H_3PW_{12}O_{40}$-catalyzed glycerol ketalization with different ketones[a]

[a]Reaction conditions: glycerol (9.23 mmol); propanone (184.6 mmol); catalyst concentration (3 mol % H^+); toluene (7.06 mmol); volume (15 mL).

Cyclohexanone was highly reactive and was almost totally converted to ketal (i.e. 1,4-dioxaspiro [4.5] decane-2-yl)methanol) (Table 4). It may be attributed to low hindrance steric on carbonylic carbon. Although cyclopentanone has also the same effect and consequently display high reactivity, the cyclohexanone has an extra destabilizing effect (Figure 12).

There is a torsional strain triggered by hydrogens on carbon atoms neighbor to carbonyl carbon (i.e. C_5 and C_9 carbon atoms) in the chair conformation of cyclohexane ring, which are eclipsed by the carbonyl oxygen [37]. This effect do not exist in the cyclopentanone.

Table 4. Effect of ketone nature in the solvent free $H_3PW_{12}O_{40}$-catalyzed glycerol ketalization[a]

Run	Ketone	Conv.[b] (%)	Ketal select.[b] (%)	Ketal[c]
1	propanone	90	97	
2	butanone	74	99	
3	cyclohexanone	98	99	
4	cyclopentanone	88	95	
5[d]	4-methyl-2-pentanone	-	47	 (*trans*)
			45	 (*cis*)
6[d]	2,4-dimethyl-3-pentanone	-	78	

[a]Reaction conditions: glycerol (9.23 mmol); $H_3PW_{12}O_{40}$ catalyst (0.0923 mmol); ketone (184.76 mmol); 298 K.
[b]Determined by GC analyses; in addition to ketal, it was formed a variable amount of not identified minority products.
[c]Determined by GC-MS, NMR and FT-IR spectroscopy analyses.
[d]The glycerol was insoluble in the ketone, it was not possible assure that reagent molecules were in contact; therefore, we do not measured the glycerol conversion.

The butanone was lesser reactive than propanone, that may be consequence of higher carbonic chain, however, the catalytic tests with linear ketones that could demonstrate this hypothesis were compromised by solubility problems with the glycerol. Although conversion has not been measured, the ketals formed in these reactions are soluble and can be detected by GC or GC-MS analyses (Table 4). In general, regardless structure of ketone, the reaction selectivity was always directed toward 1,3-dioxolane five-membered products.

Conclusions

In conclusion, $H_3PW_{12}O_{40}$ heteropolyacid was an efficient and regioselective catalyst for the synthesis of glycerol ketals (i.e. 1,3-dioxolane five-membered ring products) from cyclic and acyclic ketones. Effects of reactants stoichiometry, catalyst concentration, kind of carbonylic substrate were assessed. It was observed that conversion was dependent on the catalyst concentration and the amount of ketone used. Emphasis was given to the study of solketal synthesis using different catalysts. Among catalysts studied, $H_3PW_{12}O_{40}$ heteropolyacid was the most active. The reactions were carried out at room temperature and without solvent. The combination of inexpensive raw material (i.e. glycerol) and mild reactions conditions (i.e. room temperature), in addition to absence of solvent are positive aspects of these synthesis procedure. Although used in homogeneous conditions, $H_3PW_{12}O_{40}$ catalyst was recovered and reused without loss activity.

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Notes and references

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1. S. Bagheri, N. U. M. Julkapli, W.A Yehye, *Renew. Sust. Energ. Rev.* 2015, **41**, 113.

2. J. Calero, D. Luna, E. D. Sancho, C. Luna, F. M. Bautista, A. A. Romero, A. Posadillo, J. Berbel, C. Verdugo-Escamilla, *Renew. Sust. Energ. Rev.* 2015*,* **42**, 1437.

3. Y. Zheng, X. Chen, Y. Shen, *Chem. Rev*. 2008, **108**, 5253.

4. C. J. A. Mota, D. X. A. da Silva, N. Rosenbach Jr., J. Costa, F. da Silva, *Energ Fuels* 2010, **24**, 2733.

5. M. R. Nanda, Z. Yuan, W. Qin, H. S. Ghaziaskar, M.-A. Poirier, C. C. Xu, *Fuel* 2014, **117**, 470.

6. P. Sudarsanam, B. Malleshan, A. N Prassad, P. S. Reddy, B. M Reddy *Fuel Process. Technol.* 2013, **106**, 539.

7. L. Zhou, T.-H. Nguyen, A. A. Adesina, *Fuel Process. Technol* 2012, **104**, 310.

8. M. Trejda, K. Stawicka, M. Ziolek, *Appl. Catal. B*, 2011, **103**, 404.

9. P. Ferreira, I. M. Fonseca, A. M. Ramos, J. Vital, J. E. Castanheiro, *Appl. Catal. B*, 2010, **98**, 94.

10. P. Ferreira, I. M. Fonseca, A. M. Ramos, J. Vital, J. E. Castanheiro, *Catal. Commun*. 2011, **12**, 573.

11. S. Zhu, Y. Zhu, X. Gao, T. Mo, Y. Zhu, Y. Li, *Bioresour. Technol.* 2013, **130**, 45.

12. M. Balaraju, P. Nikhitha, K. Jagadeeswaraiah, K. Srilatha, P.S. Sai Prasad, N. Lingaiah, *Fuel Proces. Technol.* 2010, **91**, 249.

13. M. N. Timofeeva, *Appl. Catal. A* 2003, **256**, 19.

14. I. V. Kozhevnikov, *Chem. Rev*. 1998, **98**, 171.

15. M. Misono, I. Ono, G. Koyano, A. Aoshima, *Pure Appl. Chem.* 2000, **72**, 1305.

16. A. de Angelis, P. Pollesel, D. Molinari, W. O'Neal Parker Jr., A. Frattini, F. Cavani, S. Martins, C. Perego, *Pure Appl. Chem.* 2007, **79**, 1887.

17. N. Mizuno, M. Misono, *J. Mol. Catal. A*, 1994, **86**, 319.

18. M. Balaraju, P. Nikhitha, K. Jagadeeswarayah, K. Srilatha, P. S. S. Prasad, N. Lingaiah, *Appl. Catal. A*, 2009, **365**, 28.

19. P.-Y. Hoo, A. Z. Abdullah, *Chem. Engineer. J.* 2014, **250** 274.

20. M. Ayoub, M. S. Khayoon, A. Z. Abdullah, *Bioresour. Technol*. 2012, **112**, 308.

21. L. Liu, B. Wang, Y. Du, A. Borgna, *Appl. Catal. A* 2015, **489**, 32.

22. A. Patel, S. Sing, *Fuel* 2014, **118**, 358.

23. J. Deutsch, A. Martin, H. Lieske, *J. Catal.*, 2007, **245**, 428.

24. A. L. Cardoso, R. Augusti, M. J. da Silva, *J. Am. Oil Chem. Soc*. 2008, **85**, 555.

25. C. E. Gonçalves, L. O. Laier, A. L. Cardoso, M. J. da Silva, *Fuel Proces. Technol.* 2012, **102**, 46.

26. L. P. Ozorio, R. Pianzolli, M. B. S. Mota, C. J. A. Mota, *J. Braz. Chem. Soc.* 2012, **23**, 931.

27. C.-H. C. Zhou, J. N. Beltramini, Y.-X. Fan, G. G. M. Lu, *Chem. Soc. Rev.* 2008, **37**, 527.

28. V. L. C Goncalves, B. P. Pinto, C. J. A. Mota, J. C. Silva *Catal. Today* 2008, **133–135**, 673.

29. E.-E. Oprescu, E. Stepan, R. E. Dragomir, A. Radu, P. Rosca *Fuel Proces. Technol.* 2013, **110**, 214.

30. M.J. da Silva, S. A. Fernandes, A. L. Cardoso, *Fuel Proces Technol* 2012, **96**, 98.

31. F. Cavani, *Catal. Today,* 1998, **41**, 73.

32. Y. Izumi, K. Matsuo, K. Urabe, *J Mol Catal*, 1983, **18**, 299.

33. H. Shangwen, M. Hashimoto, T. Okuhara, M. Misono, Journal of catalysis, 1993, **143**, 437.

34. F. L. Menezes, M. O. Guimaraes, M. J. da Silva, *Ind. Eng. Chem. Res*. 2013, **52**, 16709.

35. R. Rodrigues, M. Gonçalves, D. Mandelli, P. P. Pescarmona, W. A. Carvalho, *Catal. Sci. Technol.* 2014, **4**, 2293.

36. C. Gonzalez-Arellano, L. Parra-Rodriguez, R. Luque, *Catal. Sci. Technol.* 2014, **4**, 2287.

37. D. Nasipuri *in "Stereochemistry of Organic Compounds: Principles and Application"*, New Age International Publishers Ltd., 1994.