



# Biodiesel Glycerin Valorization into Oxygenated Fuel Additives

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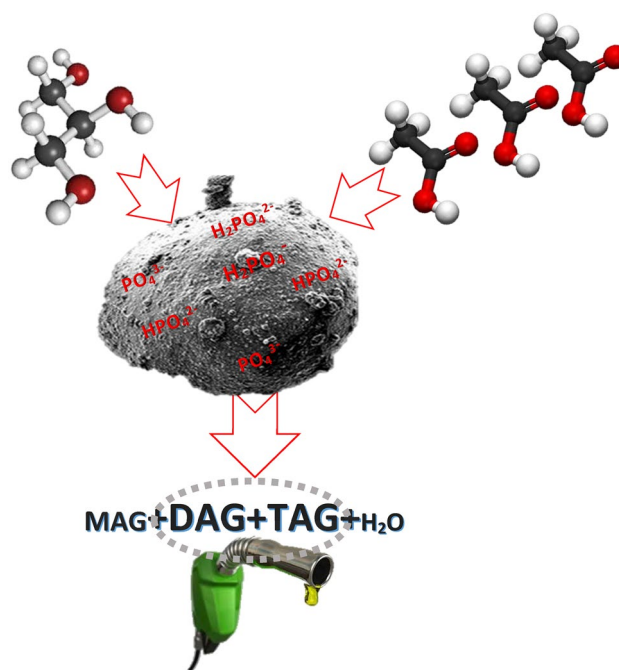
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## Abstract

Current industrial methods of biodiesel production lead to an excess of crude glycerin which requires costly purification before commercialization. Production of oxygenated fuel additives is a potential route for glycerin valorization. Glycerin acetylation was carried out over heterogeneous acid catalysts (15%, glycerol weight basis) using glacial acetic acid (molar ratio = 9). The catalysts, containing different amounts of phosphate species (P/Si from 10 to 20 atomic ratio), were prepared by wet impregnation of commercial silica with aqueous solutions of diammonium phosphate and ortho-phosphoric acid. X-ray diffraction patterns of calcined solids presented amorphous patterns like raw silica. The prepared catalysts presented, at 120 °C, glycerol conversion higher than 89.5% after 1 h of reaction, been diacetin the major product, with triacetin selectivities lower than 26.1%. Diacetin selectivity was found to be almost invariant with catalyst acidity thus underlining the relevance of catalyst porosity due to the large acetins molecules sizes. The slow rate of triacetin diffusion in narrow pores of catalyst might be responsible for the relatively low yield obtained. Surface phosphate species showed a slow rate of leaching in the reaction medium showing high catalyst stability.

## Graphical Abstract



**Keywords** Biodiesel · Catalysis · Valorization · Fuel additives · Acetylation · Acetins

Extended author information available on the last page of the article

## 1 Introduction

The increasing environmental awareness and the depletion of fossil fuel reserves have prompted the growth of the renewable biofuels market, with a greater impact on biodiesel and bioethanol, substitutes for conventional diesel and gasoline, respectively [1].

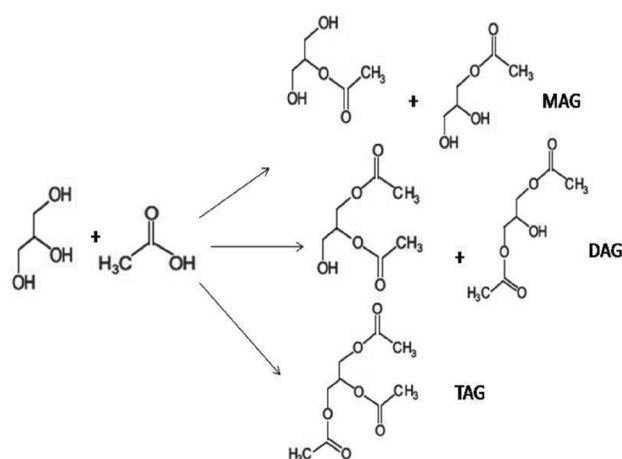
Biodiesel is typically produced by a homogeneous base-catalyzed transesterification, from vegetable oil or animal fat [2], and bioethanol is obtained by the fermentation of sugar [3]. Both processes co-produce glycerin, 10 wt% [4, 5] of the final mixture for biodiesel whereas the fermentation yields about 3 to 15 wt% (ethanol basis) [6], depending on the used feedstock.

Glycerin is mainly used in pharmaceutical, food, and cosmetic industries but these traditional uses cannot face the increasing biofuels-related production of glycerin, creating a surplus that not only affects its market value but also results in a potential environmental issue that must be addressed [4]. Simultaneously, the valorization of the co-produced glycerin would help to improve the sustainability and economic feasibility of the biodiesel production process [7].

One of the main applications of crude glycerin (non-purified glycerin co-produced with biodiesel) is an alternative fuel however, its physical and chemical properties are limiting factors in combustion [8]. Moreover, the uncontrolled combustion of glycerin leads to the formation of acrolein, a substance highly toxic for human health and ecosystems [9, 10]. On the other hand, traditional industrial uses require high glycerin purity, which would penalize even further the biodiesel production process [11]. In this context, new approaches have been studied and glycerin acetylation, to produce mono-, di-, and triacetins (MAG; DAG, and TAG), have stood out as a potential option since the three products have a wide range of applications [12], particularly TAG that can be used as an oxygenated fuel bio-additive to improve fuel combustion [13]. Additionally, DAG can be used in biodegradable polyester production, helping to mitigate the problem related to the pollution of marine and freshwater environments [7, 14].

Glycerin acetylation (Fig. 1) can be carried out using either acetic anhydride or acetic acid as an acetylation agent [15]. However, despite the former being thermodynamically favorable, achieving higher TAG selectivity, the latter is more practical since it is more stable during storage periods and has a lower price [7, 13]. Additionally, the reaction with acetic anhydride is more violent, demanding more resistant, and therefore expensive, equipment [7].

The acetylation is an acid-catalyzed reaction that can be performed in a homogeneous or heterogeneous medium. Usually, mineral acids are used as homogeneous catalysts,



**Fig. 1** Acetylation reaction of glycerin with acetic acid

which are toxic, corrosive, difficult to remove from the final reaction mixture, and generate wastes that may pose risks for human health and the environment [12]. Moreover, the main challenge regarding glycerin acetylation is the low selectivity towards TAG, which can be enhanced by increasing the catalyst acidity. However, when homogeneous catalysts are used, an increase in catalyst acidity implies higher equipment costs [11].

The use of heterogeneous catalysts in glycerin acetylation not only avoids all the mentioned problems but also offers the possibility of reuse the catalyst several times, becoming an interesting option from an economic and environmental point of view [11]. Therefore, several solid catalysts have been studied, for different reaction conditions (Table 1). For most of the tested catalysts in Table 1, the selectivity towards TAG, the most valuable acetin, remains low. Data reported by Abida et al. [16] show that  $\text{SO}_4^{2-}$  studded over silica coated  $\text{Fe}_2\text{O}_3$ , magnetic and nanostructured catalysts, permits to obtain 100% of TAG selectivity after 80 min of reaction. According to the depicted reaction mechanism, the active phase seems to be related to  $\text{Si-SO}_4\text{H}$  species on the catalyst surface. The best catalyst lost about 50% of TAG selectivity after 6 consecutive reaction batches, possibly by leaching the  $-\text{SO}_4\text{H}$  species into the reaction medium. The leaching active species into the reaction medium can have a non-negligible homogeneous catalytic contribution.

Recently data from Ramalingam et al. [17] seems to show a major role of the catalyst mesoporous on the triacetin formation. The authors reported a selectivity 50.4% of TAG selectivity obtained with mesoporous silica modified with copper and ruthenium. Both, Lewis and Brønsted acid catalysts have been used in glycerin acetylation. Brønsted acetylation mechanism (Fisher esterification) is believed to start with acetic acid protonation as schematized in Fig. 2 [18]. Theoretically, Lewis and Brønsted mechanisms are similar

**Table 1** Triacetin (TAG) selectivity in glycerin acetylation from the literature

Catalyst	Parameters (reaction time, temperature, HAc: glycerin molar ratio; catalyst loading)	% TAG selectivity	Reference
Acid-exchange resins	4 h; 120 °C; 9:1; 4 wt% (glycerin basis)	≤ 34	[34]
	4.5 h; 110 °C; 9:1; 82.96 mmol H <sup>+</sup> /L	≤ 44.5	[35]
	8 h; 80 °C; 6:1; 5 wt% (glycerin basis)	15.1	[36]
	3 h; 105 °C; 3:1; 5 wt% (glycerin basis)	12	[37]
	24 h; 80 °C; 6:1; 9 wt% (glycerin basis)	26	[12]
K-10 montmorillonite	0.5 h; Reflux temp.; 3:1; 2 mmol of acid sites	5	[32]
	1 h; 120 °C; 3:1; 1 g	≤ 56	[38]
Activated carbons	4 h; 105 °C; 9:1; 7 wt% (glycerin basis)	≤ 41.0	[39]
	3 h; 120 °C; 8:1; 0.8 g	34	[40]
	5 h; 110 °C; 3:1; 2 wt% (glycerin basis)	≤ 45	[41]
	1.5 h; 100 °C; 8:1; 5 wt% (glycerin basis) – ultrasound-assisted	100	[11]
	24 h; 80 °C; 6:1; 9 wt% (glycerin basis)	≤ 23	[12]
Mesoporous and modified silica	6 h; 80 °C; 3:1; 75 mg	≤ 18	[42]
	8 h; 80 °C; 6:1; 5 wt% (glycerin basis)	≤ 27.0	[36]
	3 h; 105 °C; 3:1; 5 wt% (glycerin basis)	≤ 49	[37]
	2 h; 50 °C; 6:1; 0.2 g	≤ 4.62	[43]
	4.5 h; 120 °C; 6:1; 4 wt% (glycerin basis)	35	[44]
	5 h; 120 °C; 10:1; wt% undefined	≤ 50.4	[17]
	8 h; 80 °C; 6:1; 5 wt% (glycerin basis)	0.5	[36]
Modified zirconia	3 h; 105 °C; 3:1; 5 wt% (glycerin basis)	≤ 5	[37]
	3 h; 120 °C; 6:1; 5 wt% (glycerin basis)	≤ 7.52	[45]
	1 h; 120 °C; 6:1; 0.1 g	≤ 16.5	[46]
	8 h; 80 °C; 6:1; 5 wt% (glycerin basis)	≤ 0.9	[36]
Heteropolyacids loaded solids	6 h; 80 °C; 3:1; 75 mg	≤ 30	[42]
	24 h; 105 °C; 6:1; 5 wt% (glycerin basis)	≤ 71.4	[47]
	20 h; 105 °C; 12:1; 10 wt% (glycerin basis)	30	[48]
	4 h; 120 °C; 5:1; 0.2 g	20	[49]
	3 h; 120 °C; 16:1; 0.2 g	≤ 14	[50]
	45 min; 80 °C; 6:1; 7%wt% (glycerin basis)	100%	[16]
Magnetic nanostructured SO <sub>4</sub> <sup>2-</sup> /(SiO <sub>2</sub> –Fe <sub>2</sub> O <sub>3</sub> )		50% for 6th reaction batch	
Phosphotungstic, silicotungstic, phosphomolybdic acids/polymeric material	6 h; 110 °C; 1:20; 7%wt% (glycerin basis)	34%	[24]
Sulphated siliceous zirconia	40 min; 80 °C; 9:1; 3%wt% (glycerin basis)	93%	[22]

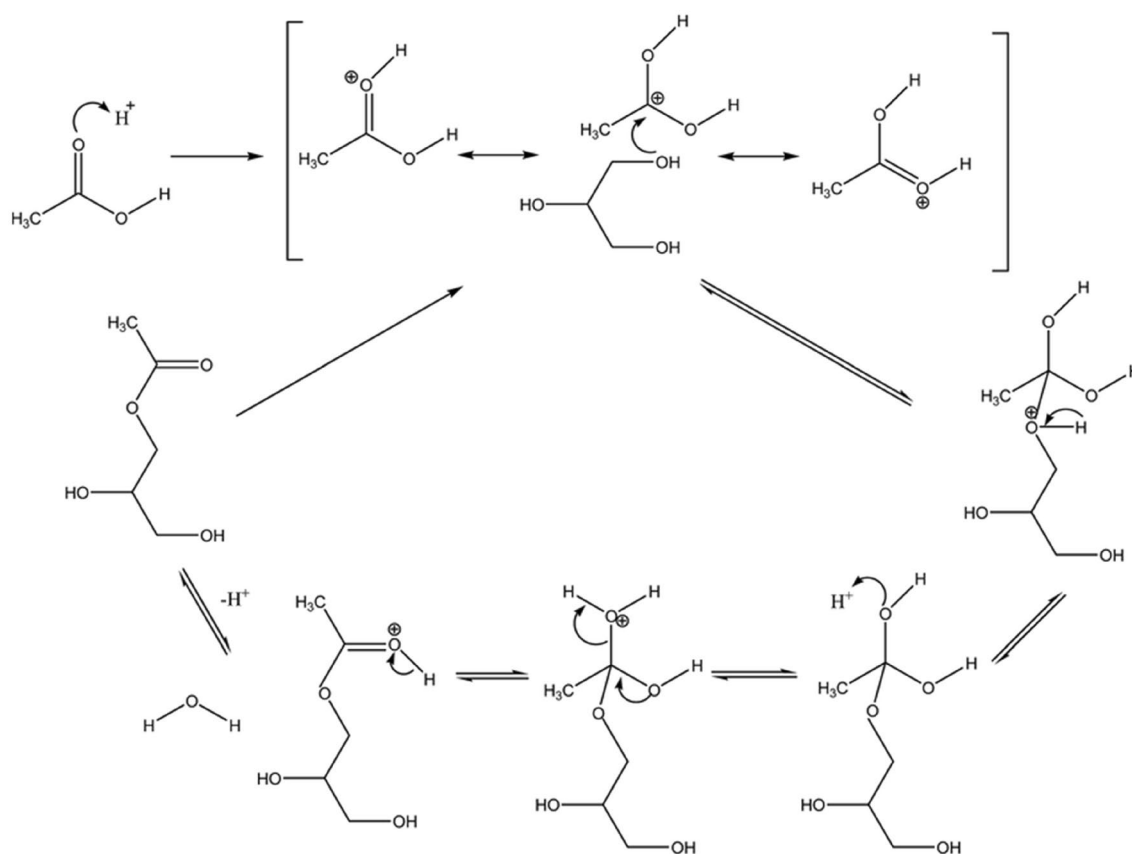
[18] and some researchers claim a synergy effect between both acid sites during glycerin acetylation over Keggin heteropolyacid catalysts [19].

Since silica can be obtained from natural sources and industrial wastes, the use of this kind of catalyst would help to further increase the sustainability of all biodiesel production processes [20]. According to published data strong Brønsted acid, sites can be created by calcination of phosphoric acid impregnated silica [21]. Abida and Ali [22] studied the catalytic behavior of sulfated siliceous zirconia catalysts. The authors reported strong Brønsted acidity, which is responsible for the exceptional TAG selectivity (Table 1). The catalyst was deactivated by leaching sulfate species into the reaction medium. Sulfate species over carbon materials

[23] are also highly active for the glycerin acetylation showing a lower leaching rate, but with lower TAG selectivity than that reported by Abida and Ali.

Magar et al. [24] reported the catalytic behavior of phosphotungstic, silicotungstic, and phosphotungstic acids supported over polymeric materials during glycerin acetylation. The authors underlined the fact that polymeric support material adsorbed the water formed during reaction thus shifting the equilibrium towards the reaction products. The best catalyst allowed 34% of TAG selectivity (Table 1).

A clever synthesis route, to avoid the glycerin co-production with biodiesel, was recently proposed by Dahwan et al. [25] The authors did not assess whether the acetin content of the methyl esters produced meets the biodiesel standards.



**Fig. 2** Brønsted acid mechanism of glycerin acetylation (adapted from [18])

Given the value of TAG as an oxygenated additive for diesel, the low TAG selectivity reported in the literature, for most of the tested catalysts, justifies further investigation in the heterogenous catalysts for glycerin acetylation reaction. The focus of this work lays in the employment of phosphate modified silica (commercial fumed silica), a non-expensive and easy to prepare catalysts while changing some reaction parameters to promote the esterification of glycerin using acetic acid.

## 2 Materials and Methods

### 2.1 Preparation and Characterization of the Catalysts

Phosphated silica catalysts were prepared by contacting commercial silica powder (Sipernat 22, characteristics in Table 2) with aqueous solutions containing the desired amount of the phosphate precursor. Samples with atomic ratios P/Si in the range 10–20 were obtained and are referred to using the mnemonic *nXprecursor* (e.g.: 10X $\text{H}_3\text{PO}_4$ ), in which *n* is the P/Si atomic ratio and

**Table 2** Evonik Sipernat 22 characteristics

Density (g/L)	$\bar{d}_{50}$ Average particle diameter laser diffraction ( $\mu\text{m}$ )	Pore volume BJH ( $\text{cm}^3/\text{g}$ )	Average pore size BJH (nm)
220	120.7	1.15	32.5

precursor can be either o-phosphoric acid ( $\text{H}_3\text{PO}_4$ , Fisher Chemical, reagent grade) or diammonium phosphate  $[(\text{NH}_4)_2\text{HPO}_4]$ , Merck, pro analysis]. Diammonium phosphate is expected to allow a better anchorage of P species on the silica surface thus contributing to better dispersion of the acidic species and improved catalytic behavior.

The slurries were slowly evaporated ( $\approx 80^\circ\text{C}$ ) under vigorous stirring until dryness. The obtained samples were dried overnight at  $120^\circ\text{C}$  and calcined for 5 h at  $475^\circ\text{C}$  in a muffle.

The crystallinity of fresh catalysts was investigated by X-ray diffraction (XRD) using a Burke D8 Advance X-ray diffractometer with Cu  $k_\alpha$  radiation at 40 kV and 40 mA. Each diffractogram was acquired in the range of  $5\text{--}70^\circ$

at  $0.02^\circ \text{ s}^{-1}$  and then compared with standard JCPDS patterns.

To identify the surface species involved in the catalytic process, which remain adsorbed, and thus infer about the stability of the catalysts, both fresh and post-reaction solid catalysts were characterized by HATR-FTIR with a Pike Elmer Spectrum Two IR spectrometer, using a  $4 \text{ cm}^{-1}$  resolution. HATR-FTIR spectra were corrected using the Kubelka–Munk function.

The acidity of catalysts was also evaluated using the standard reaction of skeletal isomerization of 1-butene. The catalytic tests were carried out at  $222^\circ \text{C}$  in a conventional apparatus for continuous catalytic tests. The reaction was carried out using 520 mg of catalyst with  $Y_{1\text{-but}}^0 = 12.8\%$  in an inert atmosphere of  $\text{N}_2$  and a total flow of  $4.3 \text{ L h}^{-1}$ . The reaction effluent was quantified by gas chromatography (GC) using an FID detector.

## 2.2 Glycerin Acetylation Catalytic Tests

The glycerin (Glyc, 99% from Fluka) acetylation with acetic acid (HAc, glacial from Fluka) was studied in a 500 mL round bottom Pyrex flask equipped with a condenser and a magnetic stirrer. The reaction temperature was kept at  $120^\circ \text{C}$  using a nest shape electrical heating jacket with temperature control, whereas the temperature sensor is immersed in the reaction medium. The catalytic tests were carried out in conditions selected from the literature [42] using 500 mg of catalyst (15 wt%, glycerin basis), HAc/Glyc = 9 molar ratio. After the reaction, the catalyst was removed by filtration and the liquid effluent was analyzed by GC using a Varian CP 3800 chromatograph equipped with a flame ionization detector. The pure MAG, DAG, TAG, glycerin, and acetic acid were injected separately to determine the retention time of each component for a fused silica capillary column (0.32 mm of internal diameter, 15 m length with a  $0.1 \mu\text{m}$  of film thickness of Methyl 5% Phenyl Silicone). Chromatograms were acquired in the conditions listed in Table 3.

**Table 3** Gas chromatograph experimental conditions

Conditions		
Carrier gas	Helium	
Initial temperature	$110^\circ \text{C}$	
Ramp	$10^\circ \text{C/min}$ to $150^\circ \text{C}$	
Injector temperature	$280^\circ \text{C}$ ; split ratio 10	
FID temperature	$300^\circ \text{C}$	
Detector gases (mL/min)	$\text{H}_2$	30
	Air	300
	He	30
Total pressure (psi)	6.7	

Samples were prepared by mixing some drops of the product with Isopropyl Alcohol (IPA) (GC grade) as an internal standard. About  $2 \mu\text{L}$  of the sample was then injected into the column. The catalyst stability was evaluated using the same sample for consecutive reaction batches without any intermediate reactivation procedure. The GC analysis was unable to distinguish MAG and DAG isomers, most likely due to their high boiling points, hence the products are simply referred to as “MAG and DAG”.

## 3 Results and Discussion

The surface acidity of raw silica and prepared catalysts was evaluated by skeletal isomerization of 1-butene. Both the reaction speed ( $r_{1\text{-but}}$ ) and the trans/cis selectivity ratio of the skeletal isomerization of 1-butene (Table 4) are directly related to the surface acidity of catalysts (zeolites) [26]. Acidic catalysts produce larger amounts of trans-isomer [26] thus having trans/cis-butene-2 ratios higher than 1. For the tested catalysts, the trans/cis butene-2 isomers ratios were always higher than 1, evidencing the acidic character of the catalysts. Also, the 1-butene conversion was usually greater for the catalysts prepared with diammonium phosphate solutions and tends to increase with the P/Si ratio, which indicates greater surface acidity and therefore greater potential for glycerin acetylation performance.

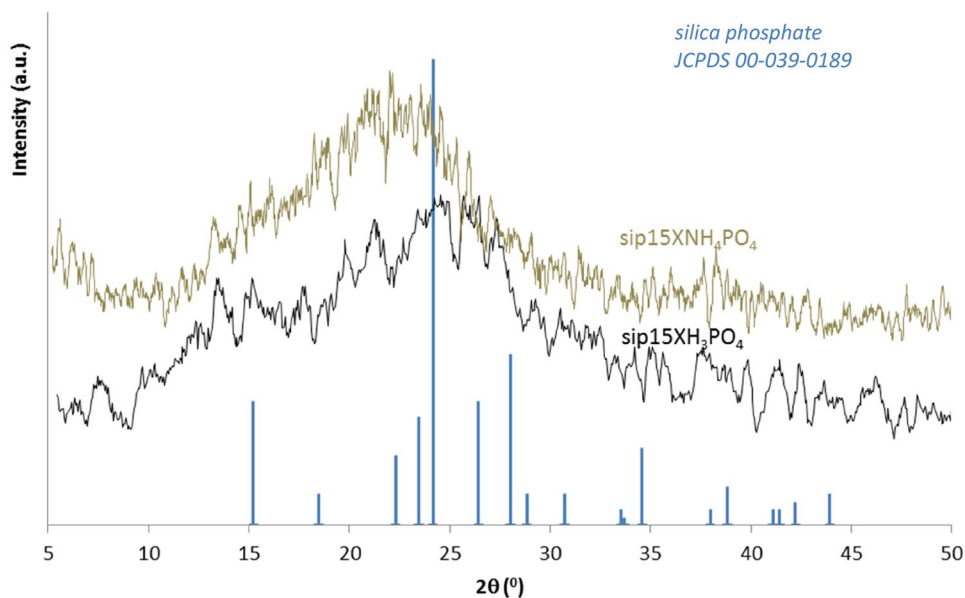
It appears that the diammonium precursor allowed a better dispersion of P species on the silica surface thus improving surface acidity. Additionally, the volatilization of ammonium species during calcination can contribute to creating a higher porosity surface layer over silica material.

The diffractograms of fresh catalysts (Fig. 3) showed patterns ascribable to amorphous materials like raw silica (amorphous according to the supplier). As reported in the literature [27], the broad feature around  $2\theta = 22.5^\circ$  belongs

**Table 4** 1-butene isomerization. Average rate of conversion ( $r_{1\text{-but}}$ ) and trans/cis selectivity ratios.  $Y_{1\text{-but}}^0 = 12.8\%$  in  $\text{N}_2$ ;  $W_{\text{cat}} = 0.52\text{g}$ ; total flow of  $4.3 \text{ L/h}$  and  $222^\circ \text{C}$

Catalyst	1-butene conversion (%)	$r_{1\text{-but}}$ ( $\mu\text{mol}\cdot\text{gcat}^{-1}\cdot\text{s}^{-1}$ )	trans/cis 2-butene selectivity ratio
Silica	3.7	0.45	1.1
$10\text{XH}_3\text{PO}_4$	12.3	1.50	1.5
$10\text{XNH}_4\text{PO}_4$	16.7	2.04	1.4
$15\text{XH}_3\text{PO}_4$	12.3	1.50	1.5
$15\text{XNH}_4\text{PO}_4$	11.7	1.43	1.4
$15\text{XNH}_4\text{PO}_4$	11.6	1.41	1.4
$20\text{XH}_3\text{PO}_4$	21.7	2.64	1.5
$20\text{XNH}_4\text{PO}_4$	29.1	3.56	1.6

**Fig. 3** XRD patterns of fresh catalysts  $15\text{XH}_3\text{PO}_4$  and  $15\text{XNH}_4\text{PO}_3$

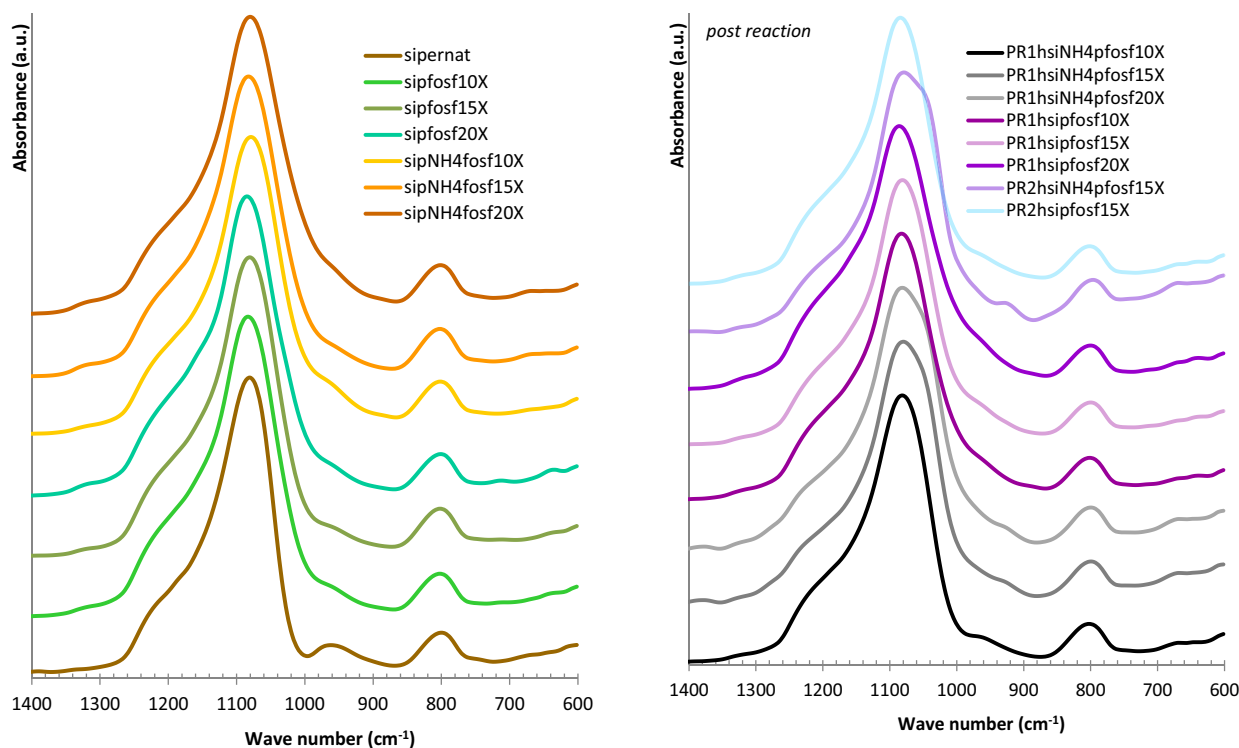


to amorphous silica. Diffraction lines of silica phosphate are absent which seems to confirm the good dispersion of P species with the probable formation of small (nanostructured) aggregates of silica phosphates.

The fresh and post-reaction catalysts were characterized by HATR-FTIR spectroscopy to identify surface species

which can be correlated with catalytic activity and deactivation. The main spectral features for fresh and post-reaction catalysts are presented in Fig. 4.

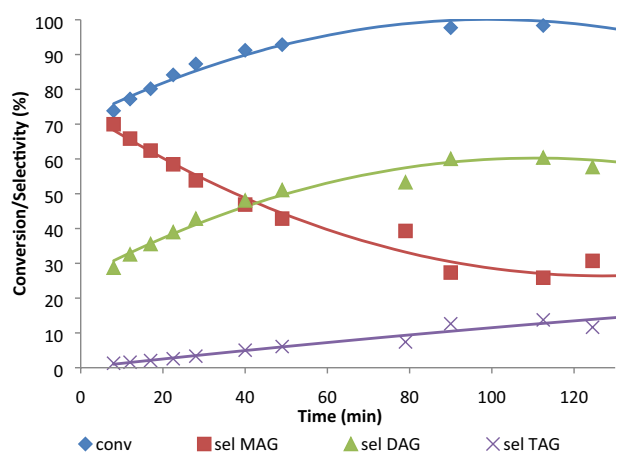
The raw silica shows absorption bands at 1080, 963, and  $802\text{ cm}^{-1}$  respectively attributable to antisymmetric Si–O–Si, in-plane Si–O, and symmetric Si–O stretching



**Fig. 4** HATR-FTIR spectra of fresh and post-reaction catalysts



vibrations [28]. The small bands at  $947\text{ cm}^{-1}$  and  $802\text{ cm}^{-1}$  are assigned to the flexion modes of SiO–H and Si–O–, respectively [29]. Fresh catalysts display analogous IR features but the most intense band became wider due to the overlay of O–P–O and O=P–O vibrations at  $1140$  and  $1230\text{ cm}^{-1}$  [30]. For the post-reaction samples, the most intense band results from the overlapping of features belonging to  $\text{SiO}_2$  and  $\text{PO}_4^{3-}$  species; for samples prepared using diammonium phosphate this effect was more noticeable. Additionally, longer reaction times (2 h instead of 1 h) faded this effect, which possibly indicates that phosphorus surface species are leached during the reaction.



**Fig. 5** Glycerin conversion and acetins (MAG, DAG and TAG) selectivities versus reaction time (120 °C; HAC/Glyc = 9 molar ratio; 15 wt.% glycerin basis; raw silica catalyst)

Kinetics data, obtained using raw silica catalyst (Fig. 5), confirmed the sequential mechanism of the acetylation reaction [31]. The total conversion of glycerin was achieved in a short time, first by MAG formation, whose maximum selectivity was reached at the beginning of the acetylation. For longer reaction times MAG concentration decreased, being replaced by DAG. On the other hand, DAG was slowly converted in TAG, at a reaction rate constant and independent of DAG concentration. A decrease in DAG concentration is only observable for low concentrations of MAG. The low rate of triacetin formation can be explained by the porosity of the catalyst since the TAG molecule is larger than the glycerin one and, therefore, more susceptible to diffusional limitations. The kinetics test was replicated 3 times, allowing to compute relative errors for conversion and selectivities (3% for conversion and 7% for selectivities).

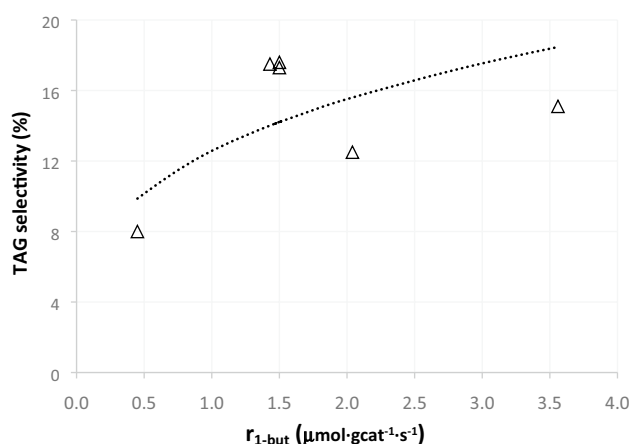
The tests performed (Table 5) allowed us to analyze the effect of the catalyst acidity and the reaction time on the total conversion and, especially, on the selectivity towards triacetin production.

The effect of higher catalyst acidity is readily noticeable as the selectivity of TAG reaction increases steadily, especially when compared to the unmodified silica (Fig. 6). The effect of the reaction temperature is observable in the  $10\text{XNH}_4\text{PO}_4$  tests and seems to impact the overall glycerin conversion more than the products' selectivity.

The effect of test duration is noticeable through higher selectivity towards heavier products (TAG) but lower overall conversion. This trend should lead to greater consumption of MAG and DAG over higher reaction times, and an

**Table 5** Catalytic performances of the prepared catalysts during the acetylation of glycerin with acetic acid

		HAc/Glyc Molar ratio	Catalyst load- ing (wt%, glyc- erin basis)	T (°C)	Reaction time (h)	Conversion, selectivities (%)				
						Conv	Acetol	MAG	DAG	TAG
Sipernat		9.0	15.0	120	1	89.5	–	41.7	50.3	8.0
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	10X	8.6	15.1	120	2	92.6	8.7	18.6	60.2	12.5
	10X	9.0	15.9	130	2	91.1	–	17.5	67.0	15.5
	10X	8.8	15.6	120	1	91.3	–	21.1	65.5	13.5
	10X	8.7	15.4	112	2	94.0	5.7	19.7	61.2	13.4
	15X	8.8	15.5	120	1	92.9	–	21.4	65.2	13.4
	15X	8.6	15.3	120	2	95.1	–	19.5	64.8	15.7
	15X, Batch#2	8.3	15.6	120	2	94.4	–	19.1	64.8	16.2
	20X	8.8	15.6	120	1	93.0	–	20.8	65.4	13.8
	20X	8.7	15.3	120	2	94.8	–	20.6	64.3	15.1
	H <sub>3</sub> PO <sub>4</sub>	10X	9.0	16.2	120	2	93.3	–	16.4	66.0
10X		9.0	14.9	120	1	91.3	–	18.7	66.4	14.9
15X		8.7	15.4	120	1	90.3	–	19.1	66.4	14.5
20X		8.6	15.2	120	2	92.7	–	17.2	65.5	17.3
20X		8.9	15.7	120	1	91.0	–	14.2	59.7	26.1



**Fig. 6** TAG selectivity (120 °C; 2h reaction time) versus rate of butene-1 isomerization (a measure of the catalysts acidity)

increasingly higher concentration of TAG in the medium, thus longer reaction times seem to favor TAG production.

Production of acetol ( $\alpha$ -hydroxyacetone) was only observed for experiments using the  $10\text{XNH}_4\text{PO}_4$  and  $15\text{XNH}_4\text{PO}_4$  catalysts and might be a product of dehydration of glycerin. Dehydration tends to be an endothermic reaction, which explains the low selectivity due to the low temperature used. However, Gonçalves et al. [32] reported better yields of acetol for lower acidity catalysts, such as the case, which might relate to the formation of this product with the acidity of the catalyst. Acetol could be an interesting intermediate in a new technological route for the production of propylene glycol from glycerin [33].

The comparison of data in Table 5 (current work) and Table 1 (from literature) is hard since there is a wide dispersion of reaction variables (catalyst loading, temperature, reaction time, and HAc/ Glyc ratio) values. Still, from data in Table 5 and Table 1, it stands out the lower TAG selectivities obtained in this study when compared with data reported for mesoporous silica catalysts. The catalyst morphology seems to have a chief role in TAG formation because the highest selectivities were reported for mesoporous silica catalysts. Despite the low porosity of the used silica data in Table 5 showed a catalytic behavior for P/Silica catalysts superior to most catalysts displayed in Table 1. P/SiO<sub>2</sub> catalysts allowed similar TAG selectivity for shorter reaction times.

The stability of the prepared catalysts was evaluated by reusing the same catalyst sample in a second consecutive reaction batch without intermediate reactivation. Data in Table 5 for the 15X sample, prepared using ammonium phosphate, show similar catalytic behavior for both reaction batches, thus indicating catalyst stability.

The results in Table 5 showed a catalytic behavior for P/Silica catalysts superior to most catalysts displayed in Table 4. P/SiO<sub>2</sub> catalysts allowed similar TAG selectivity for shorter reaction times.

## 4 Conclusions

Acetylation of glycerin with acetic acid was carried out over solid acid catalysts. Phosphate modified silica was prepared using ortho-phosphoric acid or diammonium phosphate. TAG selectivity remains almost invariant with catalyst surface acidity, while emphasizing the importance of pore size due to the large kinetic diameter of the heaviest product. It appears that slow diffusion in narrow pores might be responsible for the low selectivity of the reaction to triacetin. Diammonium phosphate precursor led to higher acidity solids. Surface phosphate species showed a slow rate of leaching in the reaction medium showing high catalyst stability.

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**Author Contributions** APSD Conceptualization, Resources, Supervision, Funding acquisition, Writing-Reviewing and editing. FGF Investigation, Formal Analysis, Writing Original Draft, Reviewing and Editing. MC Investigation, Writing Original Draft. JG Writing, Reviewing and Editing.

## Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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