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Cs₄PMo₁₁VO₄₀-Catalyzed Glycerol Ketalization to Produce Solketal: An Efficient Bioadditives Synthesis Method

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Abstract: In this work, a series of vanadium-substituted phosphomolybdic acids were synthesized and tested as the catalysts for the synthesis of solketal, a green fuel bioadditive, from the condensation reaction of glycerol with acetone. The objective was to demonstrate that an easily synthesizable solid catalyst can efficiently promote glycerol condensation with acetone at room temperature. The activity of pristine heteropolyacid (i.e., H₃PMo₁₂O₄₀) and its vanadium-substituted cesium salts (Cs_{3+n}PMo_{12-n}V_nO₄₀; n = 0–3) was evaluated in condensation reactions carried out at room temperature. Among the catalysts tested, Cs₄PMo₁₁VO₄₀ was the most active and selective towards a five-member ring solketal isomer (dioxolane). A high yield of solketal (i.e., 95% conversion and 95% selectivity to solketal) was achieved in glycerol condensation with acetone at room temperature within a short reaction time (2 h). The influence of the main reaction parameters, such as the acetone–glycerol molar ratio, catalyst load, and reaction temperatures, was investigated. The greatest activity of the Cs₄PMo₁₁VO₄₀ catalyst was correlated to its greatest acidity.

Keywords: glycerol; solketal; phosphomolybdovanadate catalysts; bioadditives; acetalization



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1. Introduction

Nowadays, due to the inevitable depletion of fossil-origin resources, the production of green fuels such as biodiesel has become essential [1,2]. However, in these processes, glycerol is co-produced at 10 wt.%, making it an inexpensive and abundant platform molecule for biorefineries of the future [3–5]. Among the several routes to valorized glycerol is its conversion to solketal, a valuable fuel bioadditive (i.e., diesel and gasoline), through condensation reactions with an aldehyde (acetalization) or ketone (ketalization) [6–8].

Condensation reactions have commonly been carried out in the presence of homogeneous mineral liquid acids, which are corrosive and require neutralization steps which generate large amounts of effluent and residues [9]. Simple Lewis acid metal salts were demonstrated to be efficient in ketalization or acetalization glycerol reactions; however, most of them were soluble in reaction conditions [10–13]. Alternatively, these Lewis acid metal acids have been supported in different solid matrixes and used as heterogeneous catalysts in reactions to produce solketal from glycerol [14].

Several solid acid catalysts are also used in glycerol ketalization reactions, such as sulfonic resins [15,16], metal oxides [17], sulfonated carbonaceous materials [18], zeolites [19–21], molecular sieves [22,23], and solid-supported acid catalysts [24–26]. Nonetheless, the high polarity of the reaction medium, in addition to the water molecules generated as a co-product of the reaction, can contribute to the leaching of the active phase of solid-supported catalysts.

In this sense, Keggin heteropolyacids (HPAs) have risen to prominence as an attractive option to traditional solid-supported catalysts [27–29]. These compounds belong to a class of metal oxides characterized as solid clusters of metal–oxygen that when protonated have been demonstrated to be very active in acid-catalyzed reactions [30]. Although solid,

HPAs have a low surface area and are soluble in polar solvents, hampering their use as solid catalysts. This drawback can be easily overcome if these HPAs are converted to solid salts [31]. If the protons of HPAs are exchanged with metal cations with low amounts of radius, lower than 1.3 Å, the catalytic properties of HPAs can be improved; however, they will remain soluble [32]. This strategy has been explored in various reactions, in which the proton exchange with metals such as Al^{3+} , Fe^{3+} , Cu^{2+} , and Sn^{2+} led to a noticeable increase in the activity of HPAs either in oxidation or acid-catalyzed reactions [33,34].

On the other hand, if the HPA protons are replaced with voluminous cations that have an ionic radius greater than 1.3 Å, such as K^+ or Cs^+ , the surface area of HPAs jumps from 1 to 3 $\text{m}^2 \text{g}^{-1}$ (i.e., acids) to 160 $\text{m}^2 \text{g}^{-1}$ (salts), making them efficient and recyclable heterogeneous catalysts which can be used in different reactions such as oxidation, esterification, or etherification reactions [35]. It is important to note that this modification is performed with Keggin heteropolyanions, keeping their primary structure intact, since the cations are placed on the secondary ones [36].

Conversely, there are three other strategies to modify the composition of the Keggin heteropolyanion, enhancing its catalytic properties but preserving its structure. However, all of them are internal modifications to the primary structure of the Keggin anion. The first can be undertaken by removing one unit MO ($\text{M} = \text{W}, \text{Mo}$), which turns the $\text{PM}_{12}\text{O}_{40}^{3-}$ anion (saturated) into a $\text{PM}_{11}\text{O}_{39}^{7-}$ lacunar anion (unsaturated) [37]. Lacunar HPAs are easily synthesized and are stable under acidic or oxidative conditions. The second approach is to fill this vacancy with transition metal cations (X^{+n}), generating metal-doped heteropolyanions ($\text{PM}_{11}\text{XO}_{39}^{(7-n)-}$) [38]. Both lacunar and metal-doped HPA salts have been effective catalysts in the oxidation reactions of alcohols and aldehydes [39–43].

The third strategy is to substitute Mo or W atoms with V, keeping the number of oxygen atoms of the heteropolyanion intact. Recently, vanadium-substituted HPA catalysts were synthesized from phosphomolybdic acid and successfully used as $\text{H}_{3+n}\text{PMo}_{12-n}\text{V}_n\text{O}_{40}$ acids with $n = 1\text{--}3$ [44]. However, despite the high conversion and selectivity achieved in these reactions, they were carried out in homogeneous conditions. To overcome this drawback, we recently prepared cesium phosphomolybdovanadate salts and used them as heterogeneous catalysts in benzaldehyde condensation reactions [45,46]. Therefore, the novelty of this work describes how two simple modifications (the replacement of protons of phosphomolybdic acid with cesium cations, and the exchange of molybdenum atoms with vanadium atoms) can transform the homogeneous acid into an active solid catalyst.

In this work, a series of cesium salts of vanadium-substituted phosphomolybdic acids with general formulae ($\text{Cs}_{3+n}\text{PMo}_{12-n}\text{V}_n\text{O}_{40}$ with $n = 1\text{--}3$) were synthesized and evaluated as catalysts in glycerol condensation reactions with acetone to produce solketal, a valuable fuel bioadditive.

2. Materials and Methods

2.1. Chemicals

All the chemicals received were used without any further treatment. Acetone (99.9 wt. %) and glycerol (99.5 wt. %) were obtained from Sigma-Aldrich (Burlington, MA, USA). The hydrated heteropolyacid (i.e., $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot n \text{H}_2\text{O}$; 99.9 wt. %), and the synthesis precursors V_2O_5 (99.6 wt. %), MoO_3 (99.5 wt. %), H_3PO_4 (85 wt. %), NaVO_3 (98 wt. %), CsCl (99 wt. %), and Na_2MoO_4 (≥ 98 wt. %), were from Sigma-Aldrich. Acetone and glycerol (99 wt. %) were also from Sigma-Aldrich.

2.2. Synthesis and Characterization of Unsubstituted and Vanadium-Substituted Cesium Phosphomolybdate Salts

The cesium phosphomolybdate salt was synthesized following a procedure described in the literature [44–46]. Typically, the catalyst was synthesized slowly by mixing 2 solutions, the first an aqueous solution of precursor $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (4.20 g; 60 mL) and the second solution CsCl (1.14 g, 40 mL). The resulting solution was heated and stirred for 3 h at 373 K,

giving a green precipitate ($\text{Cs}_3\text{PMo}_{11}\text{O}_{40}$). After water vaporization at 373 K, the solid was dried in an oven at 393 K for 24 h.

All the vanadium-substituted phosphomolybdate cesium salts were synthesized starting from the respective acid, which was also prepared following the literature [44–46]. The $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ (3.86 g) was converted to $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ salt (yellow solid) after the slow addition of $\text{CsCl}_{(\text{aq})}$ aqueous solution (20 mL, 1.46 g). The resulting suspension was stirred for 3 h and heated to 363 K. After water vaporization at 373 K, the solid $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ salt was collected and dried in an oven at 393 K/24 h. An analogous procedure was used to obtain $\text{Cs}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ from $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$, only adjusting the stoichiometry; however, a brown solid was formed. When the precursor $\text{H}_6\text{PMo}_9\text{V}_3\text{O}_{40}$ was precipitated as $\text{Cs}_6\text{PMo}_9\text{V}_3\text{O}_{40}$ salt, a white solid was obtained. The characterization of cesium salts has been discussed by us previously [44,46].

2.3. Catalytic Runs

The catalytic tests were carried out in a stirred glass reactor (50 mL) three-necked glass flask. A homogenous solution containing glycerol and acetone at an adequate molar ratio was magnetically stirred at room temperature. Then, the addition of a solid catalyst started the reaction, which was allowed to proceed for 2 h. The catalyst load was expressed concerning the glycerol. Toluene was the internal standard (0.10 mL). Blank reactions were carried out using the same conditions, with both ketone and glycerol but in the absence of the catalyst.

The reactions were monitored through GC analyses of aliquots collected periodically (Shimadzu 2010 equipment, FID, capillary column). The conditions were 80 °C/3 min, 10 °C/min to 250 °C, hold time of 5 min. The injector and FID detector were kept at 250 and 280 °C, respectively. The GC was fitted with a DB5 capillary column (0.25 m × 0.25 mm × 30 m).

The recovery and reuse of the most active catalyst were evaluated. At the end of the run, the reaction solution was centrifugated, and the supernatant was removed. The solid resultant was washed with ethyl acetate and the catalyst was dried in an oven, weighted, and then reused in another catalytic run.

Analyses of mass spectrometry in a Shimadzu GC 2010 gas chromatograph coupled with MS-QP 2010A equipment (Tokyo, Japan) with a Carbowax capillary column (0.25 mm × 0.25 mm × 30 m) were identified as the main products. Helium was the carrier gas at 2 mL/min, and the temperatures of both the GC injector and MS ion source were kept at 250 and 260 °C, respectively. The MS detector operated in EI mode at 70 eV, with a scanning range of m/z 50–400. The products were co-injected into a GC chromatograph (Shimadzu 2010) with authentic samples previously synthesized. The conversion was calculated using a calibration curve built with the glycerol and solketal, allowing the mass balance of reactions to be checked.

3. Results and Discussion

3.1. Catalytic Characterization

Cesium phosphomolybdate catalysts containing vanadium were previously characterized by us [46]. However, in this present work, only the acidity measurements will be presented to support the discussions about their catalytic activity.

In Figure 1, the EDS MEV analyses of cesium phosphomolybdate salts are shown. The composition of catalysts was confirmed by EDS measurements. The microscopy data showed that a higher cesium load increased the particle sizes.

In Table 1, we summarize the characterization data previously described, which were obtained through the potentiometric titration curves with *n*-butylamine [46]. The measurement of the initial electrode potential (E_i) allows us to classify the strength of the acid sites of the catalyst as very strong ($E_i > 100$ mV), strong ($0 < E_i < 100$ mV), weak ($-100 < E_i < 0$ mV), and very weak ($E_i < -100$ mV). On the other hand, the minimum value of the second derived curve obtained from titration provides the acid site number (mEq/g).

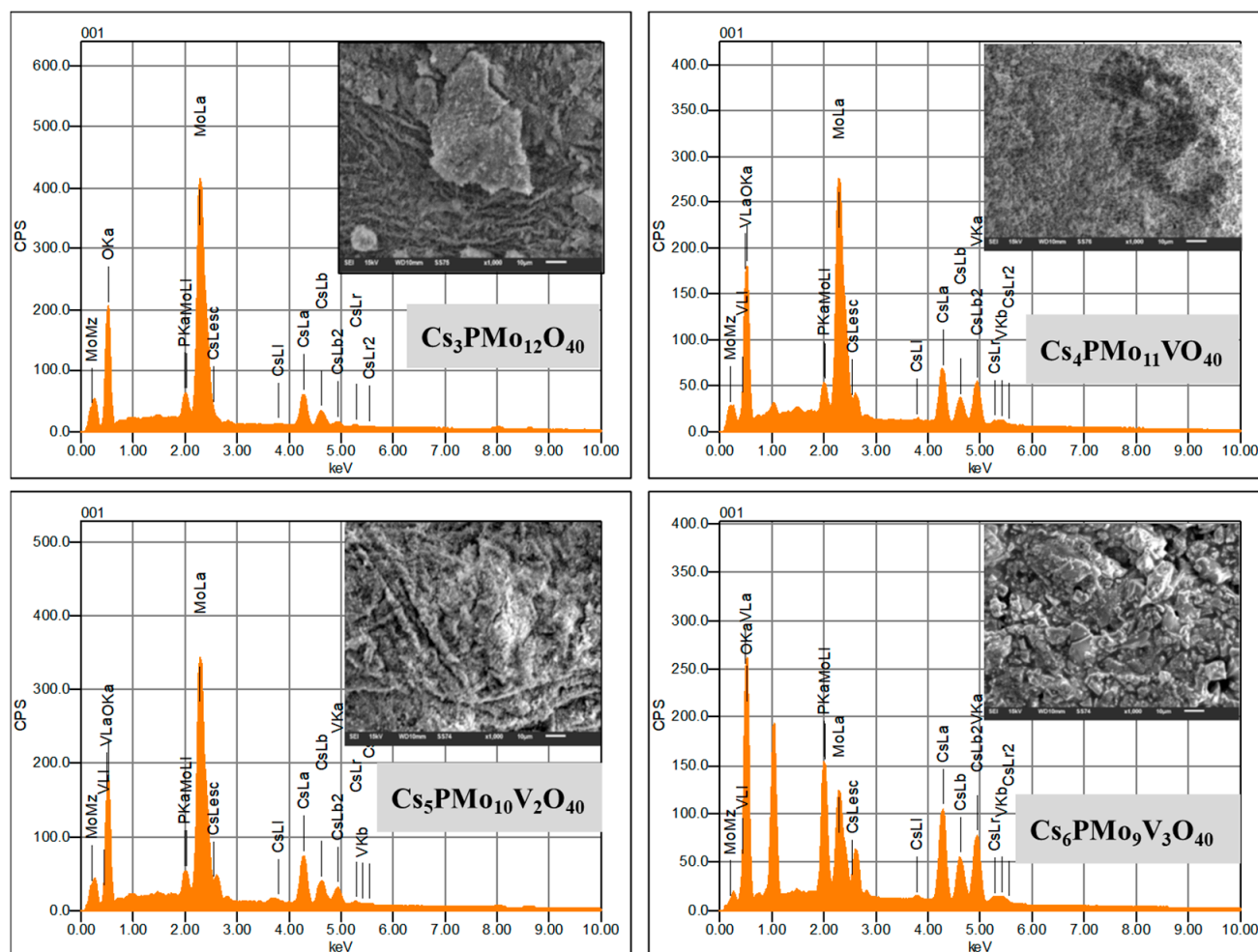


Figure 1. EDS-MEV analyses of cesium phosphomolybdates.

Table 1. Measurements of acidity of the phosphomolybdic acid and its cesium salts ^a.

Catalyst	Initial Electrode Potential (mV)	Acidity Strength ^a	Acid Site Numbers (mEq/g)
H ₃ PMo ₁₂ O ₄₀	695	Very strong	1.3
Cs ₃ PMo ₁₂ O ₄₀	450	Very strong	0.2
Cs ₄ PMo ₁₁ VO ₄₀	460	Very strong	0.6
Cs ₅ PMo ₁₀ V ₂ O ₄₀	330	Very strong	0.2
Cs ₆ PMo ₉ V ₃ O ₄₀	90	strong	0.1

^a Classified according to ref [34]; measured in acetonitrile solution (50 mg catalyst) by potentiometric titration with n-butylamine 0.025 mol L⁻¹ (adapted from ref [46]).

An increase in vanadium load led to a decrease in Ei value, suggesting that the strength of acidity was being lowered. In addition, the acid site number was progressively diminished when a higher vanadium load was used. Similarly, if the cesium content was increased, the same happened.

In Table 2, the effects of proton exchange with cesium of the phosphomolybdic acid and the replacement of the molybdenum atom with vanadium on the surface area and porosity properties of catalysts are presented.

Table 2. Measurements of surface area and porosity of the phosphomolybdic acid and its cesium salts.

Catalyst	Surface Area ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore Volume ($\text{m}^3 \cdot \text{g}^{-1}$) $\times 10^{-3}$	Diameter Pore (Å)
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	2.8	1.7	3.8
$\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$	104.1	37.3	2.0
$\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$	55.6	17.4	3.5
$\text{Cs}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$	4.1	1.0	3.1
$\text{Cs}_6\text{PMo}_9\text{V}_3\text{O}_{40}$	3.0	0.5	3.1

Phosphomolybdic acid has a very low surface area. When cesium cations replace their protons, they noticeably increase their surface area, as can be seen in the case of $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ (Table 2). However, when the cesium load is increased, there is a notable diminishment in surface area. This probably happened due to the high ionic radius of the cesium cations. A greater cesium load hampered the packing of heteropolyanions and cesium cations.

The pore volumes were also impacted by the cesium load. The proton exchange with cesium increased the pore volume remarkably ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$, 1.7 and $37.3 \text{ m}^3 \cdot \text{g}^{-1} \times 10^{-3}$). Nonetheless, similarly to the verified measurement of the surface area, a higher cesium load reduced the pore volume.

3.2. Catalytic Runs

3.2.1. The Effect of Catalyst Nature

The reaction conditions were defined according to the literature and were used for screening the most effective catalyst [46]. The kinetic curves are shown in Figure 2. Although acetone excess was found (1:30 glycerol–acetone molar ratio), only a poor conversion was achieved in the absence of a catalyst at room temperature after a 2 h reaction. Conversely, when the reactions were carried out in the presence of cesium phosphomolybdate or its derived vanadium-substituted salts, higher conversions were achieved. Among them, the $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ -catalyzed reaction was that with the greatest conversion result.

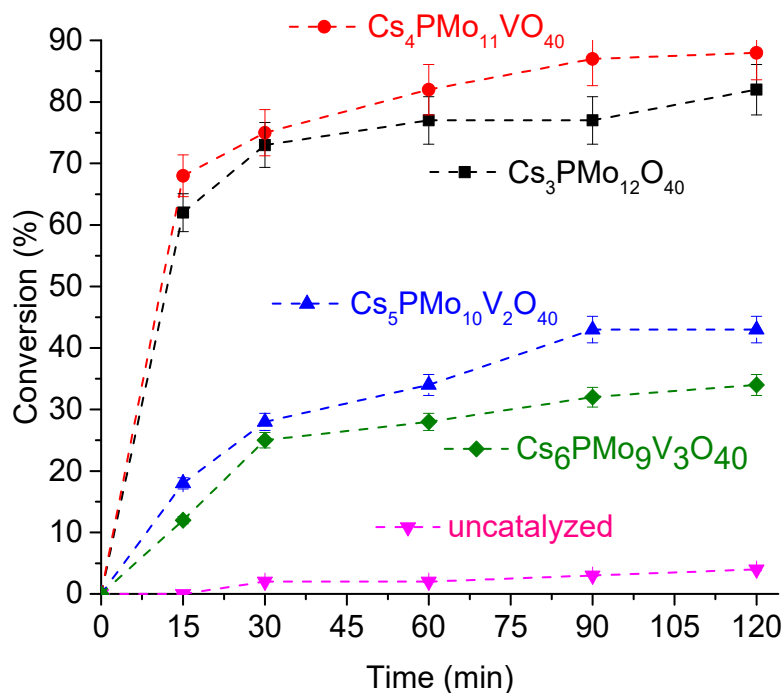
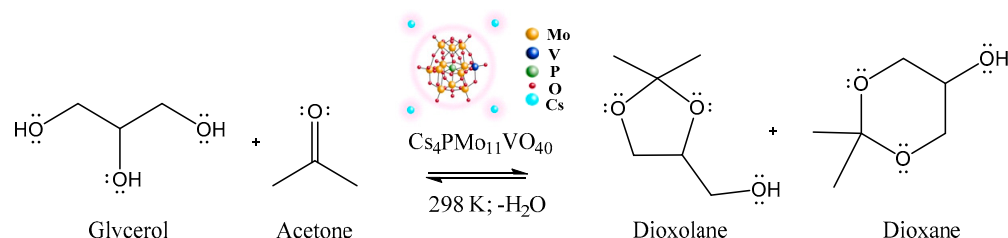


Figure 2. Effects of each kind of cesium catalyst on the kinetic curves of glycerol condensation with acetone ^a. ^a Reaction conditions: glycerol (6.0 mmol), acetone (180.0 mmol), temperature (298 K), catalyst (0.030 mol %), volume (10 mL).

The superior performance of the $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ catalyst can be correlated to its highest strength of acidity, the data of which are presented in Table 1. If a greater vanadium load is used, both acidity strength and acid site number become lower (Table 1). These results agree with the literature [10]. Curiously, if a 1:11 V:Mo molar ratio is used, the charge on the terminal oxygen is increased, making the new proton more acidic, since the exchanges of Mo^{6+} with V^{5+} in a Keggin anion weakens the P-Oa bond and its interaction with the $\text{di-H}_5\text{O}_2^+$ cations, consequently increasing the strength of the acidity. Conversely, if a greater proportion is used, the total negative charge of the Keggin anions also increases, consequently reinforcing their interaction with the new protons, which become less acidic [45,46].

In all of the reactions, dioxolane was always the main product. Even though the thermodynamic stability of five-membered ring compounds is lower than that of six-membered ring ones, when the acetalization of glycerol is performed with an excess of acetone the main product generally formed has a five-membered ring (Scheme 1). The same result was observed by Yu et al. [47].



Scheme 1. Main products of $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ -catalyzed glycerol acetalization with acetone.

Figure 3 displays the conversion and selectivity reached after 2 h of reaction. Only the most active catalysts (i.e., $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40} > \text{H}_3\text{PMo}_{12}\text{O}_{40} > \text{Cs}_3\text{PMo}_{12}\text{O}_{40}$) converted the glycerol to the solketal isomers (i.e., dioxolane and dioxane). Cesium phosphomolybdate salts containing two or three vanadium atoms failed in this reaction and in these cases, only glycerol oligomers were formed, as demonstrated by the mass balance of the process. When solketal isomers were formed, the selectivity toward the dioxolane isomer (i.e., with a five-membered ring) was significantly higher. The higher selectivity toward solketal (i.e., with a five-membered ring) can be confirmed by checking the selectivity of the reactions described herein, and in the presence of other heteropolyacid catalysts [27]. A plausible explanation is depicted in Scheme 2 in Section 3.2.2.

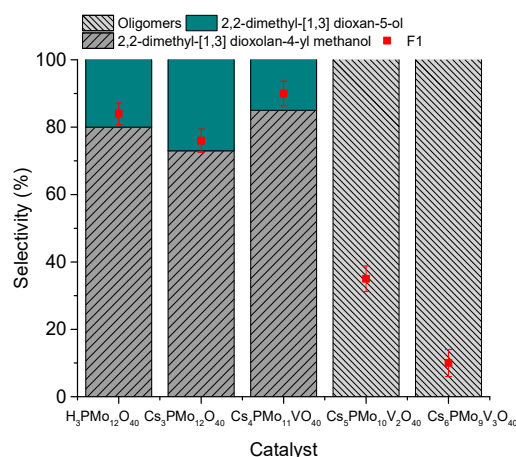


Figure 3. Conversions and selectivity of glycerol acetone condensation reactions reached after 2 h in the presence of phosphomolybdic acid or its cesium salts ^a. ^a Reaction conditions: glycerol (6.0 mmol), acetone (180.0 mmol), temperature (298 K), catalyst (0.030 mol %), volume (10 mL).

The condensation of glycerol with acetone is a reaction commonly performed using Brønsted acids in a homogeneous phase [47]. Nonetheless, there are different solid catalysts used in this reaction [14]. Table 3 summarizes the main results.

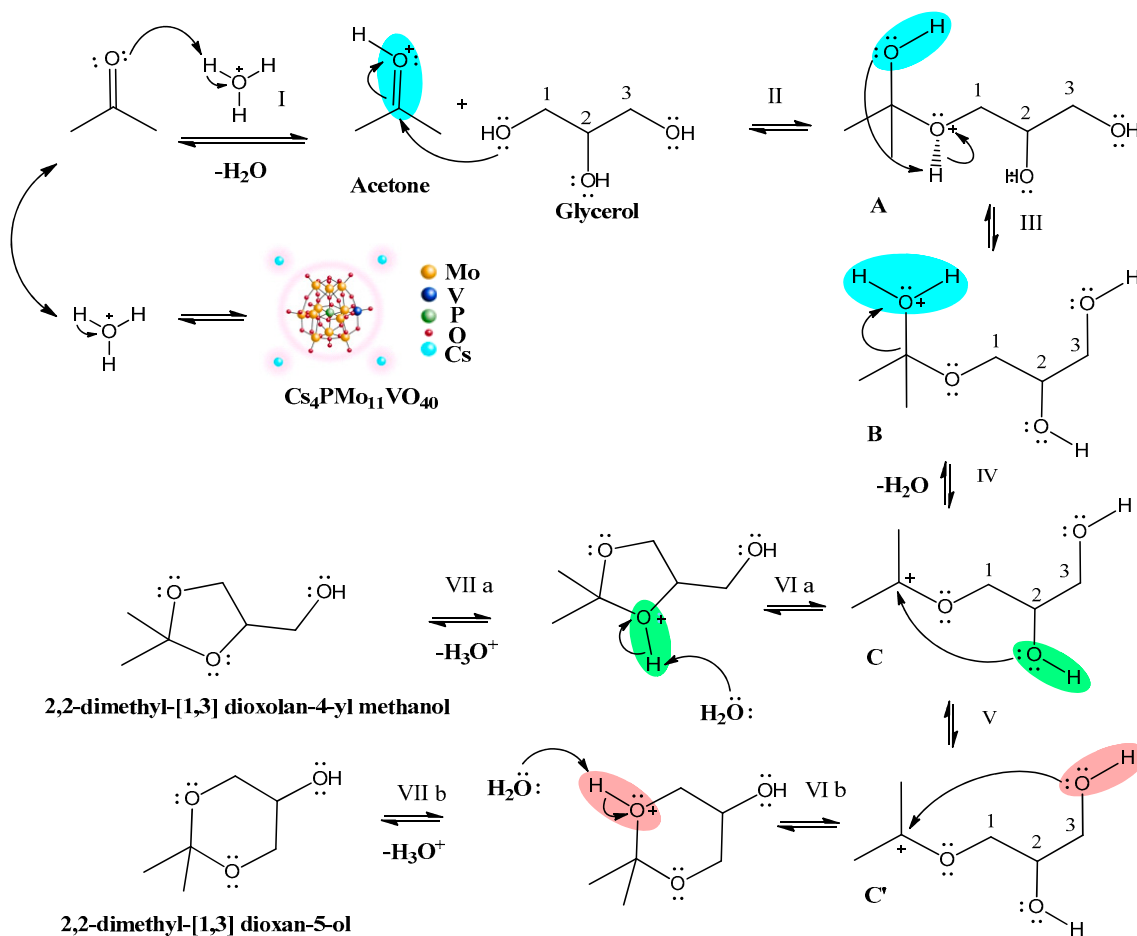
Table 3. Comparison of heterogeneous catalysts for the conversion of glycerol to solketal.

Catalyst	Load (wt. %)	Temperature (K)	Conv.	TON	Ref.
Amberlyst-36	5	313	88	33	[48]
Zeolite beta	13	343	60	22	[49]
Zeolite USY	19	343	90	33	[49]
H ₃ PW ₁₂ O ₄₀ /SiO ₂	5	343	100	121	[50]
Cs ₄ PMo ₁₁ VO ₄₀	0.36	298	90	180	This work

The cesium monovanadate phosphomolybdate catalyst achieved the highest TON (mol of glycerol converted/mol catalyst) among the different solid catalysts (Table 3). Moreover, the reaction was carried out at the lowest temperature. These are positive aspects of this catalyst.

3.2.2. Mechanistic Insights

Typically, the first step in condensation reactions of alcohols with ketones or aldehydes in an acidic medium is the activation of the carbonyl group through the protonation (step I, Scheme 2). Although the protons of HPA have been exchanged with cesium, these metal cations react with hydration water molecules, generating hydronium cations that act as catalysts in glycerol condensation with acetone.



Scheme 2. Reaction pathway of $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ -catalyzed glycerol acetalization with acetone.

The protonation of the carbonyl group makes its carbon more susceptible to the nucleophilic attack of the terminal hydroxyl group of glycerol, generating the A intermediate (step II, Scheme 2). After the prototropism step (step III), the B intermediate releases a water molecule, generating a C tertiary carbocation (step IV). This intermediate can undergo a nucleophilic attack of a secondary hydroxyl group of glycerol (step V), which after the water loss results in the dioxolane (five-membered ring) or of the secondary hydroxyl group of glycerol, which after the water elimination will generate the dioxane isomer (six-membered). These are the key steps (VIa or VIb steps) that govern the reaction selectivity. Since the secondary hydroxyl group is nearest to the positive carbon of carbocation if compared to the tertiary hydroxyl group, it is more stereochemically favorable and, therefore, the dioxolane (five-membered ring) is always predominant in the glycerol condensation of acetone.

3.2.3. The Effect of the Stoichiometry of Reactants

Glycerol acetone condensation is a reversible reaction, and therefore it is sensitive to the reactant concentration variations. An increase in the acetone amount shifted the reaction equilibrium toward products, in addition to enhancing the reaction rate (Figure 4).

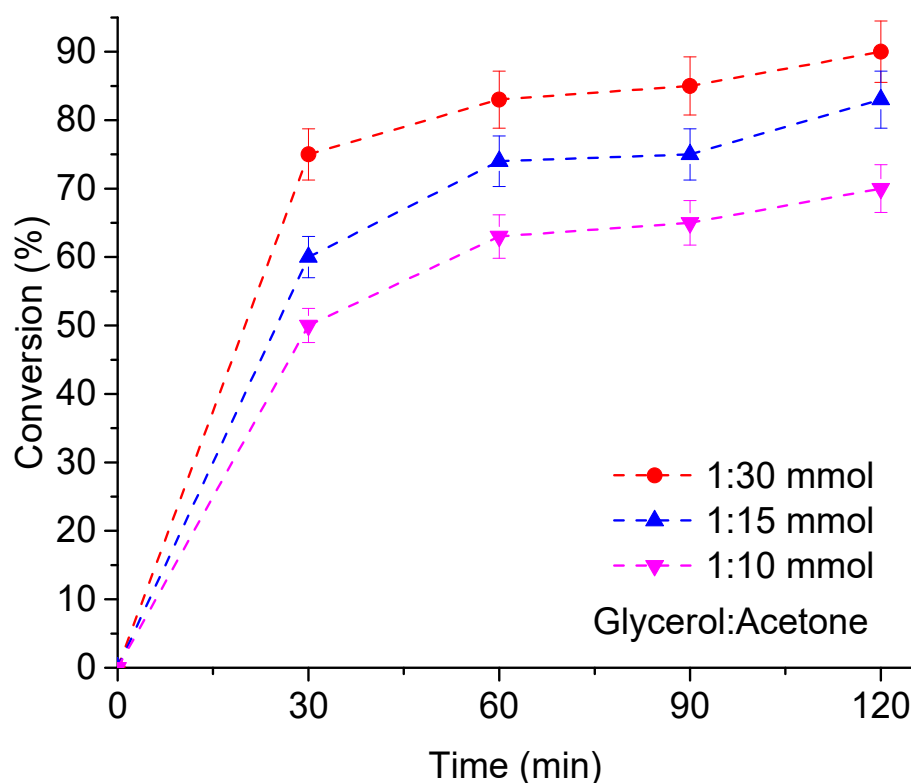


Figure 4. Effect of glycerol–acetone ratio on the kinetic curves of condensation reactions with acetone catalyzed by $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ ^a. ^a Reaction conditions: glycerol (6.0; 12.0; 18.0 mmol), acetone (180.0 mmol), temperature (298 K), catalyst (0.030 mol %), volume (10 mL).

Another effect observed was that the glycerol solubility was diminished when acetone was present in lower amounts. A biphasic system was formed at 1:5 molar proportions. It was favorable to the formation of polyglycerols, namely oligomers. For this reason, it is absent in Figure 5. Therefore, the reaction selectivity was impacted by the variation in reactant stoichiometry. It was verified that the higher the acetone excess, the lower the oligomer formation. Conversely, the solketal selectivity was progressively favored when the molar ratio of acetone to glycerol was increased. The same occurred with the reaction conversions.

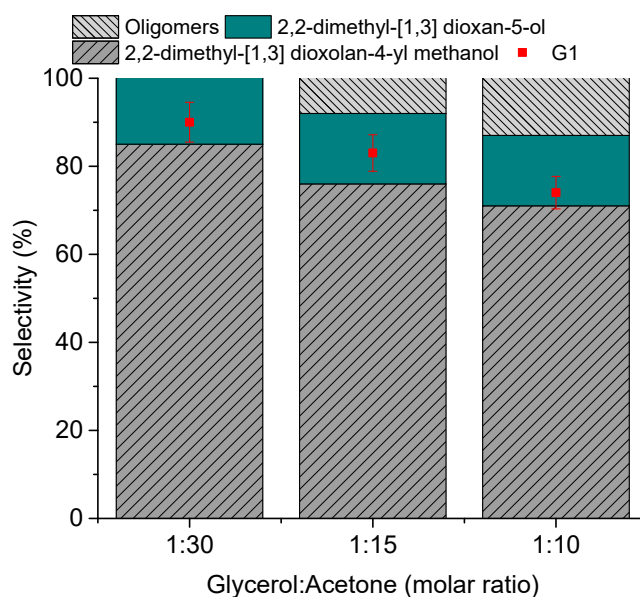


Figure 5. Effects of glycerol–acetone proportion on the conversion and selectivity of $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ -catalyzed glycerol acetone condensation after 2 h reaction ^a. ^a Reaction conditions: glycerol (6.0 mmol), acetone (variable), temperature (298 K), catalyst (0.030 mol %), volume (10 mL).

3.2.4. The Effect of Catalyst Load

The impacts of catalyst load variation on the conversion and selectivity of glycerol condensation with acetone were studied at 298 K and 1:30 molar ratio (Figure 6).

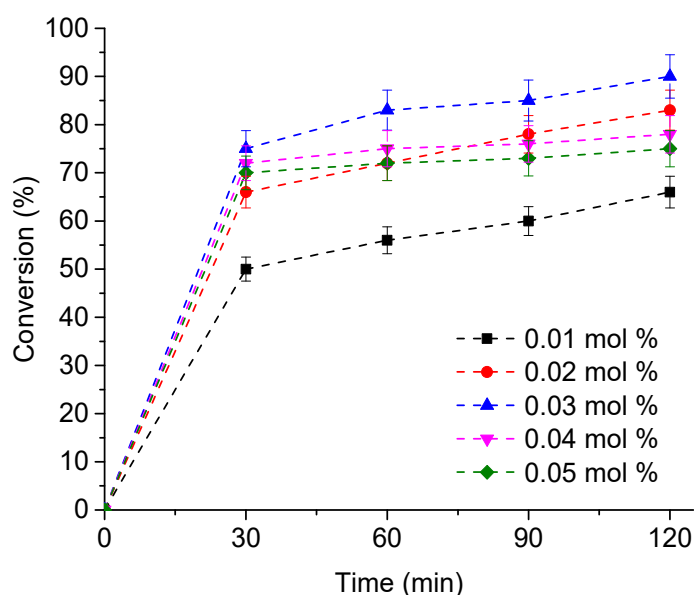


Figure 6. Effect of catalyst load on the kinetic curves of $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ -catalyzed glycerol acetone condensation reactions ^a. ^a Reaction conditions: glycerol (6.0 mmol), acetone (180 mmol), catalyst load (variable), temperature (298 K), volume (10 mL).

An increase in catalyst load had a beneficial effect until 0.03 mol %; amounts greater diminished progressively in both initial rate and conversion. This was a consequence of the lower accessibility of reactant molecules to the active sites of the catalyst triggered by the higher presence of solids in the system.

A similar effect was verified in terms of selectivity (Figure 7); until 0.03 mol %, they progressively increased with an increase in load, and afterwards, with higher loads, both selectivity and conversion were lower.

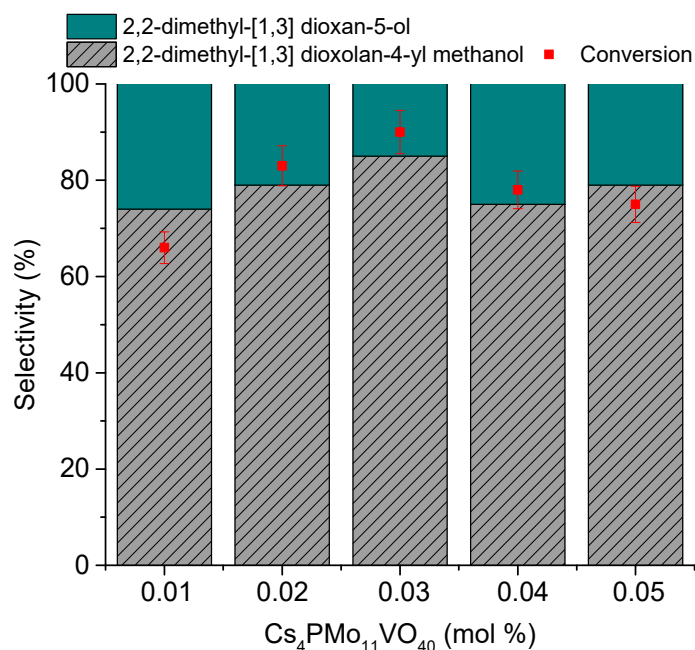


Figure 7. Effect of catalyst load on the conversion and selectivity of Cs₄PMo₁₁VO₄₀-catalyzed glycerol acetone condensation after 2 h reaction ^a. ^a Reaction conditions: glycerol (6.0 mmol), acetone (180 mmol), catalyst load (variable), temperature (298 K), volume (10 mL).

3.2.5. The Effects of Temperature

The effects of temperature were evaluated in the range of 298 to 323 K and the kinetic curves are shown in Figure 8. Initially, the reactions were carried out at each temperature without a catalyst. Despite the acetone excess, it was verified that only a poor conversion was achieved. Indeed, the highest conversion (15%) in the absence of a catalyst was achieved at the highest temperature (323 K). It was omitted by simplification.

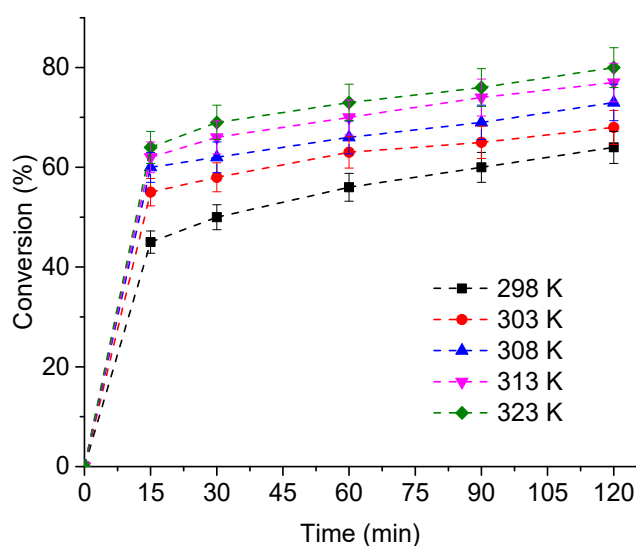


Figure 8. Effects of temperature on the kinetic curves of Cs₄PMo₁₁VO₄₀-catalyzed glycerol acetone condensation reactions ^a. ^a Reaction conditions: glycerol (6.0 mmol), acetone (180 mmol), temperature (variable), catalyst load (0.010 mol %), volume (10 mL).

Conversely, in the presence of a catalyst, the temperature effect was more visible. The initial rates were increased and the higher temperatures accelerated the reactions,

probably due to the higher number of effective collisions. The progressive increase in conversions occurred when the reactions were carried out at higher temperatures, suggesting an endothermic character (Figure 9).

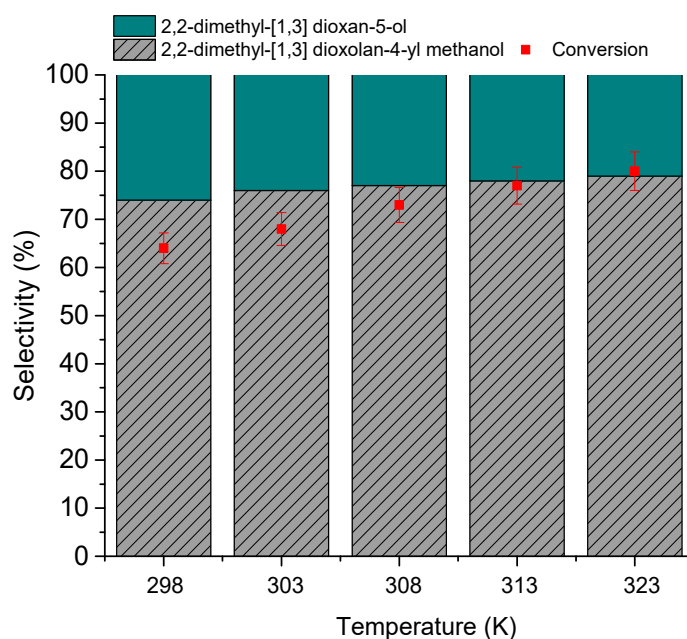


Figure 9. Impacts of temperature on the conversion and selectivity of $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ -catalyzed glycerol acetone condensation after 2 h reaction ^a. ^a Reaction conditions: glycerol (6.0 mmol), acetone (180 mmol), temperature (variable), catalyst (0.010 mol %), volume (10 mL).

Regardless of temperature, the reaction selectivity remained almost the same, with dioxolane as the major product.

3.2.6. Recovery and Reuse of the $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ Catalyst

The recovery and reuse of the $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ catalyst were assessed. The main results are shown in Table 4.

Table 4. Recovery and reuse of the $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ catalyst in condensation reactions of glycerol with acetone ^a.

Run	Conversion	Selectivity % Dioxane/Dioxolane	Recovery %
1	89	12/88	97
2	88	10/90	98
3	85	11/89	97
4	86	10/90	97

^a Reaction conditions: glycerol (6.0 mmol), acetone (180 mmol), catalyst load (0.03 mol %), temperature (298 K), time (2 h), volume (10 mL).

Initially, we investigated various solvents to select the most efficient to wash the catalyst, once the remaining glycerol had shown a strong interaction with the catalyst. Ethyl acetate was demonstrated to be the most effective solvent. Afterwards, the recovery and reuse of the catalyst were evaluated. The catalyst was easily separated through centrifugation. The catalyst was efficiently recovered, weighted, and reused without a loss of activity (Table 3). Moreover, the selectivity of solketal remained constant.

4. Conclusions

The activity of pristine heteropolyacid (i.e., $\text{H}_3\text{PMo}_{12}\text{O}_{40}$) and its vanadium-substituted cesium salts ($\text{Cs}_{3+n}\text{PMo}_{12-n}\text{V}_n\text{O}_{40}$; $n = 0\text{--}3$) was evaluated in glycerol condensation reactions with acetone. Among the catalysts tested, the $\text{Cs}_4\text{PMo}_{11}\text{VO}_{40}$ salt was the most active and selective towards the solketal. This superior activity was assigned to the highest strength of acidity when monosubstituted with vanadium, as well as the n-butylamine potentiometric titration analyses. The replacement of one molybdenum atom with vanadium increases the strength of acidity of cesium phosphomolybdate. However, if more molybdenum atoms are substituted, the heteropolyanion gains an increased negative charge; consequently, the strength of its acidity is reduced and it becomes a less efficient catalyst. Regardless of the reaction conditions or kind of catalyst, the five-membered ring isomer was always the major product, which could be attributed to the steric effects, as depicted in Scheme 2. Dioxolane was always the main product, probably due to the increased ease of attack of the secondary hydroxyl group of glycerol on the carbonylic carbon of an intermediate protonated and formed during the reaction. The impacts of the main reaction parameters were assessed. Most studies were carried out at room temperature, and it was verified that using 0.030 mol % of catalyst and 1:30 glycerol acetone molar ratio, conversion (90%) and selectivity above 90% towards dioxolane isomer were achieved. The reusability of the catalyst was evaluated. It was easily reversed and reused without loss of activity. This solid catalyst is an attractive option to the corrosive mineral acids normally used as catalysts in these reactions.

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