Accepted Manuscript

Accepted date:

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15-2-2015

PII:S1381-1169(15)00072-2DOI:http://dx.doi.org/doi:10.1016/j.molcata.2015.02.015Reference:MOLCAA 9431To appear in:Journal of Molecular Catalysis A: ChemicalReceived date:3-10-2014Revised date:23-1-2015

Please cite this article as: Swetha Sandesh, A.B.Halgeri, Ganapati V.Shanbhag, Utilization of renewable resources: Condensation of glycerol with acetone at room temperature catalyzed by organic-inorganic hybrid catalyst, Journal of Molecular Catalysis A: Chemical http://dx.doi.org/10.1016/j.molcata.2015.02.015

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Utilization of renewable resources: Condensation of glycerol with acetone at room temperature catalyzed by organic-inorganic hybrid catalyst

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Graphical abstract

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Highlights

- $(C_3H_7)_4N^+/PWA$ is reported for the first time as an efficient solid acid catalyst.
- Condensation of glycerol with acetone reaction was performed at room temperature.
- High activity of $(C_3H_7)_4N^+/PWA$ explained by its acidity and pseudo liquid behaviour.
- The catalyst performed better compared to other conventional solid acid catalysts.
- Catalyst was truly heterogeneous with good reusability for 3 catalyst recycles.

Abstract

Organic-inorganic hybrid catalyst prepared from organic ammonium salt and heteropoly acid is reported as highly active and selective heterogeneous catalyst for the condensation reaction of glycerol with acetone at room temperature. The product formed during the reaction, solketal is a highly potential compound applied majorly in petroleum and pharmaceutical industries. The $(C_3H_7)_4N^+/PWA$ catalyst performed better than other conventional solid acid catalysts like H-beta, amberlyst-15, montmorillonite K-10 and cesium salt of phosphotungstic acid with 94 % glycerol conversion and 98 % selectivity for solketal. The high activity of $(C_3H_7)_4N^+/PWA$ catalyst can be explained by its acidity and pseudo liquid behaviour. An independent study on the influence of water on catalyst deactivation was performed by adding a small amount of water (glycerol: water (1:1)) during the reaction. The $(C_3H_7)_4N^+/PWA$ catalyst showed a remarkable resistance towards deactivation due to water with only a marginal decrease in conversion (~3 %) compared to other conventional solid acid catalysts like amberlyst-15, Hbeta and montmorillonite K-10. $(C_3H_7)_4N^+/PWA$ catalyst was truly heterogeneous and showed good reusability for 3 catalyst recycles.

Keywords: Glycerol ; Solketal ; Condensation ; Heteropoly salt ; Acid catalyst

1. Introduction

Glycerol has recently gained importance as an inexpensive and abundant raw material for the synthesis of variety of value-added chemicals. There are several routes for the transformation of glycerol such as transesterification, etherification, acetylation, oxidation, condensation, hydrogenolysis and dehydration [1-7]. One such economically viable reaction is the condensation of glycerol with acetone to give 5 membered ring compound, solketal (2, 2-dimethyl-4- hydroxymethyl-1, 3-dioxolane) (ESI: Scheme S1).

Solketal is a colourless and odourless liquid, completely soluble in water and stable under normal temperature and pressures. Due to its low toxicity, it has been widely used as a solvent for maintaining single phase mixture of gasoline and ethanol [8], for cleaning metallic, electrical and plastic substrates [9] and pharmaceutical injections as water miscible solvent [10-11]. It is also used in cosmetics industry as an additive in ointments [12] in the chemical industry as an additive in low temperature transfer fluids [13] and as a fuel additive [14].

Conventionally condensation of glycerol with acetone was carried out using homogeneous acid catalyst (sulphuric acid or *p*-toulenesulphonic acid [15]. To overcome the environmental problems, many solid acid catalysts like arenesulfonic acid-functionalized mesostructured silica (Ar-SBA-15) [16], Nb₂O₅ [5], SO_4^{2-}/ZrO_2 [17], activated carbon [18], Si induced heteropoly acid [19], Hf-TUD-1 [20] and zeolites [21] have been reported for condensation reaction of glycerol and acetone. However, all these catalysts have been reported to work at reaction temperature ~70 °C. Recently, H-beta has been studied as a catalyst for acetalization of glycerol at room temperature, in which, effect of crystallite size and acidity has been investigated in detail by our group [22]. In this study, quaternary ammonium salt of heteropoly acid is reported for the first time as heterogeneous acid catalyst for glycerol transformation. Since heteropoly acids (HPA) are soluble in polar compounds they can be heterogenised by ion exchange with Cs, Rb and Sm [23, 24]. Alkyl ammonium chloride and nitrate salts were used as homogeneous acid catalysts for aldol condensation and alkylation reactions [25, 26] whereas

alkylammonium exchanged silicotungstate salt was found to act as heterogeneous catalyst for epoxidation reactions [27]. Furthermore, sulfonated organic ammonium salt of phosphotungstic acid was also reported as heterogeneous catalyst in polar medium [28].

There has been an increasing interest in recent years to develop novel solid catalysts and modify them for selective synthesis of value added chemicals. In the present communication, we report tetrapropylammonium salt of phosphotungstic acid $[(CH_3CH_2CH_2)_4N)_3PW_{12}O_{40}]$ as an efficient heterogeneous catalyst for the condensation reaction of glycerol with acetone under room temperature (30 °C). Here, heteropolytungstate is preferred as a precursor for this catalyst over heteropolymolybdate because of their stronger acidity, higher thermal stability and lower oxidation [21].

2. Experimental Section

2.1. Materials

Glycerol, acetone and ammonium carbonate were purchased from Merck India Ltd. Phosphotungstic acid (PWA), silicotungstic acid (SWA), phosphomolybdic acid (PMoA), tetraethyl ammonium bromide ((C_2H_5)_4N⁺Br⁻), tetrapropyl ammonium bromide and ((C_3H_7)_4N⁺Br⁻) and cetyltrimethyl ammonium bromide (($C_{16}H_{33}$)(CH₃)_3N⁺Br⁻) were purchased from SD fine chemicals. Amberlyst-15 (AB-15) was obtained from Alfa Aesar, USA. The montmorillonite K-10 clay (hereafter K-10 clay) was purchased from Sigma Aldrich, USA. H-beta (SAR-25) was kindly donated by Süd-Chemie India Pvt Ltd. All the chemicals were of research grade and used without any further purification.

2.2. Catalyst preparation

The organic-inorganic hybrid catalysts were prepared by adding drop wise, the required amount of aq. 1 M solution of, $(C_3H_7)_4N^+Br$ to aqueous solution of HPA hydrates (PWA, SWA, PMoA) (0.02 M) at room temperature with stirring. The obtained slurry containing precipitate was stirred for 2 h, filtered, washed with water and dried in an oven at 120 °C for 4 h and activated at 150 °C before use. The catalysts were designated as $(C_3H_7)_4N^+/PWA$, $(C_3H_7)_4N^+/SWA$, $(C_3H_7)_4N^+/PMoA$ for respective HPAs. Different organic salts on PWA were prepared by following the same procedure as mentioned above by varying the organic salt and are designated as $C_8H_{20}N^+/PWA$ and $C_{19}H_{42}N^+/PWA$. Cs/PWA and NH₄/PWA catalysts were prepared by literature methods [29-30] and other solid acid catalysts were activated at 150 °C prior to the reaction.

2.3. Catalyst Characterization

FT-IR (Alpha-T, Bruker) spectra were obtained in the range of 4000 to 600 cm⁻¹ to study the chemical property of the catalyst. The KBr pellets of samples prepared were directly used for the FT-IR analysis. PXRD and SEM data are represented in ESI (Fig. S1 and S2 respectively). Thermogravimetric analysis (TGA) was carried out under inert atmosphere, with a heating rate of 10 °C min⁻¹ in the range 35–800 °C.

The C H N analysis was performed to evaluate the extent of exchange of tetrapropylammonium ions with H^+ of HPAs.

Acidity of all catalysts were measured by potentiometric titration [31]. About 5 mg of the catalyst was suspended in 5 ml of n-butylamine solution (0.05 N) in acetonitrile and sonicated for 5 min to attain uniform dispersion. Then the above solution was suspended in excess of acetic acid (90 mL) and potentiometrically titrated against perchloric acid (0.1 N) in acetic acid. Prior to sample titration, a blank titration of acetic acid and n-butyl amine against perchloric acid was carried out to check the acidity contribution from the solutions used.

2.4 Catalytic activity

The condensation reaction of glycerol with acetone was carried out in 100 ml two-necked glass reactor equipped with a magnetic stirring bar, a Liebig condenser, and a thermometer. The required amount of glycerol and acetone were taken in the reactor and stirred at 1800 rpm for 15 min before the addition of pre-activated catalyst. The reaction was performed at 30 °C for 2 h and then the mixture was taken out and centrifuged for 10 min to separate the catalyst from the liquid phase. The obtained product was analyzed by gas chromatography (Shimadzu, GC-2014) with flame ionization detector (FID) equipped with capillary column(0.25mm I.D and 30 m length, Stabilwax, Restek). All the products were confirmed by gas chromatography with mass spectroscopy (Shimadzu, GCMS QP 2010).

An independent experiment was conducted to understand the effect of water on the catalytic activity during the reaction. For this, the reaction was conducted in the absence of water for 15 min. Then, 1 mole of water was added to the reaction mixture (glycerol: water = 1:1) and monitored the effect of water on the catalytic activity.

Leaching test was carried out for condensation reaction to investigate the heterogeneity of the catalyst. The reaction was carried out using 0.5 wt% of $(C_3H_7)_4N^+$ /PWA catalyst at reaction temperature of 30 °C with glycerol to acetone mole ratio of 1:6. Reaction was stopped after 30min and reaction mixture containing the catalyst was filtered. The reaction was continued without the catalyst for next 5 h and sample was drawn on every one hour interval and analysed.

3. Results and Discussion

Organic-inorganic hybrid catalysts were characterized by FTIR, TGA and C H N elemental analysis studies. FT-IR (Alpha-T, Bruker) spectra were obtained in the range of 4000 to 600 cm⁻¹ to study the chemical property of the catalyst. The KBr pellets of samples prepared were directly used for the FT-IR analysis. IR spectra of PWA (H₃PW₁₂O₄₀), (C₃H₇)₄N⁺/PWA and (C₃H₇)₄N⁺Br are shown in Fig. 1 (a). Four bands at 700-1100 cm⁻¹ region corresponding to Keggin unit (HPW) structural vibrations are observed for PWA and (C₃H₇)₄N⁺/PWA suggesting that the framework of primary Keggin structure remained unaltered after modification of PWA with ammonium salt. The peaks corresponding to Keggin anion vibration are as follows. The stretching frequency of P-O in the central PO₄ tetrahedron is at 1081 cm⁻¹. The peak at 987 cm⁻¹ is due to the terminal W=O vibration in the WO₆ octahedron and the peak at 897 and 815 cm⁻¹ were assigned to W-O_b-W and W-O_c-W bridges respectively. Weaker peaks appearing at 605 and 518 cm⁻¹ due to bending vibrations of the type O-P-O and W-O-W bonds respectively [32]. In addition to Keggin unit, (C₃H₇)₄N⁺/PWA exhibits other 3 characteristic peaks corresponding to tetrapropylammonium ion at 1467, 1400 cm⁻¹ (C-H stretching) and 1180 cm⁻¹ (C-H bending). The peak at 1063 cm⁻¹ is attributed to C-N stretching vibration [33].

Thermo gravimetric analysis (TGA) was carried out under inert atmosphere, with a heating rate of 10 °C min⁻¹ in the range 35–800 °C. Thermogravimmetric analysis of $(C_3H_7)_4N^+$ /PWA catalyst showed a marginal weight loss (~ 1 %) upto 120 °C due to the removal of water of hydration. Further, there was no weight loss upto 400 °C which indicates that the catalyst is thermally stable upto that temperature. Above 400 °C, there was a rapid decrease of weight by 15 % upto 450 °C which can be attributed to the loss of organic moiety (Fig. 1 (b)). The weight loss of 2.2 % from 550 to 600 °C is due to the decomposition of Keggin heteropoly anion into WO₃ and P₂O₅ [20].

C H N elemental analysis showed the extent of exchange of tetrapropyl ammonium ions with protons of HPA. It is found that protons are exchanged completely with alkyl ammonium ions in the heteropoly salts as presented in Table 1. These alkyl ammonium salts of HPA showed the acidity in the range of 0.5-0.7 mmol/ g measured by potentiometric titration which could be attributed to the presence of protons in the catalyst. The reason for generation of protons in neutral salts of HPA is still not understood completely [34]. The solid tetraalkyl ammonium salts of HPA compounds possess discrete ionic structures, comprising fairily mobile structural units; heteropoly anion and the counter cation. Completely substituted heteropoly salts gain protons upon interaction with reaction medium either by dissociation of coordinated water/ polar protic reactants (such as glycerol in this study) or by reduction of metal cations [35-38]. The structure is preserved even upon complete substitution of tetraalkyl ammonium ions and manifests itself to exhibit extremely high proton mobility and a pseudoliquid phase.

3.1. Catalytic activity study

Condensation of glycerol with acetone was carried out over organic-inorganic hybrid catalysts and compared with different types of solid acid catalysts namely, H-beta zeolite, montmorillonite K-10 (K-10 clay), amberlyst-15 (AB-15) and cesium salt of PWA (Cs/PWA) as shown in Fig. 2. A blank reaction in the absence of catalyst showed only trace conversion of glycerol.

Although glycerol conversion varied with different heterogeneous acid catalysts, selectivity towards 5-membered ring compound, solketal was invariably high for all the catalysts. Solid acid catalysts *viz.* H-beta, AB-15 and K-10 clay showed high glycerol conversion of 89, 87 and 82 % respectively for initial one hour and then remained almost constant. These highly acidic catalysts, although showed high initial activity, might be deactivated due to the blockage of active sites by water molecules formed during the reaction. Cs⁺ exchanged PWA catalyst with high acidity 1.88 showed low glycerol conversion of around 40 % with 85 % solketal selectivity. Compared to all the above acid catalysts (C₃H₇)₄N⁺/PWA catalyst with acidity of 0.6 mmol/g gave high glycerol conversion of 94 % with almost 98 % solketal selectivity in 120 min of reaction. Both (C₃H₇)₄N⁺/PWA and (C₂H₅)₄N⁺/PWA catalysts showed the highest turnover number of 120 followed by other organicinorganic hybrid catalysts made of SWA and PMoA (117 and 106 respectively) (Table 2). It is observed that solketal selectivity increases as the reaction time increases for all the reactions. The other product formed is a 6-membered cyclic acetal, 5-hydroxy-1, 3-dioxane as shown in ESI: Scheme S1. Initially, side product acetal formation was high, probably because the catalytic sites are fresh and more active in the initial phase of the reaction.

In $(C_3H_7)_4N^+/PWA$ catalyst, along with acidity (0.6 mmol/g) the combination of rigid molecule, PWA and the flexible alkyl ammonium ion contributes to the high glycerol conversion. In this study, both reactants (glycerol and acetone) are polar and the reactant molecules can penetrate into the secondary structure of heteropoly anions to come in contact easily with active sites of $(C_3H_7)_4N^+/PWA$ catalyst. Wang and co-workers observed that for esterification reaction, the synthesized alkyl quaternary ammonium salt of PWA exhibits bulk type I catalysis [28]. In bulk type I catalysis of HPA and its salts, e.g. acid-catalyzed reactions of polar molecules at relatively lower temperatures, the reactant molecules are absorbed in the inter polyanion space of ionic crystal, undergo reaction and then products desorb from the solid bulk. Polar molecules like glycerol absorb into the solid bulk and expand the distance between the poly anions. This type of catalysis is known as pseudo liquid catalysis in presence of polar reactants [38-42].

The condensation of glycerol with acetone was carried out with different tetrapropylammonium exchanged heteropoly acids namely, $(C_3H_7)_4N^+/PWA$, $(C_3H_7)_4N^+/SWA$, $(C_3H_7)_4N^+/PMoA$ and the results are represented in Fig. 3. Among these catalysts, $(C_3H_7)_4N^+/PWA$ showed highest glycerol

conversion of 94 % with 98 % selectivity to solketal in 120 min reaction time, whereas $(C_3H_7)_4N^+/SWA$ and $(C_3H_7)_4N^+/PMoA$ showed marginally lower conversion (89.8 and 86.8 % respectively) with the selectivity same as that of $(C_3H_7)_4N^+/PWA$. The similarity in performance of these catalysts which differ in the type of heteropoly anion shows that these catalysts contain similar active sites. Different organic ammonium salts like $(C_2H_5)_4N^+, (C_3H_7)_4N^+$ and $(C_{16}H_{33})(CH_3)_3N^+$ were exchanged with protons of PWA and applied as catalysts for solketal synthesis. While $(C_2H_5)_4N^+/PWA$ and $(C_3H_7)_4N^{+'}PWA$ catalysts acted as purely heterogeneous catalysts with glycerol conversion of 83.4 and 94 % respectively, $(C_{16}H_{33})(CH_3)_3N^+/PWA$ with a long alkyl chain of 16 carbon atoms acted as homogeneous catalyst with a low conversion of 77 %. The ammonium salt of PWA without alkyl groups (NH_4^+/PWA) was applied as a catalyst for this reaction and the activity was compared with $(C_3H_7)_4N^+/PWA$. The NH_4^+/PWA catalyst acted as heterogeneous catalyst but gave low glycerol conversion of 30 % with 73 % selectivity for solketal. Interestingly, PWA without ion exchange acted as homogeneous catalyst with glycerol conversion of 90 % within 10 min of reaction. Pure $(C_3H_7)_4N^+Br$ salt was also used as a homogeneous catalyst which showed negligible activity for this reaction.

It is known that certain catalysts deactivate due to water formed as a byproduct during the reaction. As it is difficult to confirm this effect for the batch reactions where conversions get stable at longer reaction period, independent experiments were conducted by adding small amount of water (glycerol: water = 1:1) after 15 min of reaction (Fig. 4). It is observed that K-10 and H-beta were highly affected due to the addition of water and glycerol conversion decreased remarkably by 30 and 35 % compared with neat reaction. AB-15 showed comparatively more resistance to the effect of water (about 15 % decrease in conversion). Among the 4 catalysts taken for this study, $(C_3H_7)_4N^+/PWA$ catalyst showed a remarkable resistance towards deactivation due to water with only a marginal decrease in conversion (~3 %). This study shows that byproduct water can block the active sites for certian catalysts and highly hydrophilic catalysts like H-beta and K-10 are more affected by deactivation of acidic sites due to water.

3.2. Influence of reaction conditions

The effect of catalyst weight percent and mole ratio of glycerol to acetone was studied for $(C_3H_7)_4N^+/PWA$ catalyst at room temperature and depicted in Fig. 5 (a). The glycerol conversion increased from 10 to 79.8 % in 15 min of reaction as the catalyst concentration increased from 0.3 to 3 wt % (with respect to total weight of the reactants). Further increase in the catalyst concentration from 3 to 7 wt% did not improve the glycerol conversion.

The effect of mole ratio of glycerol to acetone was studied at room temperature using $(C_3H_7)_4N^+/PWA$ catalyst. The mole ratio of glycerol to acetone was varied from 1:1 to 1:8 as shown in Fig. 5 (b). The

glycerol conversion increased with increase in mole ratio. The conversion was 57 % for 1:1 mole ratio after 15 min reaction and it increased to 79.5 % upon increasing mole ratio from 1: 1 to 1: 8 whereas selectivity towards products remained almost the same (98%) with different acetone concentrations.

Based on the above results, the optimized conditions using $(C_3H_7)_4N^+/PWA$ are 30 °C (room temperature), 3 wt % catalyst with respect to total reactant weight and glycerol to acetone mole ratio of 1 : 6.

Based on activity of the catalyst, a plausible mechanism is proposed. The acid sites in $(C_3H_7)_4N^+/PWA$ facilitate the reaction by activating the carbonyl group of acetone forming a carbocation. The hydroxyl group of glycerol then attacks the carbocation to form an intermediate which then undergoes cyclization with the removal of water to form solketal (Scheme 1).

Leaching test was carried out to confirm the heterogeneity of the catalyst [Fig. 6 (a)]. The catalyst was removed from the reaction mixture after 30 min (at 48 % conversion) and the reaction was continued without the catalyst for 5 h. The conversion remained the same at 48 % even after five hours of reaction time, indicating no leaching of active sites into the reaction media. It is further confirmed by measuring FT-IR spectra of the catalyst and product mixture. The band between 1200 to 500 cm⁻¹ corresponding to the Keggin structure of PWA was absent in the product mixture [Fig. 6 (b)].

Catalyst recyclability test was performed for $(C_3H_7)_4N^+/PWA$ by employing washed (with acetone) and dried (at 120 °C) catalyst under optimized reaction conditions. The catalyst showed good recyclability with marginal decrease in activity after 3 recycles (Fig. 7 (a)). XRD of fresh and 3rd spent catalyst showed no change in the phase purity of the catalyst (Fig. 7 (b)). Moreover, C, H, N analysis of recycled catalyst showed marginally higher percentage of C, H and N compared to fresh catalyst *viz*. C = 14.2 wt %, H = 3.1 wt % and N = 1.9 wt %. Higher percentage of C and H could be due to small amount of adsorbed organics remained even after regeneration. However, from % of nitrogen, it is confirmed that all the ammonium groups are fully preserved in the recycled catalyst (Table 1).

4. Conclusions

Organic- inorganic hybrid catalysts such as $(C_3H_7)_4N^+/PWA$ were synthesized and applied as highly active and selective heterogeneous catalysts for glycerol condensation reaction with acetone to give solketal. Among all the tetrapropylammonium ions exchanged HPA catalysts, $(C_3H_7)_4N^+/PWA$ gave high glycerol conversion of 94 % with 98 % solketal selectivity. The high activity of $(C_3H_7)_4N^+/PWA$ catalyst can be explained by its acidity and pseudo liquid behaviour. The catalyst showed better performance compared to other conventional solid acid catalysts. This organic-inorganic hybrid catalyst also exhibited a remarkable resistance towards deactivation due to water compared to other conventional solid acid catalysts like amberlyst-15, H-beta and montmorillonite K-10. Different Keggin heteropoly salts with same alkyl ammonium cation showed similar catalytic activity. $(C_3H_7)_4N^+/PWA$

catalyst was truly heterogeneous and showed good reusability for 3 catalyst recycles.

Acknowledgements

SS acknowledges CSIR, New Delhi for providing Senior Research Fellowship and also thankful to Manipal University for permitting this research as a part of the PhD programme.

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Fig. 1 a) FT-IR spectra of $(C_3H_7)_4N^+/PWA$, PWA and $(C_3H_7)_4N^+Br$ and b) TGA plot of $(C_3H_7)_4N^+/PWA$ catalyst.gr1

Fig. 2 Catalytic activity of different solid acid catalysts. Conditions: Temperature = $30 \degree$ C, Glycerol: acetone = 1:6, Catalyst weight = $3 \ \text{wt\%}$ of total reactant weight.gr2

Fig. 3 Catalytic activity of tetrapropylammonium exchanged HPAs. (Conditions as mentioned in Fig. 2).gr3

Fig. 4 The effect of addition of water during the reaction. Conditions: Temperature = 30 °C, Glycerol: acetone: water = 1:6:1, Catalyst weight = 3 wt% of total reactant weight, Water was added after 15 min of reaction time.gr4

Fig. 5 Effect of conditions on performance a) catalyst wt % (Conditions: Glycerol to acetone mole ratio = 1: 6, temperature = 30 °C) and b) Glycerol to acetone mole ratio (Conditions: Catalyst weight = 3 wt % of total reactant weight, Temperature = 30 °C).gr5

Fig. 6 a) Leaching test and b) Confirmation of heterogeneity from FT-IR.gr6

Fig. 7 a) Reusability of $(C_3H_7)_4N^+/PWA$ catalyst. Conditions: Temperature = 30 °C, Glycerol: acetone = 1:6, Catalyst weight = 3 wt% of total reactant weight and **b**) XRD patterns of $(C_3H_7)_4N^+/PWA$ fresh and 3rd recycled catalyst.gr7

Scheme 1 Plausible reaction mechanism for condensation reaction of glycerol with acetone.sc1

Table 1 Elemental analysis of organic-inorganic hybrid catalysts.

Catalysts	N (wt%)	C (wt%)	H (wt%)
$(C_3H_7)_4N^+/PWA$	1.4	12.5	2.4
$(C_3H_7)_4N^+/SWA$	1.8	15.6	3.0
(C ₃ H ₇) ₄ N ⁺ /PMoA	2.1	18.1	3.4
$(C_{16}H_{33})(CH_3)_3N^+/PWA$	1.3	18.4	3.4
$(C_3H_7)_4N^+/PWA$ 3rd recycle	1.9	14.2	3.1

Catalysts	Acidity (mmol/g)	Glycerol Conversion (mol %)	TON
$(C_3H_7)_4N^+/PWA$	0.60	94	120
AB-15	0.95	89	72
H-beta	1.5	88	23
K-10 clay	1.1	87	61
Cs/PWA	1.88	38	24
$(C_3H_7)_4N^+/SWA$	0.65	90	106
(C ₃ H ₇) ₄ N ⁺ /PMoA	0.57	87	117
$(C_2H_5)_4N^+/PWA$	0.53	83	120
(C ₁₆ H ₃₃)(CH ₃) ₃ N ⁺ /PWA*	0.56	77	106

Table 2 Potentiometric analysis of acidity and catalytic activity of all the catalysts.

Conditions: Temperature = $30 \,^{\circ}$ C, Glycerol: acetone = 1: 6, Catalyst = 3 wt % of total reactant weight, Time = $120 \,\text{min}$, TON = moles of glycerol converted per mole of acid sites. * Homogeneous phase

Table 3 Catalytic activities of NH₄⁺/PWA, organic salt of PWA and its precursors.

Catalyst	Phase	Glycerol conversion (mol %)	Solketal selectivity (mol %)	Solketal yield (mol %)
NH4 ⁺ /PWA	Hetero	30	73	22
$(C_2H_5)_4N^+/PWA$	Hetero	83	96	82
$(C_3H_7)_4N^+/PWA$	Hetero	94	98	93
$(C_{16}H_{33})(CH_3)_3N^+/PWA$	Homo	77	94	75
$(C_3H_7)_4N^+Br$	Homo	0.2	98	0.15
PWA	Homo	90*	98	88

Conditions: Glycerol: acetone = 1: 6, Temperature = $30 \degree C$, Catalyst = 3 wt % of total reactant weight, Time = $120 \min$, * Time = $10 \min$.