CHAPTER V

Synthesis of solketal from condensation of glycerol with acetone
5.1. 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) (Scheme 5.1.).

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 Ar-SBA-15 [16], Nb₂O₅ [5], SO₄²⁻/ZrO₂ [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, 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 \( [(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)\text{N}]_3\text{PW}_{12}\text{O}_{40} \) 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].

5.2. Chemicals and Reagents

Glycerol and acetone were purchased from Merck India Ltd. Phosphotungstic acid (PWA), silicotungstic acid (SWA), phosphomolybdic acid (PMoA), tetraethyl ammonium bromide ((C\(_2\)H\(_5\))\(_4\)N\(^+\)Br), tetrapropyl ammonium bromide and ((C\(_3\)H\(_7\))\(_4\)N\(^+\)Br) and cetyltrimethyl ammonium bromide ((C\(_{16}\)H\(_{33}\))(CH\(_3\))\(_3\)N\(^+\)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.

5.3. Catalyst preparation

The organic-inorganic hybrid catalysts were prepared by adding drop wise, the required amount of aq. 1 M solution of, (C\(_3\)H\(_7\))\(_4\)N\(^+\)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\(_3\)H\(_7\))\(_4\)N\(^+\)/PWA, (C\(_3\)H\(_7\))\(_4\)N\(^+\)/SWA, (C\(_3\)H\(_7\))\(_4\)N\(^+\)/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\(_8\)H\(_{20}\)N\(^+\)/PWA and C\(_{19}\)H\(_{42}\)N\(^+\)/PWA.
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Ammonium salt of heteropolyacid (NH₄⁺/PWA) was prepared by adding dropwise a required amount of ammonium carbonate (0.47 M) to aqueous phosphotungstic acid (0.75 M) at room temperature. The reaction mixture was aged for 20 h at room temperature, followed by evaporation in water bath. Then obtained precipitate was dried in oven at 120 °C and finally calcined at 150 °C for 3 h.

Preparation of cesium exchanged phosphotungstic acid (Cs/PWA) is given in Chapter II Section 2.2.3.2.

5.4. Characterization- Results and Discussion

5.4.1. Powder X-ray diffraction pattern (PXRD)

![PXRD patterns of organic-inorganic hybrid catalysts.](image)

The PXRD patterns of different organic salts [(C₃H₇)₄N⁺Br, C₈H₂₀N⁺Br and C₁₉H₄₂N⁺Br] exchanged phosphotungstic acid and tetrapropyl ammonium exchanged heteropoly acids (PWA, SWA, PMoA) are shown in Fig. 5.1. The patterns show that the alkylammonium salts of heteropoly acids were localized in the crystal lattice.
5.4.2. Fourier transform infrared spectroscopy patterns (FT-IR)

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 (H\(_2\)PW\(_{12}\)O\(_{40}\)), (C\(_3\)H\(_7\))\(_4\)N\(^+\)/PWA and (C\(_3\)H\(_7\))\(_4\)N\(^+\)Br are shown in Fig. 5.2. Four bands at 700-1100 cm\(^{-1}\) region corresponding to Keggin unit (HPW) structural vibrations are observed for PWA and (C\(_3\)H\(_7\))\(_4\)N\(^+\)/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 PO\(_4\) tetrahedron is at 1081 cm\(^{-1}\). The peak at 987 cm\(^{-1}\) is due to the terminal W=O vibration in the WO\(_6\) 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 [31]. In addition to Keggin unit, (C\(_3\)H\(_7\))\(_4\)N\(^+\)/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 [32].

![FT-IR spectra of (C\(_3\)H\(_7\))\(_4\)N\(^+\)/PWA, PWA and (C\(_3\)H\(_7\))\(_4\)N\(^+\)Br.](image-url)
5.4.3. Thermo gravimetric analysis (TGA)

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\(_3\)H\(_7\))\(_4\)N\(^+\)/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. 5.3). The weight loss of 2.2 % from 550 to 600 °C is due to the decomposition of Keggin heteropoly anion into WO\(_3\) and P\(_2\)O\(_5\) [20].

5.4.4. Carbon, Hydrogen and Nitrogen analysis (C, H, N)

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 5.1. 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 [33]. The solid tetraalkyl ammonium
salts of HPA compounds possess discrete ionic structures, comprising fairly 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.

Table 5.1. Elemental analysis of organic-inorganic hybrid catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>N (wt%)</th>
<th>C (wt%)</th>
<th>H (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C₃H₇)₄N⁺/PWA</td>
<td>1.4</td>
<td>12.5</td>
<td>2.4</td>
</tr>
<tr>
<td>(C₃H₇)₄N⁺/SWA</td>
<td>1.8</td>
<td>15.6</td>
<td>3.0</td>
</tr>
<tr>
<td>(C₃H₇)₄N⁺/PMoA</td>
<td>2.1</td>
<td>18.1</td>
<td>3.4</td>
</tr>
<tr>
<td>(C₁₆H₃₃)(CH₃)₃N⁺/PWA</td>
<td>1.3</td>
<td>18.4</td>
<td>3.4</td>
</tr>
<tr>
<td>(C₃H₇)₄N⁺/PWA 3rd recycle</td>
<td>1.9</td>
<td>14.2</td>
<td>3.1</td>
</tr>
</tbody>
</table>

5.4.5. Acidity measurement by potentiometric titration

Acidity of all catalysts were measured by potentiometric titration [30]. 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. Acidity of all the catalyst measured is given in Table 5.2.

5.4.6. Scanning Electron Microscopy (SEM) measurement

SEM measurement was performed to determine the morphology of the (C₃H₇)₄N⁺/PWA catalyst. It exhibited irregular spherical shaped particles with approximately 1 µm particle size as shown in Fig. 5.4.
5.5. Catalytic activity studies

5.5.1. Experimental Procedure

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 presence of water.
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.

5.6. Results and Discussion

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), cesium salt of PWA (Cs/PWA) as shown in Fig. 5.5. 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/PWA catalyst with acidity 1.88 mmol/g gave low glycerol conversion of around 40 % with 85 % selectivity to solketal. Compared to all the above acid catalysts \((\text{C}_3\text{H}_7)_4\text{N}^+\)/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 \((C_3H_7)_4N^+/PWA\) and \((C_2H_5)_4N^+/PWA\) catalysts showed the highest turnover number of 120 followed by other organic- inorganic hybrid catalysts made of SWA and PMoA (117 and 106 respectively) (Table 5.2). 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 Scheme 5.1. Initially, side product acetal formation was high, probably because the catalytic sites are fresh and more active in the initial phase of the reaction.

### Table 5.2. Potentiometric analysis of acidity and catalytic activity of all the catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Acidity (mmol/g)</th>
<th>Glycerol Conversion (mol %)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>((C_3H_7)_4N^+/PWA)</td>
<td>0.60</td>
<td>94</td>
<td>120</td>
</tr>
<tr>
<td>AB-15</td>
<td>0.95</td>
<td>89</td>
<td>72</td>
</tr>
<tr>
<td>H-beta</td>
<td>1.5</td>
<td>88</td>
<td>23</td>
</tr>
<tr>
<td>K-10 clay</td>
<td>1.1</td>
<td>87</td>
<td>61</td>
</tr>
<tr>
<td>Cs/PWA</td>
<td>1.88</td>
<td>38</td>
<td>24</td>
</tr>
<tr>
<td>((C_3H_7)_4N^+/SWA)</td>
<td>0.65</td>
<td>90</td>
<td>106</td>
</tr>
<tr>
<td>((C_3H_7)_4N^+/PMoA)</td>
<td>0.57</td>
<td>87</td>
<td>117</td>
</tr>
<tr>
<td>((C_2H_5)_4N^+/PWA)</td>
<td>0.53</td>
<td>83</td>
<td>120</td>
</tr>
<tr>
<td>((C_{16}H_{33})(CH_3)_3N^+/PWA*)</td>
<td>0.56</td>
<td>77</td>
<td>106</td>
</tr>
</tbody>
</table>

**Reaction conditions:** Temperature = 30 °C, Glycerol: acetone = 1 : 6, Catalyst = 3 wt % of total reactant weight, Time = 120 min, TON = moles of glycerol converted per mole of acid sites. * Homogeneous phase

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, (C₃H₇)₄N⁺/PWA, (C₃H₇)₄N⁺/SWA, (C₃H₇)₄N⁺/PMoA and the results are represented in Fig. 5.6. Among these catalysts, (C₃H₇)₄N⁺/PWA showed highest glycerol conversion of 94 % with 98 % selectivity to solketal in 120 min reaction time, whereas (C₃H₇)₄N⁺/SWA and (C₃H₇)₄N⁺/PMoA showed marginally lower conversion (89.8 and 86.8 % respectively) with the selectivity same as that of (C₃H₇)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

![Fig. 5.6. Catalytic activity of tetrapropylammonium exchanged HPAs](image)

**Conditions:** Temperature = 30 °C, Glycerol: acetone = 1:6, Catalyst weight = 3 wt% of total reactant weight
(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}N\textsuperscript{+}, (C\textsubscript{3}H\textsubscript{7})\textsubscript{4}N\textsuperscript{+} and (C\textsubscript{16}H\textsubscript{33})(CH\textsubscript{3})\textsubscript{3}N\textsuperscript{+} were exchanged with protons of PWA and applied as catalysts for solketal synthesis (Table 5.3.). While (C\textsubscript{2}H\textsubscript{5})\textsubscript{4}N\textsuperscript{+}/PWA and (C\textsubscript{3}H\textsubscript{7})\textsubscript{4}N\textsuperscript{+}/PWA catalysts acted as purely heterogeneous catalysts with glycerol conversion of 83.4 and 94 % respectively, (C\textsubscript{16}H\textsubscript{33})(CH\textsubscript{3})\textsubscript{3}N\textsuperscript{+}/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\textsubscript{4}+/PWA) was applied as a catalyst for this reaction and the activity was compared with (C\textsubscript{3}H\textsubscript{7})\textsubscript{4}N\textsuperscript{+}/PWA. The NH\textsubscript{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\textsubscript{3}H\textsubscript{7})\textsubscript{4}N\textsuperscript{+}Br salt was also used as a homogeneous catalyst which showed negligible activity for this reaction.

Table 5.3. Catalytic activities of NH\textsubscript{4}+/PWA, organic salt of PWA and its precursors

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Phase</th>
<th>Glycerol conversion (mol %)</th>
<th>Solketal selectivity (mol %)</th>
<th>Solketal yield (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH\textsubscript{4}+/PWA</td>
<td>Hetero</td>
<td>30</td>
<td>73</td>
<td>22</td>
</tr>
<tr>
<td>(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}N\textsuperscript{+}/PWA</td>
<td>Hetero</td>
<td>83</td>
<td>96</td>
<td>82</td>
</tr>
<tr>
<td>(C\textsubscript{3}H\textsubscript{7})\textsubscript{4}N\textsuperscript{+}/PWA</td>
<td>Hetero</td>
<td>94</td>
<td>98</td>
<td>93</td>
</tr>
<tr>
<td>(C\textsubscript{16}H\textsubscript{33})(CH\textsubscript{3})\textsubscript{3}N\textsuperscript{+}/PWA</td>
<td>Homo</td>
<td>77</td>
<td>94</td>
<td>75</td>
</tr>
<tr>
<td>(C\textsubscript{3}H\textsubscript{7})\textsubscript{4}N\textsuperscript{+}Br</td>
<td>Homo</td>
<td>0.2</td>
<td>98</td>
<td>0.15</td>
</tr>
<tr>
<td>PWA</td>
<td>Homo</td>
<td>90*</td>
<td>98</td>
<td>88</td>
</tr>
</tbody>
</table>

Reaction conditions: Glycerol : acetone = 1 : 6, Temperature = 30 °C, Catalyst = 3 wt % of total reactant weight, Time = 120 min, * Time = 10 min.

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. 5.4.). 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, \((\text{C}_3\text{H}_7)_4\text{N}^+/\text{PWA}\) 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 certain catalysts and highly hydrophilic catalysts like H-beta and K-10 are more affected by deactivation of acidic sites due to water.

**Fig. 5.4. 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.
5.7. Optimization of reaction conditions

In order to find the best reaction conditions to get high yield of solketal following conditions were studied at room temperature (30 °C),

5.7.1. Effect of catalyst concentration
5.7.2. Effect of glycerol to acetone mole ratio

5.7.1. Effect of catalyst concentration

The effect of catalyst weight percent and mole ratio of glycerol to acetone was

![Graphs showing the effect of catalyst concentration and glycerol to acetone mole ratio on glycerol conversion.](image)

**Fig. 5.7. a) Effect of catalyst concentration** (Conditions: Glycerol to acetone mole ratio = 1:6, temperature = 30 °C) and **b) Effect of Glycerol to acetone mole ratio** (Conditions: Catalyst weight = 3 wt % of total reactant weight, temperature = 30 °C)

studied for (C₃H₇)₄N⁺/PWA catalyst at room temperature and depicted in Fig. 5.7 (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.
5.7.2. Effect of glycerol to acetone mole ratio

The effect of mole ratio of glycerol to acetone was studied at room temperature using \((\text{C}_3\text{H}_7)_4\text{N}^+ / \text{PWA}\) catalyst. The mole ratio of glycerol to acetone was varied from 1:1 to 1:8 as shown in Fig. 5.7 (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 \((\text{C}_3\text{H}_7)_4\text{N}^+ / \text{PWA}\) are 30 °C (room temperature), 3 wt % catalyst with respect to total reactant weight and glycerol to acetone mole ratio of 1:6.

5.8. Leaching test

Leaching test was carried out to confirm the heterogeneity of the catalyst (Fig. 5.8 (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 5 h 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. 5.8 (b)).

5.9. Reusability test

Catalyst recyclability test was performed for \((C₃H₇)₄N⁺/PWA\) 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. 5.9 (a)). XRD of fresh and 3rd spent catalyst showed no change in the phase purity of the catalyst (Fig. 5.9 (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 5.1.).

5.10. Proposed reaction mechanism

Based on activity of the catalyst, a plausible mechanism is proposed. The acid sites in \((C₃H₇)₄N⁺/PWA\) catalyst facilitates 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 5.2.).
Scheme 5.2. Plausible reaction mechanism for condensation reaction of glycerol with acetone
5.11. References


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