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Glycerol acetins: Fuel additive synthesis by acetylation and esterification of glycerol using cesium phosphotungstate catalyst

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Abstract

Glycerol acetylation and esterification reactions with acetic anhydride and acetic acid respectively give acetins, in which di and tri acetins are commercially important products used as fuel additives. Acetylation and esterification of glycerol were studied over various solid acid catalysts namely, cesium phosphotungstate, amberlyst-15, H-beta, sulfated zirconia and montmorillonite K-10 under mild reaction conditions. The catalysts were characterized by XRD, FTIR, SEM and acidity measurements. Among all the catalysts evaluated in this study, cesium phosphotungstate showed highest activity with > 98% conversion for both the reactions, whereas di and triacetins selectivity was 99.1% for acetylation and 75% for esterification reaction. The catalyst with high Brønsted acidity gave high activity for both the reactions, whereas selectivity for di and tri acetins depends on nature of active sites.

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2 **1. Introduction**

3 The growing scarcity of fossil hydrocarbons made the researchers to find alternative
4 source of energy. Biomass is considered to be a potential raw material for making renewable
5 fuels. Transesterification of vegetable oils or animal fats through catalytic route produces
6 biodiesel as the main product (90 wt%) and glycerol as a byproduct (10 wt%).¹ Increase in
7 the production of biodiesel causes increase in glycerol availability in tons. Glycerol is a
8 propanetriol containing three hydroxyl groups which can be functionalized as well as
9 removed through catalytic processes. Transformation of available glycerol to value-added
10 products like oxygenated fuel additives, chemicals, solvents etc. can add value to it and make
11 the process economically viable and valuable.²⁻⁸

12 Glycerol undergoes acetylation with acetic acid or acetic anhydride in presence of
13 acid catalyst to yield acetins namely monoacetin, diacetin and triacetin. Di and triacetins can
14 be used as fuel additive which have been introduced in biodiesel formulation to improve its
15 viscosity property as cold flow improver and it has also been used as an antiknock additive
16 for gasoline. Triacetin is also used in cosmetics, whereas monoacetin and diacetin are used as
17 plasticizer in cigarette filters and as raw materials for the production of biodegradable
18 polyesters.⁹

19 Homogeneous acids such as $H_3PW_{12}O_{40}$ showed higher catalytic activities towards
20 acetylation reaction^{10,11} but faced several practical difficulties in separation of catalyst,
21 recyclability and handling. To overcome these practical difficulties, variety of Brønsted solid
22 acid catalysts have been reported for the reaction of glycerol with acetic acid or acetic
23 anhydride. Solid acid catalysts such as amberlyst-15, montmorillonite K-10, beta zeolite and
24 H-USY^{12,13} were applied as catalysts for this reaction which showed 100% glycerol
25 conversion using higher catalyst concentrations. Supported sulfonic acid catalysts¹⁴⁻²⁰ and

1 mixed oxides like $\text{MoO}_3/\text{TiO}_2\text{-ZrO}_2$,²¹ Y/SBA-3²² have been reported to be active catalysts
2 for acetylation of glycerol. Even supported heteropoly acid catalysts like PW on silica, Cs-
3 containing zirconia, carbon, niobic acid with high thermal stability and high surface area have
4 been used but showed less efficiency for this reaction.²³⁻²⁷ Silver ion exchanged
5 phosphotungstic acid catalyst is also used for the esterification of glycerol with acetic acid.²⁸

6 Recently, cesium exchanged heteropoly acid has received greater attention as a
7 catalyst in many reactions due to its heterogeneous property, high thermal stability and higher
8 surface area compared to parent heteropoly acid. The catalytic properties of metal ion
9 exchanged heteropoly acid can be tuned by choosing appropriate metal salt and by varying
10 the extent of ion exchange. The studies in the literature show that the cesium
11 phosphotungstate is more active than parent PWA due to its high surface protonic acidity
12 with high acid strength of the proton associated to the polyanion.²⁹⁻³²

13 The aim of this work is to explore a catalyst for the synthesis of glycerol acetins under
14 mild reaction conditions (low temperature, mole ratio and catalyst concentration) and to get
15 higher activity and selectivity for di and triacetins. Different well known solid acid catalysts
16 like cesium phosphotungstate, zeolites, resin, clay and sulfated zirconia were studied for both
17 acetylation and esterification reactions of glycerol. The best catalyst was taken further for
18 detailed studies. The physicochemical properties of the catalysts were correlated with
19 catalytic activity and selectivity for acetins.

20 **2. Experimental**

21 *2.1. Chemicals and catalysts*

22 Glycerol and acetic acid were purchased from Merck India Ltd. Cesium carbonate and
23 phosphotungstic acid (PWA) were procured from SD fine chemicals, India. Amberlyst-15
24 (hereafter AB-15) was obtained from Alfa Aesar, USA. The montmorillonite K-10 clay
25 (hereafter K-10) was purchased from Sigma Aldrich, USA. H-beta (SAR-25) was kindly

1 donated by Süd-Chemie India Pvt Ltd. All the chemicals were of research grade and used
2 without any further purification.

3 The acidic cesium phosphotungstate (hereafter CsPWA) was prepared following a
4 literature procedure.³³ The final composition of the salt was found to be $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$.
5 Other solid acid catalyst, sulfated zirconia (SZ) was synthesized by literature method.³⁴

6 *2.2. Catalyst characterization*

7 Powder X-ray diffraction patterns of CsPWA and PWA were recorded with Bruker
8 D2 phaser X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$) with high resolution
9 Lynxeye detector. All the samples were scanned in the 2θ range of $5 - 80^\circ$. The specific
10 surface areas of the catalysts were determined by nitrogen sorption measurement using
11 Quantachrome NOVA instrument at 77 K.

12 The nature of acidic sites of catalysts was investigated by pyridine adsorption study
13 using Pyridine-FT-IR (alpha-T, Bruker) and the spectra were obtained in the range of 1400–
14 1600 cm^{-1} . The catalyst pellets were saturated by pyridine followed by degassing at 150°C
15 for 1 h. The FTIR spectra in absorbance mode for pyridine treated sample were subtracted
16 with pyridine untreated sample to obtain the peaks only due to pyridine–acid interaction.³⁴

17 In addition to above method, acidity of the catalysts was determined by
18 potentiometric titration. About 0.05 g of sample was suspended in 5 ml of n-butylamine
19 solution (0.05 N) in acetic acid and sonicated for 5 min to attain uniform dispersion. Then the
20 above solution was suspended in excess of acetic acid (90 mL) and potentiometrically titrated
21 against perchloric acid (0.1 N) in acetic acid. Prior to sample titration, a blank titration of
22 acetic acid and n-butyl amine against perchloric acid was carried out to check the acidity
23 contribution from solutions used. ICP-OES was performed using a Thermo-iCAP 6000 series
24 in order to study the leaching of cesium in the reaction mixture.

1 Scanning electron microscope (SEM) images of CsPWA catalyst were recorded on
2 Zeiss microscope to investigate the crystallite size and morphology.

3 *2.3 Catalytic activity studies*

4 Catalytic activity studies were performed in a liquid phase glass batch reactor. Prior to
5 the reaction, the catalysts (except Amberlyst-15) were activated at 120 °C to remove the
6 moisture.

7 a) Acetylation reaction of glycerol with acetic anhydride: In a typical procedure, the reaction
8 was performed in a 100 ml two-necked glass reactor equipped with a magnetic stirring bar, a
9 Liebig condenser, and a thermometer. The glycerol and acetic anhydride were taken in the
10 ratio of 1: 3 in the glass reactor and 4 wt% of catalyst (with respect to total reactants) were
11 added into it. The reaction was performed under stirring at room temperature.

12 b) Esterification reaction of glycerol with acetic acid: In a typical procedure, the reaction was
13 carried out in a 100 ml two-necked glass reactor equipped with a magnetic stirring bar, a
14 Liebig condenser, and a thermometer. The required amounts of glycerol and acetic acid were
15 taken in the reactor and desired catalyst weight was added into it. The reaction was performed
16 under stirring at desired temperature.

17 For both the reactions, same separation procedure was followed; the reaction mixture
18 was taken out and centrifuged for 10 min to separate the catalyst from liquid phase. The
19 obtained product was analyzed in gas chromatography (Shimadzu, GC-2014) with flame
20 ionization detector (FID) equipped with capillary column (0.25mm I.D and 30 m length,
21 Stabilwax, Restek). All the products were confirmed by gas chromatography with mass
22 spectroscopy (Shimadzu, GCMS QP 2010).

23 **3. Results and discussion**

24 *3.1. Catalyst characterization*

1 The formation of crystalline phase of CsPWA catalyst was confirmed by XRD in
2 comparison with phosphotungstic acid (Fig. 1a). XRD pattern of PWA shows the diffraction
3 peaks corresponding to cubic Pn3m crystalline structure. Interestingly, the diffraction peak of
4 CsPWA became significantly broader with a right shift in 2θ value (25°) compared to PWA.
5 The shift of diffraction peak towards higher angle in CsPWA is attributed to the formation of
6 body centered cubic structure.^{29,35}

7 The characteristic presence of Keggin structure of CsPWA and phosphotungstic acid
8 was confirmed by FTIR studies (Fig. 1b). Four bands at 700-1100 cm^{-1} region corresponding
9 to Keggin unit (PWA) structural vibrations are observed for PWA and CsPWA suggesting
10 that the framework of primary Keggin structure remained unaltered after modification of
11 PWA with cesium salt. The peaks corresponding to Keggin anion vibration are as follows.
12 The stretching frequency of P–O in the central PO_4 tetrahedron is at 1084 cm^{-1} . The peak at
13 991 cm^{-1} is due to the terminal W=O vibration in the WO_6 octahedron and the peak at 890
14 and 794 cm^{-1} were assigned to W– O_b –W and W– O_c –W bridges respectively. Weaker peak
15 appearing at 595 cm^{-1} is due to bending vibrations of W–O–W bonds.³²

16 The physicochemical properties of CsPWA, AB-15, K-10, H-beta and sulfated
17 zirconia are tabulated in Table 1. The specific surface area of as-prepared CsPWA was found
18 to be 110 m^2/g . H-beta and K-10 exhibited higher surface area of 450 and 250 m^2/g
19 respectively, whereas amberlyst-15 and sulfated zirconia gave lower surface areas $< 60 \text{ m}^2/\text{g}$.

20 The interaction of pyridine nitrogen with acidic sites gave two different frequency of
21 bending vibrations. The bending vibrations around 1445 cm^{-1} and 1540 cm^{-1} are assigned as
22 Lewis (L) and Brönsted (B) acid sites respectively and B/L ratio were measured using the
23 peak intensities. Pyridine-FTIR spectra of CsPWA catalyst showed a strong Brönsted acidity
24 due to the presence of protons (peak at 1540 cm^{-1}) and weak Lewis acid sites (peak at 1445
25 cm^{-1}) as depicted in Fig. 2. The CsPWA contained high B/L ratio of 3.86 compared to other

1 solid acid catalysts used in this study except AB-15 (Table 1). AB-15 is a pure Brønsted acid
2 catalyst with sulfonic acid groups on polystyrene chain. The B/L ratio decreased in the order;
3 AB-15 > CsPWA > K-10 > H-beta > sulfated zirconia.

4 Potentiometric acid-base titration revealed the total acidity of the catalysts (tabulated
5 in Table 1). The total acidity of CsPWA, H-beta, K-10 and SZ was found to be 1.87, 1.49,
6 1.10 and 1.48 mmol/g respectively. H-beta zeolite and sulfated zirconia has same amount of
7 acidic sites. Acidity of AB-15 was 4.7 mmol/g as given by the manufacturer.

8 CsPWA catalyst exhibited the morphology of the spherical shaped particles with size
9 ranging from 70-200 nm as shown in Fig. 3.

10 3.2. Catalyst screening

11 Acetylation and esterification of glycerol was studied over various solid acid catalysts
12 namely, CsPWA, AB-15, H-beta, sulfated zirconia and K-10 using acetic anhydride and
13 acetic acid respectively. The performance of the catalyst is measured by glycerol conversion
14 and the selectivity to di and triacetins.

15 Acetylation of glycerol using acetic anhydride was carried out over different Brønsted
16 solid acid catalysts at room temperature (30 °C) (Fig. 4.). Prior to the catalytic reaction, a
17 blank run was carried out without a catalyst, which resulted in negligible glycerol conversion
18 (2.5%) with 100% selectivity to monoacetins. Among the solid acid catalysts screened, the
19 catalyst containing higher amount of acid sites *viz.* CsPWA (1.87 mmol/g) and AB-15 (4.7
20 mmol/g) resulted in maximum glycerol conversion (100%) with higher glycerol diacetins and
21 glycerol triacetin selectivity of 99.1 and 99.9% respectively. Among the solid acid catalysts
22 screened, the catalyst containing higher amount of acid sites *viz.* CsPWA (1.87 mmol/g) and
23 AB-15 (4.7 mmol/g) gave maximum glycerol conversion (100%) with higher selectivity
24 towards diacetins (17 and 23%) and triacetin (82 and 77%) respectively. The catalytic
25 activity of CsPWA showed higher triacetin selectivity of 82% at room temperature compared

1 to all other solid acid catalysts for 2 h of reaction time. This result shows that the utilization
2 of acetic anhydride is maximum for CsPWA and AB-15 with higher selectivity to triacetin
3 compared with other catalysts namely K-10, H-beta and sulfated zirconia. The glycerol
4 conversion reached to a maximum of 100% at the initial time period, but the triacetin
5 selectivity was found to increase with time for CsPWA and AB-15 with a decrease in mono
6 and diacetins selectivity (Fig. 4). K-10 containing B/L ratio of 2.3 gave lower triacetin
7 selectivity of 32%, whereas H-beta catalyst (B/L ratio of 1.92) showed 80% diacetin
8 selectivity. Sulfated zirconia, the catalyst with higher Lewis acidic sites showed very low
9 glycerol conversion of 25%. These results clearly show that the catalyst with higher Brønsted
10 acidic sites gives higher glycerol conversion with high di and triacetins selectivity. The
11 glycerol conversion and triacetin selectivity increased for the catalysts in the following order;
12 SZ < H-beta < K10 < AB-15 < Cs/PWA.

13 Since CsPWA and AB-15 showed complete glycerol conversion at 30 min, it was not
14 possible to decide the best catalyst among the two. Therefore, the catalyst concentration was
15 reduced to 1 wt% (w.r.t. total reactants) and as a result, the catalytic performance of AB-15
16 showed lower glycerol conversion of 25% at 30 min. As the time increased, glycerol
17 converted completely with increase in triacetin selectivity. But CsPWA catalyst showed 99.8
18 % glycerol conversion even at less catalyst amount for 30 min with higher triacetin selectivity
19 compared to AB-15 (Fig. S1†). The turn over frequency of all the catalysts (Table 1)
20 increased in the following order; SZ < AB-15 < H-beta < K-10 < CsPWA. Highest TOF/h of
21 267 was obtained for CsPWA which clearly proves that CsPWA is highly active catalyst for
22 acetylation reaction of glycerol. The high selectivity towards triacetin using acetic anhydride
23 as acetylating agent compared to acetic acid can be explained on the basis of formation of
24 intermediate acylium ion (Scheme S1†).¹²

1 In order to study the catalytic behaviour at lower reactant mole ratio, the reaction was
2 studied with glycerol : acetic anhydride of 1:1.5 and 1:2 (Table 2). It showed relatively lower
3 selectivity towards triacetin compared to higher reactant mole ratio of 1:3 suggesting that the
4 formation of triacetin is greater with higher amount of acetylating agent.

5 Further, the esterification of glycerol was studied using acetic acid under reaction
6 conditions; glycerol : acetic acid of 1:8, 85 °C and 7 wt% of catalyst referred to total
7 reactants (Fig. 5). As observed in the acetylation reaction, a similar catalytic performance was
8 observed with high performance of CsPWA and AB-15 compared with other catalysts. The
9 glycerol conversion reached to 98% using CsPWA and AB-15 within 2 h with increase in
10 diacetins and triacetin selectivity. CsPWA exhibited higher catalytic performance with
11 triacetin selectivity of 27%, whereas AB-15 gave 22% triacetin selectivity. Among these two
12 catalysts, CsPWA exhibited much higher TOF at 30.5 h⁻¹ compared to AB-15 (12.3 h⁻¹)
13 (Table 1).

14 Among lower active catalysts, large pore H-beta zeolite exhibited comparatively
15 greater catalytic performance than K-10 and sulfated zirconia. Glycerol conversion increased
16 from 28 to 80% with increase in time from 1 to 5 h using H-beta and finally reached to 37%
17 diacetins selectivity (5 h). Triacetin did not form with H-beta catalyst. In contrast, K-10 clay
18 showed lower glycerol conversion (63%) compared to H-beta zeolite but it gave triacetin
19 selectivity of 4% (5 h). Glycerol conversion of 70% with 20% diacetin selectivity was
20 observed for sulfated zirconia catalyst. It exhibited lower activity compared to other acid
21 catalysts which could be due to lower B/L ratio (1.46), since the esterification reactions are
22 predominantly catalyzed by Brönsted acid sites. Thus, the catalytic activity towards
23 esterification of glycerol with acetic acid gives a clear picture with respect to nature of acidic
24 sites (B/L ratio) of the catalyst. The turn over frequency of the screened catalysts increased in
25 the following order; SZ < AB-15 ≈ H-Beta < K-10 < CsPWA.

1 3.3 Influence of reaction conditions on esterification reaction of glycerol with acetic acid

2 The influence of reaction parameters *viz.* catalyst concentration, reaction temperature,
3 and reactants mole ratio on catalytic activity using CsPWA catalyst were studied for glycerol
4 esterification with acetic acid.

5 Effect of catalyst concentration was studied with glycerol to acetic acid mole ratio of
6 1 : 8 at 85 °C for 2 h. The catalyst concentration was varied from 3 to 9 wt% (Table 3). The
7 glycerol conversion was found to increase from 56 to 98% with increase in the catalyst
8 concentration from 3 to 7 wt%. The lesser catalytic activity with catalyst concentration of 3
9 and 5 wt% indicates the requirement of higher active sites for the reaction. Selectivity to
10 diacetins (31 and 34%) was almost the same for 3 and 5 wt% catalysts, but the triacetin was
11 formed with 5 wt% catalyst (5% selectivity), whereas for 3 wt% catalyst, triacetin was not
12 observed. The catalytic activity was found to be almost the same with 7 and 9 wt% catalyst
13 concentrations. The glycerol conversion increased from ~ 84 to 98% as the time increased
14 from 30 min to 2 h. The maximum of 98% glycerol conversion was attained at 1 h using 7
15 wt% catalyst concentration, but the selectivity to diacetin varied from 55 to 59% after 2 h.
16 The maximum triacetin selectivity of 16% was obtained after 2 h. No major variation in
17 catalytic performance was observed with further increase in catalyst concentration to 9 wt%.
18 Moreover, the selectivity to all the acetins remained the same as in the case of 7 wt% catalyst
19 concentration. This indicates that the amount of active acidic sites in 7 wt% catalyst
20 concentration is sufficient to get the maximum activity of glycerol conversion and selectivity
21 to the desired product.

22 The effect of glycerol to acetic acid mole ratio was studied from 1:4 to 1:10 at 85 °C
23 for 2 h (Table 4). The conversion of glycerol increased with increase in mole ratio from 1:4 to
24 1:8 due to increase in availability of accessible acetic acid with glycerol. The glycerol
25 conversion and selectivity to acetins remained almost the same with further increase in mole

1 ratio of reactants from 1:8 to 1:10. The reaction condition with 1:8 mole ratio was found to be
2 the best compared with other mole ratios. A gradual increase in glycerol conversion from 45
3 to 69% with increase in reaction time was observed for 1:4. Formation of triacetin was found
4 to be nil at this mole ratio. This indicates that at 1:4 mole ratio, the amount of accessible
5 acetic acid was not sufficient for the maximum conversion of glycerol to yield higher amount
6 of diacetin and triacetin. For mole ratio 1:6, the glycerol conversion increased from 67 to
7 92% with the increase in time from 30 to 120 min. The catalytic activity with 1:8 and 1:10
8 mole ratio was found to be almost the same. The glycerol reached a maximum conversion of
9 98% with negligible changes in the acetins selectivity (diacetins and triacetin was 59 and
10 16% respectively). Therefore, 1:8 reactants mole ratio was found to be the best mole ratio for
11 further studies.

12 The effect of temperature was studied at four different temperatures ranging from 65
13 to 95 °C using glycerol to acetic acid mole ratio of 1:8 for 2 h. From Table 5, it is observed
14 that the glycerol conversions were low and slowly increased with time at temperatures of 65
15 and 75 °C, which could be attributed to lesser formation of acylium ion from acetic acid at
16 lower temperatures. At higher temperatures of 85 and 95 °C, glycerol conversion reached to a
17 maximum of 98% and remained almost the same, indicating that the formation of acylium ion
18 is faster at these temperatures. It is also observed that di and triacetins increased with increase
19 in reaction time. The catalytic activity at 85 °C was found to be best temperature for
20 esterification reaction since the glycerol reached a maximum conversion of 98% with the
21 selectivity to di and triacetin of 59 and 16% respectively.

22

23 *3.4. Plausible reaction mechanism for esterification reaction of glycerol with acetic acid*

24 The plausible reaction mechanism for esterification of glycerol with acetic acid
25 proceeds by the activation of acetic acid carbonyl group by CsPWA catalyst whereby

1 electrophilicity of carbonyl carbon increases (Scheme 1). Then the carbonyl carbon is
2 attacked by the oxygen of glycerol. The transfer of proton from the intermediate to the second
3 hydroxyl group of glycerol gives an activated complex with the formation of water molecule.
4 Later, with the loss of water molecule gives monoacetin. The above-mentioned mechanism
5 continues sequentially further by the reaction of monoacetin with acetic acid to form diacetin
6 and triacetin.

7

8 *3.5. Catalyst reusability and leaching studies*

9 Catalyst recyclability test was performed for CsPWA catalyst under optimized
10 reaction conditions for both acetylation and esterification reactions. The catalyst showed
11 good recyclability with similar activity after 3 recycles (Table 6). In case of acetylation, the
12 selectivity of triacetin was retained after initial decrease in the 1st recycle. For esterification
13 reaction, with each recycle, triacetin decreased marginally with the increase of monoacetin
14 and diacetin. XRD analysis of the fresh and 3 times recycled catalyst showed no change in
15 the phase purity of the catalyst (Fig. 6). FTIR analysis of the spent CsPWA catalyst was also
16 performed and it showed no change in the characteristic peak of Keggin structure after the
17 recycle (Fig. S2†).

18 The leaching test was carried out for acetylation and esterification reactions by
19 investigating the leaching of Cs in the catalyst into the reaction media. The study was
20 performed under the optimized reaction conditions where the reaction was stopped at 2 and 5
21 h for acetylation and esterification reactions respectively and the catalyst was filtered out.
22 Thus obtained filtrate was subjected to ICP-OES analysis of Cs in order to find the leaching
23 of Cs. The analysis confirmed the absence of Cs in the reaction mixture under the detection
24 limit of 0.01ppm which suggests that the catalyst is truly heterogeneous.

25

1

2 *3.6. Comparison of CsPWA with the reported catalysts for the esterification of glycerol*

3 The active CsPWA catalyst was compared with the reported catalysts for the
4 esterification of glycerol and the data was tabulated in Table S1†. Among the reported
5 catalysts, supported heteropoly acids *viz.* HSiW/ZrO₂ and HPW/ZrO₂ catalysts showed
6 slightly higher selectivity for di and triacetins compared to CsPWA catalyst. However, higher
7 reaction temperature (difference of 35 °C) and glycerol to acetic acid mole ratio were used
8 for these catalysts. At lower temperature and reactants mole ratio, CsPWA catalyst showed
9 higher activity and selectivity towards di and triacetins compared to the reported catalysts.

10 **4. Conclusions**

11 Acetylation and esterification of glycerol were studied with acetic anhydride and
12 acetic acid respectively using different solid acid catalysts. The yields of mono, di and
13 triacetins were differed with the nature of acid catalysts. Among the solid acid catalysts
14 screened, the catalyst containing higher amount of acid sites *viz.* CsPWA (1.87 mmol/g) and
15 AB-15 (4.7 mmol/g) resulted in maximum glycerol conversion (100%) with higher di and
16 triacetins selectivity of 99.1 and 99.9% respectively for acetylation reaction. CsPWA showed
17 highest triacetin selectivity of 82% at room temperature compared to all other solid acid
18 catalysts. The turn over frequency for acetylation of glycerol increased in the following order;
19 SZ < Amberlyst-15 < H-beta < K-10 < CsPWA with highest TOF/h of 267 for CsPWA
20 catalyst. CsPWA catalyst also gave highest activity and selectivity for di and triacetins for
21 esterification of glycerol with acetic acid. The catalytic activity towards the reaction was
22 correlated with B/L ratio of the catalyst. Higher catalytic activities of CsPWA and AB-15 are
23 due to higher B/L ratio of the catalysts. Among the two catalysts, CsPWA gave highest di and
24 triacetins selectivity which could be due to the nature of active sites present in the catalyst.

1 The catalyst exhibited good recyclability with marginal decrease in the activity after 3
2 recycles.

3 **5. Acknowledgement**

4 Swetha S. acknowledges CSIR, New Delhi for providing Senior Research Fellowship
5 and also thankful to Manipal University for permitting this research as a part of the Ph. D
6 programme.

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Figures

Fig. 1. XRD patterns (a) and FTIR spectra (b) of CsPWA and PWA.

Fig. 2. Pyridine-FTIR spectra of catalysts.

Fig. 3. SEM images of CsPWA.

Fig. 4. Catalytic activity of different solid acid catalysts with glycerol and acetic anhydride.
Reaction conditions: Glycerol : Acetic anhydride = 1 : 3, Temperature = 30 °C, Catalyst weight = 3 wt%.

Fig. 5. Catalytic activity of different solid acid catalysts with glycerol and acetic acid.
Reaction conditions: Glycerol : Acetic acid = 1 : 8, Temperature = 85 °C, Time= 5 h, Catalyst weight = 7 wt%.

Fig. 6. XRD patterns of fresh and recycled catalyst

Scheme 1. Plausible reaction mechanism for the esterification

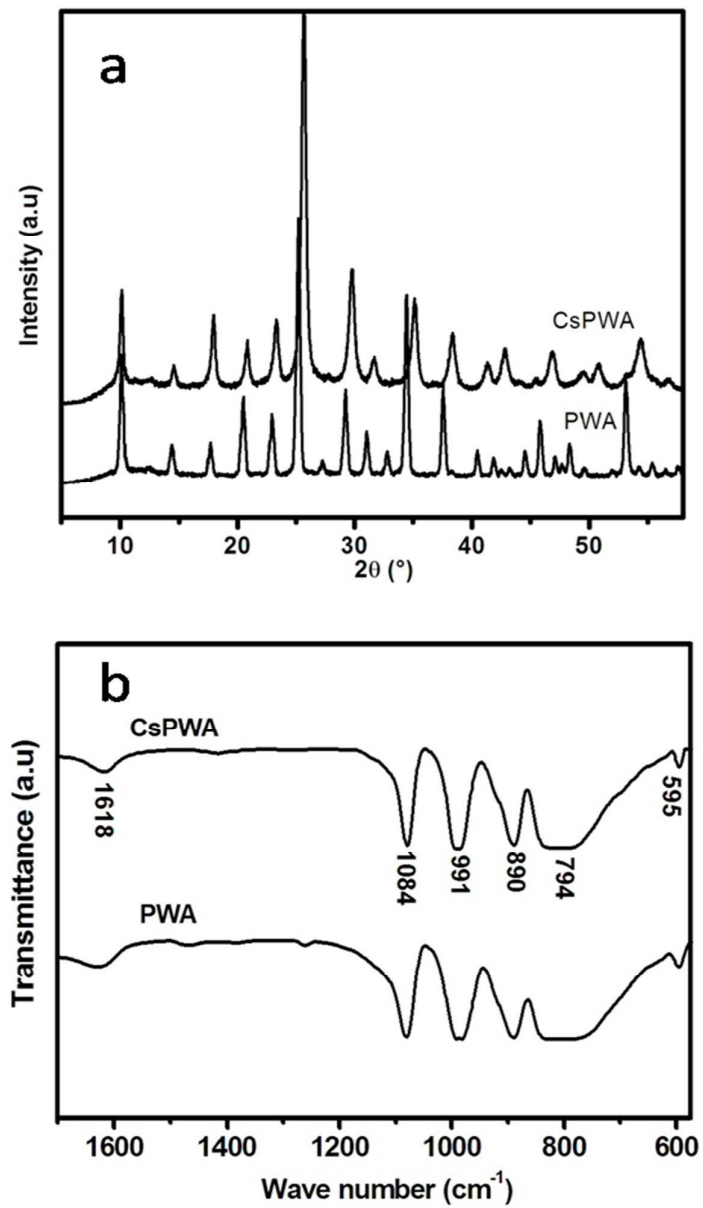


Fig. 1. XRD patterns (a) and FTIR spectra (b) of CsPWA and PWA.

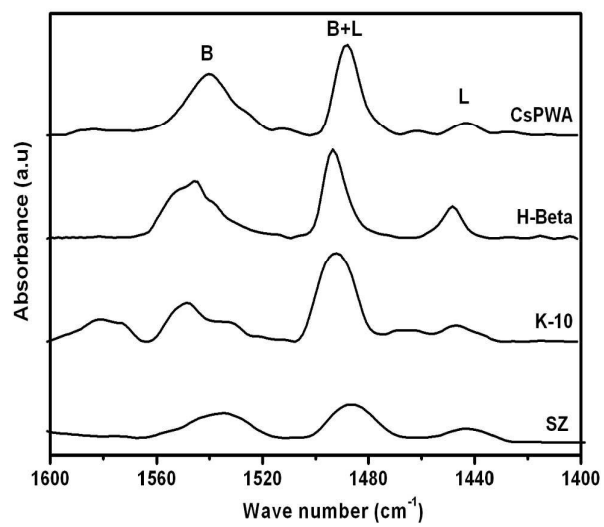


Fig. 2. Pyridine-FTIR spectra of catalysts.

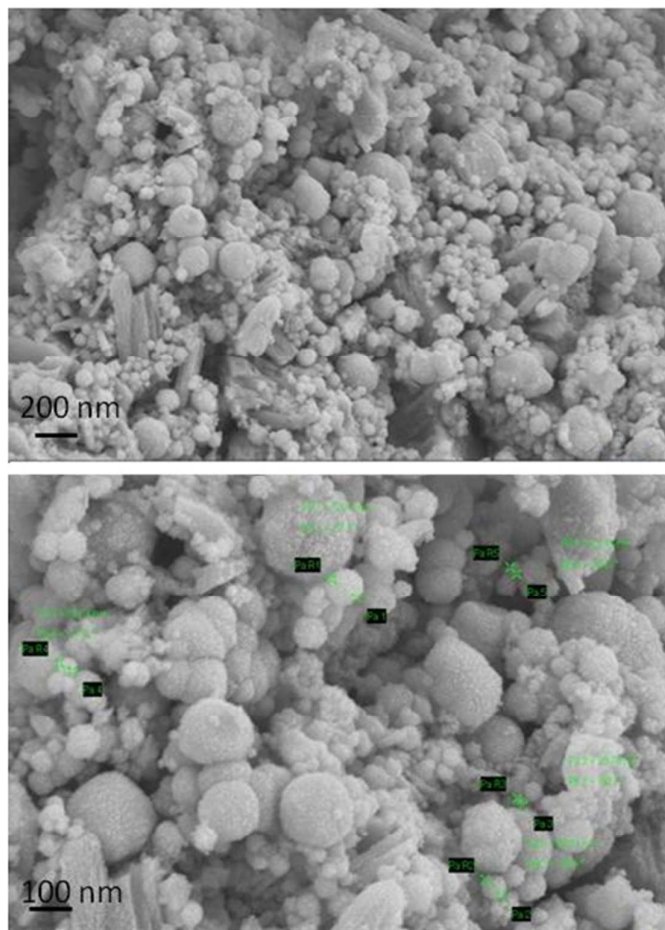


Fig. 3. SEM images of CsPWA catalyst

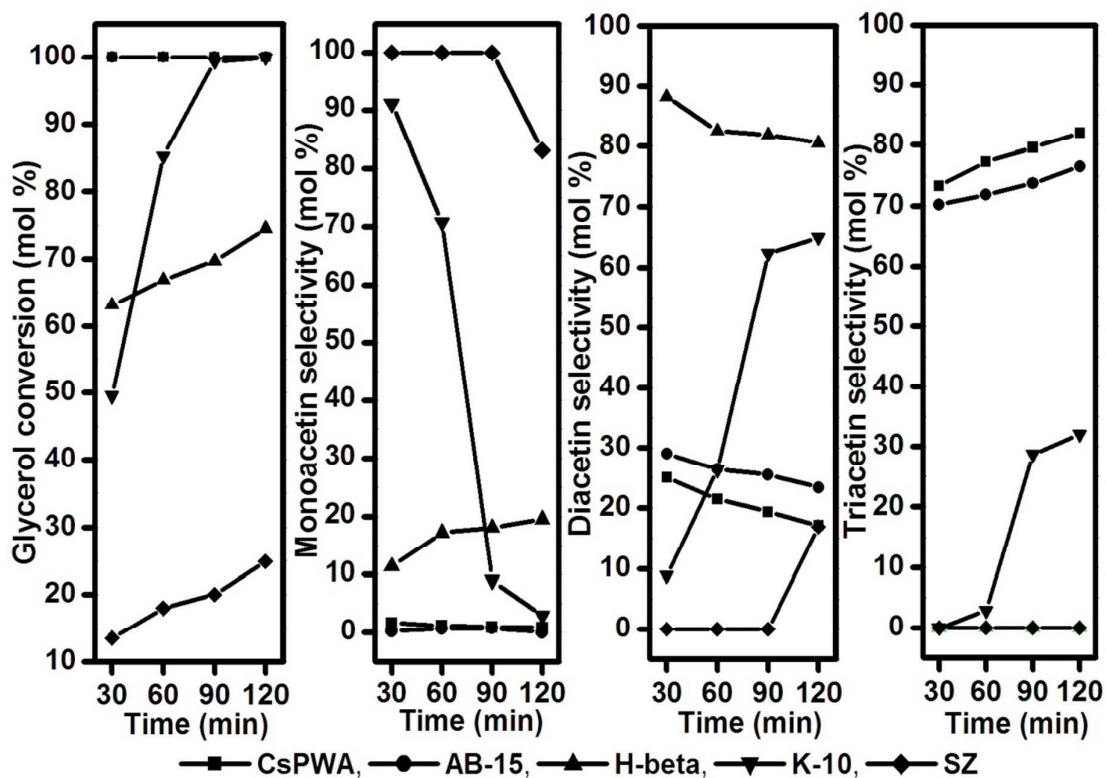


Fig. 4. Catalytic activity of different solid acid catalysts with glycerol and acetic anhydride. Reaction conditions: Glycerol : Acetic anhydride = 1 : 3, Temperature = 30 °C, Time= 120 min, Catalyst weight = 4 wt%.

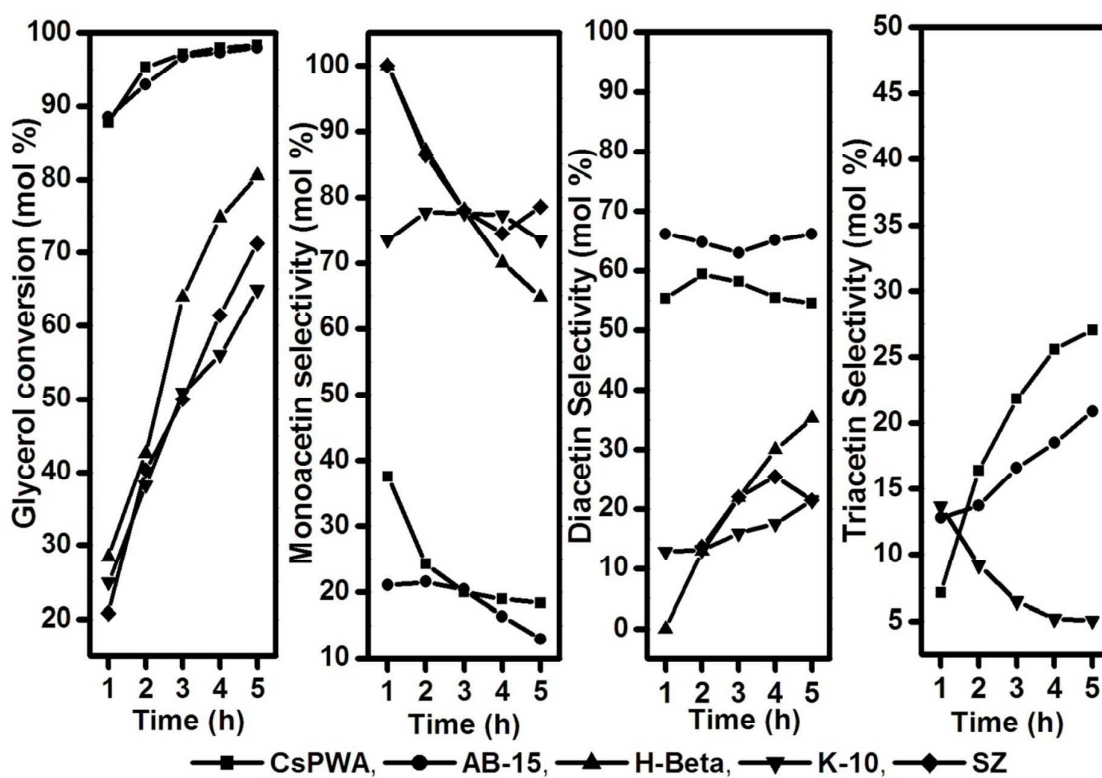


Fig. 5. Catalytic activity of different solid acid catalysts with glycerol and acetic acid.

Reaction conditions: Glycerol : Acetic acid = 1 : 8, Temperature = 85 °C, Time= 5 h, Catalyst weight = 7 wt%.

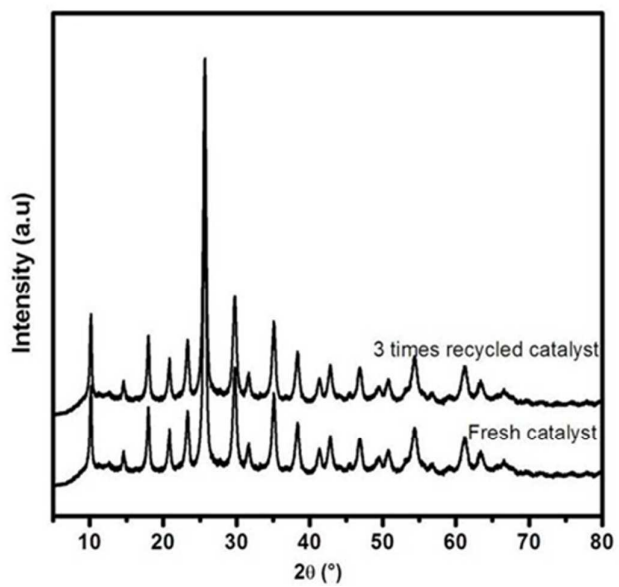
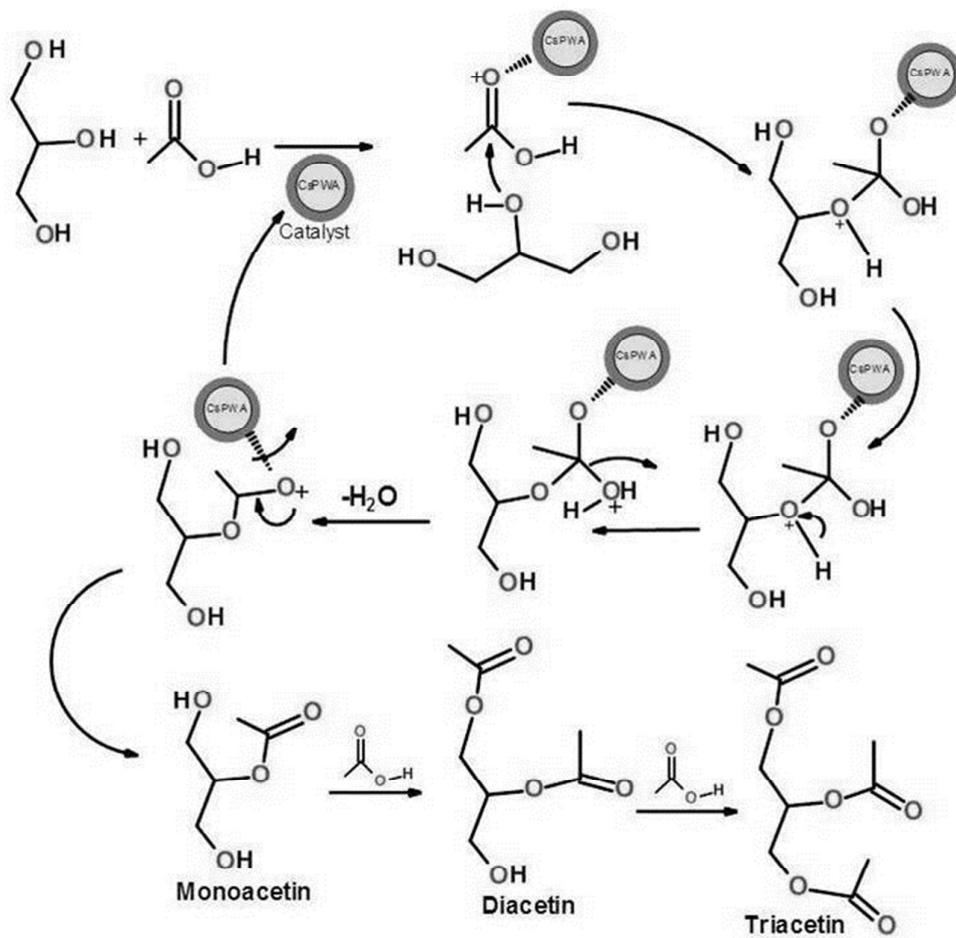


Fig. 6. XRD patterns of fresh and recycled CsPWA catalyst

Scheme 1. Plausible reaction mechanism for the esterification

Tables

Table 1. Physicochemical properties and activities of different catalysts for acetylation and esterification of glycerol.

Table 2. Effect of reactant mole ratio on catalytic performance in acetylation of glycerol with acetic anhydride.

Reaction conditions: Temperature = 30 °C, Time= 120 min, CsPWA catalyst = 4 wt%.

Table 3. Effect of catalyst concentration on catalytic activity in esterification of glycerol with acetic acid.

Reaction conditions: Glycerol : Acetic acid = 1 : 8 , Temperature = 85 °C, Catalyst = CsPWA.

Table 4. Effect of reactant mole ratio on catalyst performance in esterification of glycerol with acetic acid.

Reaction conditions: Temperature = 85 °C, CsPWA catalyst = 7 wt%.

Table 5. Effect of temperature on catalyst performance in esterification of glycerol with acetic acid.

Reaction conditions: Glycerol : Acetic acid = 1: 8 , CsPWA catalyst = 7 wt%.

Table 6. Reusability test of CsPWA catalyst on acetylation and esterification of glycerol.

Table 1: Physicochemical properties and activities of different catalysts for acetylation and esterification of glycerol.

Catalyst	S _{BET} (m ² /g)	Amount of acidity (mmol /g)	Py-FTIR B/L ratio	Acetylation ^a TOF (h ⁻¹)	Esterification ^c TOF (h ⁻¹)
CsPWA	110	1.87	3.86	69.7 267 ^b	30.5
AB -15	39	4.7	-	27.7 28.3 ^b	12.3
H-beta	450	1.49	1.92	55.2	12.4
K-10	250	1.1	2.30	58.6	14.7
Sulfated zirconia	57	1.48	1.44	11.9	9.2

Turn over frequency (TOF) = Moles of glycerol converted per mole of acid site per hour.

^aReaction conditions as in Fig. 4, ^b 1wt% catalyst, ^c Reaction conditions as in Fig. 5

Table 2. Effect of reactant mole ratio on catalytic performance in acetylation of glycerol with acetic anhydride.

Time (h)	Glycerol : Acetic anhydride	Glycerol conversion (mol%)	Acetin Selectivity (mol%)		
			Mono	Di	Tri
1 h	1:1.5	92.6	19.3	40.3	40.4
2 h	1:1.5	98	13.3	41.2	45.5
1 h	1:2	98.1	12.8	33.3	54.0
2 h	1:2	98.3	12.7	31.3	56.1
1 h	1:3	100	1.2	21.5	77.3
2 h	1:3	100	0.9	17.1	82

Reaction conditions: Temperature = 30 °C, Time= 120 min, CsPWA catalyst = 4 wt%.

Table 3. Effect of catalyst concentration on catalytic activity in esterification of glycerol with acetic acid.

Catalyst wt%	Time (min)	Glycerol conversion (mol%)	Acetin Selectivity (mol%)		
			Mono	Di	Tri
3	30	30	95	5	0
3	60	35.4	80	20	0
3	90	40	72	28	0
3	120	56	69	31	0
5	30	40	86	14	0
5	60	52	75	25	0
5	90	62	68	30	2
5	120	70	61	34	5
7	30	84	37	55	8
7	60	97.5	35	56	9
7	90	98	27	58	15
7	120	98.1	25	59	16
9	30	85	36	54	10
9	60	95.6	30	58	12
9	90	97	28	58	14
9	120	98.2	26	58	16

Reaction conditions: Glycerol : Acetic acid = 1 : 8 , Temperature = 85 °C, Catalyst = CsPWA.

Table 4. Effect of reactant mole ratio on catalyst performance in esterification of glycerol with acetic acid.

Mole ratio Gly : Acetic acid	Time (min)	Glycerol conversion (mol%)	Acetin Selectivity (mol%)		
			Mono	Di	Tri
1:4	30	45.4	81	19	0
1:4	60	58.7	75	25	0
1:4	90	62	73	27	0
1:4	120	69	65	35	0
1:6	30	67	77	23	0
1:6	60	85.4	74	26	0
1:6	90	90	73	24	3
1:6	120	92	59	35	6
1:8	30	84	37	55	8
1:8	60	97.5	35	56	9
1:8	90	98	27	58	15
1:8	120	98.1	25	59	16
1:10	30	85	36	54	10
1:10	60	90.7	31	57	12
1:10	90	97	28	58	14
1:10	120	98.2	26	58	16

Reaction conditions: Temperature = 85 °C, CsPWA catalyst = 7 wt%.

Table 5. Effect of temperature on catalyst performance in esterification of glycerol with acetic acid.

Temp (°C)	Time (min)	Glycerol conversion (mol%)	Acetin Selectivity (mol%)		
			Mono	Di	Tri
65	30	35.4	93	7	0
65	60	45.8	75	25	0
65	90	52	69	31	0
65	120	65.4	68	32	0
75	30	57	90	10	0
75	60	62.5	84	16	0
75	90	88	74	23	3
75	120	92	60	34	6
85	30	84	37	55	8
85	60	97.5	35	56	9
85	90	98	27	58	15
85	120	98.1	25	59	16
95	30	85	35	55	10
95	60	87.3	32	56	12
95	90	97	27	59	14
95	120	98.2	25	59	16

Reaction conditions: Glycerol : Acetic acid = 1: 8 , CsPWA catalyst = 7 wt%.

Table 6. Reusability test of CsPWA catalyst on acetylation and esterification of glycerol.

Catalyst	Temp (°C)	Glycerol conversion (mol%)	Acetins Selectivity (mol%)		
			Mono	Di	Tri
Fresh	30	100	1	17	82
Recycle-1	30	100	2	23	75
Recycle-2	30	100	6	19	75
Recycle-3	30	100	4	20	76
Reaction conditions: Glycerol : Acetic anhydride = 1:3, CsPWA catalyst = 4 wt%, Temp : 30 °C, Time = 2 h					
Fresh	85	98.1	20	53	27
Recycle-1	85	98.2	22	54	24
Recycle-2	85	98.5	23	57	20
Recycle-3	85	98	25	59	16
Reaction conditions: Glycerol : Acetic acid = 1:8, CsPWA catalyst = 7 wt%, Temp : 85 °C, Time = 5 h					

Graphical abstract

