A GREEN AND EFFICIENT ROUTE TO SYNTHESIS OF DIACETALS WITH PENTAERYTHRITOL USING SOLID ACID CATALYSTS

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ABSTRACT

In the present endeavour, diacetals have been synthesized replacing the conventional catalyst with environment friendly solid acid catalysts. Two types of catalysts possessing similar elemental composition have been explored for their potential utility as solid acid catalyst. M(IV) Phosphotungstates which possess inherent acidity have been synthesized by sol-gel route, while in another case, acidity has been induced into M(IV) oxides, by process of anchoring and calcination, using 12-Tungstophosphoric acid (12-TPA) [M(IV) = Zr, Ti, Sn]. All the catalysts have been characterized for elemental analysis by ICP-AES, TGA, FTIR, SEM, EDX, XRD, surface area (BET method) and surface acidity (NH_3-TPD method). The diacetal synthesis involves acetalization of carbonyl compounds with pentaerythritol. The synthesis conditions have been optimized by varying parameters such as reaction time, catalyst amount and mole ratio of the reactants. The catalytic activity of synthesized materials has been compared and correlated with acid properties of the materials. It is observed that catalytic activity of M(IV) phosphotungstates > 12-TPA supported oxides. The highlighting feature is the good % yield of diacetals obtained and the possible regeneration and reuse of M(IV) phosphotungstates upto three catalytic runs without significant loss in % yields of diacetals.

Keywords: Diacetal Formation, Pentaerythritol, Phosphotungstates, Solid Acid Catalyst, Supported Catalysts.

I. INTRODUCTION

Tetravalent Metal Acid (TMA) salts are inorganic cation exchangers possessing general formula M(IV) $(HXO_4)_2.nH_2O$ [M(IV)=Zr, Ti, Sn, Ce, Th, etc. X=P, W, Mo, As, Sb, etc] where, H^+ of the structural hydroxyl groups are responsible for cation exchange, due to which TMA salts indicate good potential for application as solid acid catalysts, the acidic sites being bronsted acid sites in nature [1,2]. From our laboratory, TMA salts have been used as solid acid catalysts for esterification [3-5], cyclodehydration [6], ketalisation of ketones [7], hydration of nitriles [8], cyclodehyration of 1,n-diols [9] and for synthesis of coumarin derivatives [10]. When we used a mixed material of the class of Tetravalent Bimetallic acid (TBMA) salts such as Zirconium Titanium Phosphate (ZTP) [5] (containing two different cations and an anion) and a mixed material of the class of Tetravalent Metal Bianionic Acid (TMBA) salts (containing two different anions and a cation) such as Zr(IV) Phosphotungstate (ZrPW) [11] as a solid acid catalyst, for synthesis of esters and coumarin derivatives respectively, enhanced catalytic activity was observed compared to their single salt counter parts. Heteropoly acids (HPAs) have proved to be the alternative for traditional acid catalysts due to both strong acidity and appropriate redox properties. The major disadvantage of HPAs, as catalyst lies in their low thermal stability, low surface area (1-10m^2/g) and separation problems from reaction mixture. HPAs can be made eco-friendly, insoluble solid acids, with high thermal stability and high surface area by supporting them onto suitable supports. The support provides an opportunity for HPAs to be dispersed over a large surface area which increases catalytic activity [12]. Acetalization is an acid catalyzed reaction wherein acetals are derived from carbonyl compounds and alcohols, intensely used in organic synthesis to protect the carbonyl group of ketones and aldehydes, which is sometimes necessary in the manipulation of organic molecules with multiple functional groups [13]. Protection of the carbonyl groups of aldehydes and ketones can be accomplished by alcohols, diols or trioxanes. Besides, the interest of acetals as protecting groups, many of them have found direct applications as solvents in fragrance industries [14], cosmetics [15], food and beverage additives [16], pharmaceuticals [17], in the synthesis of enantiomerically pure compounds [18], in detergent and lacquer industries [15], and in polymer chemistry [19]. Acetals have been also used in motor oils, lubricating oils and hydraulic fluids, and as an invert-emulsion for drilling petroleum operations [20]. A number of acetalization procedures include the use of corrosive protic acids (HCl, H_2SO_4), Lewis acids ($ZnCl_2$, $FeCl_3$) [13], p-toluenesulphonic acid [21], camphorsulphonic acid [22], iodine [23], formic acid [24] and a series of cationic diphosphine Lewis acidic complexes of Pt(II), Pd(II), and Rh(III) etc [25]. However, acetalization procedures mentioned above, require expensive reagents, tedious work-up procedure and neutralization of the strongly acidic media leading to the production of harmful wastes. The use of solid acid catalyst eliminates the corrosive action of liquid acids. Currently, there is a global effort to replace the conventional homogeneous liquid acids by heterogeneous solid acids. A number of solid acid catalysts [26-41] have been reported for the acetalization reactions with advantages such as ease of work up as well as regeneration and reuse of catalyst, on the other hand with disadvantages such as leaching of active components, long reaction times, use of large amounts of catalyst and poor yields of diacetal. Therefore, the need for an ideal solid acid catalyst is on. Pentaerythritol (PET) is an alcohol with formula $C(CH_2OH)_4$ [2,2-bis (hydroxymethyl) propane-1,3-diol]. Pentaerythritol reacts with carbonyl compounds to give pentaerythritol acetals which are useful in many fields. They can be applied as plasticizers and vulcanizers of various polymeric materials, as raw materials for production of valuable resins and lacquers, as physiologically active substances [36], defoamers for washing solution containing anionic surfactant, in motor oils, lubricating oils and hydraulic fluids [20]. In the present endeavour, M(IV) Phosphotungstates [M(IV)PWs], mixed materials of the class of TMBA salts such as Zr(IV) Phosphotungstate (ZrPW), Ti(IV) Phosphotungstate (TiPW) and Sn(IV) Phosphotungstate (SnPW) possessing inherent acidity have been synthesized by sol-gel route. Looking to the potential utility of supported HPAs and for comparison of catalytic performance, we have supported 12-Tungstophosphoric acid (12-TPA) onto ZrO_2, TiO_2 and SnO_2 by process of anchoring and calcination, resulting in 12-TPA/ZrO_2, 12-TPA/TiO_2 and 12-TPA/SnO_2 which possess induced acidity and same components (i.e. Zr, Ti, Sn, P and W) as the TMBA salts. All synthesized materials have been characterized for elemental analysis by ICP-AES, TGA, FTIR, SEM, EDX, XRD, surface area (BET method) and surface acidity (NH_3-TPD method). The potential utility of these materials as solid acid catalysts has been explored by studying diacetal formation as a model reaction. A simple, efficient and environment friendly route is described for the acetalization of benzaldehyde, cyclohexanone, acetophenone and benzophenone with PET by varying parameters such as reaction time, catalyst amount and mole ratio of the reactants. The catalytic activity of synthesized materials has been compared and correlated with acid properties of the materials.

II. EXPERIMENTAL

2.1 Synthesis of M (IV) Phosphotungstates [M (IV) Pws]

M(IV)PWs were synthesized by sol-gel method, the main objective being to obtain a material with high ion exchange capacity (IEC)/protonating ability, varying several parameters such as mole ratio of reactants, temperature, mode of mixing (metal salt solution to anion salt solution or vice versa), *p*H and rate of mixing. Several sets of materials were prepared varying conditions in each case using IEC as the indicative tool. The optimized parameters for synthesis of ZrPW, TiPW and SnPW have been presented in SM - Tables 1 to 3 respectively.

2.1.1 Synthesis of ZRPW (At Optimized Condition)

An aqueous mixture of $NaH_2PO_4.2H_2O$ (0.1M, 50ml) and $Na_2WO_4.2H_2O$ (0.1M, 50ml) was added dropwise (flow rate 1 $ml{\cdot}min^{-1}$) to an aqueous solution of $ZrOCl_2.8H_2O$ (0.2M, 50ml) with continuous stirring for an hour at 70^0C. The gelatinous precipitates obtained was filtered, washed with double distilled water and dried at room temperature. The material was then broken down to the desired particle size (30-60 mesh) by grinding and sieving and acid treated by method reported earlier [4]. This material was used for all studies.

2.1.2 Synthesis Of Tipw (At Optimized Condition)

An aqueous mixture of $NaH_2PO_4.2H_2O$ (0.1M, 50ml) and $Na_2WO_4.2H_2O$ (0.1M, 50ml) was added dropwise (flow rate 1 $ml{\cdot}min^{-1}$) to a solution of $TiCl_4$ (0.2M, 50ml) (prepared in 10% W/V H_2SO_4 solution) with continuous stirring for an hour at room temperature. The gelatinous precipitates obtained are kept for ageing for 1h, then filtered and washed with double distilled water followed by drying at room temperature. The material was then broken down to the desired particle size (30-60 mesh) by grinding and sieving and acid treated by method reported earlier [4]. This material was used for all studies.

2.1.3 Synthesis of SNPW (At Optimized Condition)

An aqueous mixture of $NaH_2PO_4.2H_2O$ (0.1M, 50ml) and $Na_2WO_4.2H_2O$ (0.1M, 50ml) was added dropwise (flow rate 1 $ml{\cdot}min^{-1}$) to a solution of $SnCl_4$ (0.1M, 100ml) (prepared in 0.1M HCl) with continuous stirring for an hour at room temperature. The gelatinous precipitates obtained are kept for ageing for 3h, then filtered and washed with double distilled water followed by drying at room temperature. The material was then broken down to the desired particle size (30-60 mesh) by grinding and sieving and acid treated by method reported earlier [4]. This material was used for all studies.

2.2 Synthesis of 12-TPA Supported Oxides (12-TPA/Zro_2, 12-TPA/Tio_2, 12-TPA/Sno_2)

For preparation of ZrO_2, TiO_2 and SnO_2, aqueous solutions of $ZrOCl_2.8H_2O$ (0.3M, 100 ml), $TiCl_4$ (0.9M, 100 ml) and $SnCl_4.5H_2O$ (0.3M, 100 ml) were prepared to which liq. NH_3 (25%) was added dropwise with vigorous stirring. The pH of the solutions was adjusted to 9.5. In all the cases, white precipitates obtained were filtered and washed with double distilled water till removal of adhering ions and then dried at 120^oC for 3 h followed by calcination at 550^oC for 5h. For the preparation of 12-TPA supported catalysts, a series of aqueous solutions containing 10-30 wt % of 12-TPA per gram of precalcined oxides were used, and the mixture was stirred for 36 h. The excess water was removed at 70^oC under vacuum. The resulting solid was dried at 120^oC for 3h, followed by grinding to get a fine powder. In each case surface acidity was used as the indicative tool. The optimization of wt. % loading of 12-TPA onto oxides have been presented in SM – Table 4. Amongst the different wt. % of 12-TPA loaded, 20 wt. % loading of 12-TPA onto oxides gives maximum surface acidity. Thus, for all studies 20 wt.% 12-TPA/M(IV)Oxides have been used and abbreviated as 12-TPA/M(IV)Oxides-20, where M(IV) = Zr, Ti and Sn.

2.3 Catalyst Characterization

The ion exchange capacity (IEC)/protonating ability of M(IV)PWs (possessing inherent acidity) was determined by measurement of Na^+ IEC using column method reported earlier [42]. Chemical stability of all synthesized materials in various media such as acids (HCl, H_2SO_4 and HNO_3), bases (NaOH and KOH) and organic solvents (ethanol, benzene, acetone and acetic acid) was studied by taking 0.5 g of material in 50 ml of the particular medium and allowed to stand for 24 h. The change in colour, weight, solubility, etc. was observed. Elemental analysis was performed on ICP-AES spectrometer (Thermo Scientific iCAP 6000 series). FTIR spectra was recorded using KBr pellet on Shimadzu (Model 8400S). Thermal analysis (TGA) was carried out on a Shimadzu (Model TGA 50) thermal analyzer at a heating rate of 10 $^{\circ}C \cdot min^{-1}$ using an air as career gas. X-ray diffractogram (2θ = 10 - 80°) was obtained on X-ray diffractometer (Brucker AXS D8) with Cu-K_{α} radiation with nickel filter. SEM and EDX of the sample were scanned on Jeol JSM-5610-SLV scanning electron microscope. Surface area measurement (by BET method) was carried out on Micromeritics Gemini at -196^{o}C using nitrogen adsorption isotherms. Surface acidity was determined on Micromeritics Chemisorb 2720, by a temperature programmed desorption of ammonia. The synthesized materials were preheated at 150^{o}C, 200^{o}C and 700^{o}C. Ammonia was chemisorbed at 120^{o}C and then desorption was carried out upto 700^{o}C at a heating rate of 10^{o}C/min.

2.4 Catalytic Activity: Acetalization of Carbonyl Compounds with PET

In a typical reaction, a 100 mL round bottomed flask equipped with a Dean and Stark apparatus, attached to a reflux condenser was used and charged with carbonyl compound (5-20 mmol), PET (5-10 mmol), catalyst (0.15 - 0.35 g) and toluene as solvent (10 mL) in nitrogen atmosphere. The reactions were carried out varying several parameters such as reaction time, amount of catalyst, mole ratio of reactants etc. The progress of the reaction was monitored by TLC (20% of ethyl acetate in petroleum ether). After cooling, the catalyst was filtered off and washed with CH_2Cl_2. The crude product was isolated by distillation and purified through recrystallization in ethanol.

2.5. Regeneration of Catalyst

Regeneration of catalyst possessing inherent acidity [M(IV)PWs]

After separation of catalyst from reaction mixture by decantation, it is first refluxed in ethanol for 30 minutes to solubilise and remove adsorbed molecules, followed by drying at room temperature and acid treatment by method reported earlier [4]. This regeneration procedure was followed in subsequent recycle reaction for M(IV)PWs. Regeneration of catalyst possessing induced acidity [12-TPA/M(IV)Oxides-20]

After separation of catalyst from reaction mixture by decantation, it is first refluxed in ethanol for 30 minutes to solubilise and remove adsorbed molecules, followed by drying at 120^{o}C for 3 hrs. This regeneration procedure was followed in subsequent recycle reaction for 12-TPA/M(IV) oxides-20.

III. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

Elemental analysis performed by ICP-AES for all the synthesized materials have been presented in Table 1, which is well supported by EDX analysis for all the materials (Table 1, SM - Fig. 1-6).

Table 1 Elemental Analysis by ICP-AES and EDX

Materials	% by ICP-AES analysis			% by EDX analysis (atomic %)			
	M(IV)	P	W	M(IV)	P	W	O
ZrPW	Zr=26.87	5.67	25.37	Zr=60.79	18.53	20.67	-
TiPW	Ti=17.24	9.24	23.36	Ti=46.61	37.99	15.40	-
SnPW	Sn=41.21	4.67	16.47	Sn=59.33	23.31	17.37	-
12-TPA/ZrO_2-20	Zr=79.14	0.26	21.79	Zr=28.75	0.11	3.44	67.70
12-TPA/TiO_2-20	Ti=81.44	0.25	20.40	Ti=28.63	0.15	0.88	70.34
12-TPA/SnO_2-20	Sn=76.22	0.23	22.76	Sn=18.40	0.12	2.57	78.92

A study on the chemical stability of M(IV)PWs and 12-TPA/M(IV)Oxides-20 shows that these materials are stable in acid and organic solvent media, however not so stable in base medium. The maximum tolerable limits for all synthesized materials have been presented in Table 2.

Table 2 Chemical Stability Data of M (IV) PWS and 12-TPA/M (IV) Oxides-20.

Materials	Chemical media	Maximum tolerable limits
M(IV)PWs	Acids	18N H_2SO_4, 16N HNO_3, 11.3N HCl
	Bases	5 N NaOH, 5 N KOH
	Organic Solvents	Ethanol, Benzene, Toluene, Acetone and Acetic acid
12-TPA/ M(IV)Oxides-20	Acids	5N H_2SO_4, 16N HNO_3, 11.3N HCl
	Bases	Not Stable
	Organic Solvents	Ethanol, Benzene, Toluene, Acetone and Acetic acid

FTIR spectrum of M(IV)PWs (SM - Fig. 7) exhibits broad band in the region ~ 3400 cm^{-1} which is attributed to asymmetric and symmetric –OH stretching in all the samples. A medium band around ~ 1635 cm^{-1} is attributed to P-O-H bending, indicating presence of structural –OH protons contained in all samples. A band in the region ~ 1083 cm^{-1} is attributed to the presence of P-O stretching in all samples. FTIR spectrum of 12-TPA/ZrO_2-20, 12-TPA/TiO_2-20 and 12-TPA/SnO_2-20 (SM - Fig. 8) exhibits peaks at ~3450 cm^{-1}, ~1635 cm^{-1}, ~1083 cm^{-1}, ~987 cm^{-1}, which corresponds to asymmetric and symmetric –OH stretching, P-O-H bending, P-O stretching and W=O stretching respectively. TGA thermogram (SM - Fig. 9) shows weight loss in the temperature range of 40 – 150^0C for ZrPW, TiPW and SnPW to be 19.78%, 21.02% and 15.26% respectively, which corresponds to loss of surface moisture and hydrated water. Weight loss in the temperature range of 150^0C - 650^0C for ZrPW, TiPW and SnPW is found to be 7.25%, 4.28% and 6.04% respectively, which is probably due to the condensation of structural hydroxyl groups. TGA thermograms of 12-TPA/ZrO_2-20, 12-TPA/TiO_2-20 and 12-TPA/SnO_2-20 (SM - Fig. 10) exhibit 0.9%, 0.4% and 1.4% weight loss in the temperature range of 30 – 150^0C which corresponds to the loss of surface moisture. Thereafter in the region 200-600°C there is a negligible weight loss which indicates fairly stable nature of the materials. SEM images (SM - Fig. 11-19) of all the synthesized materials exhibit irregular morphology. Absence of sharp peaks in X-ray diffractogram of M(IV)PWs (SM - Fig. 20) reveals the amorphous nature of M(IV)PWs. X-ray diffractogram of pure 12-TPA has been presented in SM – Fig. 21. X-ray diffractogram of 12-TPA/ZrO_2-20 (SM - Fig. 22) shows intense and well defined characteristic diffraction peaks at 2θ values of 31.4, 35.2, 50.1, and 59.9 (JCPDS data card no. 17-923). X-ray diffractogram pattern of 12-TPA/TiO_2-20 (SM - Fig. 23) shows characteristic diffraction peaks at 2θ values of 25.2, 37.8, 48.0, 53.8, 55.0, 62.1 and 75.0 correspond to the crystal planes of (101), (004), (200), (105), (211), (213) and (215) respectively, indicates formation of anatase TiO_2 (JCPDS data card no. 21-1272). X-ray diffractogram pattern of 12-TPA/SnO_2-20 (SM - Fig. 24) shows characteristic diffraction peaks at 2θ values of 26.5, 33.8 and 51.8 correspond to the crystal planes of (110), (101) and (211) respectively, indicates formation tetragonal SnO_2 (JCPDS data card no. 41-1445). Surface area values determined (by BET method) for all materials have been presented in Table 3.

Table 3 Surface Area, Surface Acidity and IEC Values for M (IV) PWS and 12-Tpa/M (IV) Oxides-20

Materials	Surface Area (BET method) (m^2/g)	Surface acidity (NH_3-TPD method)		IEC (meq./g)
		Preheating Temperature (°C)	Acidity (mmol/g)	
ZrPW	81.0	150	9.34	0.98
		200	6.05	0.76
		700	3.90	0.49
TiPW	86.5	150	11.05	2.97
		200	11.02	2.39
		700	8.28	1.07
SnPW	171.0	150	10.28	2.00
		200	7.54	1.64
		700	4.50	0.73
12-TPA/ ZrO_2-20	33.9	150	1.07	-
		200	0.89	-
		700	0.17	-
12-TPA/ TiO_2-20	60.5	150	2.03	-
		200	1.68	-
		700	0.27	-
12-TPA/ SnO_2-20	139.5	150	1.42	-
		200	1.11	-
		700	0.22	-

3.2 Evaluation of Acid Property

Surface acidity for all the materials was determined by NH_3-TPD at 150°C, 200°C and 700°C preheating temperatures (Fig. 1-6, Table 3). M(IV)PWs exhibit broad desorption peaks compared to 12-TPA/M(IV)Oxides-20, which is in accordance with the amorphous and crystalline nature of the materials respectively [10]. As already discussed earlier in the text, acidity in the M(IV)PWs is due to the presence of structural hydroxyl protons, H^+ of the – OH being the Bronsted acid sites. Further, surface acidity values of M(IV)PWs depend on the size and charge of the cation. Smaller size and higher charge of the cation indicates greater tendency to release a proton, i.e. H^+ of the –OH groups present in M(IV)PWs. In the present study Zr^{4+}, Ti^{4+} and Sn^{4+}, all metal ions being tetravalent as well as bearing common anion PO_4^{3-} and WO_4^{2-}, size of the cation (Zr^{4+}-0.86 Å, Ti^{4+}-0.74 Å, Sn^{4+}-0.83 Å) seems to play a dominant role. Thus the acidity in the materials follows the order

TiPW > SnPW > ZrPW. Decrease in surface acidity for M(IV)PWs with increasing preheating temperatures could be attributed to condensation of structural hydroxyl groups as discussed above in thermal behavior of these materials. This is well supported by IEC values, which reflect on the protonating ability and thus the acidity of the materials, which also decreases with increasing calcination/preheating temperature (Table 3).

In case of 12-TPA supported catalysts, anchoring of 12-TPA onto the various oxides induces acidity into the oxides. A decrease in surface acidity for 12-TPA/M(IV)Oxides-20 with increasing preheating temperatures could be attributed to decomposition of 12-TPA into WO_3 crystallites [43].

3.2. Catalytic Activity: Acetalization of Carbonyl Compounds with PET

Acetal formation is a reversible reaction, which proceeds by a two-step mechanism [44]. Scheme 1 shows the mechanism of the acetal formation of carbonyl compounds using solid acid catalyst. In this, carbonyl compound is first protonated by the Brønsted acid sites (H^+ ions of the catalyst) to produce the intermediate which then combine with alcohol to form the hemiacetal liberating a significant amount of heat [45]. Protonation of this intermediate leads to subsequent dehydration followed by the formation of the diacetal [45]. Reaction conditions were optimized using ZrPW and 12-TPA/ZrO_2-20 as solid acid catalyst for preparation of diacetal from benzaldehyde and ketones (cyclohexanone and acetophenone/benzophenone) with PET by varying parameters such as reaction time, catalyst amount and mole ratio of the reactants. The optimized reaction conditions have been presented in SM – Fig. 25-27.

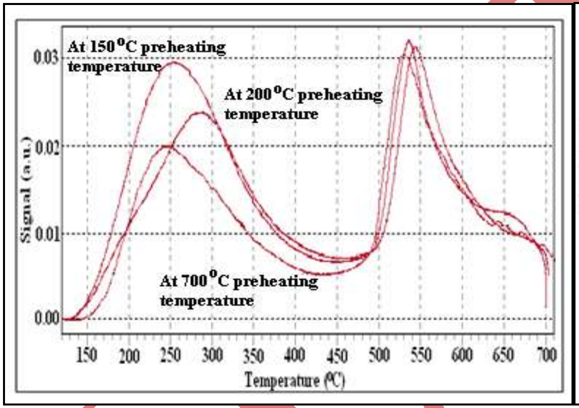


Fig. 1 NH_3-TPD Patterns of ZRPW

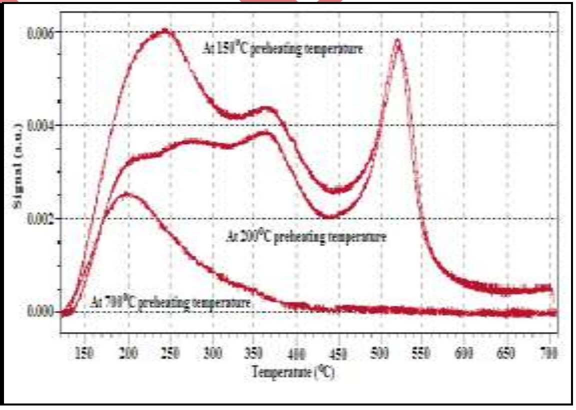


Fig. 2 NH_3-TPD Patterns of 12-TPA/Zro_2-20

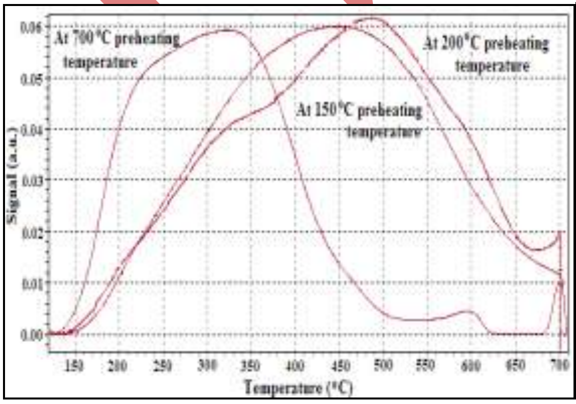


Fig. 3 NH_3-TPD patterns of TiPW

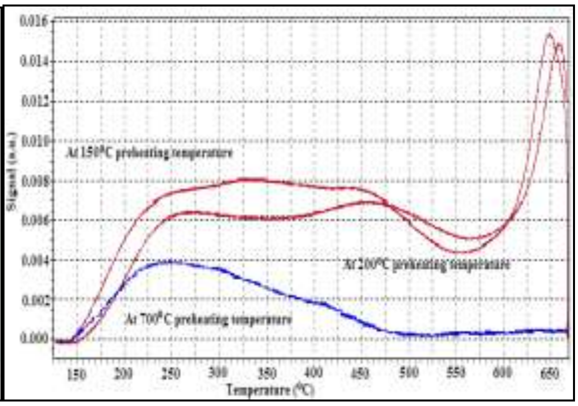


Fig. 4 NH_3-TPD patterns of 12-TPA/TiO_2-20

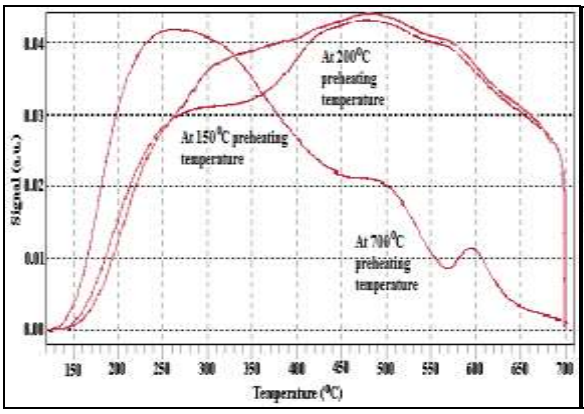


Fig. 5 NH_3-TPD patterns of SnPW

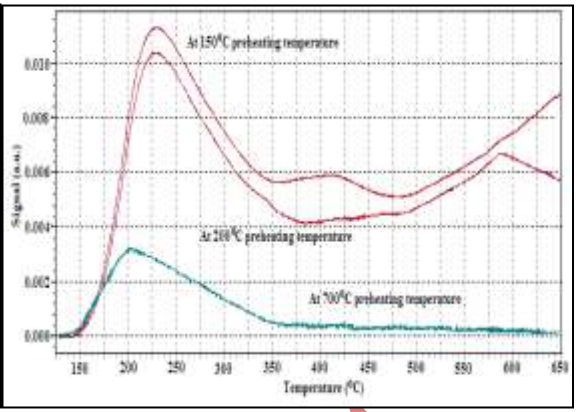
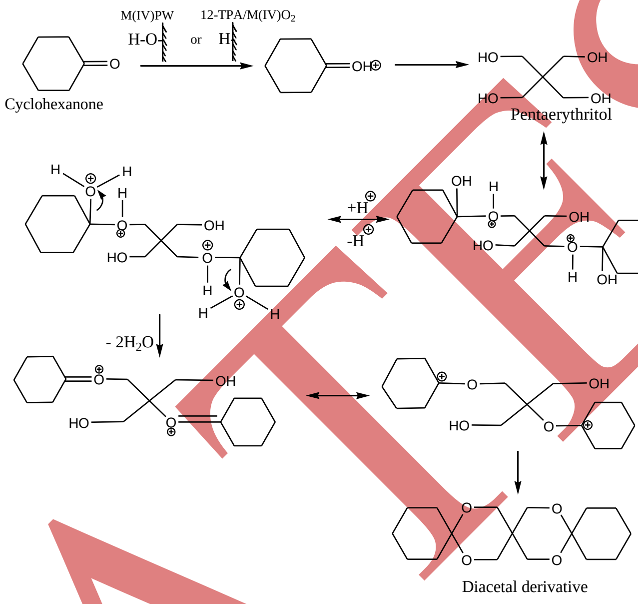


Fig. 6 NH_3-TPD patterns of 12-TPA/SnO_2-20



Scheme 1. Mechanism for Acetalization of Cyclohexanone with Pentaerythritol

The effect of reaction time on the product yield of diacetal formed in all cases was studied at refluxing temperature (110°C) using toluene as solvent with 1:1 mole ratio of PET: benzaldehyde/ketones and 0.15g of catalyst (ZrPW). The reaction reached equilibrium within 4 h (benzaldehyde), 6 h (cyclohexanone) and 8 h (acetophenone and benzophenone). With increasing catalyst amount, which was varied from 0.15g to 0.35 g, % yield increases probably due to increase in the number of acid sites. With reference to mechanism described in scheme 1, step 1 is protonation whereas step 3 is formation of hemiacetal followed by deprotonation. For deprotonation to occur an optimum acidity is required or else if acidity is higher, then the further reaction to form the acetal is inhibited or reaction slows down and thus, the excess acid amount may promote the occurrence of the reverse reaction. Therefore in all cases, optimum catalyst amount was taken as 0.3 g. Acetal formation is a reversible reaction, the reverse reaction being acetal hydrolysis with same mechanism going in the backward direction to give alcohol and carbonyl compound. Considering thermodynamics of the acetal reaction, equilibrium constants of the acetal reaction are low [46]. As in any equilibrium reaction, the reaction may be driven to the product side (forward direction) by controlling the concentration of one of the reactants or removing water molecule formed continuously to avoid the reverse reaction (Le Chatlier's Principle). In the present study, in order to obtain higher yields of acetal, Le Chatlier's Principle has been followed. A Dean and Stark apparatus has been used for removal of water as binary azeotrope using toluene as solvent. Further, mole ratio of the reactants PET to carbonyl compound has been varied taking one of the reactants in excess. Thus, precautions are taken to avoid the backward reaction to arrive at maximum yields. The presented % yields are isolated yields. The influence of mole ratio of reactants on product yield was studied using 0.3 g of catalyst at the refluxing temperature at optimized reaction time. The mole ratio PET: benzaldehyde/ketones were varied from 1:1 to1:5 and 2:1. It is observed that when the mole ratio increased from 1:1 to 1:4, the product yield increased which is attributed to an increase in chemisorption of benzaldehyde/ketones on the Brønsted acid sites which leads to the polarization of the carbonyl bond where PET makes a nucleophilic attack. Further, for mole ratio 2:1, yield decreased which may be due to the dilution of benzaldehyde/ketones. In the present study, 1:4 mole ratio of PET: benzaldehyde/ketones were used. Diacetal of PET was observed as the single product over all mole ratios of PET and benzaldehyde/ketones. At optimized condition, acetalization of benzaldehyde, cyclohexanone, acetophenone and benzophenone with PET was performed using using all synthesized materials (Table 4). In all the reactions, acetal derivative of benzaldehyde (dibenzal acetal) was obtained with high % yield. This is probably due to the fact that aldehyde undergoes nucleophilic addition more readily than ketones. Compared to benzophenone and acetophenone, benzophenone being more bulky than acetophenone, shows the lowest reactivity and thus low yields. The rate determining step of acetalization is the formation of a cation from the protonated hemiacetal. Hence, the bulkiness of hemiacetals might prevent the attack of the alcohol on the carbonyl carbon atom there by effecting a change in the rate-determining step. Further, the electron withdrawing power of phenyl group (1 for acetophenone and 2 for benzophenone) in these compounds reduces the easy release of the pair of electron on the carbonyl carbon during the reaction. However, cyclohexanone is more reactive towards nucleophiles than both acetophenone and Benzophenone [44]. Therefore the reactivity of the ketones decrease in the order cyclohexanone > acetophenone > benzophenone. Regeneration and reusability for all the catalysts under study was conducted and results presented in Table 4. After each catalytic run, all the catalysts turn dark brown, probably due to the fact that reactant molecules get adsorbed on the surface of the catalysts. In case of M(IV)PWs, after each subsequent run the catalysts were regenerated as described earlier in experimental section. It is observed that, on regeneration M(IV)PWs exhibit only a marginal decrease in yields upto three catalytic runs. However, when catalysts are reused, the decrease in

Table 4. Synthesis of Diacetals at Optimized Condition Using M (IV) Pws and 12-Tpa/M (IV) Oxides-20.

Reactants	% Yield							
	Catalytic run	ZrPW	TiPW	SnPW	Catalytic run	12-TPA/ ZrO_2	12-TPA/ TiO_2	12-TPA/ SnO_2
PET: Benzaldehyde	1(F)	77.87	81.45	79.09	1(F)	69.32	76.88	72.53
	2(Rg)	76.11	80.14	77.96	2(Ru)	58.41	62.00	61.00
	2(Ru)	63.47	69.00	65.32				
	3(Rg)	74.44	77.68	76.00	3(Ru)	44.00	50.06	48.10
	3(Ru)	50.00	59.22	53.98				
PET: Cyclohexanone	1(F)	74.41	79.66	76.55	1(F)	64.00	70.80	67.62
	2(Rg)	73.00	78.02	75.48	2(Ru)	51.36	61.37	54.69
	3(Rg)	71.16	77.69	73.94	3(Ru)	40.87	49.79	41.99
PET: Acetophenone	1(F)	65.28	70.12	68.99	1(F)	60.82	64.81	63.49
	2(Rg)	63.56	68.56	67.19	2(Ru)	48.56	51.00	50.08
	3(Rg)	61.89	67.35	66.03	3(Ru)	32.40	40.49	37.00
PET: Benzophenone	1(F)	54.19	62.00	57.35	1(F)	51.24	53.55	52.94
	2(Rg)	53.48	60.81	56.47	2(Ru)	39.78	41.30	40.06
	3(Rg)	50.89	59.02	55.11	3(Ru)	30.33	29.89	30.36

(Mole ratio of PET: aldehyde/ketones -1:4; Catalysts amount -0.3g; Reaction temperature -110°C; Solvent: Toluene; Reaction Time: PET:Benzaldehyde -4h, PET:Cyclohexanone -6h, PET:Acetophenone/Benzophenone -8h; F: Fresh; Rg: Regenerated; Ru: Reused)

% yields are much higher which is probably due to the deactivation of catalysts due to substrate molecules getting adsorbed on surface or also entering interstices of the catalyst material [10]. Table 5 provides atomic wt. % of various components (Zr, P, W and O) for both fresh and spent catalysts in case of synthesis of dibenzal aceatal (SM - Fig. 28 and 29). Decrease in atomic wt. % of Zr in ZrPW and Zr and W in 12-TPA/ZrO$_2$-20 indicates leaching of ions which could be the probable reason for decrease in % yields of diacetals.

Table 5. Elemental Analysis By Edx For Both Fresh And Spent Zrpw And 12-Tpa/Zro$_2$-20 In The Synthesis Of Diacetal Of Benzaldehyde.

Reactants	Materials	% by EDX analysis			
		Zr	P	W	O
PET: Benzaldehyde	ZrPW (Fresh)	60.79	18.53	20.67	-
	ZrPW (Spent)	53.55	25.64	20.80	-
	12-TPA/ZrO$_2$-20 (Fresh)	28.75	0.11	3.44	67.70
	12-TPA/ZrO$_2$-20 (Spent)	14.28	0.83	1.97	82.92

(Mole ratio of PET:Benzaldehyde -1:4; Catalysts amount - 0.3 g; Reaction temperature - 110 °C; Solvent: Toluene; Reaction Time- 4h)

In the present study, amongst M(IV)PWs performance of catalyst is found to be TiPW > SnPW > ZrPW whereas, amongst 12-TPA/M(IV)Oxides-20, the order is found to be 12-TPA/TiO$_2$-20 > 12-TPA/SnO$_2$-20 > 12-TPA/ZrO$_2$-20 which could be attributed to increased surface acidity of these materials (Table 3). Comparing inherent and induced catalysts, with reference to performance of catalysts, M(IV)PWs scores over 12-TPA/M(IV)Oxides-20 in terms of % yields of diacetal formed as well as reusability of catalysts. Comparing catalyst efficiency/performance of M(IV)PWs and 12-TPA/M(IV)Oxides-20 with M(IV) phosphates of the class of TMA salts [M(IV) = Ce and Th] [47] (Table 6) it is observed that % yields range from low to marginal to comparative yields. TiPW, works as the most efficient catalyst giving excellent yields for all diacetals especially, 81.45% in case of synthesis of acetal derivative of benzaldehyde.

TABLE 6. Comparison of % yield of acetal derivative of benzaldehyde using TMA salts, TMBA salts [M (IV) PWs] and 12-TPA/M (IV) Oxides-20.

Catalyst Used	Substrates (mole ratio)	% yield
CP [47]	PET:Benzaldehyde (1:4)	74.51
TP [47]		68.13
TiPW*		81.45
12-TPA/TiO$_2$-20*		76.88

*(*Present work; Catalyst amount:0.30g; Reaction temperature: 110^{o}C; Reaction time: 4h)*

3.3 Characterization of the Products

The isolated products were characterized by FTIR, ^{1}H-NMR spectroscopy and melting point.

Acetal derivative of benzaldehyde: λ_{max}/cm^{-1} 2910 (CH), 2862 (CH), 1600 (C=C Aromatic), 1460 (C=C Aromatic), 1390 (CH), 1050 (C-O-C), 805 (C_6H_5), 710 (C_6H_5). δH (100 MHz; $CDCl_3$; Me_4Si), 3.51 (6H, m, $H_{ax,}$ H_{eq}), 4.70 (2H, d, J 11.7, 2 H_{eq}), 5.42 (2H, s, 2 × PhCH), 7.10–7.60 (10H, m, 2 × Ph). Melting Point: 155°C.

Acetal derivative of cyclohexanone: λ_{max}/cm^{-1} 2960 (CH), 2870 (CH), 1140 (C-O-C). δH H(100 MHz; $CDCl_3$; Me_4Si) 1.4-1.7(20H, m, 2 × $(CH_2)_5$), 3-3.5 (8H, m, $(CH_2O)_4$). Melting Point: 116°C.

Acetal derivative of acetophenone: λ_{max}/cm^{-1} 2970 (CH), 2890 (CH), 1600 (C=C Aromatic), 1468 (C=C Aromatic), 1365 (CH), 1150 (C-O-C), 790 (C_6H_5), 700 (C_6H_5). δH (100 MHz; $CDCl_3$; Me_4Si) 1.51 (6H, s, 2 × Me), 3.15 (2H, dd, J 11.1, 2.4, 2 × H_{eq}), 3.30 (2H, d, J 11.1, 2 × H_{ax}), 3.60 (2H, d, J 11.7, 2 × H_{ax}), 4.48 (2H, dd, J 11.7, 2 × H_{eq}), 7.25-7.70 (10H, m, 2 × Ph). Melting Point: 146°C.

Acetal derivative of benzophenone: λ_{max}/cm^{-1} 2975 (CH), 2880 (CH), 1615 (C=C Aromatic), 1480 (C=C Aromatic), 1390 (CH), 1050 (C-O-C), 755 (C_6H_5), 770 (C_6H_5). δH (100 MHz; $CDCl_3$; Me_4Si) 3.6 (8H, s, $(CH_2O)_4$), 7.14–7.32 (20H, m, 2 × $(Ph)_2$). Melting Point: 160°C (Ethanol).

IV. CONCLUSIONS

The work outlined herein reveals the promising use of both the types of solid acid catalysts in acetal formation with advantages of high selectivity of the products formed with no catalyst contamination, operational simplicity, mild reaction conditions, no acid waste generation, and regeneration and reuse of catalysts. Amongst the two types of catalysts synthesized possessing same elemental composition, *(i)* M(IV)PWs (possessing inherent acidity) scores over *(ii)* 12-TPA/M(IV)Oxides-20 (possessing induced acidity) in terms of catalyst performance in the synthesis of diacetals. Finally, TiPW exhibiting the best performance has potential for commercialization.

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REFERENCES

[1] A. Bhaumik, S. Inagaki, Mesoporous Titanium Phosphate Molecular Sieves with Ion-Exchange Capacity, *J. Am. Chem. Soc*, *123*, 2001, 691-696.

[2] R. C. T. Slade, J. A. Knowels, D. J. Jones, J. Roziere, The isomorphous acid salts α-$Zr(HPO_4)_2 \cdot H_2O$, α-$Ti(HPO_4)_2 \cdot H_2O$ and α-$Zr(HAsO_4)_2 \cdot H_2O$: Comparative thermochemistry and vibrational spectroscopy, *Solid State Ionics*, *96*, 1997, 9-19.

[3] R. Joshi, H. Patel, U.Chudasama, Synthesis of monoester and diesters using eco-friendly solid acid catalysts M(IV) tungstates and phosphates, *Ind. J. Chem. Technol*, *15*, 2008, 238-243.

[4] H. Patel, R. Joshi, U. Chudasama, Use of zirconium(IV) phosphate as a solid acid catalyst in some esterification reactions, *Ind. J. Chem*, *47(A)*, 2008, 348-352.

[5] R. Thakkar, U. Chudasama, Synthesis of mono and diesters using eco-friendly solid acid catalyst - zirconium titanium phosphate, *Green Chemistry Letters and Reviews*, 2(1), 2009, 1-9.

[6] S. Patel, U. Chudasama, P. Ganeshpure, Cyclodehydration of 1,4-butanediol catalyzed by metal (IV) phosphates, *React. Kinet. Catal*, *76*, 2002, 317-325.

[7] S. Patel, U. Chudasama, P. Ganeshpure, Ketalization of Ketones with diols catalyzed by Metal (IV) phosphates as solid acid catalysts, *J. Mol. Catal. A: Chem*, *194*, 2003, 267-271.

[8] S. Patel, U. Chudasama, P. Ganeshpure, Tetravalent metal acid salts: Solid acid catalysts for hydration of nitriles to amindes, *Indian J. Chem. 42B*, 2003, 1168-1169.

[9] S. Patel, U. Chudasama, P. Ganeshpure, Metal (IV) Phosphates as solid acid catalysts for selective cyclodehydration of 1,N - diols, *Green Chem. 3*, 2001, 143-145.

[10] R. Joshi, U. Chudasama, Synthesis of coumarins via the pechmann condensation using inorganic ion exchangers as solid acid catalysts, *J. Sci. Ind. Res. 67*, 2008, 1092-1097.

[11] S. Ghodke, U. Chudasama, Solvent Free Synthesis of Coumarins Using Environment Friendly Solid Acid Catalysts, *Appl. Catal. A: Gen*, *453*, 2013, 219-226.

[12] A. E. R. S. Khder, Preparation, characterization and catalytic activity of tin oxide-supported 12-tungstophosphoric acid as a solid catalyst, *Appl. Catal. A: Gen. 343(1-2)*, 2008, 109-116.

[13] T. W.Greene, *Protective Groups in Organic Synthesis*, Wiley, New York, 1981.

[14] M. J. Climent, A. Velty, A. Corma, Design of a solid catalyst for the synthesis of a molecule with blossom orange scent, *Green Chem. 4*, 2002, 565-569.

[15] K. Bauer, D. Garbe, H. Surburg, *Common Fragrances and Flavour Materials*, IInd Ed, VCH: New York, 1990.

[16] S. V. Ley, H. W. M. Priepke, Eintopfsynthese einer trisaccharideinheit des gemeinen polysaccharid-antigens von *Streptococci* der Gruppe B unter verwendung cyclohexan-1,2-diacetal(CDA)-geschützter rhamnoside, *Angew. Chem. 106*, 1994, 2412-2414.

[17] K. Bruns, J. Conard, A. Steigel, Stereochemistry of cyclic compounds-I: Synthesis and conhgurational assignment of diawereomeric 2,4-dioxaspir[5.5]undec-8-enes, *Tetrahed. 35*, 1979, 2523-2530.

[18] M. K. Cheung, N. L. Douglas, B. Hinzen, S. V. Ley, X. Pannecoucke, One-pot synthesis of tetra- and pentasaccharides from monomeric building blocks using the principles of orthogonality and reactivity tuning, *Synlett. 3*, 1997, 257-260.

[19] A. J. Elliot, *1,3-Dioxalane Polymers in Comprehensive Heterocyclic Polymers*. Pergamon Press: Oxaford, UK, 1984.

[20] A. O. Barros, A. T. Faisca, E. R. Latcher, R. S. V. Nascimento, R. A. S. Gil, Acetalization of hexanal with 2-ethyl hexanol catalyzed by solid acids, *J. Braz. Chem. Soc. 22(2)*, 2011, 359-363.

[21] C. A. McKinzie, J. H. Stocker, Preparation of ketals. A reaction mechanism, *J. Org. Chem. 20*, 1955, 1695-1701.

[22] F. P. Boulineau, A. Wei, Stereoselective synthesis of [^{13}C] methyl 2-[^{15}N] amino-2-deoxy-β-D-glucopyranoside derivatives, *Carbohydrate Res. 334*, 2001, 271-279.

[23] K. P. R. Kartha, Iodine, a novel catalyst in carbohydrate reactions I. o-isopropylidination of carbohydrates, *Tetra. Lett. 27*, 1986, 3415-3416.

[24] F. M. Winnik, J. P. Carver, J. J. Krepinsky, Syntheses of model oligosaccharides of biological significance. Synthesis of a tetramannoside and of two lyxose-containing trisaccharides, *J. Org. Chem. 47*, 1982, 2701-2707.

[25] M. Cataldo, F. Neiddu, R. Gavagnin, F. Pinna, G. Strukul, Hydroxy complexes of palladium (II) and platinum (II) as catalysts for the acetalization of aldehydes and ketones, *J. Mol. Catal. A: Chem.*, *142*, 1999, 305-316.

[26] C. H. Lin, S. D. Lin, Y. H. Yang, T. P. Lin, The synthesis and hydrolysis of dimethyl acetals catalyzed by sulfated metal oxides. An efficient method for protecting carbonyl groups, *Catal. Lett. 73 (2-4)*, 2001, 121-125.

[27] J. Tateiwa, H. Hiriuchi, S. Uemura, Ce^{3+}-Exchanged montmorillonite (Ce^{3+}-Mont) as a useful substrate-selective acetalization catalyst, *J. Org. Chem. 60*, 1995, 4039-4043.

[28] R. Ballini, G. Bosica, B. Frullanti, R. Maggi, G. Sartori, F.Schroer, 1,3-Dioxolanes from carbonyl compounds over zeolite HSZ-360 as a reusable, heterogeneous catalyst, *Tetrahedron Lett. 39*, 1998, 1615-1618.

[29] F. Algarre, A. Corma, H. Garcia, J.Primo, Acid zeolites as catalysts in organic reactions. Highly selective condensation of 2-alkylfurans with carbonylic compounds, *Appl. Catal. A: Gen. 128*, 1995, 119-126.

[30] M. Iwamoto, Y. Tanaka, N. Sawamura, S. Namba, Remarkable effect of pore size on the catalytic activity of mesoporous silica for the acetalization of cyclohexanone with methanol, *J. Am. Chem. Soc. 125 (43)*, 2003, 13032-13033.

[31] M. J. Climent, A. Corma, S. Iborra, M. C. Navarro, J. Primo, Use of mesoporous MCM-41 aluminosilicates as catalysts in the production of fine chemicals: preparation of dimethylacetals, *J. Catal. 161*, 1996, 783-789.

[32] Y. Tanaka, N. Sawamura, M. Iwamoto, Highly effective acetalization of aldehydes and ketones with methanol on siliceous mesoporous material, *Tetrahedron Lett. 39*, 1998, 9457-9460.

[33] B. F. Mirjalili, A. M. Zolfigol, C. A. Bamoniri, A. Hazar, $Al(HSO_4)_3$ as an efficient catalyst for acetalization of carbonyl compounds under heterogeneous or solvent-free conditions, *J. Braz. Chem. Soc. 16*, 2005, 877-880.

[34] E. P. Mayoral, R. M. Martin-Aranda, A. J. Lopez-Peinado, P. Ballestreos, A. Zukla, J. Cejka, Green synthesis of acetals/ketals: efficient solvent-free process for the carbonyl/hydroxyl group protection catalyzed by SBA-15 materials, *Top. Catal. 52,*2009,148-152.

[35] C. C. Silveria, S. R. Mendes, F. I. Ziembowiscz, E. J. Lenardao, G. Perin, The use of anhydrous $CeCl_3$ as a recyclable and selective catalyst for the acetalization of aldehydes and ketones, *J. Braz. Chem. Soc. 21*, 2010, 371-374.

[36] V. Kannan, K. Sreekumar, A. Gil, M. A. Vicente, Acetalation of pentaerithritol catalyzed by an Al-pillared saponite, *Catal. Lett. 141*, 2011, 1118-1122.

[37] B. R. Jermy, A. Pandurangan, Efficient synthesis of diacetal of pentaerythritol under microwave irradiation using heteropoly acid $H_3PW_{12}O_{40}$, *Cata. Comm, 7*, 2006, 921-925.

[38] H. R. Shaterian, K. Azizi, N. Fahimi, Protection of Carbonyl Compounds as Diacetals Using P_2O_5/SiO_2 and P_2O_5/Al_2O_3 as Catalysts, *Chem. Sci. Trans. 1(1)*, 2012, 85-90.

[39] H R Shaterian, F. Rigi, Acetalization of carbonyl compounds as pentaerythritol diacetals and diketals in the presence of cellulose sulfuric acid as an efficient, biodegradable and reusable catalyst, *Chin. J Chem. 30(3)*, 2012, 695-698.

[40] Y. Wang, X. Gong, Z. Wang, L. Dai, SO_3H-functionalized ionic liquids as efficient and recyclable catalysts for the synthesis of pentaerythritol diacetals and diketals, *J. Mol. Cata. A: Chem. 322(1-2)*, 2010 7-16.

[41] Y. Y. Wang, Y. N. Xu, Z. Z. Wang, L. Y. Dai, A new approach to the synthesis of diacetals (diketals) pentaerythritol catalyzed by SO_3H-functionalized ionic liquids, *Chin. Chem. Lett. 21(5)*, 2010, 524-528.

[42] P. Patel, U. Chudasama, Synthesis and characterization of a novel hybrid cation exchange material and its application in metal ion separations, *Ion Exch. Lett. 4*, 2011, 7-15.

[43] N. G. Waghmare, P. Kasinathan, A. Amrute, N. Lucas, S. B. Halligudi, Titania supported silicotungstic acid: An efficient solid acid catalyst for veratrole acylation, *Cata. Commu, 9*, 2008, 2026-2029.

[44] B. Thomas, P. Sreedharan, S. Sugunan, Synthesis of dimethyl acetal of ketones: design of solid acid catalysts for one-pot acetalization reaction, *Micro. Meso. Mater. 80*, 2005, 65-72.

[45] I. Agirre, V. L. Barrio, B. Güemez, J. F. Cambra, P. L. Arias, Catalytic reactive distillation process development for 1,1 diethoxy butane production from renewable sources, *Biores. Technol. 102*, 2011, 1289-1297.

[46] P. V. Rui, C. S. M. Pereira, V. M. T. M. Silva, J. M. Loureiro, A. E. Rodrigues, Glycerol Valorization as Biofuel: Thermodynamic and Kinetic Study of the Acetalization of Glycerol with Acetaldehyde, *Ind. Eng. Chem. Res*, *52(4)*, 2013, 1538-1547.

[47] T. Parangi, U. Chudasama, Acetalization of carbonyl compounds with pentaerythritol catalyzed by metal (IV) phosphates as solid acid catalysts, *Ind. Eng. Chem. Res.* 52*(26)*, 2013, 8969-8977.

[48]