An Alternate Green Route to Synthesis of Mono and Diesters using Solid Acid Catalysts

Ghodke Shrinivas and Chudasama Uma*
Applied Chemistry Department, Faculty of Technology and Engineering, The M. S. University of Baroda, Vadodara, 390 001, Gujarat, INDIA

Abstract

The conventional catalysts used in esterification reactions are liquid acids that are not environment friendly. Keeping with global trends, in the present endeavour, an effort has been made to replace the conventional homogeneous liquid acid catalysts by heterogeneous solid acid catalysts. M(IV) Phosphotungstates [M(IV)= Zr, Ti and Sn] which possess inherent acidity have been synthesized by sol-gel route whereas, 12-Tungstophosphoric acid (12-TPA) has been supported onto ZrO_2, TiO_2 and SnO_2 resulting in 12-TPA/ZrO_2, 12-TPA/TiO_2 and 12-TPA/SnO_2 which possesses induced acidity have been synthesized by process of anchoring and calcination. All the catalysts have been characterized for elemental analysis by ICP-AES, TGA, FTIR, SEM, EDX, XRD, surface area (by BET method) and surface acidity (by NH_3-TPD method). The potential utility of these materials as solid acid catalysts have been explored by studying esterification as a model reaction wherein mono and diesters have been synthesized. The catalytic activity of synthesized materials has been compared and correlated with acid properties of the materials.

Keywords: Phosphotungstate, solid acid catalyst, esterification, supported catalysts.

Introduction

Esterification is an industrially important reaction for synthesis of plasticizers, perfumes, fragrance in cosmetics, flavors in food, diluents in paints and coatings and intermediates in drugs, dye stuffs, and fine chemicals[1]. The conventional catalyst used in esterification reactions is sulfuric acid, methanesulfonic acid, or p-toluenesulfonic acid that are cited as potential environmentally hazardous chemicals, that pose problems such as difficulty in handling, causing an acidic waste water, difficulty of catalyst recovery, etc.[2,3]. The corrosive action of liquid acids can be reduced by using solid acid catalyst. Currently, there is a global effort to replace the conventional homogeneous liquid acids by heterogeneous solid acids.

Several solid acid catalysts[4-11] have been reported for esterification reactions with advantages such as ease of work up as well as regeneration and reuse of catalyst, however with disadvantages such as leaching of active components, long reaction times, use of large amounts of catalyst, poor yields of ester formed, etc. Thus, the need for an ideal solid acid catalyst is on.

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[12,13].

TMA salts have been used as solid acid catalysts for esterification[14-16], cyclodehydration[17], ketalisation of ketones[18], hydration of nitriles[19], cyclodehyration of 1,n-diols[20] and for synthesis of coumarin derivatives[21].

When we used a mixed material of the class of Tetravalent Bimetallic acid (TBMA) salts such as Zirconium Titanium Phosphate (ZTP)[16] 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)[22] 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[23].

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 esterification as a model reaction wherein monoesters such as ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA), benzyl acetate (BzA) and diesters such as diethyl malonate (DEM), diethyl succinate (DES), dioctyl phthalate (DOP) and dibutyl phthalate (DBP) have been synthesized. The catalytic activity of synthesized materials has been compared and correlated with acid properties of the materials.

Material and Methods

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), pH and rate of mixing. Several sets of materials were prepared varying conditions in each case using IEC as the indicative tool (SM - tables 1 to 3).

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·min^{-1}) to an aqueous solution of $ZrOCl_2.8H_2O$ (0.2M, 50ml) with constant 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[14]. This material was used for all studies.

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·min^{-1}) to a solution of $TiCl_4$ (0.2M, 50ml) (prepared in 10% W/V H_2SO_4 solution) with constant 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[14]. This material was used for all studies.
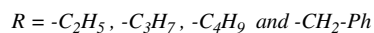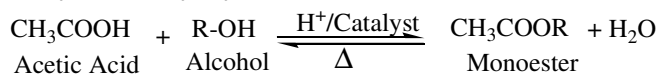
Synthesis of SnPW (at optimized condition): An aqueous mixture of $NaH_2PO_4.2H_2O$ (0.1M, 50ml) and $Na_2WO_4.2H_2O$ (0.1M, 50ml) was added dropwise (flow rate 1 ml·min^{-1}) to a solution of $SnCl_4$ (0.1M, 100ml) (prepared in 0.1M HCl) with constant stirring for an hour at room temperature. The gelatinous 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[14]. This material was used for all studies.

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. Amongst the different wt. % of 12-TPA loaded, 20 wt. % loading of 12-TPA onto oxides gives maximum surface acidity (SM – table 4). 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.

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[14]. 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 ºC·min^{-1}. X-ray diffractogram (2θ = 10 - 80°) was obtained on X-ray diffractometer (Brucker AXS D8) with Cu-K$_\alpha$ 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°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°C, 200°C and 700°C. Ammonia was chemisorbed at 120°C and then desorption was done upto 700°C with heating rate of 10°C/min.

Catalytic Activity: Synthesis of mono esters:

$$CH_3COOH + R\text{-}OH \xrightarrow[\Delta]{H^+/\text{Catalyst}} CH_3COOR + H_2O$$

Acetic Acid   Alcohol   Monoester

$$R = \text{-}C_2H_5 \,, \text{-}C_3H_7 \,, \text{-}C_4H_9 \text{ and } \text{-}CH_2\text{-}Ph$$

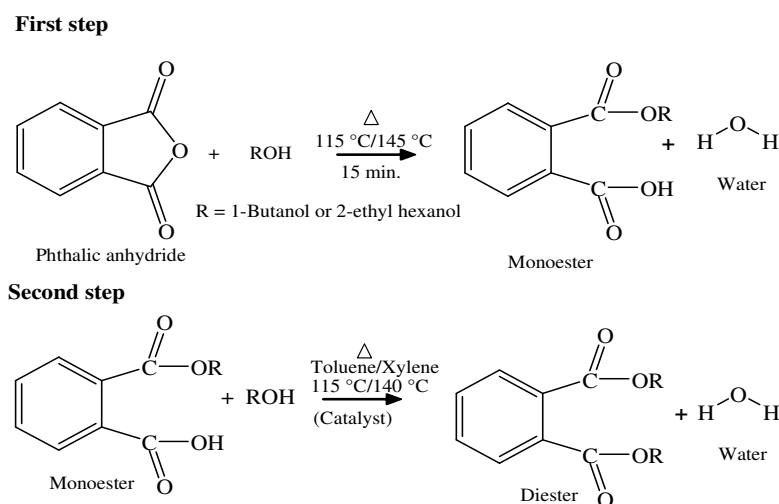**Scheme-1**
Synthesis of monoesters

In this reaction, round bottomed flask equipped with a Dean and Stark apparatus, attached to a reflux condenser was used and charged with acetic acid (0.050 - 0.075 M), alcohol (0.050 - 0.075 M), catalyst (0.05 - 0.20 g) and a suitable solvent (10 mL) (scheme 1). The reactions were carried out varying several parameters such as reaction time, catalyst amount, mole ratio of reactants and these parameters optimized. The temperature parameter has not been varied as the reaction temperature is sensitive to boiling points of reactants as well as solvents used as azeotrope. After completion of reaction, catalyst was separated by decantation and reaction mixture was distilled to obtain the product.

Synthesis of diesters: The diesters have been synthesized in two steps (scheme 2 and 3).

The mono ester was prepared in first step by taking equimolar proportion of acid and alcohol were taken in a round bottomed flask and the reaction mixture stirred at ~80°C for DEM and DES, ~115°C for DBP and ~140°C for DOP for about 10-15 min in absence of any catalyst and solvent. The dicarboxylic acid/anhydride gets completely converted to the monoester, and the acid concentration at this stage is taken as the initial concentration. The obtained product was then subjected to further esterification reaction by adding second mole of respective alcohol, catalyst (0.10 - 0.25 g) and 10 mL solvent. The reactions were carried out optimizing several parameters such as reaction time, catalyst amount and mole ratio of reactants. The temperature parameter has not been varied as discussed in synthesis of monoesters. After completion of reaction, catalyst was separated by decantation and reaction mixture was distilled to obtain the product.

First step

Second step
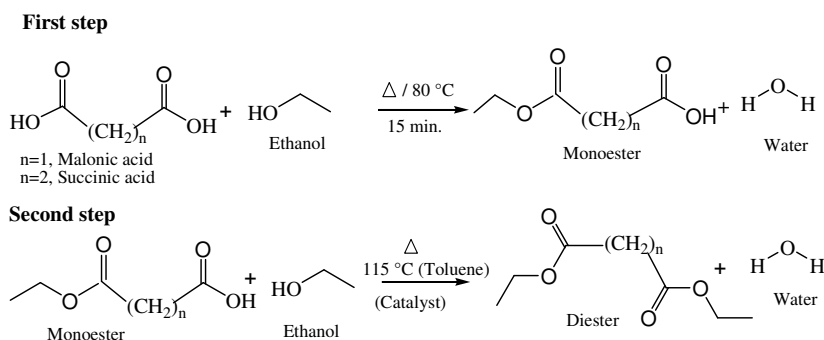
Scheme-2
Synthesis of DEM and DES

First step

Second step

Scheme-3
Synthesis of DBP and DOP

Calculation of % yield of esters: The yields of the mono and diesters formed were determined by titrating the reaction mixture with 0.1 M alcoholic KOH solution using the formula 1.

$$\% \text{ yield} = [(A - B) / A] \times M \times 100 \qquad (1)$$

Where, A and B are acid values of the sample withdrawn before and after reaction, respectively and M is mole ratio of acid: alcohol. The yield of ester formed was also confirmed by GC.

Regeneration of catalyst: In case of M(IV)PWs, spent catalyst obtained from reaction mixture was first refluxed in ethanol for 30 minutes and then dried at room temperature followed by acid treatment[14]. In case of 12-TPA/M(IV) oxides-20, spent catalyst was refluxed in ethanol for 30 minutes and then dried at 120°C for 3 hrs.

Results and Discussion

Catalyst characterization: Elemental analysis 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 - figure 1-6).

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.

FTIR spectrum of M(IV)PWs (SM–figure-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 - figure 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 - figure 9) shows weight loss in the temperature range of 40 – 150^{0}C 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^{0}C - 650^{0}C 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 - figure 10) exhibit 0.9%, 0.4% and 1.4% weight loss in the temperature range of 30 – 150^{0}C 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 - figure 11-16) of all the synthesized materials exhibit irregular morphology. Absence of sharp peaks in X-ray diffractogram of M(IV)PWs (SM - figure 17) reveals the amorphous nature of M(IV)PWs.

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=26.88	4.96	25.37	Zr=60.79	18.53	20.67	-
TiPW	Ti=14.84	4.64	24.97	Ti=46.61	37.99	15.40	-
SnPW	Sn=36.82	4.67	29.41	Sn=59.33	23.31	17.37	-
12-TPA/ZrO$_2$-20	Zr=58.62	0.09	16.48	Zr=28.75	0.11	3.44	67.70
12-TPA/TiO$_2$-20	Ti=46.76	0.08	16.17	Ti=28.63	0.15	0.88	70.34
12-TPA/SnO$_2$-20	Sn=60.01	0.08	18.04	Sn=18.40	0.12	2.57	78.92

Table-2
Chemical stability data of M(IV)PWs (Maximum tolerable limits)

Materials	Chemical media	Maximum tolerable limits
M(IV)PWs	Acids	18N H$_2$SO$_4$, 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	Acids	5N H$_2$SO$_4$, 16N HNO$_3$, 11.3N HCl
	Bases	Not Stable
	Organic Solvents	Ethanol, Benzene, Toluene, Acetone and Acetic acid

X-ray diffractogram of 12-TPA/ZrO$_2$-20 (SM - figure 18) 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 - figure 19) 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 - figure 20) 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.

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 (figure 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[21]. Acidity of the M(IV)PWs is due to the presence of structural hydroxyl protons where, H$^+$ of the – OH are 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).
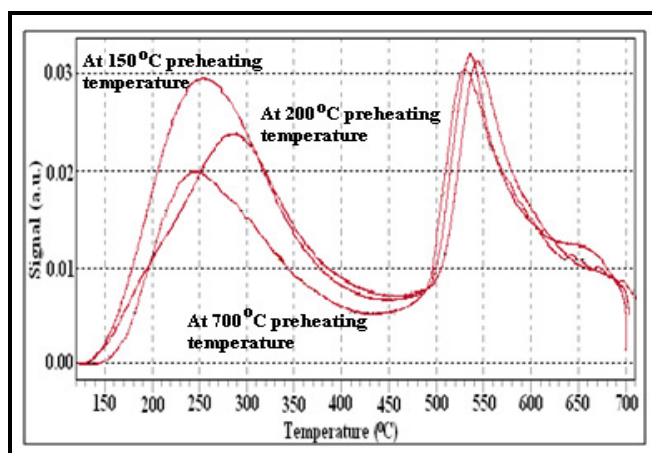
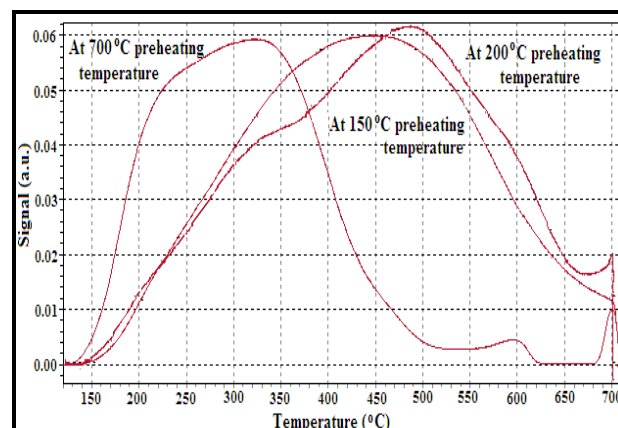

Figure-1
NH$_3$-TPD patterns of ZrPW

Figure-2
NH$_3$-TPD patterns of TiPW
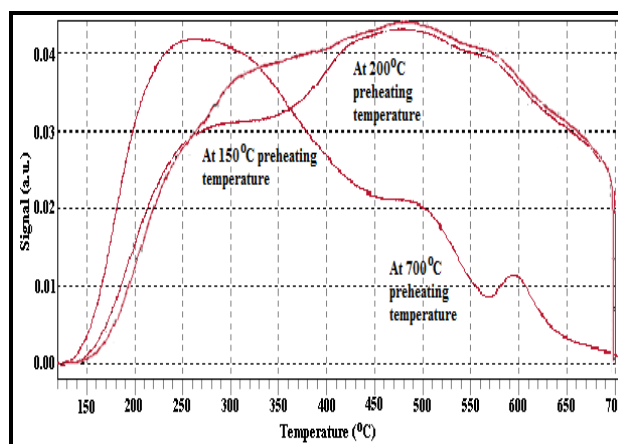

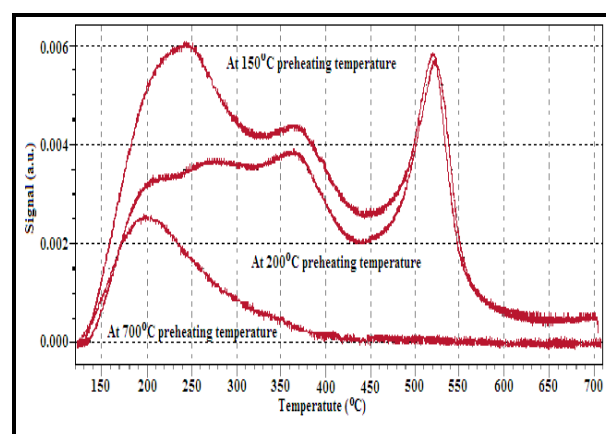**Figure-3**
NH$_3$-TPD patterns of SnPW

Figure-4
NH$_3$-TPD patterns of 12-TPA/ZrO$_2$-20

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[24].
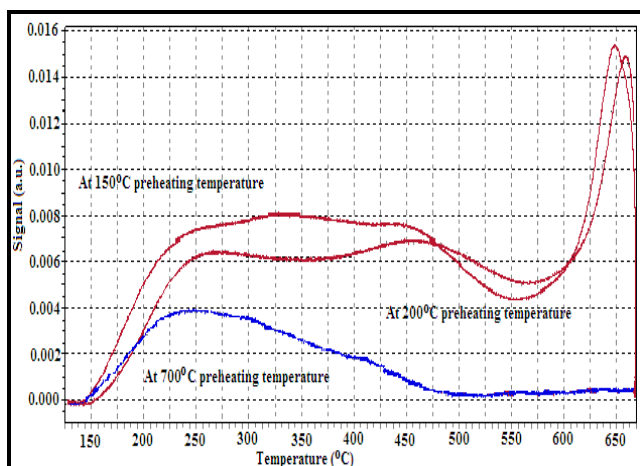
Figure-5
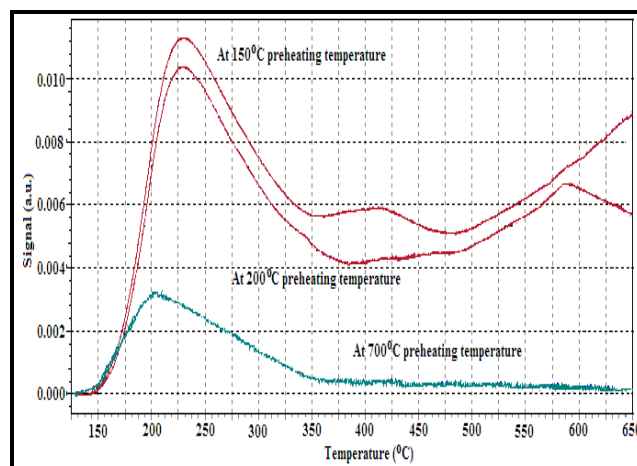**NH₃-TPD patterns of 12-TPA/TiO₂-20**

Figure-6
NH₃-TPD patterns of 12-TPA/SnO₂-20

Table-3
Surface area, surface acidity and IEC values for M(IV)PWs and 12-TPA/M(IV)Oxides

Materials	Surface Area (BET method) (m^2/g)	Surface acidity (NH₃-TPD method)		IEC (meq./g)
		Preheating Temperature (°C)	Acidity (mmol/g)	
ZrPW	80.96	150	9.34	0.98
		200	6.05	0.76
		700	3.90	0.49
TiPW	86.48	150	11.05	2.97
		200	11.02	2.39
		700	8.28	1.07
SnPW	171.04	150	10.28	2.00
		200	7.54	1.64
		700	4.50	0.73
12-TPA/ ZrO₂-20	33.90	150	1.07	-
		200	0.89	-
		700	0.17	-
12-TPA/ TiO₂-20	60.50	150	2.03	-
		200	1.68	-
		700	0.27	-
12-TPA/ SnO₂-20	139.54	150	1.42	-
		200	1.11	-
		700	0.22	-

Catalytic Activity

Synthesis of mono esters: Equilibrium constants of the esterification reactions are low. Following Le Chatlier's Principle, solvent was employed to remove the water formed during the reaction as a binary azeotrope using Dean and Stark apparatus, so that reverse reaction is avoided. Firstly, reaction conditions were optimized using ZrPW (inherent acidity) and 12-TPA/ZrO₂-20 (induced acidity) as solid acid catalysts for EA synthesis by varying several parameters (SM - table 5).

For both the catalysts, it is observed that as reaction time increases (1-10h), percentage yield increases. However, there is

not much gain in product after 8 h. With increasing amount of the catalyst (0.05g – 0.20g), the % yield increases which is probably due to proportional increase in the number of active sites. The influence of reactant mole ratio was studied by increasing mole ratio from 1:1.5 to 1.5:1 (acid:alcohol). The % yield of ester increases with increase in mole ratio of acid while decreases with increasing mole ratio of alcohol[16]. Further, at optimized conditions synthesis of EA, PA, BA and BzA was performed using all synthesized materials.

Synthesis of monoesters, EA, PA, and BA has been reported in absence of catalyst and exhibit poor yields. Therefore catalyst is a must for these reactions. In case of BzA, it is observed that

with an excess of acetic acid and in the absence of any catalyst the yield is high, which is attributed to auto catalysis[16]. The %

yield of ester formed is observed to be BzA > BA > EA > PA.

Table-4
Synthesis of mono esters at optimized condition using M(IV)PWs and 12-TPA/M(IV)Oxides

Catalysts	Catalytic run	Yields of mono ester (%) / (TON)			
		EA	PA	BA	BzA
ZrPW (regenerated)	1	76.92(34.87)	56.95(28.47)	84.92(45.87)	87.35(57.65)
	2	75.11(34.04)	55.44(27.72)	82.11(44.88)	86.00(56.69)
	3	72.98(33.08)	52.10(26.05)	81.68(44.65)	83.69(55.17)
ZrPW (reused)	1	76.92(34.87)	56.95(28.47)	84.92(45.87)	87.35(57.65)
	2	64.25(28.70)	48.31(24.15)	70.14(38.33)	78.11(51.55)
	3	51.87(23.51)	36.78(18.38)	62.88(34.36)	65.42(43.17)
TiPW (regenerated)	1	99.64 (45.10)	68.11 (34.00)	89.81 (49.03)	88.19 (58.14)
	2	96.22 (43.55)	65.11 (32.50)	87.32 (47.67)	86.72 (57.17)
	3	95.02 (43.01)	63.88 (31.89)	85.90 (46.90)	83.99 (55.37)
SnPW (regenerated)	1	85.54 (38.71)	66.78 (33.34)	87.38 (47.70)	87.81 (57.89)
	2	84.10 (38.06)	65.10 (32.50)	86.10 (47.01)	86.78 (57.21)
	3	82.12 (37.16)	64.52 (32.21)	84.78 (46.28)	85.10 (56.10)
12-TPA/ZrO$_2$-20 (reused)	1	64.41 (29.14)	48.69 (24.30)	75.29 (41.09)	78.44 (51.70)
	2	49.11 (22.22)	34.60 (17.27)	62.99 (36.02)	64.57 (42.56)
	3	39.10 (17.69)	28.10 (14.02)	49.00 (26.74)	52.99 (34.93)
12-TPA/TiO$_2$-20 (reused)	1	73.67 (33.33)	53.88 (26.89)	84.05 (45.88)	85.00 (56.03)
	2	62.54 (28.29)	44.67 (22.30)	68.99 (37.66)	69.19 (45.61)
	3	51.44 (23.27)	38.98 (19.45)	55.10 (30.07)	54.65 (36.02)
12-TPA/SnO$_2$-20 (reused)	1	70.17 (31.75)	51.00 (25.46)	80.85 (44.13)	82.01 (54.06)
	2	58.29 (26.37)	40.18 (20.05)	62.80 (34.79)	65.07 (42.89)
	3	48.12 (21.77)	32.19 (16.07)	51.98 (28.37)	53.09 (34.99)

Mole ratio Acid:Alcohol=1.5:1, Reaction temperature: 80^0C for EA, 115^oC for PA, BA and BzA; Reaction time: 8 h; Amount of catalyst: 0.15g; Solvent: cyclohexane for EA and toluene for PA, BA and BzA

Turn over number (TON) is defined as the number of substrate molecules reacting per mole of catalyst which reflects the effectiveness of a catalyst and this also follows the order BzA > BA > EA > PA. High yields of BzA obtained could be attributed to an enhanced nucleophilicity due to presence of aromatic ring in benzyl alcohol. In another report[25], high yields of BzA were obtained with small amount of the catalyst but the reaction time was relatively high. When the boiling point of the alcohol is less than the temperature of the reaction, most of the alcohol will end up in the vapor phase and not be available in the liquid phase. This is the reason why heavier alcohols react more than the lighter ones.

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[14].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 % 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[21]. Table 6 provides atomic wt. % of various components (Zr, P, W and O) for both fresh and spent catalysts in case of synthesis of EA. 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 monoesters (SM – figure 21, 22).

Many esterification reactions have been performed by using solid acid catalysts[4-7]. However, sulfated zirconia is a good catalyst, it gets easily deactivated by losing the sulfate ions, thus restricting recycling of the catalyst. The main disadvantage of heteropoly acids is low efficiency due to low surface area, rapid deactivation and poor stability, and when supported on carbon the activity decreases[26]. Sulfonic acid-based resin (Nafion-H) has also been found to be unacceptable due to its low operating temperature. Reddy and coworkers[27] have reported the use of ZrO$_2$ impregnated with molybdenum and tungsten as solid acids for esterification reactions which are also associated with the problem of leaching of acidity and hence gives low yields of esters. Nagaraju et. al. have reported modified zeolites for esterification of benzyl alcohol with acetic acid which require long reaction time as well as large amount of catalyst to carry out reaction and also few of modified zeolites gives poor yields of ester.

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 monoester formed as well as reusability of catalysts. % yields of monoester formed using TMA salts[14,15], TBMA salts[16] and TMBA salts are presented in Table 7. It is observed that, TMBA salt TiPW, works as the most efficient catalyst giving excellent yields for all monoesters especially, 99.64% in case of synthesis of EA, compared to TMA salts (i.e. TiP, TiW) and TBMA salts (i.e. ZTPA).

Synthesis of diesters: DEM, DES, DOP, and DBP were synthesized in two steps. The first step is so rapid, that it can be carried out in the absence of catalyst attributed to the fact that, the electron withdrawing effect of one carboxyl group enhances the ionization of the other causing the -COOH groups to be protonated in this region of pH. However, esterification of the second carboxylic group (second step) is very slow and needs to be facilitated by acid catalyst wherein the resulting water must also be removed from the reaction mixture[28]. Reaction conditions were optimized using ZrPW and 12-TPA/ZrO$_2$-20 as solid acid catalysts for DEM synthesis by varying parameters such as reaction time, catalyst amount and initial mole ratio of the reactant (SM - table 6). At optimized conditions synthesis of

DEM, DES, DOP and DBP was performed using all synthesized materials.

In the present work, % yield of diester formed is observed to be DEM > DES > DOP > DBP. The yields of DOP are higher than DBP which could be attributed to higher boiling point of 2-ethyl-1-hexanol compared to 1-butanol. High yields in the case of DEM and DES, compared to DOP and DBP is probably due to less steric hindrance felt by incoming ethanol from monoester formed in the first step.

Regeneration and reusability for all the catalysts under study was conducted and results presented in Table 5. After each catalytic run, all the catalysts turn dark brown as in the case of monoesters, is 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[14]. 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 % 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[21]. Table 6 provides atomic wt. % of various components (Zr, P, W and O) for both fresh and spent catalysts in case of synthesis of DEM. 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 diesters (SM – figure 23, 24).

Table-5
Synthesis of diesters at optimized condition using M(IV)PWs and 12-TPA/M(IV)Oxides

Catalysts	Catalytic run	Yields of diester / (TON)			
		DEM	DES	DOP	DBP
ZrPW (regenerated)	1	88.64 (28.95)	81.10 (28.38)	80.87 (55.04)	63.00 (31.08)
	2	86.71 (28.32)	80.98 (28.34)	79.67 (54.22)	61.89 (30.53)
	3	84.07 (27.46)	78.10 (27.33)	78.00 (53.09)	60.10 (29.64)
ZrPW (reused)	1	88.64 (28.95)	81.10 (28.38)	80.87 (55.04)	63.00 (31.08)
	2	76.14 (24.86)	70.38 (24.62)	71.19 (48.45)	54.32 (26.79)
	3	65.72 (21.46)	59.17 (20.70)	60.20 (40.97)	45.27 (22.33)
TiPW (regenerated)	1	92.10 (30.02)	88.84 (31.03)	84.00 (57.12)	68.02 (33.55)
	2	90.13 (29.38)	87.08 (30.41)	83.12 (56.52)	67.61 (33.35)
	3	89.41 (29.14)	85.12 (29.37)	82.78 (56.29)	65.69 (32.40)
SnPW (regenerated)	1	90.14 (29.38)	84.57 (29.54)	81.04 (55.10)	66.84 (32.97)
	2	89.51 (29.18)	82.12 (28.68)	80.00 (54.40)	66.14 (32.62)
	3	87.32 (28.46)	80.10 (27.97)	78.14 (53.13)	65.00 (32.06)
12-TPA/ZrO$_2$-20 (reused)	1	81.12 (26.43)	70.42 (24.58)	67.54 (45.92)	55.25 (27.25)
	2	60.45 (19.70)	59.74 (20.86)	54.45 (37.02)	45.12 (22.25)
	3	45.55 (14.84)	45.42 (15.86)	41.45 (28.18)	30.80 (15.19)
12-TPA/TiO$_2$-20 (reused)	1	86.00 (28.02)	80.75 (28.19)	71.42 (48.56)	60.17 (29.67)
	2	68.41 (22.29)	65.05 (22.71)	59.78 (40.64)	52.81 (26.04)
	3	54.00 (17.60)	53.90 (18.82)	43.99 (29.91)	41.89 (20.66)
12-TPA/SnO$_2$-20 (reused)	1	84.50 (27.54)	75.78 (26.46)	69.59 (47.13)	57.78 (28.49)
	2	66.11 (21.54)	60.00 (20.95)	59.57 (40.50)	48.00 (23.67)
	3	49.88 (16.25)	49.08 (17.13)	42.00 (28.55)	38.17 (18.82)

*Mole ratio Acid:Alcohol=1:2, Reaction temperature: 115^{0}C for DEM, DES and DBP, 140°C for DOP; Reaction time: 8 h; Amount of catalyst: 0.15g; Solvent: xylene for DOP and toluene for DEM, DES and DBP

Jai Prakash et al have reported synthesis of DEM by using montmorillonite clay, but the disadvantages are low yields and large amount of catalyst used for reaction[25]. DES synthesis and kinetics has been reported by Kolah et al using amberlyst catalyst with good yields[29]. DOP formation has been catalyzed by zeolites[4], solid super acids[7,30] and heteropoly acids[30]. Further, Amini et. al.[28] have performed esterification of phthalic anhydride with 1-butanol and 2-ethylhexanol catalyzed by some heteropolyacids of keggin, Wells-Dawson and Preyssler type. Though these catalysts require short reaction time, in some cases it gives poor yields of esters. When homogeneous liquid acids are used as catalysts for synthesis of diesters, the result is a product that is coloured and of a poor quality.

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 diester formed as well as reusability of catalysts. % yields of diester formed using TMA salts[14,15], TBMA salts[16] and TMBA salts are presented in table-7.

It is observed that, TMBA salt TiPW, works as the most efficient catalyst giving excellent yields for all diesters especially, 92.10% in case of synthesis of DEM compared to TMA salts (i.e. TiP, TiW) and TBMA salts (i.e. ZTPA).

Proposed mechanism of solid acid catalyzed esterification reaction: Based on the classical mechanism for acid catalyzed esterification, we have reported a mechanism (scheme-3) for esterification of ethanol with acetic acid[16].

Conclusion

In the present study, amongst the two types of catalysts synthesized possessing same elemental composition, *(i)* M(IV)PWs (possessing inherent acidity) and *(ii)* 12-TPA/M(IV)Oxides (possessing induced acidity), M(IV)PWs score over 12-TPA/M(IV)Oxides-20 in terms of catalyst performance in the synthesis of monoesters and diesters. Amongst all the catalysts, TiPW which gives excellent yield of EA (99.64%) and DEM (92.10%) has potential for commercialization.

Table-6
**Elemental analysis by EDX for both fresh and spent ZrPW and 12-TPA/ZrO$_2$-20 in the synthesis of EA and DEM**

Ester formed	Materials	% by EDX analysis			
		Zr	P	W	O
EA	ZrPW (Fresh)	60.79	18.53	20.67	-
	ZrPW (Spent)	54.93	22.24	22.82	-
	12-TPA/ZrO$_2$-20 (Fresh)	28.75	0.11	3.44	67.70
	12-TPA/ZrO$_2$-20 (Spent)	26.09	1.03	0.94	71.94
DEM	ZrPW (Fresh)	60.79	18.53	20.67	-
	ZrPW (Spent)	55.73	22.25	22.02	-
	12-TPA/ZrO$_2$-20 (Fresh)	28.75	0.11	3.44	67.70
	12-TPA/ZrO$_2$-20 (Spent)	20.53	1.09	1.28	77.10

Mole ratio for EA Acid:Alcohol=1.5:1, Mole ratio for DEM Acid:Alcohol=1:2, Reaction temperature: 80°C for EA, 115°C for DEM; Reaction time: 8 h; Amount of catalyst: 0.15g; Solvent: toluene

Table-7
Comparison of % yield of EA and DOP using TMA, TBMA and TMBA salts

Catalyst Used	Substrates (mole ratio)	Product formed	Catalyst amount (g)	Reaction temperature(°C)	Reaction time (h)	% yield
TiP [15]	E:AA (1:1.5)	EA	0.15	80	8	76.10
TiW [14]	E:AA (1:1.5)	EA	0.15	80	8	71.10
TiP [16]	E:AA (1:2)	EA	0.20	80	10	80.20
ZTPA [16]	E:AA (1:1.5)	EA	0.20	80	10	86.40
TiPW*	E:AA (1:1.5)	EA	0.15	80	8	99.64
TiP [15]	PA:2-EH (1:2)	DOP	0.15	155	10	51.70
TiW [14]	PA:2-EH (1:2)	DOP	0.10	155	10	30.70
TiP [16]	PA:2-EH (1:2)	DOP	0.20	145	10	70.30
ZTPA [16]	PA:2-EH (1:2)	DOP	0.20	145	10	72.60
TiPW*	PA:2-EH (1:2)	DOP	0.15	140	8	84.00

*: Present work; E: Ethanol; AA: Acetic acid; PA: Phthalic anhydride; 2-EH: 2-Ethyl-1-Hexanol; Solvent: xylene for DOP and cyclohexane for EA
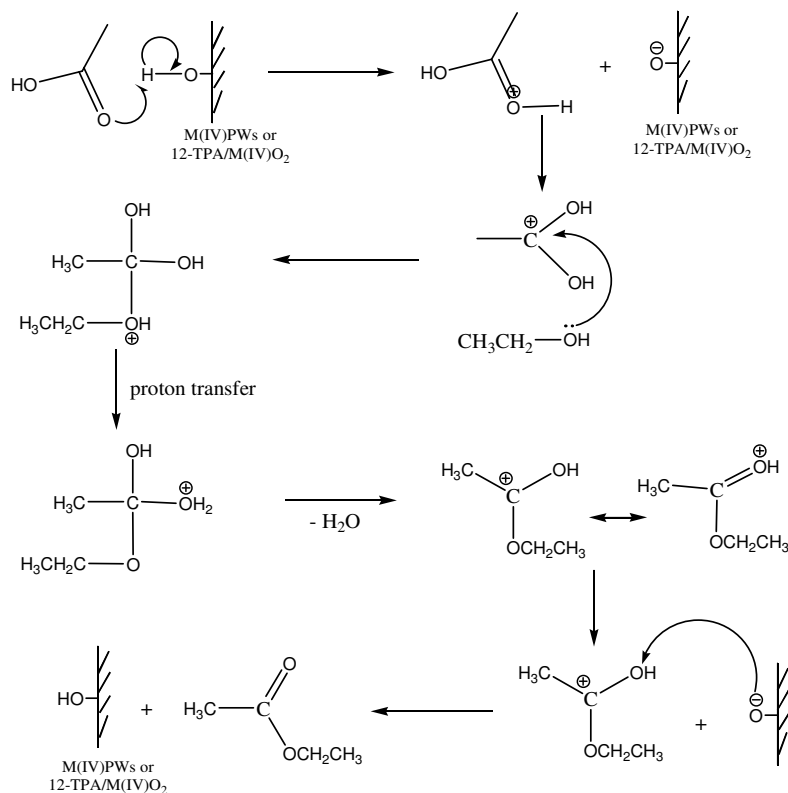
Scheme-3
Reaction mechanism for esterification of ethanol with acetic acid

Acknowledgement

References

1. Otera J., Esterification, Wiley-VCH: Weinheim, Germany, **(2003)**

2. Yadav G.D. and Murkute A.D., Kinetics of synthesis of perfumery grade p-tert-butylcyclohexyl acetate over ion exchange resin catalyst, *Int. J. Chem. Reactor Eng.*, **1,** 1-11 **(2003)**

3. Ma Y., Jin T., Wang Z. and Li T., A rapid and efficient method for acetylation of phenols with acetic anhydried catalyzed by TiO_2/SO_4^{2-} solid super acids, *Indian J. Chem.*, **42B,** 1777-1778 **(2003)**

4. Ma Y., Wang Q. L., Yan H., Ji X. and Qiu Q., Synthesis of nano-sized $Ce_{0.85}M_{0.1}Ru_{0.05}O_{2-\delta}$ (M = Si, Fe) solid solution exhibiting high CO oxidation and water gas shift activity, *Appl. Catal. A: Gen.*, **139,** 51-57 **(1996)**

5. Okudan S. and Baktir A., Esterification Reaction of polystyrene modified with maleic anhydride in the presence of resin catalyst, *Adv. Poly. Technol.*, 1-11 **(2012)**

6. Cheng Y., Feng Y., Ren Y., Liu X., Gao A., Benqiao H., Yan F. and Jianxin L., Comprehensive kinetic studies of acidic oil continuous esterification by cation-exchange resin in fixed bed reactors, *Bioresource Technol.*, **113,** 65-72 **(2012)**

7. Zhang B., Ren J., Liu X., Guo Y., Lu G. and Wang Y., Novel sulfonated carbonaceous materials from p-toluenesulfonic acid/glucose as a high-performance solid-acid catalyst, *Catal. Commu.*, **11,** 629-632 **(2010)**

8. Toor A. P., Sharma M. and Kumar G., Wanchoo R. K., Ion exchange resin catalyzed esterification of lactic acid with isopropanol : A kinetic study, *Bull. Chem. React. Engg. Catal.,* **6(1),** 24-31 **(2011)**

9. Brahamkhatri V. and Patel A., Biodiesel Production by Esterification of Free Fatty Acids over 12-Tungstophosphoric Acid Anchored to MCM-41, *Ind. Eng. Chem. Res.*, **50(24),** 13693-13702 **(2011)**

10. Nascimento L.A.S., Tito L.M.Z., Angelica A.S., Costa C.F.F., Zamian J.M. and Rocha Filho G.N., Esterification of oleic acid over solid acid catalysts prepared from Amazon flint kaolin, *Appl. Catal. B: Environ.*, **101,** 495-503 **(2011)**

11. Helen L.N., Nicholas A., Zafiropoulos A., Thomas Foglia T., Edward D., Samulski L. and Wenbin L.,

Mesoporous silica-supported diarylammonium catalysts for esterification of free fatty acids in greases, *J. Am. Oil Chem. Soc.*, **87,** 445-449 **(2010)**

12. Bhaumik A. and Inagaki S., Mesoporous Titanium Phosphate Molecular Sieves with Ion-Exchange Capacity, *J. Am. Chem. Soc.*, **123,** 691-696 **(2001)**

13. Slade R.C.T., Knowels J.A., Jones D.J. and Roziere J., The isomorphous acid salts α-Zr(HPO$_4$)$_2$·H$_2$O, α-Ti(HPO$_4$)$_2$·H$_2$O and α-Zr(HAsO$_4$)$_2$·H$_2$O: Comparative thermochemistry and vibrational spectroscopy, *Solid State Ionics*, **96,** 9-19 **(1997)**

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

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

16. Thakkar R. and Chudasama U., Synthesis of mono and diesters using eco-friendly solid acid catalyst - zirconium titanium phosphate, *Green Chemistry Letters and Reviews*, **2,** 61-69 **(2009)**

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

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

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

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

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

22. Ghodke S. and Chudasama U., Solvent free synthesis of coumarins using environment friendly solid acid catalysts, *Appl. Catal. A: Gen.*, **453,** 219-226 **(2013)**

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

24. Waghmare N.G., Kasinathan P., Amrute A., Lucas N. and Halligudi S.B., Titania supported silicotungstic acid: An efficient solid acid catalyst for veratrole acylation, *Cata. Comm.*, **9,** 2026-2029 **(2008)**

25. Reddy C., Iyengar P., Nagendrappa G. and Prakash B.J., Esterification of dicarboxylic acids to diesters over M^{n+}-montmorillonite clay catalysts, *Catal. Lett.*, **101,** 87-91 **(2005)**

26. Shanmugam S., Viswanathan B. and Varadarajan B.K., Esterification by solid acid catalysts : A comparison, *J. Mol. Catal. A: Chem.*, **223,** 143-147 **(2004)**

27. Manohar B., Reddy V.R. and Reddy B.M., Esterification by ZrO$_2$ and Mo-ZrO$_2$ eco-friendly solid acid catalysts, *Synth. Comm.*, **28,** 3183-3187 **(1998)**

28. Arabi M., Amini M.M., Abedini M., Nemati A. and Alizadeh M., Esterification of phthalic anhydride with 1-butanol and 2-ethylhexanol catalyzed by heteropolyacids, *J. Mol. Catal. A: Chem.*, **200,** 105-110 **(2003)**

29. Kolah A., Ashtana N.S., Vu D.T., Lira C.T. and Miller D.J., Reaction kinetics for the heterogeneously catalyzed esterification of succinic acid with ethanol, *Ind. Eng. Chem. Res.*, **47,** 5313-5317 **(2008)**

30. Thorat T.S., Yadav V.M. and Yadav G.D., Esterification of phthalic anhydride with 2-ethylhexanol by solid superacidic catalysts, *Appl. Catal.*, **90,** 73-96 **(1992)**