3.1 INTRODUCTION

Esters represent an imperative class of aroma compounds. Esters are useful as solvents, plasticizers, perfumes, fragrance in cosmetics, flavours in foods, diluents in paints and coatings as well as intermediates in drugs, dye stuffs, fine chemicals and pharmaceutical industries. Monoesters are very important industrially and find a wide range of applications in perfumery, flavours, pharmaceuticals and as solvents. Diesters [diethyl malonate (DEM), diethyl succinate (DES), dioctyl phthalate (DOP) and dibutyl phthalate (DBP)] are important bulk chemicals. DEM occurs naturally in grapes and strawberries as a colourless liquid with an apple-like odour, and is used in perfumes. It is also used to synthesize other compounds such as barbiturates, artificial flavourings and as intermediates for synthesis of vitamin B_1, and vitamin B_6. Succinate esters are intermediates in the production of poly butylene succinate (PBS) polymers, a polyester composed of succinic acid and 1,4-butanediol having attractive properties for broad application in automobiles and consumer goods. The 1,4-butanediol is produced by hydrogenation of succinate ester, hence the entire PBS polymer is a succinate based, biorenewable material. Esters of succinic acid (primarily dimethyl esters) are also being investigated for their insulinotropic potential in rats [1]. DOP and DBP are used as additives in the form of plasticizer, to the important plastic polyvinyl chloride.

Esterification is an industrially important reaction. The reaction between an organic acid and an alcohol is known as “esterification”. The synthesis of monoesters can be presented as shown in Scheme 3.1.The reaction is generally carried out with large excess of alcohol and in presence of a strong acid catalyst. The esterification procedure introduced by E. Fischer and A. Speier (1895) consists in refluxing acid and excess methanol or ethanol in the presence of about 3 % hydrogen chloride.

$$\mathrm{RCOOH} \quad + \quad \mathrm{R`OH} \quad \overset{\overset{+}{\mathrm{H}}}{\rightleftharpoons} \quad \mathrm{RCOOR`} \quad + \quad \mathrm{H_2O}$$

where, R and R` are alkyl and aryl groups

Scheme 3.1 *Esterification reaction*

Esterification is a reversible reaction and gives water as the second product. For a stoichiometric mixture of acid and alcohol, equilibrium generally reaches ~68% [2] of conversion for the straight chain saturated alcohol. In order to obtain maximum yields, Le Chatlier’s principle is followed and the reaction is driven to the right hand side/forward direction, as follows:

Addition of one of the reactants in excess: The reaction usually reaches a point of equilibrium at ~60% conversion, but in a small scale experiment a conversion of 60-80% can be achieved by use of a large excess of either acid or alcohol.

Removal of one of the products: Either ester or water formed is removed as soon as it is formed. Generally, suitable organic solvents are employed to remove the water formed during the reaction as a binary azeotrope or employing dehydrating agents such as anhydrous magnesium sulfate or molecular sieves [3].

To avoid equilibrium reaction, other paths have been suggested for ester synthesis. Such reactions involve the use of acyl halides (Eq. 3.1) or anhydrides (Eq. 3.2) or by alkylation of salts of carboxylic acids with alkyl halides. With acid halides, though the reactions are rapid and irreversible, HCl is obtained as a byproduct which is difficult to remove from the product. Mostly pyridine is used as an HCl acceptor. However, these reactions are efficient for only primary alcohols, secondary alcohols give lower yields and no reaction occurs at all with tertiary alcohols. Further, aromatic acid chlorides are considerably less reactive than aliphatic acid chlorides.

$$\mathrm{RCOCl + R'OH \longrightarrow RCOOR' + HCl} \qquad \textbf{\textit{(Eq. 3.1)}}$$

When acid anhydrides are used, the reaction is slow and produces one mole of carboxylic acid in place of HCl. This process is widely accepted in industry for the esterification of polyhydroxy compounds such as carbohydrates, cellulose etc.

$$\mathrm{(RCO)_2O + R'OH \longrightarrow RCOOR' + RCOOH} \qquad \textbf{\textit{(Eq. 3.2)}}$$

Other methods include the use of alkyl tert-butyl ether or by alkylation of salts of carboxylic acids with alkyl halides, transesterification, carbonylation of olefins, alcoholysis of nitriles etc.

3.2 MONOESTERS

Monoesters are typically synthesized by [4] (1) Solvolytic reactions (2) Condensation reactions (3) Free radical processes (4) Miscellaneous processes.

Solvolytic Reactions: Conversion of carboxylic acids and acid derivatives into esters by reaction with hydroxylic compounds are solvolytic reactions, which include (a) direct esterification of acids (b) alkylation of carboxylic acid salts (c) alcoholysis of acyl halides (d) alcoholysis of anhydrides (e) alcoholysis of nitriles and amides (f) alcoholysis of ketenes (g) transesterification.

Condensation Reactions: Reactions involving carbanion intermediates can be used to prepare carboxylic acid esters. Some well-known reactions of this category are (a) Knoevenagel reaction (b) Darzens reaction (c) Wittig reaction (d) Reformatsky reaction (e) Acetoacetic ester synthesis (f) malonic ester synthesis (g) derivatives of α-anions of esters (h) Michael reaction and (i) Claisen condensation.

Free-Radical Processes: This includes (a) radical additions and substitution reaction (b) acyloxylation reaction (c) anodic dimerization.

Miscellaneous processes: These include ester formation (a) using organoboranes (b) using acetylenes (c) using diazo esters (d) by carbonylation of alcohol (e) by phase transfer catalyzed reaction of alkyl or aryl halide with inorganic salt of the carboxylic acid (both liquid-liquid and solid-liquid).

For the preparation of perfumery and flavour grade esters, only a few of the above mentioned routes can be considered, due to the stringent specifications of the final product. Normally, liquid phase catalysts such as sulphuric acid, p-toluene sulfonic acid, methanesulfonic acid, hydrochloric acid, phosphoric acid etc. have been used, that are cited as potential environmentally hazardous chemicals that pose problems such as difficulty in handling, causing acidic waste water, difficulty of catalyst recovery etc. [5]. These catalysts are known to colour the product and cannot be reused. Due to these problems, accompanied by the increasing environmental awareness, there is a global effort to replace the conventional liquid acids by suitable solid acids. The most widely employed and supposedly cleaner production technique for such esters, involves the reaction of the appropriate carboxylic acid with an alcohol using a heterogeneous catalyst such as solid acid catalyst under reflux conditions, followed by separation of the ester by distillation.

3.3 LITERATURE SURVEY IN THE CURRENT AREA OF STUDY (MONOESTERS)

Cation exchange resins Dowex 50W and Amberlite IR-120 [6,7] have been used as solid acid catalysts in the esterification of acetic acid with isobutanol. Esterification of acrylic and lactic acids with butanol using Amberlyst-15 [8,9] and lactic and salicylic acids with methanol using Dowex 50W resin as solid acid catalysts [10,11] has been reported. Salmi et al have studied methyl acetate formation on new polyolefin supported sulfonic acid catalysts [12]. Meunier has reported esterification reactions using Nafion as solid acid catalyst [13]. Kaolinite [14] as well as montmorillonite [15] clay has been used as catalyst in the esterification of carboxylic acids. Giovanni Sartori has written an excellent review on clay catalyst for monoesterification reaction [16]. Manohar et al [17] have reported esterification of acetic acid and benzoic acid using ZrO_2 and Mo-ZrO_2 as solid acid catalysts and found that Mo-ZrO_2 exhibits better catalytic activity than ZrO_2. Valdeilson et al [18] have studied esterification of acetic acid with alcohols using supported niobium pentoxide on silica-alumina catalysts. Vishwanathan et al [19] have reported esterification by solid acid catalysts including clays, zeolites, sulphated metal oxides and heteropolyacids. Toor et al [20] have reported kinetic study of esterification of acetic acid with n-butanol and isobutanol catalyzed by ion exchange resin. Silicotungstic acid supported zirconia is reported as an effective catalyst for esterification reactions using formic, acetic, propionic, *n*-butyricacid and *n*-butyl alcohol, isobutyl alcohol and *sec*-butyl alcohol [21]. Chu et al [22] have reported the vapour phase synthesis of ethyl and butyl acetate by immobilized dodecatungstosilicic acid on activated carbon. The rate of esterification was found to be dependent on the partial pressure of the reactants.

Dupont et al [23] have reported heteropolyacids (HPA) supported on activated carbon as catalysts for the esterification of acrylic acid by butanol. Deactivation of the catalyst was observed under flow condition (from 43 to 32% conversion) which was attributed to the dissolution of the supported HPA in the reaction medium (25 %). Timofeeva et al [24] have reported esterification of acetic acid and *n*-butyl alcohol using Keggin and Dawson type HPAs and found that the reaction rate depends on the acidity, as well as on the structure and composition of HPAs. 12-TPA supported on hydrous zirconia was used as solid acid catalyst in esterification of primary and secondary alcohols [25]. Sharath et al studied benzyl acetate formation in the presence of zeolites and their ion exchanged forms. They reported reasonably good yield with 100 % selectivity [26]. Ma et al have reported the synthesis of ethyl, butyl and benzyl acetates with high yields using zeolite catalyst [27]. Jiang et al have studied catalytic activity of mesoporous TiO_2 solid super acid for esterification of iso-amyl alcohol and salicylic acid [28].

Sugi et al [29] have reported 12-TPA supported onto MCM-48 as an efficient catalyst for the esterification of long chain fatty acid and alcohols in supercritical

CO_2.Yarmo et al [30] have reported 12-TPA supported on MCM-41 for esterification of fatty acid under solvent free condition. The workers have also reported synthesis, characterization and catalytic performance of porous nafion resin/silica nanocomposites for esterification of lauric acid and methanol [31]. Nascimento et al have reported catalytic esterification of oleic acid over SO_4^{2-}/MCM-41 nanostructured materials [32]. Helen et al [33] have reported use of mesoporous silica supported diarylammonium catalysts for esterification of free fatty acid in greases. Zhu et al have reported synthesis, characterization and application of sulfated zirconia/ hexagonal mesoporous silica (HMS) catalyst in the esterification of gossypol [34]. Pandurangan et al have reported vapour phase esterification of butyric acid with 1-pentanol and tert-butylbenzene with iso-propyl acetate over Al-MCM-41 mesoporous molecular sieves [35]. Srinivas et al have reported the kinetics of esterification of fatty acids over solid acid catalysts including large pore zeolite-β (Hβ), micro-mesoporous Fe/Zn double-metal cyanide (DMC) and mesoporous Al-MCM-41 [36]. Said et al have reported perspective catalytic performance of Brønsted acid sites during esterification of acetic acid with ethyl alcohol over 12-TPA supported on silica [37].

Rhijn et al have reported sulfonic acid functionalized ordered mesoporous materials as catalysts for condensation and esterification reactions [38]. Zhang Yijun et al have reported synthesis, characterization and catalytic application of HPA/MCM-48 in the esterification of methacrylic acid with n-butyl alcohol [39]. Lingaiah et al have reported 12-TPA with varying contents on SnO_2 as efficient solid acid catalysts for esterification of free fatty acids with methanol for the production of biodiesel [40]. Guo et al have reported simultaneous esterification and transesterification of soybean oil with methanol catalyzed by mesoporous Ta_2O_5/SiO_2–[H_3PW/R] (R = Methyl or Phenyl) hybrid catalysts [41]. Khire et al have reported esterification of lower aliphatic alcohols with acetic acid in presence of sulfated zirconia and silica supported zirconia catalysts and these catalysts have been evaluated and compared with other acid catalysts [42]. Chopade et al have reported use of various heterogeneous solid acid catalysts for production of biodiesel via transesterification of triglycerides with methanol [43].

Feng et al have reported the use of sulfonated based NKC-9 cation exchange resin for acidic oil continuous esterification process in a fixed bed reactor [44]. Nage and Kulkarni et al have reported biodiesel production by a continuous process using heterogeneous catalysts (mixed oxides of Zr and Al) [45]. Keat Teong Lee et al have written an excellent review on heterogeneous catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel [46]. Park et al have reported heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel [47]. The authors have also reported esterification of used vegetable oils using the heterogeneous WO_3/ZrO_2 catalyst for production of biodiesel [48,49]. Gang et al have reported solvent free esterifications of various carboxylic acids and alcohols catalyzed by surfactant-combined catalysts dodecylbenzene sulfonic acid (DBSA) and copper dodecylbenzene sulfonate (CDBS) in moderate to excellent yield at room temperature [50]. Liao Sen et al have reported synthesis of ammonium cerium phosphate via low heating state reaction and its use for benzyl acetate synthesis [51].

From our laboratory, TMA salts have been widely investigated as solid acid catalysts for synthesis of monoesters such as ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA) and benzyl acetate (BzAc) [52-61].

3.4 OBJECTIVES OF THE PRESENT WORK (MONOESTERS)

In the present chapter, the potential utility of M(IV)PWs (Type-I Inherent SACs) and 12-TPA/M(IV)O_2 (Type-II Induced SACs) has been explored by studying esterification as a model reaction, wherein monoesters ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA) and benzyl acetate (BzA) have been synthesized. Reaction parameters, reaction time, catalyst amount and mole ratio of the reactants have been optimized. Catalytic performance of Type-I and Type-II catalysts have been compared at optimized condition and correlated with acid properties of the materials. The performance ability of the catalysts have also been assessed for regenerated/ reactivated catalysts. A reaction mechanism has been proposed for solid acid catalyzed esterification reaction.

3.5 EXPERIMENTAL (MONOESTERS)

Catalyst Synthesis and Characterization

The synthesis and characterization of Type-I catalysts ZrPW, TiPW, SnPW [Inherent SACs - M(IV)PWs] and Type – II catalysts 12-TPA/ZrO_2-20, 12-TPA/TiO_2-20, 12-TPA/SnO_2-20 [Induced SACs - 12-TPA/M(IV)O_2-20] have been discussed in Chapter 2.

Materials and Methods

Acetic acid, ethanol, 1-propanol, 1-butanol, benzyl alcohol, cyclohexane, and toluene were procured from Loba chemicals (India). Yields of ester formed were determined by GC performed on Chemito 800 plus, equipped with flame-ionization detector (FID), oven temperature: 150°C, injector temperature: 200°C, detector temperature: 220°C and split ratio is 1:2. EDX analysis for catalysts (fresh and spent) has been performed on Jeol JSM-5610-SLV scanning electron microscope.

Experimental setup

In a typical reaction, a 100 mL round bottomed flask equipped with a Dean and Stark apparatus, attached to a reflux condenser, was 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) (used as azeotrope to remove water formed during the reaction) and refluxed at particular temperature for particular time (1-10h). Cyclohexane (b.p. 80°C) was used as a solvent for the synthesis of EA and toluene (b.p. 110°C) for PA, BA and BzA. Reaction parameters reaction time, catalyst amount and mole ratio of the reactants have been varied and conditions optimized. The temperature parameter has not been varied as the reaction temperature is sensitive to boiling points of reactants [ethanol (78°C), 1-propanol (97°C), 1-butanol (118°C), benzyl alcohol (205°C) and acetic acid (115°C)] as well as solvents (used as azeotrope). After completion of reaction, catalyst was separated by decantation/filtration and reaction mixture was distilled to obtain the product.

Calculation of % yield of esters

The yields of monoesters formed were determined by titrating the reaction mixture with 0.1 M alcoholic KOH solution. The yields of the esters were calculated using the formula, $\%\ yield = [(A - B) / A] \times M \times 100$, where A and B are acid values of the sample withdrawn before and after reaction and M is mole ratio of acid: alcohol. The yield of ester formed was also confirmed by GC.

Regeneration/Reactivation of catalyst

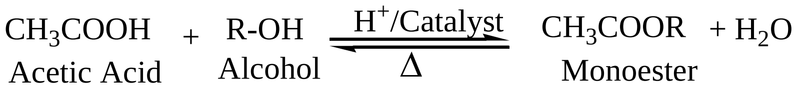
After separation of catalyst (Type-I and Type-II) from reaction mixture by filtration/decantation, it is refluxed in ethanol for 30 minutes to solubilise/remove adsorbed molecules of reactants/products.

After refluxing in ethanol, M(IV)PWs (Type-I catalysts) were dried at room temperature followed by acid treatment (by method reported earlier in chapter 2). This regeneration procedure was followed for subsequent catalytic run.

In case of 12-TPA/M(IV)O_2-20 (Type-II catalysts), after refluxing in ethanol, the catalysts were dried at room temperature followed by drying at 120°C for 3 hrs. This reactivation procedure was followed for subsequent catalytic run.

3.6 RESULTS AND DISCUSSION (MONOESTERS)

Monoesters (EA, PA, BA and BzA) were synthesized as described in experimental section which can be presented as Scheme 3.2.



$$\underset{\text{Acetic Acid}}{CH_3COOH} + \underset{\text{Alcohol}}{R\text{-}OH} \underset{\Delta}{\overset{H^+/\text{Catalyst}}{\rightleftharpoons}} \underset{\text{Monoester}}{CH_3COOR} + H_2O$$

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

Scheme 3.2 *Synthesis of monoesters (EA, PA, BA and BzA)*

Equilibrium constants of the esterification reactions are low. As in any equilibrium reaction, the reaction may be driven to the product side by controlling the concentration of one of the reactants (Le Chatlier’s Principle) or by removing the water produced. Following this principle, solvent (cyclohexane/toluene) 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 (Type-I catalyst) and 12-TPA/ZrO_2-20 (Type-II catalyst) as solid acid catalysts for synthesis of EA by varying several parameters such as reaction time, catalyst amount and mole ratio of the reactants (Table 3.1).

For both the catalysts, it is observed that as reaction time increases (1-10h), percentage yield increases (Figure 3.2). However, there is not much gain in % yield after 8 h. The temperature parameter has not been varied as the reaction temperature is sensitive to boiling points of reactants [ethanol (78°C), 1-propanol (97°C), 1-butanol (118°C), benzyl alcohol (205°C) and acetic acid (115°C)] as well as solvents (used as azeotrope). 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 (Figure 3.3). The influence of reactant mole ratio was studied by increasing mole ratio from 1:1.5 to 1.5:1 (acid:alcohol) (Figure 3.4). As observed from Table 3.1, the % yield of ester increases with increase in mole ratio of acid while decreases with increasing mole ratio of alcohol. This may be attributed to preferential adsorption of alcohol on the catalyst which results in blocking of active sites. For economic reasons also, the reactant that is usually less expensive of the two is taken in excess. In the present study, acids were used in excess. As observed from Table 3.2 to 3.5, the yields of the monoesters are always high when acid is taken in excess. Apart from driving the equilibrium toward product side, the excess acid catalyzes the reaction.

Further, at optimized conditions [Table 3.1, mole ratio of reactants = 1:1.5 (alcohol:acid); catalyst amount = 0.15 g; reaction time = 8 h] synthesis of EA, PA, BA and BzA was performed using ZrPW, TiPW, SnPW, 12-TPA/ZrO_2-20, 12-TPA/TiO_2-20 and 12-TPA/SnO_2-20 (Table 3.2 - 3.5, Figure 3.5 – 3.8).

Synthesis of monoesters, EA, PA, and BA has been reported [62] 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. In another report [26], high yields of BzA were obtained with small amount of the catalyst but the reaction time was relatively high. In the present work, order of % yield of monoester formed is observed to be 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. 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 [1-butanol (118^oC)] react more than the lighter ones [ethanol (78^oC) and 1-propanol (97^oC)]. Further, yields are lower for PA compared to EA is attributed to the boiling point of 1-propanol (97^oC) which is less than the temperature of the reaction (110^oC). 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 (Table 3.2 – 3.5).

In the present study, amongst M(IV)PWs performance of catalyst in terms of % yield/TON of monoesters formed is found to be TiPW > SnPW > ZrPW whereas, amongst 12-TPA/M(IV)O_2-20, 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 2.5 – 2.10). Comparing performance of M(IV)PWs (Type - I catalysts) and 12-TPA/M(IV)O_2-20 (Type - II catalysts), M(IV)PWs scores over 12-TPA/M(IV)O_2-20 in terms of % yield/TON of monoesters formed.

Regeneration/reactivation and reuse of catalysts

After each catalytic run, there is change in colour of the catalysts [pale yellow in case of 12-TPA/M(IV)O_2-20 and light brown in case of M(IV)PWs]. This is probably due to the fact that reactant molecules come onto surface of catalyst and enter into reaction to give the product, while a few of them get adsorbed on surface. After each subsequent run, the acid sites were regenerated in case of type – I catalysts [M(IV)PWs] and reactivated in case of type – II catalysts [12-TPA/M(IV)O_2-20] as described in experimental section. All subsequent catalytic runs were performed at optimized conditions (Table 3.2 – 3.5).

It is observed that, on regeneration M(IV)PWs exhibited only a marginal decrease in % yields in each subsequent run, probably due to regeneration of the acid sites. However, a reactivation in case of 12-TPA/M(IV)O_2-20 exhibited a much higher decrease in % yields. In case of synthesis of EA, EDX analysis for both fresh and spent catalysts (ZrPW and 12-TPA/ZrO_2-20) has been performed after first catalytic run (Table 3.6; Figure 3.9 – 3.12). Decrease in atomic wt. % of Zr in ZrPW and Zr and W in 12-TPA/ZrO_2-20 is observed, indicating leaching of ions, which could be the probable reason for decrease in % yields.

When M(IV)PWs were used as such after each subsequent run (i.e. without regeneration), the decrease in % yields are much higher compared to regenerated M(IV)PWs, which is probably attributed to the deactivation of catalysts, due to substrate molecules getting adsorbed on surface or also entering interstices of the catalyst material [59].

Proposed mechanism of solid acid catalyzed esterification reaction

The mechanism of esterification can be different for the various solid acid catalysts and also depends on gas- or liquid-phase operation as well as the substrate. Chu et al [22] claim that the esterification mechanism of acetic acid with butanol over carbon-supported HPA catalysts proceeds via a protonated alcohol intermediate, but most authors [63-65] proposed a protonated carboxylic acid as the reaction intermediate.

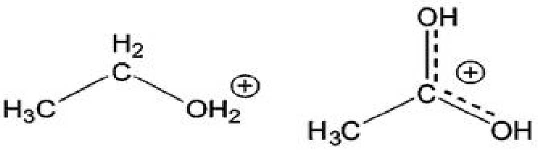
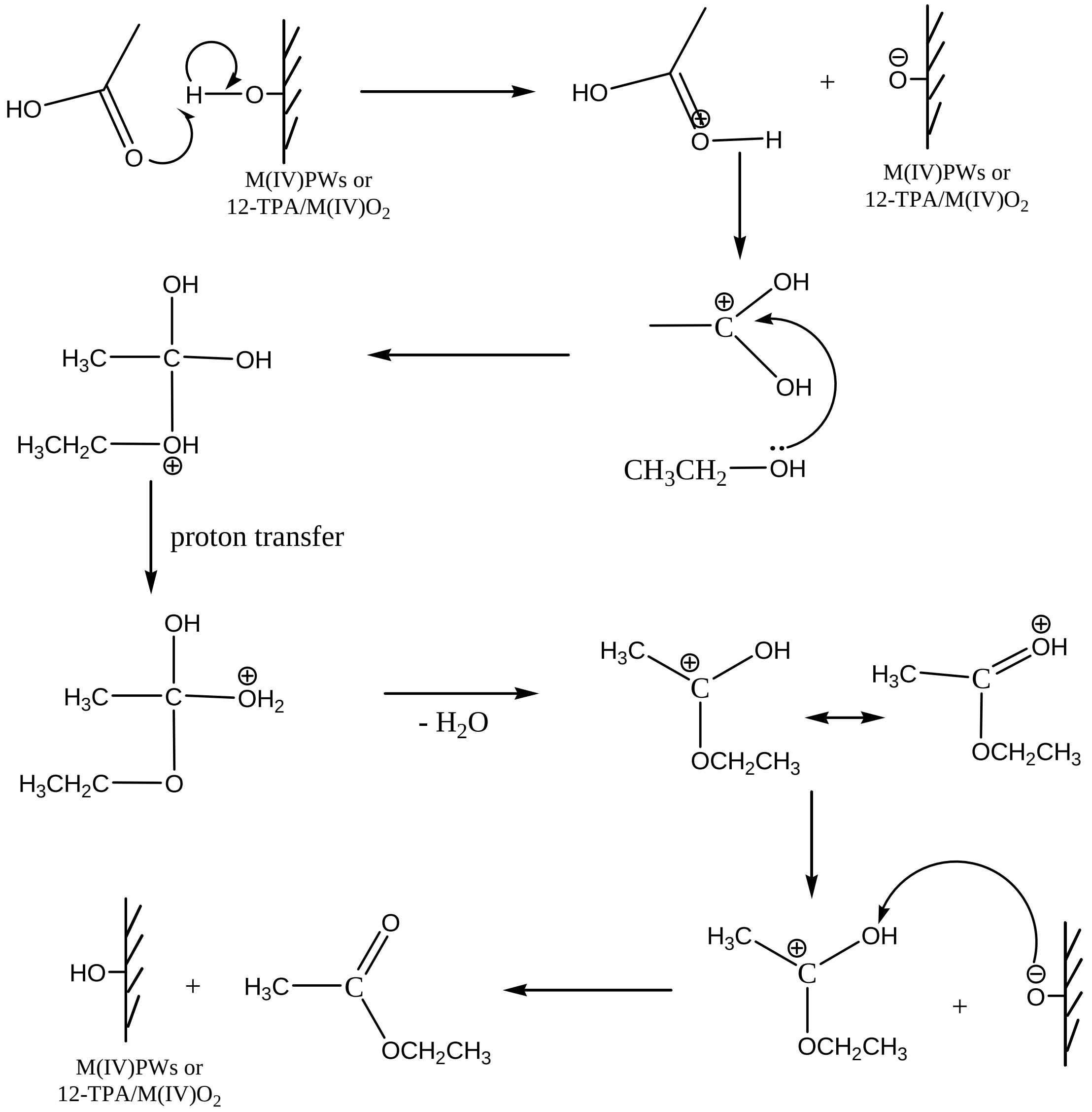


***Figure 3.1** Possible protonated intermediates in esterification reaction*

The two possible intermediates, protonated ethanol and protonated acetic acid, are shown in figure 3.1. Based on the classical mechanism for acid catalyzed esterification reaction, a mechanism is proposed (Scheme 3.3) for esterification of ethanol with acetic acid as a typical case, involving a protonated acetic acid intermediate [61].



***Scheme 3.3** Proposed mechanism for esterification of ethanol with acetic acid using M(IV)PWs and 12-TPA/M(IV)O$_2$*

Table 3.1 *Optimization of reaction conditions for synthesis of EA using ZrPW and 12-TPA/ZrO$_2$-20.*

Set No.	**Substrates with their mole ratio**	**Product formed**	**Catalyst amount (g)**	**Reaction temperature (^{o}C)#**	**Reaction time (h)**	**% Yield of EA**	
						ZrPW	**12-TPA/ ZrO$_2$-20**
(A) Reaction time variation							
1	E:AA (1:1)	EA	0.05	80	1	16.82	14.12
2	E:AA (1:1)	EA	0.05	80	2	29.01	27.19
3	E:AA (1:1)	EA	0.05	80	3	41.90	34.09
4	E:AA (1:1)	EA	0.05	80	4	40.13	37.96
5	E:AA (1:1)	EA	0.05	80	5	42.34	40.58
6	E:AA (1:1)	EA	0.05	80	6	43.72	42.00
7	E:AA (1:1)	EA	0.05	80	7	42.62	42.22
8	E:AA (1:1)	EA	0.05	**80**	**8**	**43.91**	**43.10**
9	E:AA (1:1)	EA	0.05	80	9	44.06	43.60
10	E:AA (1:1)	EA	0.05	80	10	44.89	43.92
(B) Catalyst amount variation							
11	E:AA (1:1)	EA	0.10	80	8	60.00	55.10
12	E:AA (1:1)	EA	**0.15**	80	8	**64.30**	**58.99**
13	E:AA (1:1)	EA	0.20	80	8	65.80	60.89
(C) Mole ratio variation							
14*	**E:AA (1.5:1)**	**EA**	**0.15**	**80**	**8**	**22.05**	**20.54**
15	E:AA (1:1.5)	EA	0.15	80	8	76.92	64.41

*(#Cyclohexane was used as solvent at 80^{o}C and toluene was used at 110^{o}C; E: Ethanol; AA: Acetic acid; *Optimum condition)*

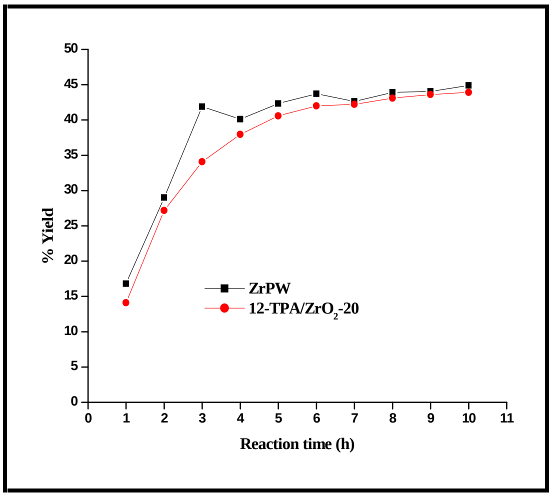


Figure 3.2 *Optimization of reaction time for synthesis of EA*

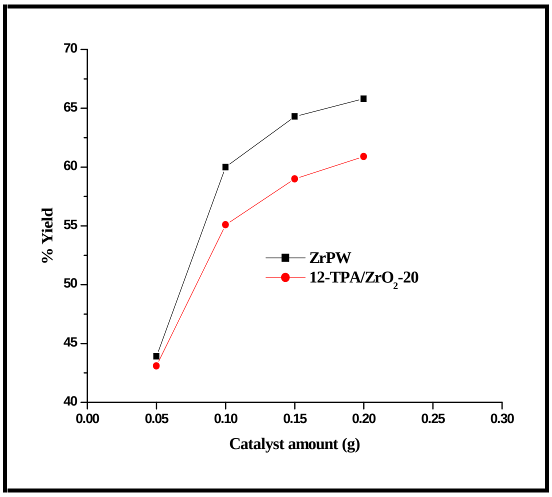


Figure 3.3 *Optimization of amount of catalyst for synthesis of EA*

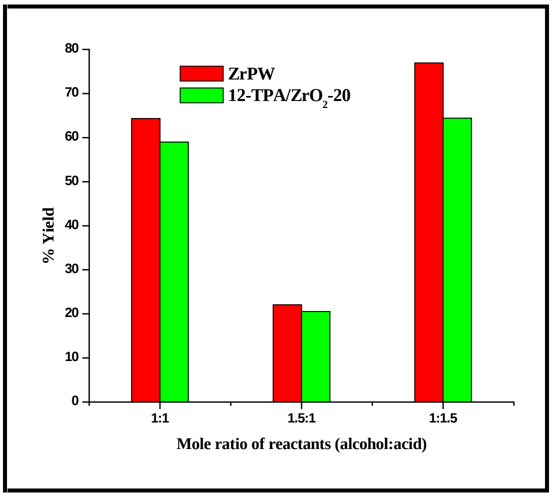


Figure 3.4 *Optimization of mole ratio of reactants for synthesis of EA*

Table 3.2 *Synthesis of mono ester - ethyl acetate (EA) at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Catalyst	**% Yield (TON) of EA**		
	Catalytic Run		
	1	***2***	***3***
ZrPW	76.92 (34.87) *(F)*	75.11 (34.04) *(Rg)*	72.98 (33.08) *(Rg)*
TiPW	99.64 (45.10) *(F)*	96.22 (43.55) *(Rg)*	95.02 (43.01) *(Rg)*
SnPW	85.54 (38.71) *(F)*	84.10 (38.06) *(Rg)*	82.12 (37.16) *(Rg)*
ZrPW	76.92 (34.87) *(F)*	64.25 (28.70) *(Ru)*	51.87 (23.51) *(Ru)*
TiPW	99.64 (45.16) *(F)*	89.25 (39.86) *(Ru)*	78.55 (35.60) *(Ru)*
SnPW	85.54 (38.77) *(F)*	76.45 (34.14) *(Ru)*	68.08 (30.85) *(Ru)*
12-TPA/ ZrO_2-20	64.41 (29.14) *(F)*	49.11 (22.22) *(Ra)*	39.10 (17.69) *(Ra)*
12-TPA/ TiO_2-20	73.67 (33.33) *(F)*	62.54 (28.29) *(Ra)*	51.44 (23.27) *(Ra)*
12-TPA/ SnO_2-20	70.17 (31.75) *(F)*	58.29 (26.37) *(Ra)*	48.12 (21.77) *(Ra)*

[Mole ratio Acetic acid:Ethanol=1.5:1, Reaction temperature: 80^{0}C; Reaction time: 8 h; Catalyst amount: 0.15g; Solvent: cyclohexane; F: Fresh catalyst; Rg: Regenerated catalyst; Ru: Reused catalyst (used as such, without regeneration); Ra: Reactivated catalyst]

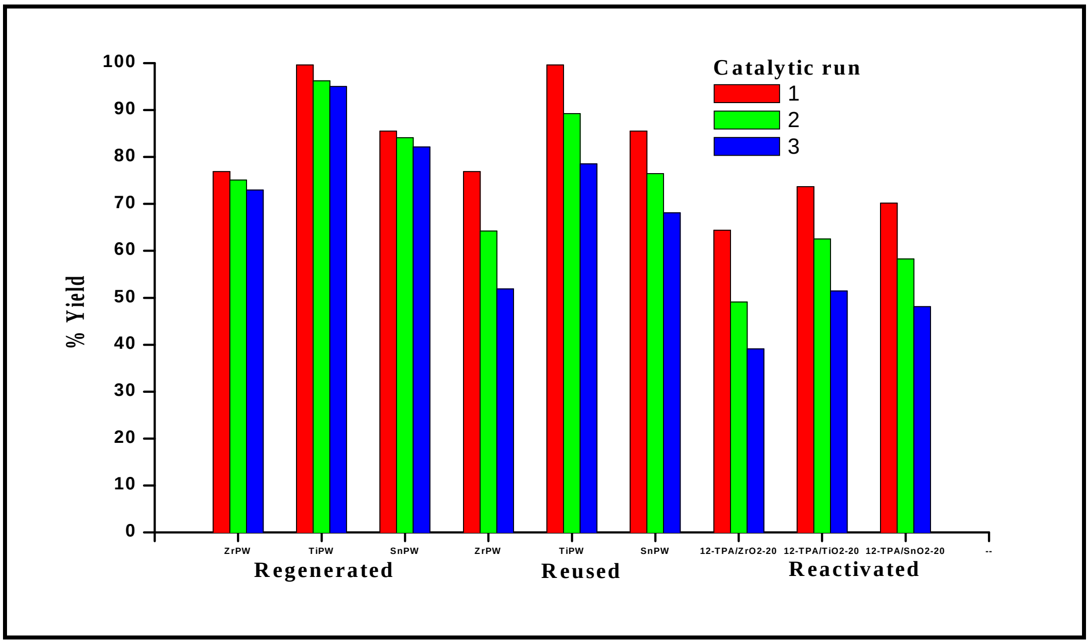


***Figure 3.5** Comparison of % yields of EA at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Table 3.3 *Synthesis of mono ester - propyl acetate (PA) at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Catalyst	**% Yield (TON) of PA**		
	Catalytic Run		
	1	***2***	***3***
ZrPW	56.95 (28.47) *(F)*	55.44 (27.72) *(Rg)*	52.10 (26.05) *(Rg)*
TiPW	68.11 (34.00) *(F)*	65.11 (32.50) *(Rg)*	63.88 (31.89) *(Rg)*
SnPW	66.78 (33.34) *(F)*	65.10 (32.50) *(Rg)*	64.52 (32.21) *(Rg)*
12-TPA/ ZrO_2-20	48.69 (24.30) *(F)*	34.60 (17.27) *(Ra)*	28.10 (14.02) *(Ra)*
12-TPA/ TiO_2-20	53.88 (26.89) *(F)*	44.67 (22.30) *(Ra)*	38.98 (19.45) *(Ra)*
12-TPA/ SnO_2-20	51.00 (25.46) *(F)*	40.18 (20.05) *(Ra)*	32.19 (16.07) *(Ra)*

(Mole ratio Acetic acid:Propanol=1.5:1, Reaction temperature: 110°C; Reaction time: 8 h; Catalyst amount: 0.15g; Solvent: Toluene; F: Fresh catalyst; Rg: Regenerated catalyst; Ra: Reactivated catalyst)

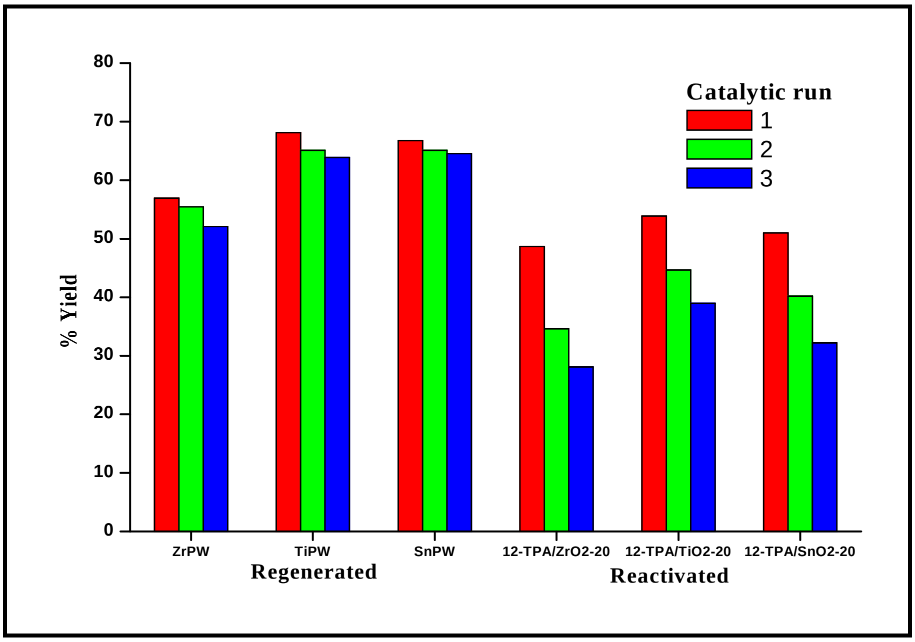


Figure 3.6 *Comparison of % yields of PA at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Table 3.4 *Synthesis of mono ester - butyl acetate (BA) at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Catalyst	**% Yield (TON) of BA**		
	Catalytic Run		
	1	***2***	***3***
ZrPW	84.92 (45.87) *(F)*	82.11 (44.88) *(Rg)*	81.68 (44.65) *(Rg)*
TiPW	89.81 (49.03) *(F)*	87.32 (47.67) *(Rg)*	85.90 (46.90) *(Rg)*
SnPW	87.38 (47.70) *(F)*	86.10 (47.01) *(Rg)*	84.78 (46.28) *(Rg)*
12-TPA/ ZrO_2-20	75.29 (41.09) *(F)*	62.99 (36.02) *(Ra)*	49.00 (26.74) *(Ra)*
12-TPA/ TiO_2-20	84.05 (45.88) *(F)*	68.99 (37.66) *(Ra)*	55.10 (30.07) *(Ra)*
12-TPA/ SnO_2-20	80.85 (44.13) *(F)*	62.80 (34.79) *(Ra)*	51.98 (28.37) *(Ra)*

(Mole ratio Acetic acid:n-butanol=1.5:1, Reaction temperature: 110^{o}C; Reaction time: 8 h; Catalyst amount: 0.15g; Solvent: Toluene; F: Fresh catalyst; Rg: Regenerated catalyst; Ra: Reactivated catalyst)

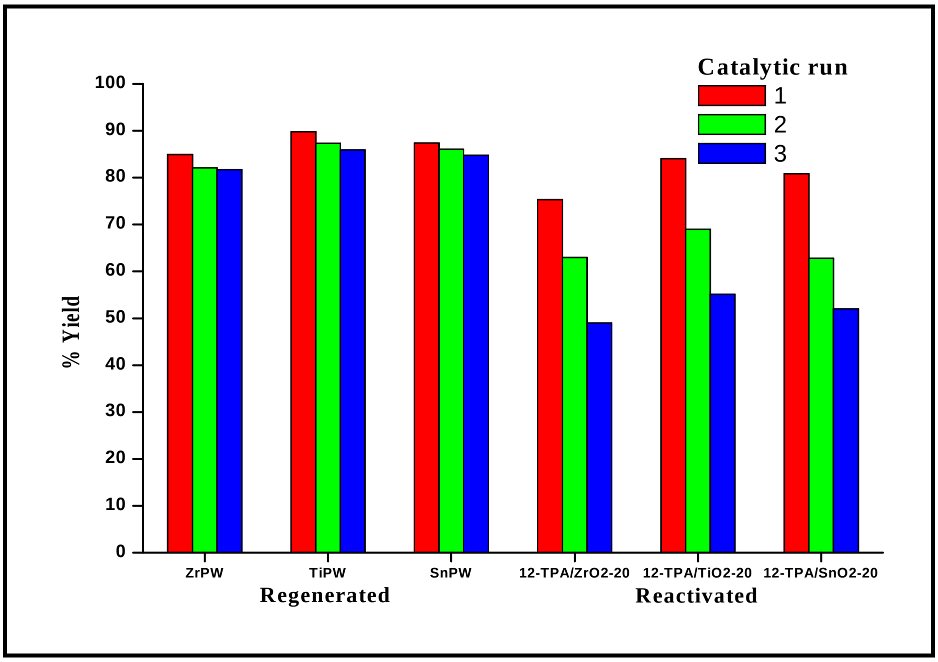


Figure 3.7 *Comparison of % yields of BA at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Table 3.5 *Synthesis of mono ester - benzyl acetate (BzA) at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Catalyst	**% Yield (TON) of BzA**		
	Catalytic Run		
	1	***2***	***3***
ZrPW	87.35 (57.65) *(F)*	86.00 (56.69) *(Rg)*	83.69 (55.17) *(Rg)*
TiPW	88.19 (58.14) *(F)*	86.72 (57.17) *(Rg)*	83.99 (55.37) *(Rg)*
SnPW	87.81 (57.89) *(F)*	86.78 (57.21) *(Rg)*	85.10 (56.10) *(Rg)*
12-TPA/ ZrO_2-20	78.44 (51.70) *(F)*	64.57 (42.56) *(Ra)*	52.99 (34.93) *(Ra)*
12-TPA/ TiO_2-20	85.00 (56.03) *(F)*	69.19 (45.61) *(Ra)*	54.65 (36.02) *(Ra)*
12-TPA/ SnO_2-20	82.01 (54.06) *(F)*	65.07 (42.89) *(Ra)*	53.09 (34.99) *(Ra)*

(Mole ratio Acetic acid:Benzyl alcohol=1.5:1, Reaction temperature: 110^{o}C; Reaction time: 8 h; Catalyst amount: 0.15g; Solvent: Toluene; F: Fresh catalyst; Rg: Regenerated catalyst; Ra: Reactivated catalyst)

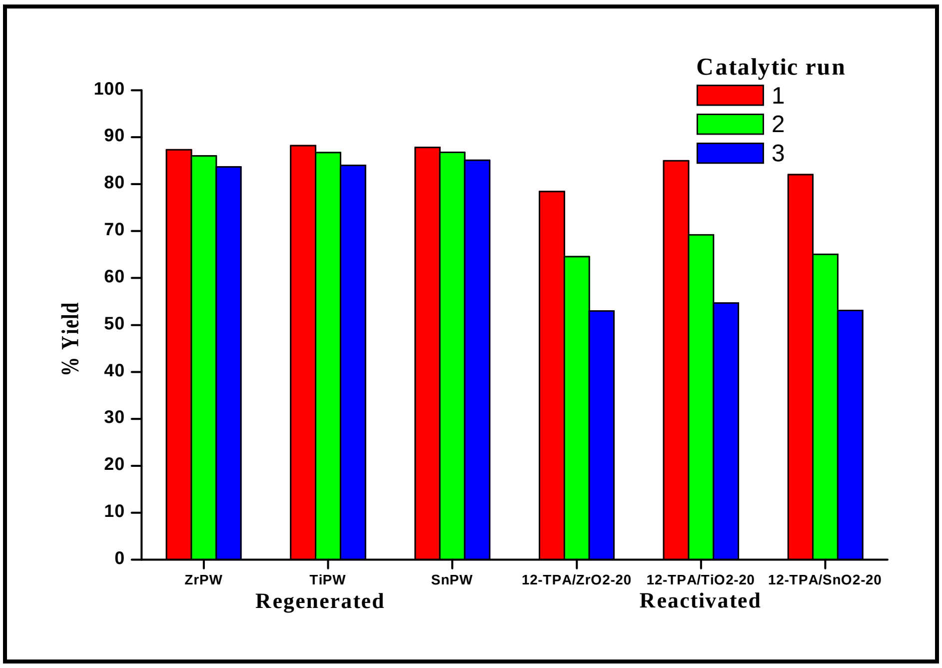


Figure 3.8 *Comparison of % yields of BzA at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

***Table 3.6** Elemental analysis by EDX for both fresh and spent ZrPW and 12-TPA/ZrO_2-20 in the synthesis of EA.*

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

(Mole ratio Acid:Alcohol=1.5:1, Reaction temperature: 80°C; Reaction time: 8 h; Amount of catalyst: 0.15g; Solvent: cyclohexane)

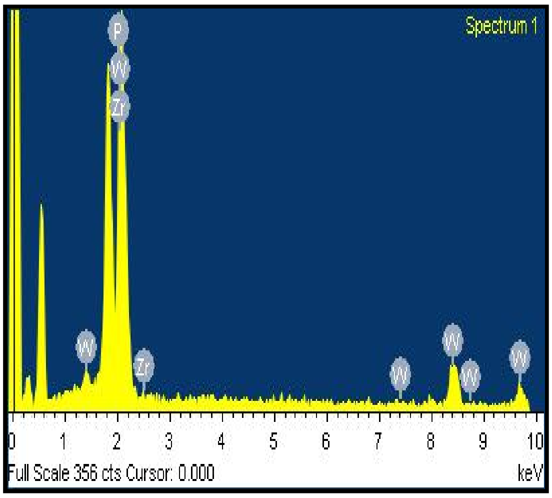


Figure 3.9 *EDX of fresh ZrPW*

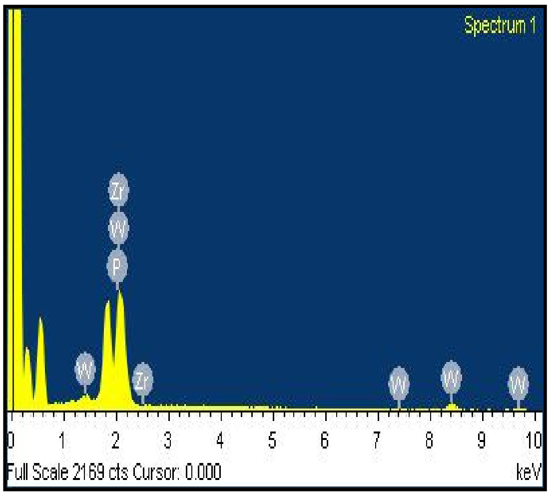


Figure 3.10 *EDX of spent ZrPW in synthesis of EA*

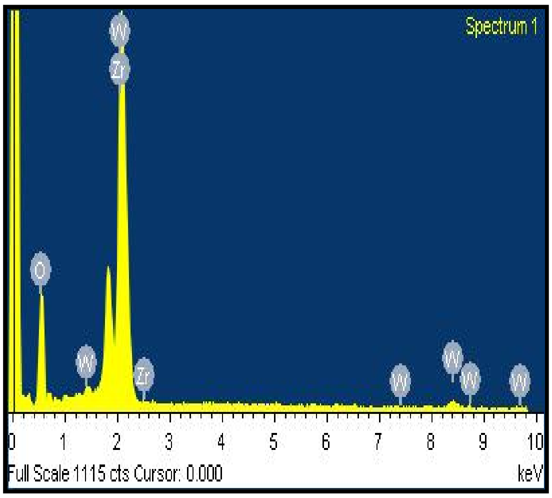


Figure 3.11 *EDX of fresh 12-TPA/ZrO_2-20*

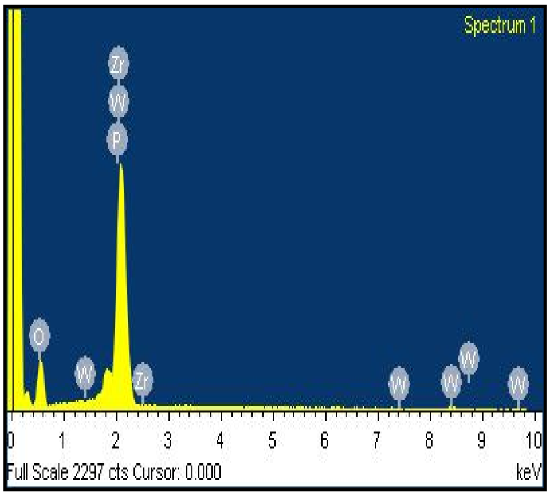
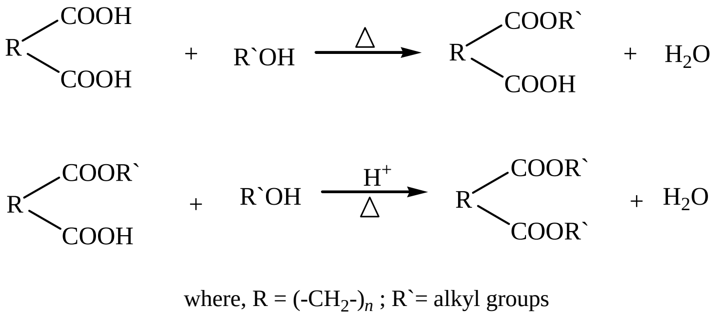


Figure 3.12 *EDX of spent 12-TPA/ZrO_2-20 in synthesis of EA*

3.7 DIESTERS

Reactions involved for diester synthesis are presented in Scheme 3.4.



Scheme 3.4 *Schematic presentation of diester formation*

Diesters can be prepared using dicarboxylic acid or anhydride. Diesters are prepared in two stages (Scheme 3.4) [66-68]. The first stage is very rapid and can be carried out in the absence of a catalyst. However, esterification of the second carboxylic group is very slow and needs to be facilitated by an acid catalyst, resulting in the formation of water as a byproduct. The reaction is an equilibrium one and hence to facilitate it in the forward direction, the water molecule must be removed by azeotrope formation. The current commercial process is a batch method which is very efficient with respect to its feed stocks. Conversion (based on phthalic anhydride) and selectivity can reach 99.2 and 99.8 %, respectively [66]. To reach this high conversion, a 20 % excess of alcohol is used [66]. The excess is recovered after reaction by a steam stripping process. Hardly any purification is required after synthesis because of the high selectivity, usually only a decolorization is carried out. A typical byproduct is the dialkyl ether formed by the condensation of two molecules of alcohol.

A large number of catalysts have been reported for the synthesis of diesters. Normally, liquid phase catalysts such as sulphuric acid, p-toluene sulfonic acid (PTSA), methanesulfonic acid (MSA), hydrochloric acid, phosphoric acid etc. have been used. The kinetics of esterification reaction have been studied by Bhutada and Pangarkar [69] by using homogeneous catalysts such as tetrabutyl titanate (TBT), tetra butyl zirconate (TBZ) and p-toluene sulfonic acid (PTSA). The alkyl titanates have the advantage of very low byproduct formation when compared with PTSA or sulphuric acid. However, their very low activity as compared to the bronsted acids, necessitates reaction temperatures as high as 200°C. Further, homogeneous catalysts are known to colour the product and cannot be reused. As already mentioned, liquid acids have several disadvantages. Due to these problems accompanied by the increasing environmental awareness, efforts are being focused for replacement of these conventional liquid acids by suitable solid acids.

3.8 LITERATURE SURVEY IN THE CURRENT AREA OF STUDY (DIESTERS)

Bhagiyalakshmi et al [70] have studied effect of hydrophobic and hydrophilic properties of Al-MCM-41 (Si/Al = 50,100 and 150) and Hβ zeolite on the esterification of maleic anhydride with ethanol. Wang et al studied the synthesis of n-butyl, isopentyl and benzyl acetates, ethyl and n-butyl benzoates and DOP using ZSM-5 and HY zeolites [57]. HY was found to be an excellent catalyst for the synthesis of phthalates and benzoates compared to ZSM-5.

Suter has reported a noncatalytic process for the manufacture of DOP, at very high temperatures, at which autocatalysis occurs [71]. Bekkum and Schwegler investigated the use of HPAs (homogeneous and carbon supported) for DOP synthesis [72]. They obtained a superior activity at low temperatures in both homogeneous and supported form. Thorat et al [73] have reported the use of solid super acids (sulfated and HPA supported onto oxides) for the synthesis of DOP. They have reported a selectivity > 99 % and demonstrated that selection of optimum calcination temperature is a must for the optimum yield. Yadav et al [74] also have reported esterification of maleic acid with ethanol over cation-exchange resin catalysts. G Lu [75] also investigated DOP synthesis over solid superacids SO_4^{2-}/Ti-M-O (M = Al, Fe, Sn). They obtained superior activity in case of SO_4^{2-}/Ti-Al-Sn-O system and found that acid strength, surface area and catalytic activity of the system is affected by the preparation conditions. Ma et al [76] studied the synthesis of DOP using ZSM-5 and HY zeolites. Z H Zhao [62] has also reported the use of aluminophosphate and silicoaluminophosphate molecular sieves as solid acid catalyst for the synthesis of DOP. Amini et al [66] have reported the use of heteropoly acids for the production of DOP and DBP. DEM synthesis has been reported by Reddy et al [77] using montmorillonite clay, but the yield is low (41 %) and relatively high amount of catalyst (0.5 g) was used. In another report, DEM was synthesized by Jiang et al [78] using the reaction of CO with $ClCH_2COOC_2H_5$. In this case high yield was observed but the reaction was carried out at high pressure. Kolah et al [1] have reported esterification of succinic acid with ethanol and also have reported esterification of triethyl citrate via mono and di-ethyl citrate catalyzed by macro porous Amberlyst-15 ion exchange resin. Patel et al [79] have reported synthesis and characterization of 12-TPA anchored to MCM-41 as well as its use as environmentally benign catalyst for synthesis of succinate and malonate diesters. Ren et al have reported catalytic activity of a novel carbon-based solid acid catalyst for esterification of succinic acid with ethanol [80]. Okudan et al have reported esterification reaction of polystyrene modified with maleic anhydride in the presence of resin catalyst [81].

From our laboratory, TMA salts have been widely investigated as solid acid catalysts for synthesis of diesters such as dioctyl phthalate (DOP), dibutyl phthalate (DBP) and diethyl malonate (DEM) [59-61].

3.9 OBJECTIVES OF THE PRESENT WORK (DIESTERS)

In the present study, the potential utility of M(IV)PWs (Type-I Inherent SACs) and 12-TPA/M(IV)O_2 (Type-II Induced SACs) has been explored by studying esterification as a model reaction, wherein diesters diethyl malonate (DEM), diethyl succinate (DES), dioctyl phthalate (DOP) and dibutyl phthalate (DBP) have been synthesized. Reaction parameters, reaction time, catalyst amount and mole ratio of the reactants have been optimized. Catalytic performance of Type-I and Type-II catalysts have been compared at optimized condition and correlated with acid properties of the materials. The performance ability of the catalysts have also been assessed for regenerated/ reactivated catalysts.

3.10 EXPERIMENTAL (DIESTERS)

Catalyst Synthesis and Characterization

The synthesis and characterization of Type-I catalysts ZrPW, TiPW, SnPW [Inherent SACs - M(IV)PWs] and Type – II catalysts 12-TPA/ZrO_2-20, 12-TPA/TiO_2-20, 12-TPA/SnO_2-20 [Induced SACs - 12-TPA/M(IV)O_2-20] have been discussed in Chapter 2.

Materials and Methods

Ethanol, 1-butanol, toluene, xylene, phthalic anhydride, 2-ethyl-1-hexanol, succinic acid and malonic acid were procured from Loba chemicals (India). Yields of ester formed were determined by GC performed on Chemito 800 plus, equipped with flame-ionization detector (FID), oven temperature: 150°C, injector temperature: 200°C, detector temperature: 220°C, split ratio is 1:2. EDX analysis for fresh and spent catalysts has been performed on Jeol JSM-5610-SLV scanning electron microscope.

Experimental setup

The diesters have been synthesized in two steps (Scheme 3.5 and 3.6). The mono ester was prepared in first step by taking equimolar proportion (0.025 M) of acid and alcohol (malonic acid and ethanol for DEM, succinic acid and ethanol for DES, phthalic anhydride and 1-butanol for DBP, phthalic anhydride and 2-ethyl-1-hexanol for DOP) 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 and anhydride gets completely converted to the monoester, so that the acid concentration at this stage is taken as the initial concentration. The obtained product (monoester) was then subjected to esterification reaction by addition of a second mole (0.025 M) of respective alcohol, catalyst (0.10 - 0.25 g) and 10 mL solvent [toluene (b.p. 110°C) for DEM, DES and DBP, and xylene (b.p. 140°C) for DOP]. 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 the reaction temperature is sensitive to boiling points of reactants as well as solvents (used as azeotrope). In all cases the round bottomed flask was fitted with Dean and Stark apparatus, with a condenser to remove water formed during the reaction. The reaction mixture was distilled to obtain the product.

Calculation of % yield of esters

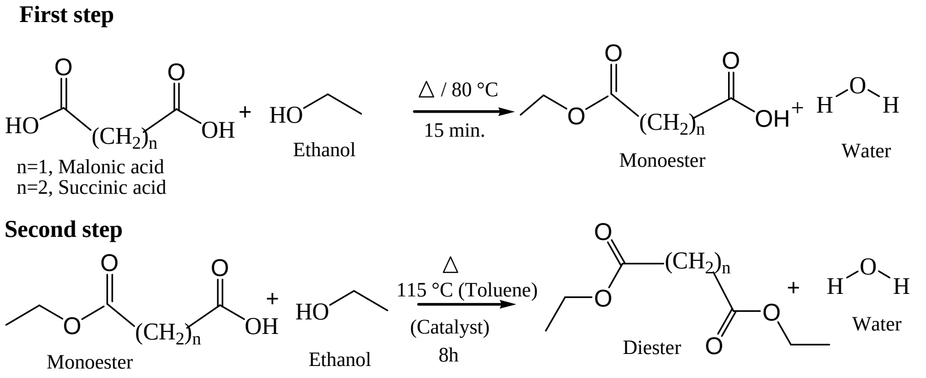
The yields of the diesters formed were determined by method described earlier in experimental for monoesters.

Regeneration/Reactivation of catalyst

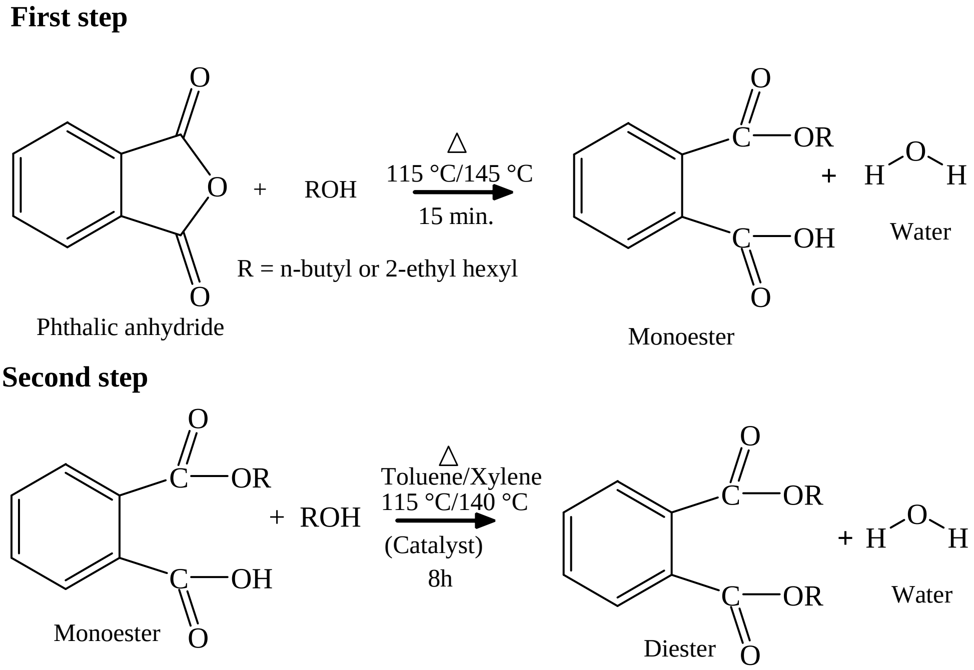
All the catalysts (Type-I and II) were regenerated/reactivated by method described earlier in experimental for monoesters.

3.11 RESULTS AND DISCUSSION (DIESTERS)

Diesters DEM, DES, DOP, and DBP were synthesized in two steps as described in experimental section and have been presented in scheme 3.5 and 3.6. 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. 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 [61].



Scheme 3.5 *Synthesis of DEM and DES*



Scheme 3.6 *Synthesis of DBP and DOP*

Firstly, reaction conditions were optimized in case of synthesis of DEM by varying parameters such as reaction time, catalyst amount and mole ratio of the reactants using ZrPW and 12-TPA/ZrO_2-20 as solid acid catalysts (Table 3.7).

For both type of catalysts, it is observed that as reaction time increases (1-10h), percentage yield increases (Figure 3.13). However, there is not much gain in product after 8 h. 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). With increasing amount of the catalyst (0.10g – 0.25g), the % yield increases which is probably due to proportional increase in the number of active sites (Figure 3.14). The influence of reactant mole ratio was studied by increasing mole ratio from 2:1 to 2.4:1 (alcohol:acid/anhydride) (Figure 3.15). As observed from Table 3.7, the % yields of diester are higher in case of mole ratio 2:1 (alcohol:acid/anhydride).

At optimized conditions [Table 3.7, mole ratio of reactant = 2:1 (alcohol: acid/anhydride), catalyst amount = 0.15 g and reaction time = 8 h] synthesis of DEM, DES, DOP and DBP using ZrPW, TiPW, SnPW, 12-TPA/ZrO_2-20, 12-TPA/TiO_2-20 and 12-TPA/SnO_2-20 has been performed (Table 3.8 - 3.11, Figure 3.16-3.19).

In all cases, order of % yields of diesters formed is 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. 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 the heavier alcohols react more than the lighter ones. Further, higher yields in case of DEM and DES compared to DOP and DBP is probably due to less steric hindrance felt by incoming ethanol from monoethyl malonate formed in the first step. Also the stability of carbocation is higher for an intermediate containing branched alcohol (2-ethyl-1-hexanol) compared to straight chain alcohol (n-butanol).

DEM synthesis has been reported by Reddy et al [77] using montmorillonite clay, but the yield is low (41 %) and relatively high amount of catalyst (0.5 g) was used. In another report, DEM has been synthesized by Jiag et al using the reaction of CO with $ClCH_2COOC_2H_5$. In this case high yield was observed but the reaction was carried out at high pressure [82]. Succinic acid esterification (diethyl succinate – DES) kinetics has been studied by Kolah et al using Amberlyst-15 ion exchange resin as solid acid catalyst [1]. However, study on % yields of DES has not been discussed. DOP formation has been catalyzed by solid super acids [73] and heteropoly acids [78]. Though, % yields of DOP are high, these solid acid catalysts suffer leaching and cannot be reused. Suter [71] has reported a non-catalytic process for the manufacture of DOP, at very high temperatures, at which autocatalysis occurs.

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 work good % yields of diesters are obtained with the advantage that the diester is the single product and colourless.

In the present study, amongst M(IV)PWs performance of catalyst in terms of % yield/TON of diesters formed is found to be TiPW > SnPW > ZrPW whereas, amongst 12-TPA/M(IV)O_2-20, 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 2.5 – 2.10). Comparing performance of M(IV)PWs (Type-I catalysts) and 12-TPA/M(IV)O_2-20 (Type-II catalysts), M(IV)PWs (Type-I catalysts) scores over 12-TPA/M(IV)O_2-20 (Type-II catalysts) in terms of % yield/TON of diesters formed.

Regeneration/reactivation and reuse of catalysts

After each catalytic run, there is change in colour of the catalysts [pale yellow in case of 12-TPA/M(IV)O_2-20 and light brown in case of M(IV)PWs]. This is probably due to the fact that reactant molecules come onto surface of catalyst and enter into reaction to give the product, while a few of them get adsorbed on surface. After each subsequent run, the acid sites were regenerated in case of type – I catalysts [M(IV)PWs] and reactivated in case of type – II catalysts [12-TPA/M(IV)O_2-20] as described in experimental section. All subsequent catalytic runs were performed at optimized conditions (Table 3.8 – 3.11).

It is observed that, on regeneration M(IV)PWs exhibited only a marginal decrease in % yields in each subsequent run, probably due to regeneration of the acid sites. However, a reactivation in case of 12-TPA/M(IV)O_2-20 exhibited a much higher decrease in % yields. In case of synthesis of DEM, EDX analysis for both fresh and spent catalysts (ZrPW and 12-TPA/ZrO_2-20) has been performed after first catalytic run (Table 3.12; Figures 3.20-3.23). Decrease in atomic wt. % of Zr in ZrPW and Zr and W in 12-TPA/ZrO_2-20 is observed, indicating leaching of ions, which could be the probable reason for decrease in % yields.

When M(IV)PWs were used as such after each subsequent run (i.e. without regeneration), the decrease in % yields are much higher compared to regenerated M(IV)PWs, which is probably attributed to the deactivation of catalysts, due to substrate molecules getting adsorbed on surface or also entering interstices of the catalyst material [59].

The mechanism of diester formation over solid acid catalyst is similar to that of conventional mechanism involving the formation of protonated dicarboxylic acid, using proton donated by the catalyst, followed by nucleophilic attack of alcoholic group to yield the respective monoester. The second carboxylic group present in monoester gets further esterified by the same mechanism in a repeat reaction, which ultimately results in the diester formation [83].

Table 3.7 *Optimization of reaction conditions for synthesis of DEM using ZrPW and 12-TPA/ZrO_2-20.*

Set No.	**Substrates with their mole ratio**	**Product formed**	**Catalyst amount (g)**	**Reaction temperature $(^{o}C)^{\#}$**	**Reaction time (h)**	**%Yield of DEM**	
						ZrPW	**12-TPA/ ZrO_2-20**
(A) Reaction time variation							
1	E:MA (2:1)	DEM	0.10	115	1	74.04	54.08
2	E:MA (2:1)	DEM	0.10	115	2	75.84	55.32
3	E:MA (2:1)	DEM	0.10	115	3	76.96	56.84
4	E:MA (2:1)	DEM	0.10	115	4	78.00	58.12
5	E:MA (2:1)	DEM	0.10	115	5	80.66	62.69
6	E:MA (2:1)	DEM	0.10	115	6	82.00	66.47
7	E:MA (2:1)	DEM	0.10	115	7	83.36	68.95
8	E:MA (2:1)	DEM	0.10	115	**8**	**83.70**	**72.18**
9	E:MA (2:1)	DEM	0.10	115	9	83.66	72.32
10	E:MA (2:1)	DEM	0.10	115	10	84.00	73.01
(B) Catalyst amount variation							
11*	**E:MA (2:1)**	**DEM**	**0.15**	**115**	**8**	**88.64**	**81.12**
12	E:MA (2:1)	DEM	0.20	115	8	89.76	81.40
13	E:MA (2:1)	DEM	0.25	115	8	90.87	81.89
(C) Mole ratio variation							
14	E:MA (2.2:1)	DEM	0.15	115	8	88.04	74.10
15	E:MA (2.4:1)	DEM	0.15	115	8	87.00	69.80

*($^{\#}$Solvent used: Toluene; E: Ethanol; MA: Malonic acid; DEM: Diethyl malonate; *Optimum condition)*

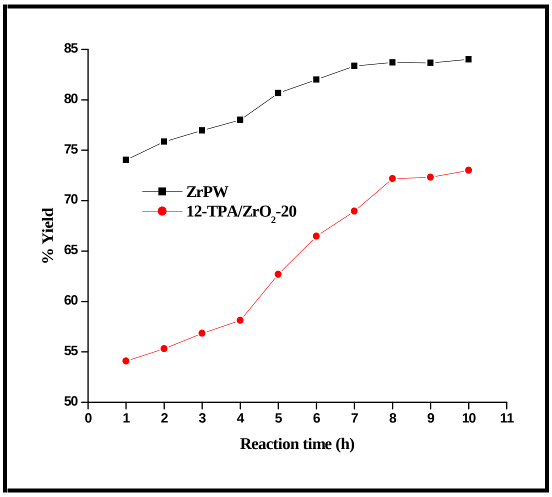


Figure 3.13 *Optimization of reaction time for synthesis of DEM*

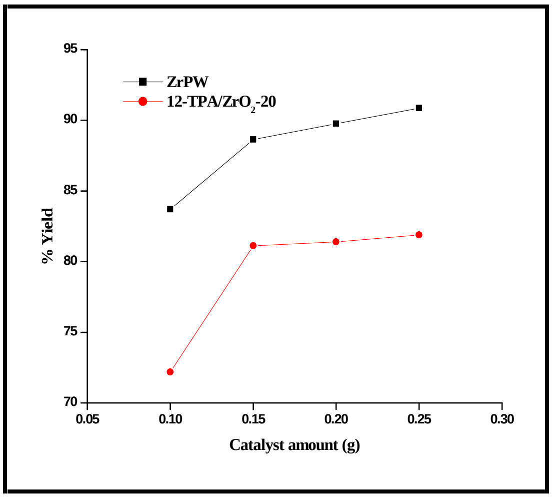


Figure 3.14 *Optimization of amount of catalyst for synthesis of DEM*

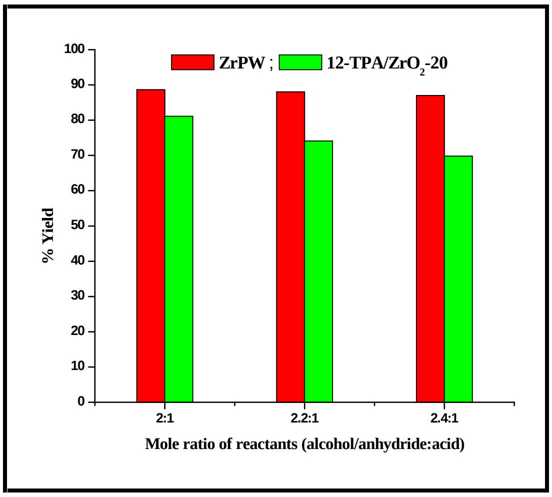


Figure 3.15 *Optimization of mole ratio of reactants for synthesis of DEM*

Table 3.8 *Synthesis of diester – diethyl malonate (DEM) at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Catalyst	**% Yield (TON) of DEM**		
	Catalytic Run		
	1	***2***	***3***
ZrPW	88.64 (28.95) *(F)*	86.71 (28.32) *(Rg)*	84.07 (27.46) *(Rg)*
TiPW	92.10 (32.02) *(F)*	90.13 (29.38) *(Rg)*	89.41 (29.14) *(Rg)*
SnPW	90.14 (29.38) *(F)*	89.51 (29.18) *(Rg)*	87.32 (28.46) *(Rg)*
ZrPW	88.64 (28.95) *(F)*	76.14 (24.86) *(Ru)*	65.72 (21.46) *(Ru)*
TiPW	92.10 (30.08) *(F)*	81.55 (26.62) *(Ru)*	70.33 (22.96) *(Ru)*
SnPW	90.14 (29.43) *(F)*	79.36 (25.91) *(Ru)*	66.80 (21.81) *(Ru)*
12-TPA/ ZrO_2-20	81.12 (26.43) *(F)*	60.45 (19.70) *(Ra)*	45.55 (14.84) *(Ra)*
12-TPA/ TiO_2-20	86.00 (28.02) *(F)*	68.41 (22.29) *(Ra)*	54.00 (17.60) *(Ra)*
12-TPA/ SnO_2-20	84.50 (27.54) *(F)*	66.11 (21.54) *(Ra)*	49.88 (16.25) *(Ra)*

[Mole ratio Malonic acid:Ethanol=1:2, Reaction temperature: 115^0C; Reaction time: 8 h; Catalyst amount: 0.15g; Solvent: Toluene; F: Fresh catalyst; Rg: Regenerated catalyst; Ru: Reused catalyst (used as such, without regeneration); Ra: Reactivated catalyst]

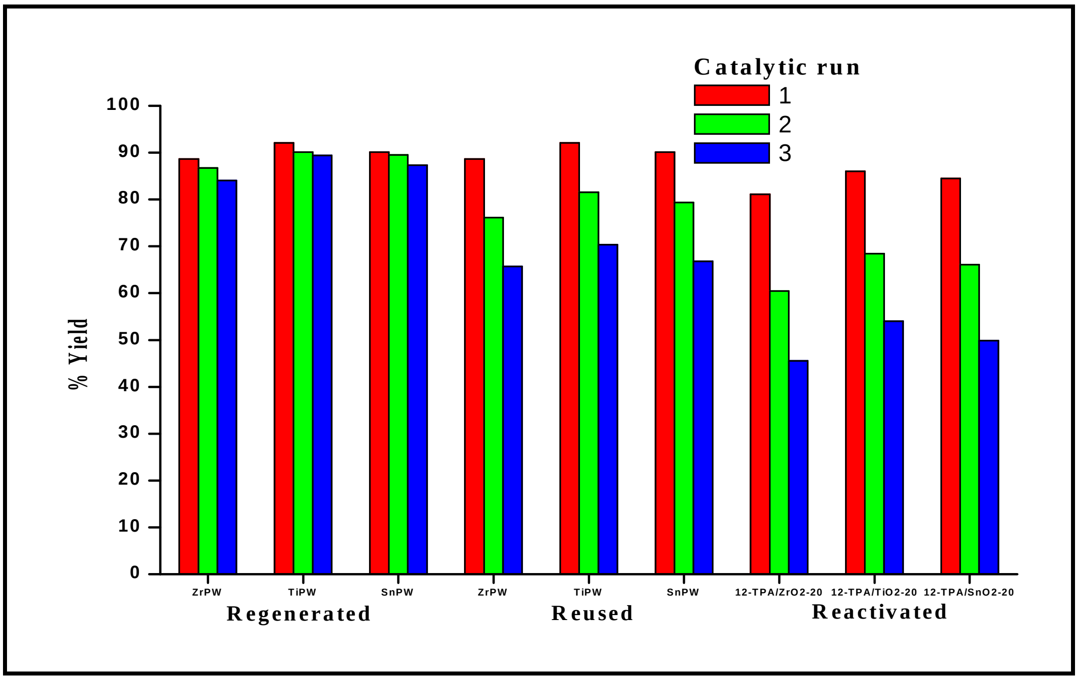


Figure 3.16 *Comparison of % yields of DEM at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Table 3.9 *Synthesis of diester – diethyl succinate (DES) at optimized condition using M(IV)PWs and 12-TPA/M(IV)O$_2$-20.*

Catalyst	**% Yield (TON) of DES**		
	Catalytic Run		
	1	***2***	***3***
ZrPW	81.10 (28.38) *(F)*	80.98 (28.34) *(Rg)*	78.10 (27.33) *(Rg)*
TiPW	88.84 (31.03) *(F)*	87.08 (30.41) *(Rg)*	85.12 (29.37) *(Rg)*
SnPW	84.57 (29.54) *(F)*	82.12 (28.68) *(Rg)*	80.10 (27.97) *(Rg)*
12-TPA/ ZrO_2-20	70.42 (24.58) *(F)*	59.74 (20.86) *(Ra)*	45.42 (15.86) *(Ra)*
12-TPA/ TiO_2-20	80.75 (28.19) *(F)*	65.05 (22.71) *(Ra)*	53.90 (18.82) *(Ra)*
12-TPA/ SnO_2-20	75.78 (28.46) *(F)*	60.00 (20.95) *(Ra)*	49.08 (17.13) *(Ra)*

(Mole ratio Succinic acid:Ethanol=1:2, Reaction temperature: 115^{0}C; Reaction time: 8 h; Catalyst amount: 0.15g; Solvent: Toluene; F: Fresh catalyst; Rg: Regenerated catalyst; Ra: Reactivated catalyst)

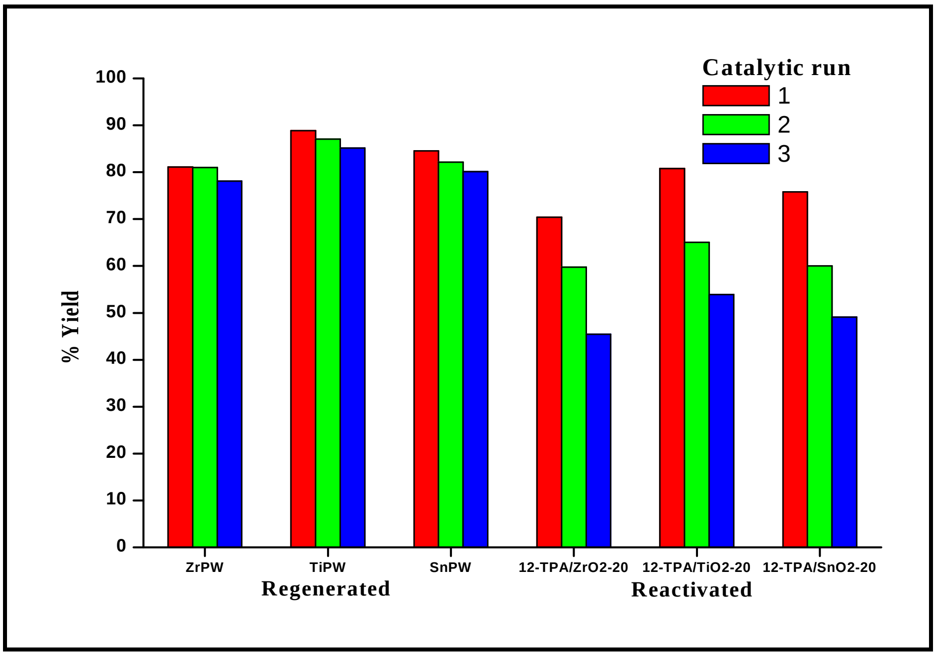


Figure 3.17 *Comparison of % yields of DES at optimized condition using M(IV)PWs and 12-TPA/M(IV)O$_2$-20.*

Table 3.10 *Synthesis of diester – dioctyl phthalate (DOP) at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Catalyst	**% Yield (TON) of DOP**		
	Catalytic Run		
	1	***2***	***3***
ZrPW	80.87 (55.04) *(F)*	79.67 (54.22) *(Rg)*	78.00 (5309) *(Rg)*
TiPW	84.00 (57.12) *(F)*	83.12 (56.52) *(Rg)*	82.78 (56.29) *(Rg)*
SnPW	81.04 (55.10) *(F)*	80.00 (54.40) *(Rg)*	78.14 (53.13) *(Rg)*
12-TPA/ ZrO_2-20	67.54 (45.92) *(F)*	54.45 (37.02) *(Ra)*	41.45 (28.18) *(Ra)*
12-TPA/ TiO_2-20	71.42 (48.56) *(F)*	59.78 (40.64) *(Ra)*	43.99 (29.91) *(Ra)*
12-TPA/ SnO_2-20	69.59 (47.13) *(F)*	59.57 (40.50) *(Ra)*	42.00 (28.55) *(Ra)*

(Mole ratio Phthalic anhydride:2-ethyl-1-hexanol=1:2, Reaction temperature: 140^0C; Reaction time: 8 h; Catalyst amount: 0.15g; Solvent: Xylene; F: Fresh catalyst; Rg: Regenerated catalyst; Ra: Reactivated catalyst)

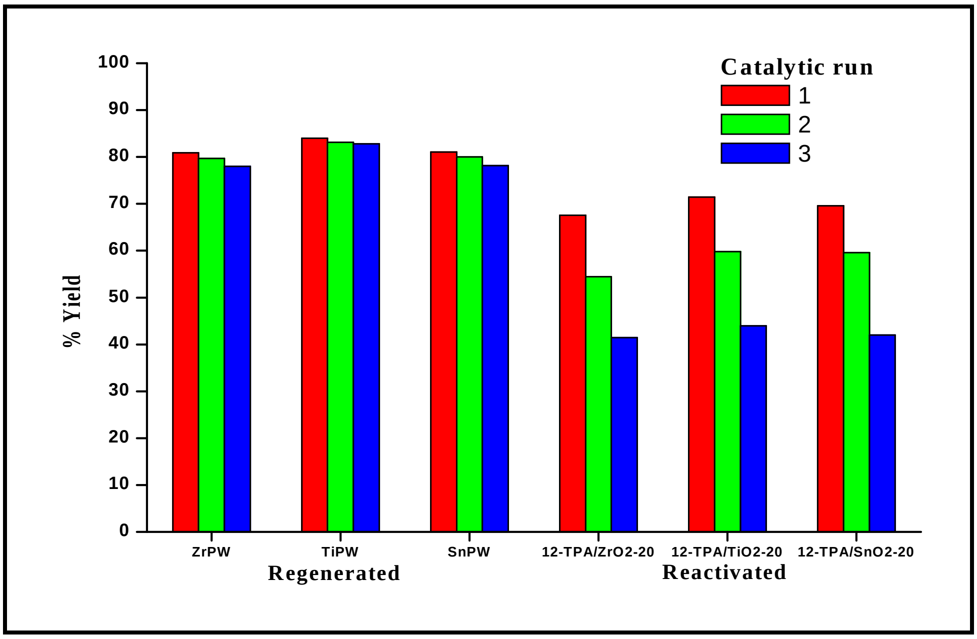


Figure 3.18 *Comparison of % yields of DOP at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Table 3.11 *Synthesis of diester – dibutyl phthalate (DBP) at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Catalyst	% Yield (TON) of DBP		
	Catalytic Run		
	1	*2*	*3*
ZrPW	63.00 (31.08) *(F)*	61.89 (30.53) *(Rg)*	60.10 (29.64) *(Rg)*
TiPW	68.02 (33.55) *(F)*	67.61 (33.35) *(Rg)*	65.69 (32.40) *(Rg)*
SnPW	66.84 (32.97) *(F)*	66.14 (32.62) *(Rg)*	65.00 (32.06) *(Rg)*
12-TPA/ ZrO_2-20	55.25 (27.25) *(F)*	45.12 (22.25) *(Ra)*	30.80 (15.19) *(Ra)*
12-TPA/ TiO_2-20	60.17 (29.67) *(F)*	52.81 (26.04) *(Ra)*	41.89 (20.66) *(Ra)*
12-TPA/ SnO_2-20	57.78 (28.49) *(F)*	48.00 (23.67) *(Ra)*	38.17 (18.82) *(Ra)*

(Mole ratio Phthalic anhydride:n-butanol=1:2, Reaction temperature: 115^0C; Reaction time: 8 h; Amount of catalyst: 0.15g; Solvent: Toluene; F: Fresh catalyst; Rg: Regenerated catalyst; Ra: Reactivated catalyst)

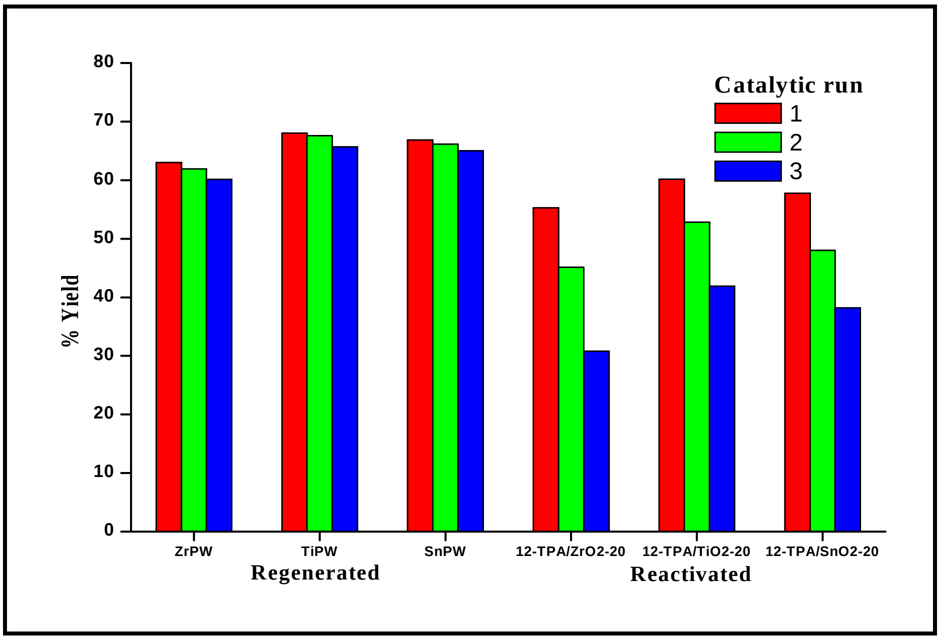


Figure 3.19 *Comparison of % yields of DBP at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Table 3.12 *Elemental analysis by EDX for both fresh and spent ZrPW and 12-TPA/ZrO_2-20 in the synthesis of DEM.*

Ester formed	**Materials**	**% by EDX analysis**			
		Zr	**P**	**W**	**O**
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 Acid:Alcohol=1:2, Reaction temperature: 115^0C; Reaction time: 8 h; Amount of catalyst: 0.15g; Solvent: toluene)

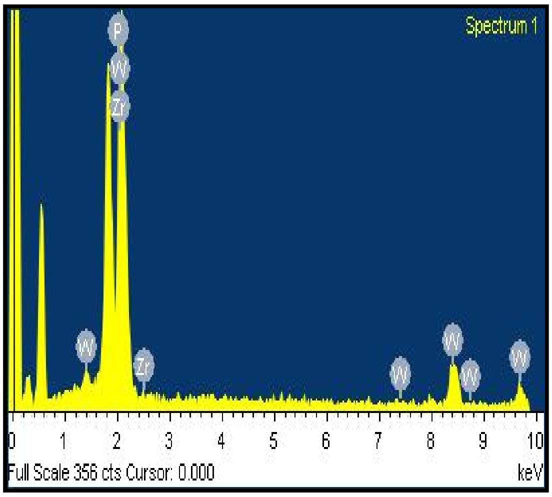


Figure 3.20 *EDX of fresh ZrPW*

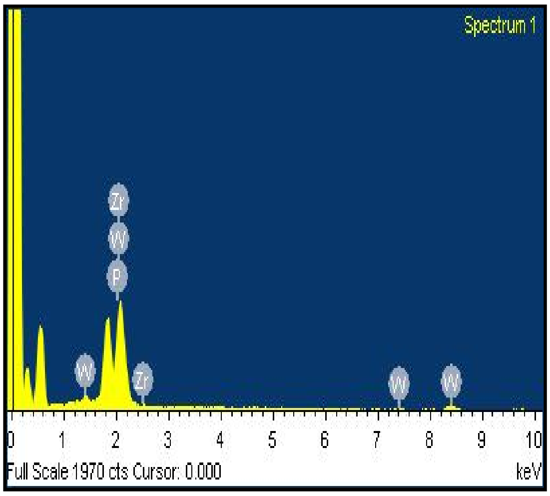


Figure 3.21 *EDX of spent ZrPW in synthesis of DEM*

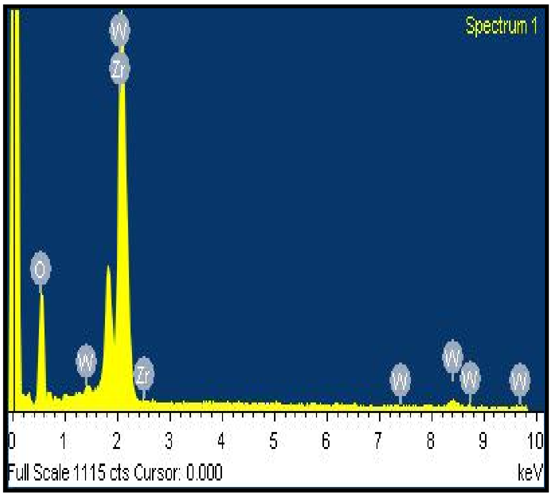


Figure 3.22 *EDX of fresh 12-TPA/ZrO_2-20*

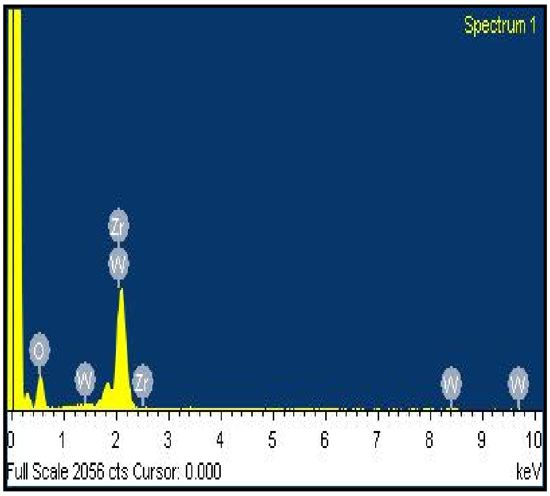


Figure 3.23 *EDX of spent 12-TPA/ZrO_2-20 in synthesis of DEM*

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