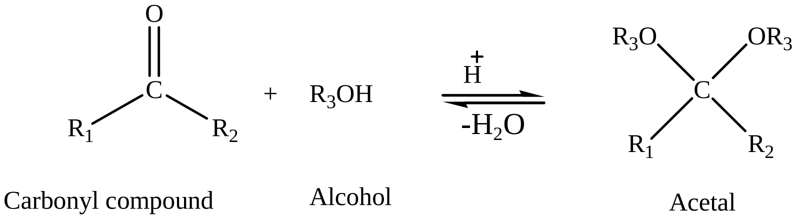
6.1 INTRODUCTION

Acetalization is an acid catalyzed reaction wherein acetals are derived from carbonyl compounds and alcohols (Scheme 6.1), intensely used in organic synthesis to protect the carbonyl group of ketones and aldehydes, which is sometimes necessary in the manipulation of organic molecules with multiple functional groups [1,2]. Protection of the carbonyl groups of aldehydes and ketones can be accomplished by alcohols [3], diols [4] or trioxanes [5]. Based on the alcohol used, a variety of mono and di-acetal derivatives are obtained. Most of the acetalization processes involve the reaction of carbonyl compound with ethylene glycol in presence of an appropriate acid catalyst.



Scheme 6.1 *Acetalization of carbonyl compound* [1,2]

(R_1 = H/alkyl/aryl groups, R_2 & R_3= alkyl/aryl groups)

Acetals are oxygenated compounds that can be prepared following different types of reactions:

- Filley et al have studied the reaction between methyl 9,10-dihydroxystearate and long chain aldehydes to form the corresponding cyclic acetal in the presence of *p*-toluenesulfonic acid (PTSA) [6].
- Reaction of glyoxylic acid with aliphatic alcohols using cation exchange resins as catalysts [7].
- From allylic ethers using cobalt compounds as catalysts [8].
- Reacting aldehydes and ketones with trimethyl/triethyl orthoformate at room temperature in the presence of copper(II) tetrafluoroborate as catalyst [9].
- Reacting ethanol and acetaldehyde in the presence of an acid catalyst. The main reaction implies the production of 1,1-diethoxy ethane and water [10].
- Acetalization of D-gluconolactones with long-chain aldehydes. [11]
- Preparing a peroxyacetal from the aldehyde and 1,1-dimethylprop-2-enyl hydroperoxide [12-15].

Sharma and Chopade et al have reported innovative reaction systems like reactive distillation or reactors integrating dehydration membranes in order to achieve high conversions for acetal formation [13-18]. In both these systems the reaction products, or at least one of the products, are removed from the reaction, shifting the reaction in the forward direction following Le Chatlier's principle.

The importance of acetals lies in the great synthetic utility and their stability to a variety of organic environments/reagents. Cyclic acetals and ketals are the most useful protective groups for the carbonyl functionality widely used in carbohydrate synthesis [19].

Besides, the interest of acetals as protecting groups, many of them have found direct applications as solvents in fragrance industries [20,21], cosmetics [21], food and beverage additives [2,22], pharmaceuticals [23], in the synthesis of enantiomerically pure compounds [24,25], in detergent and lacquer industries [21], and in polymer chemistry [26].

Pentaerythritol (PET) is an alcohol with formula $C(CH_2OH)_4$ [2,2-bis(hydroxymethyl)propane-1,3-diol]. It is a white, crystalline polyol with the neopentane backbone, a versatile building block for the preparation of many polyfunctional compounds. The pentaerythritol react with carbonyl compounds to give pentaerythritol acetals which are useful in many fields. They can be applied as plasticizers and vulcanizers for various polymeric materials, as raw materials for production of valuable resins and lacquers, as physiologically active substances [27], defoamers for washing solution containing anionic surfactant, in motor oils, lubricating oils and hydraulic fluids [28]. 1,2-diacetals are efficient protecting groups for vicinal 1,2-diol units in carbohydrates. Acetonide formation is the commonly used protection for 1,2-(*cis*)- and 1,3-diols, which have extensively been used in carbohydrate chemistry to selectively mask the hydroxyls of different sugars [29].

6.2 LITERATURE SURVEY IN THE CURRENT AREA OF STUDY

A number of acetalization procedures include the use of corrosive protic acids (HCl, H_2SO_4), Lewis acids ($ZnCl_2$, $FeCl_3$) [2,30], *p*-toluenesulphonic acid [31], camphorsulphonic acid [32], iodine [33], formic acid [34] and a series of cationic diphosphine Lewis acid complexes of Pt(II), Pd(II), and Rh(III) etc. [35,36]. However, acetalization procedures mentioned above, require expensive reagents, tedious work-up procedures and neutralization of the strongly acidic media leading to the production of harmful wastes. Though the conventional catalysts are very effective, they produce highly corrosive media and chemically reactive waste streams, whose treatment can be both difficult and hazardous. Hence, these methods suffer limitations, derived from high E-factors and low atom utilization as the catalysts are irreversibly lost [37]. In this context, the use of heterogeneous acid catalysts for the reaction is attractive and it may allow carrying it out without the generation of wastes.

In contrast, solid acid catalysts (SACs) are easier to handle, the general operation of a large chemical process is safer and eco-friendly, obtained product is of high purity and finally the possibility of recycling and reuse of catalysts. Environmentally benign solid acid catalysts such as SO_4^{-2}/ZrO_2, SO_4^{-2}/TiO_2 [38], Ce exchanged montmorillonite [39], acidic zeolites [40-42], mesoporous silica [43] and siliceous mesoporous material [44,45], $Al(HSO_4)_3$ [46], SBA-15 [47] and $CeCl_3$ [48] have been reported to be active for the acetalization reactions. Lachter et al [29] have reported catalytic activity of ion exchange resins such as niobium phosphate and amberlyst-35 as solid acid catalyst for the acetalization of hexanal with 2-ethyl-hexanol and also observed higher performance of niobium phosphate compared with Amberlyst-35. Güemez et. al. have reported acetalization of glycerol and n-butyraldehyde using Amberlyst 47 (acidic ion exchange resin) as heterogeneous catalyst [49].

Kannan et al [27] have reported acetalization of pentaerythritol with several carbonyl compounds in the presence of an Al-pillared saponite. Firouzabadi et al [50] have described application of solid silica chloride, an easily available and efficient catalyst for the preparation of diacetal of pentaerythritol from aldehydes that gives good yields with short reaction times. Pandurangan et al [51] have reported synthesis of diacetal from pentaerythritol with carbonyl compounds using MCM-41 molecular sieves. However, catalyst regeneration and reuse studies have not been reported [50,51]. It has been earlier reported that Ce exchanged H-Y zeolites and K-10 montmorillonite clays possess more acid sites and produce larger amount of acetal compared to other rare earth exchanged zeolites and clays [39].

Shaterian et. al. have reported application of P_2O_5/SiO_2 [52], P_2O_5/Al_2O_3 [52] and cellulose sulfuric acid [53] as heterogeneous catalysts in acetalization of pentaerythritol to give the diacetal and diketal derivatives. Dai et. al. have reported the synthesis of diacetals (diketals) of pentaerythritol using SO_3H-functionalized ionic liquids as catalysts [54,55]. Pandurangan et. al. [56] have reported synthesis of diacetal of pentaerythritol under microwave irradiation using $H_3PW_{12}O_{40}$.

6.3 OBJECTIVES OF THE PRESENT WORK

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 acetal formation as a model reaction wherein acetalization of carbonyl compounds (benzaldehyde, cyclohexanone, acetophenone and benzophenone) with pentaerythritol (PET) has been performed to yield the corresponding diacetal derivative. 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 acetalization of carbonyl compound with PET.

6.4 EXPERIMENTAL

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

Benzaldehyde, cyclohexanone, acetophenone, benzophenone, dichloromethane, silica gel (for TLC), ethyl acetate and petroleum ether were procured from Loba Chemicals (India). Pentaerythritol was obtained from Across Organics (India). FTIR spectra of the synthesized diacetal derivatives were scanned on Shimadzu (Model 8400S) using KBr pellet. ^{1}H-NMR spectra were scanned on Bruker 400 MHz instrument using tetramethylsilane (TMS) as internal standard in $CDCl_3$ (solvent). EDX analysis for catalysts (fresh and spent) has been performed on Jeol JSM-5610-SLV scanning electron microscope.

Experimental setup

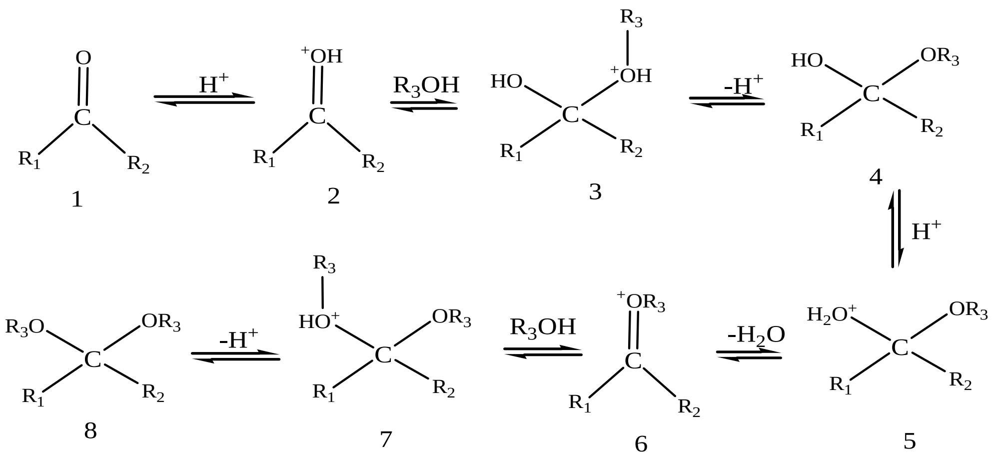
In a typical reaction, a 100 mL round bottomed flask equipped with a Dean and Stark apparatus attached to a reflux condenser was charged with carbonyl compound [benzaldehyde, cyclohexanone, acetophenone, benzophenone] (5-25 mmol), PET (5-10 mmol), catalyst (0.15 - 0.35 g), toluene (10 mL) and refluxed for particular time (1-10 h) at 110^{o}C under nitrogen atmosphere. In all the reactions, toluene was used as solvent and therefore the reaction temperature was kept at 110^{o}C (b.p of toluene). The progress of the reaction was monitored by TLC (20% of ethyl acetate in petroleum ether). Reaction parameters reaction time, catalyst amount and mole ratio of the reactants have been varied and reaction conditions optimized.

After cooling, the catalyst was filtered off and washed with dichloromethane (DCM). The crude product was isolated by distillation and purified by recrystallization in ethanol. All synthesized diacetal derivatives were characterized for IR spectroscopy, ^{1}H-NMR spectroscopy and melting point. % yields were calculated on the basis of conversion of carbonyl compounds.

After separation of catalyst from reaction mixture by decantation/filtration, it is first refluxed in ethanol for 30 minutes to solubilise and remove adsorbed molecules, followed by drying at room temperature (~30^{o}C) and then regenerated/reactivated as described in Chapter 3. The regenerated/reactivated catalysts were used to assess the performance ability at optimized condition in subsequent run.

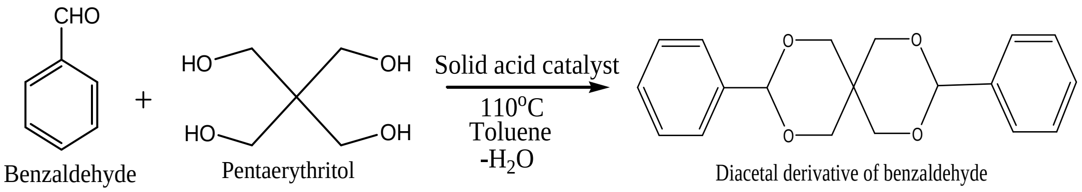
6.5 RESULTS AND DISCUSSION

Acetal formation is a reversible reaction (Scheme 6.1) which proceeds by a two-step mechanism (Scheme 6.2) [14,15,38]. Scheme 6.2 envisages the general mechanism of acetalization of carbonyl compounds using acid catalysts. In this reaction, carbonyl compound is first protonated by the Brønsted acid sites (H^+ ions of the catalyst) to produce the intermediate 2 which then combines with alcohol to form the hemiacetal 4. Protonation of 4 leads to intermediate 5 which undergoes subsequent dehydration to give 6. Reaction of 6 with a molecule of alcohol gives intermediate 7. Removal of a proton from 7 leads to the formation of the acetal 8 [14,15,38].

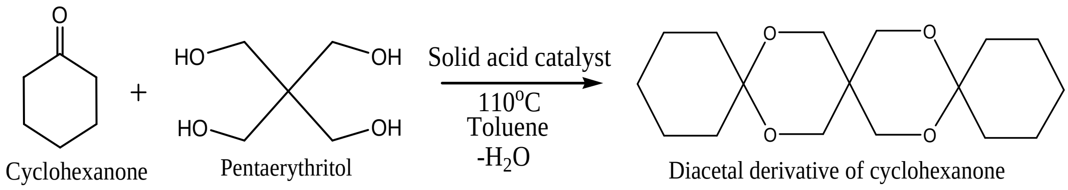


Scheme 6.2 *General mechanism for acetalization of carbonyl compounds* [39]

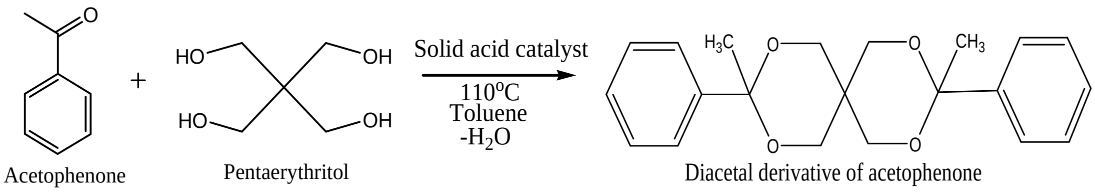
In the present study acetalization of aldehyde (benzaldehyde) and ketones (cyclohexanone, acetophenone, benzophenone) with PET has been performed as described in experimental section. The acetalization reaction of aldehydes/ketones with PET can be presented as Scheme 6.3 – 6.6.



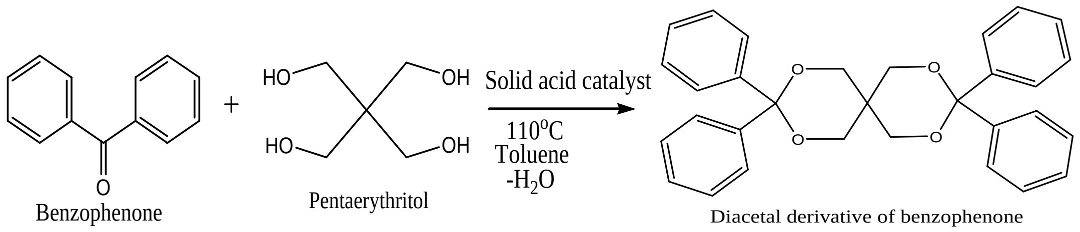
Scheme 6.3 *Reaction of benzaldehyde with PET to give diacetal of benzaldehyde*



Scheme 6.4 *Reaction of cyclohexanone with PET to give diacetal of cyclohexanone*



Scheme 6.5 *Reaction of acetophenone with PET to give diacetal of acetophenone*



Scheme 6.6 *Reaction of benzophenone with PET to give diacetal of benzophenone*

Firstly, reaction conditions were optimized for preparation of diacetal from benzaldehyde and ketones (cyclohexanone and acetophenone) with PET 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 catalyst (Table 6.1 – 6.3).

The effect of reaction time on the product yield of diacetal formed in all cases was studied at refluxing temperature (110°C) using toluene as solvent with 1:1 mole ratio of PET: benzaldehyde/ketones and 0.15g of catalyst (ZrPW). The reaction reached equilibrium within 4 h (benzaldehyde), 6 h (cyclohexanone) and 8 h (acetophenone and benzophenone) (Figure 6.1). With increasing catalyst amount (0.15g to 0.35 g) yield increased, probably due to increase in the number of acid sites (Figure 6.2). With reference to mechanism described in scheme 6.2, step 1 is protonation whereas step 3 is formation of hemiacetal followed by deprotonation. For deprotonation to occur an optimum acidity is required. If acidity is higher, then the further reaction to form the acetal is inhibited/reaction slows down. The excess acid amount may thus promote the occurrence of the reverse reaction. Therefore in all cases, optimum catalyst amount was taken as 0.3 g.

Acetal formation is a reversible reaction, the reverse reaction being acetal hydrolysis (with same mechanism) going in the backward direction to give alcohol and carbonyl compound. Considering thermodynamics of the acetal reaction, equilibrium constants of the acetal reaction are low. As in any equilibrium reaction, the reaction may be driven to the product side (forward direction) by controlling the concentration of one of the reactants or removing water molecule formed continuously to avoid the reverse reaction (Le Chatlier's Principle). In the present study, in order to obtain higher yields of acetal, Le Chatlier's Principle has been followed. A Dean and Stark apparatus has been used for removal of water as binary azoetrope using toluene as solvent. Further, mole ratio of the reactants PET to carbonyl compound has been varied taking one of the reactants in excess. Thus, precautions are taken to avoid the backward reaction to arrive at maximum yields.

The influence of mole ratio of reactants on product yield was studied using 0.3 g of catalyst at the refluxing temperature at optimized reaction time. The mole ratio PET: benzaldehyde/ketones were varied as 1:1, 1:2, 1:3, 1:4, 1:5 and 2:1 (Figure 6.3). It is observed that when the mole ratio increased from 1:1 to 1:4, the product yield increased which is attributed to an increase in chemisorption of benzaldehyde/ketones on the Brønsted acid sites which leads to the polarization of the carbonyl bond where PET makes a nucleophilic attack. Further, for mole ratio 2:1, yield decreased which may be due to the dilution of benzaldehyde/ketones. In the present study, 1:4 mole ratio of PET: benzaldehyde/ketones were used. Diacetal of PET was observed as the single product over all mole ratios of PET and benzaldehyde/ketones.

At optimized condition (mole ratio of PET:aldehyde/ketones- 1:4; catalyst amount- 0.3g; reaction temperature- 110°C; solvent- toluene; reaction time- PET:benzaldehyde - 4h, PET:cyclohexanone - 6h, PET:acetophenone/benzophenone - 8h), acetalization of benzaldehyde (Figure 6.4), cyclohexanone (Figure 6.5), acetophenone (Figure 6.6) and benzophenone (Figure 6.7) with PET using ZrPW, TiPW, SnPW, 12-TPA/ZrO_2-20 12-TPA/TiO_2-20 and 12-TPA/SnO_2-20 as solid acid catalysts has been performed (Table 6.4 – 6.7).

Acetal derivative of benzaldehyde (dibenzal acetal) was obtained with high % yield. This is probably due to the fact that aldehyde undergoes nucleophilic addition more readily than ketones. Comparing benzophenone and acetophenone, benzophenone being more bulky than acetophenone, shows the lowest reactivity and thus low yields. The rate determining step of acetalization is the formation of a cation from the protonated hemiacetal. Hence, the bulkiness of hemiacetals might prevent the attack of the alcohol on the carbonyl carbon atom thereby effecting a change in the rate-determining step. Further, the electron withdrawing power of phenyl group (1 for acetophenone and 2 for benzophenone) in these compounds reduces the easy release of the pair of electron on the carbonyl carbon during the reaction. However, cyclohexanone is more reactive towards nucleophiles than both acetophenone and benzophenone [38]. Therefore, the reactivity of the ketones decrease in the order cyclohexanone > acetophenone > benzophenone.

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

Regeneration/reactivation and reuse of catalysts

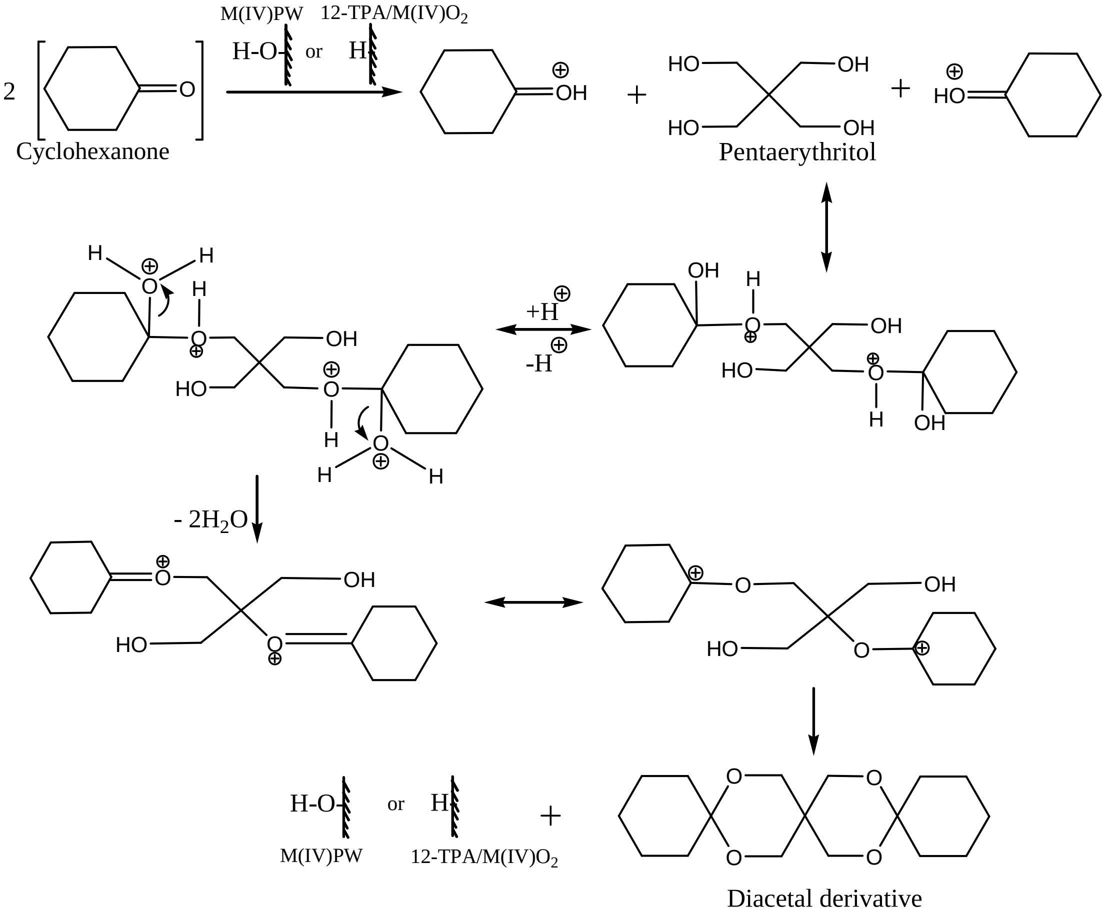
After each catalytic run, there is change in colour of the catalysts [pale yellow/light brown in case of 12-TPA/M(IV)O_2-20 and dark brown in case of M(IV)PWs]. This is probably due to the fact that reactant molecules come onto surface of catalyst and enter into reaction to give the product, while a 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 6.4 – 6.7; Figure 6.4 – 6.7).

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 diacetal derivative of benzaldehyde, EDX analysis for both fresh and spent catalysts (ZrPW and 12-TPA/ZrO_2-20) has been performed after first catalytic run (Table 6.8; Figure 6.8 - 6.11). 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 [57].

Reaction mechanism for solid acid catalyzed acetalization reaction

Acetal formation is believed to proceed through hemiacetal intermediates [27]. Kanan et al [27] have reported acetalization mechanism for cyclohexanone with PET using pillared clay catalyst. The carbonyl compound is first protonated by Brønsted acid sites (H^+ ions of the catalyst), which provides successive protonation to produce intermediates which combine with hydroxyl groups of PET to form hemiacetals. Protonation and subsequent dehydration gives corresponding acetal. The rate determining step of acetalization is the formation of a cation from the protonated hemiacetal. The bulkiness of hemiacetals might prevent the attack of the second alcohol group thereby changing the rate determining step [30]. In scheme 6.7, a probable mechanism (diacetal formation from cyclohexanone and PET) is presented using M(IV)PWs (Type – I catalysts) and 12-TPA/M(IV)O_2-20 (Type – II catalysts).



Scheme 6.7 *Proposed mechanism for acetalization of cyclohexanone with pentaerythritol using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Table 6.1 *Optimization of reaction conditions for preparation of diacetal from benzaldehyde and PET using ZrPW and 12-TPA/ZrO$_2$-20.*

Set No.	**Reactants with their mole ratio**	**Catalyst amount (g)**	**Reaction time (h)**	**% Yield of benzaldehyde diacetal**	
				ZrPW	**12-TPA/ ZrO$_2$-20**
(A)Reaction time variation					
1	PET : Benzaldehyde (1:1)	0.15	1	No Product	No Product
2	PET : Benzaldehyde (1:1)	0.15	2	20.11	4.39
3	PET : Benzaldehyde (1:1)	0.15	3	26.32	9.82
4	PET : Benzaldehyde (1:1)	0.15	**4**	**28.86**	**19.77**
5	PET : Benzaldehyde (1:1)	0.15	5	29.12	20.01
6	PET : Benzaldehyde (1:1)	0.15	6	29.26	20.13
(B)Catalyst amount variation					
7	PET : Benzaldehyde (1:1)	0.20	4	31.22	23.32
8	PET : Benzaldehyde (1:1)	0.25	4	39.10	29.61
9	PET : Benzaldehyde (1:1)	**0.30**	4	**45.88**	**37.00**
10	PET : Benzaldehyde (1:1)	0.35	4	46.06	37.19
(C)Mole ratio variation					
11	PET : Benzaldehyde (1:2)	0.30	4	51.84	44.00
12	PET : Benzaldehyde (1:3)	0.30	4	68.14	57.81
13*	**PET : Benzaldehyde (1:4)**	**0.30**	**4**	**77.87**	**69.32**
14	PET : Benzaldehyde (1:5)	0.30	4	78.04	69.67
15	PET : Benzaldehyde (2:1)	0.30	4	51.47	40.18

(: Optimum condition; Reaction temperature: 110°C; Solvent: Toluene; Yields refer to the isolated pure products)*

Table 6.2 *Optimization of reaction conditions for preparation of diacetal from cyclohexanone and PET using ZrPW and 12-TPA/ZrO$_2$-20.*

Set No.	**Reactants with their mole ratio**	**Catalyst amount (g)**	**Reaction time (h)**	**% Yield of cyclohexanone diacetal**	
				ZrPW	**12-TPA/ ZrO$_2$-20**
(A)Reaction time variation					
1	PET : Cyclohexanone (1:1)	0.15	1	No Product	No Product
2	PET : Cyclohexanone (1:1)	0.15	2	No Product	No Product
3	PET : Cyclohexanone (1:1)	0.15	3	No Product	10.00
4	PET : Cyclohexanone (1:1)	0.15	4	14.59	12.56
5	PET : Cyclohexanone (1:1)	0.15	5	18.22	17.13
6	PET : Cyclohexanone (1:1)	0.15	**6**	**25.87**	**19.97**
7	PET : Cyclohexanone (1:1)	0.15	7	26.44	20.02
8	PET : Cyclohexanone (1:1)	0.15	8	26.95	20.08
(B)Catalyst amount variation					
9	PET : Cyclohexanone (1:1)	0.20	6	27.79	21.83
10	PET : Cyclohexanone (1:1)	0.25	6	31.41	27.11
11	PET : Cyclohexanone (1:1)	**0.30**	6	**39.27**	**35.60**
12	PET : Cyclohexanone (1:1)	0.35	6	39.80	35.93
(C)Mole ratio variation					
13	PET : Cyclohexanone (1:2)	0.30	6	46.10	43.03
14	PET : Cyclohexanone (1:3)	0.30	6	61.02	53.17
15*	**PET : Cyclohexanone (1:4)**	**0.30**	**6**	**74.41**	**64.00**
16	PET : Cyclohexanone (1:5)	0.30	6	75.00	64.24
17	PET : Cyclohexanone (2:1)	0.30	6	48.70	39.13

(: Optimum condition; Reaction temperature: 110°C; Solvent: Toluene; Yields refer to the isolated pure products)*

Table 6.3 *Optimization of reaction conditions for preparation of diacetal from acetophenone and PET using ZrPW and 12-TPA/*ZrO_2*-20.*

Set No.	**Reactants with their mole ratio**	**Catalyst amount (g)**	**Reaction Time (h)**	**% Yield of acetophenone diacetal**	
				ZrPW	**12-TPA/ ZrO_2-20**
(A)Reaction time variation					
1	PET : Acetophenone (1:1)	0.15	1	No Product	No Product
2	PET : Acetophenone (1:1)	0.15	2	No Product	No Product
3	PET : Acetophenone (1:1)	0.15	3	No Product	No Product
4	PET : Acetophenone (1:1)	0.15	4	No Product	No Product
5	PET : Acetophenone (1:1)	0.15	5	8.41	6.32
6	PET : Acetophenone (1:1)	0.15	6	11.22	12.48
7	PET : Acetophenone (1:1)	0.15	7	15.87	16.00
8	PET : Acetophenone (1:1)	0.15	**8**	**19.00**	**17.37**
8	PET : Acetophenone (1:1)	0.15	9	19.42	17.60
8	PET : Acetophenone (1:1)	0.15	10	19.65	17.81
(B)Catalyst amount variation					
9	PET : Acetophenone (1:1)	0.20	8	21.54	20.00
10	PET : Acetophenone (1:1)	0.25	8	29.11	26.47
11	PET : Acetophenone (1:1)	**0.30**	8	**36.00**	**32.01**
12	PET : Acetophenone (1:1)	0.35	8	36.12	32.37
(C)Mole ratio variation					
13	PET : Acetophenone (1:2)	0.30	8	44.96	40.81
14	PET : Acetophenone (1:3)	0.30	8	58.45	51.00
15*	**PET : Acetophenone (1:4)**	**0.30**	**8**	**65.28**	**60.82**
16	PET : Acetophenone (1:5)	0.30	8	65.95	60.94
17	PET : Acetophenone (2:1)	0.30	8	41.05	34.68

(: Optimum condition; Reaction temperature: 110°C; Solvent: Toluene; Yields refer to the isolated pure products)*

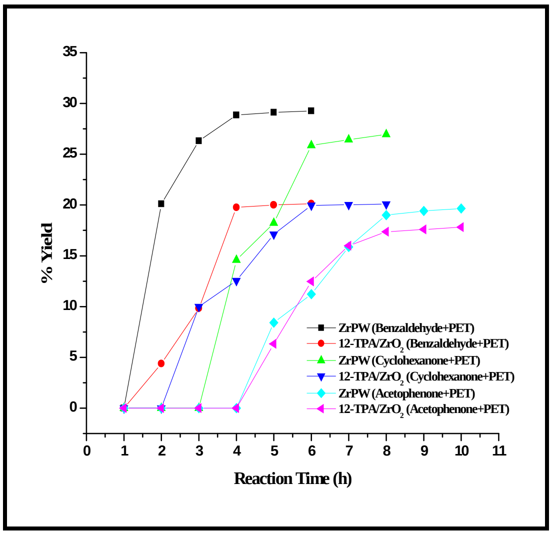


Figure 6.1 *Optimization of reaction time for synthesis of diacetals*

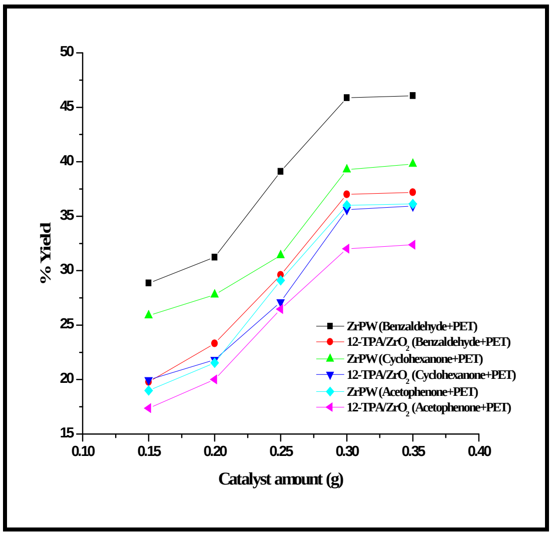


Figure 6.2 *Optimization of catalyst amount for synthesis of diacetals*

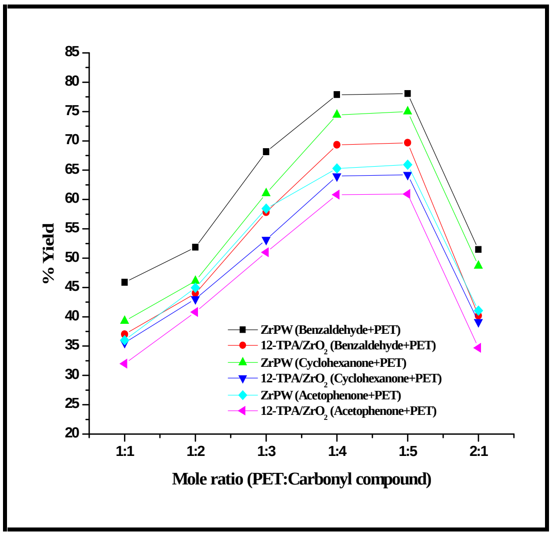


Figure 6.3 *Optimization of mole ratio of reactants for synthesis of diacetals*

Table 6.4 *Synthesis of diacetal derivative of benzaldehyde at optimized condition using M(IV)PWs and 12-TPA/M(IV)O$_2$-20.*

Catalyst	**% Yield (TON) of benzaldehyde diacetal**		
	Catalytic Run		
	1	***2***	***3***
ZrPW	77.87 (7.26) *(F)*	76.11 (7.10) *(Rg)*	74.44 (6.94) *(Rg)*
TiPW	81.45 (7.60) *(F)*	80.14 (7.47) *(Rg)*	77.68 (7.25) *(Rg)*
SnPW	79.09 (7.38) *(F)*	77.96 (7.27) *(Rg)*	76.00 (7.09) *(Rg)*
ZrPW	77.87 (7.26) *(F)*	63.47 (5.92) *(Ru)*	50.00 (4.66) *(Ru)*
TiPW	81.45 (7.60) *(F)*	69.00 (6.44) *(Ru)*	59.22 (5.52) *(Ru)*
SnPW	79.09 (7.38) *(F)*	65.32 (6.09) *(Ru)*	53.98 (5.03) *(Ru)*
12-TPA/ ZrO$_2$-20	69.32 (6.46) *(F)*	58.41 (5.45) *(Ra)*	44.00 (4.10) *(Ra)*
12-TPA/ TiO$_2$-20	76.88 (7.17) *(F)*	62.00 (5.78) *(Ra)*	50.06 (4.67) *(Ra)*
12-TPA/ SnO$_2$-20	72.53 (6.76) *(F)*	61.00 (5.69) *(Ra)*	48.10 (4.48) *(Ra)*

[Mole ratio of PET:benzaldehyde-1:4; Catalyst amount:0.3g; Reaction temperature:110°C; Solvent: Toluene; Reaction Time: 4h; F: Fresh catalyst; Rg: Regenerated catalyst; Ru: Reused catalyst (used as such, without regeneration); Ra: Reactivated catalyst; Yields refer to the isolated pure products]

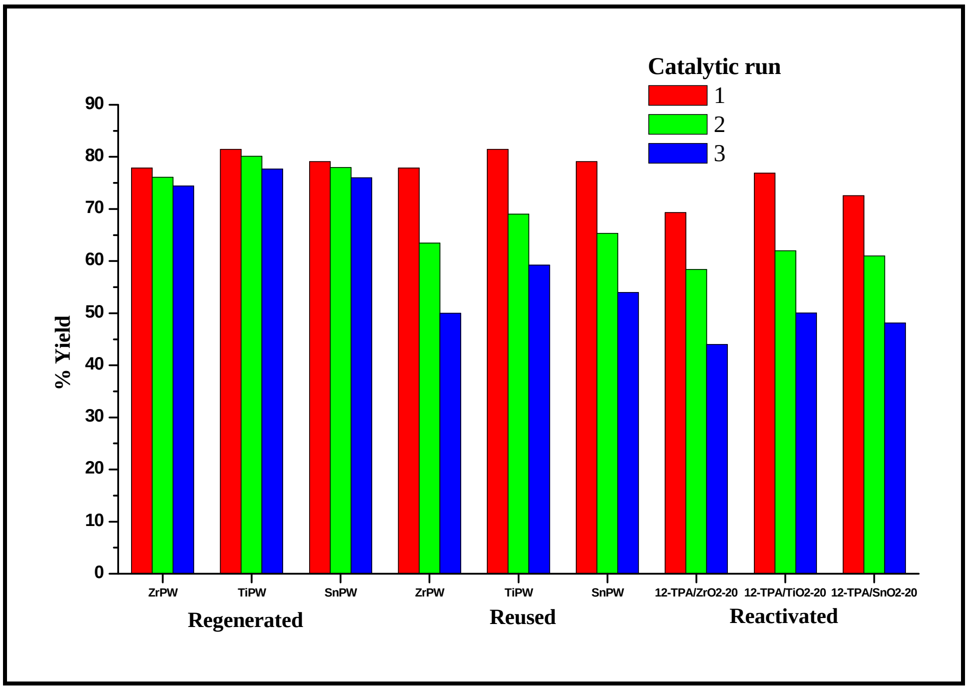


Figure 6.4 *Comparison of % yields of diacetal derivative of benzaldehyde at optimized condition using M(IV)PWs and 12-TPA/M(IV)O$_2$-20.*

Table 6.5 *Synthesis of diacetal derivative of cyclohexanone at optimized condition using M(IV)PWs and 12-TPA/M(IV)O$_2$-20.*

Catalyst	**% Yield (TON) of cyclohexanone diacetal**		
	Catalytic Run		
	1	***2***	***3***
ZrPW	74.41 (6.54) *(F)*	73.00 (6.42) *(Rg)*	71.16 (6.26) *(Rg)*
TiPW	79.66 (7.01) *(F)*	78.02 (6.86) *(Rg)*	77.69 (6.83) *(Rg)*
SnPW	76.55 (6.73) *(F)*	75.48 (6.64) *(Rg)*	73.94 (6.50) *(Rg)*
12-TPA/ ZrO$_2$-20	64.00 (5.63) *(F)*	51.36 (4.51) *(Ra)*	40.87 (3.59) *(Ra)*
12-TPA/ TiO$_2$-20	70.80 (6.23) *(F)*	61.37 (5.40) *(Ra)*	49.79 (4.38) *(Ra)*
12-TPA/ SnO$_2$-20	67.62 (5.95) *(F)*	54.69 (4.81) *(Ra)*	41.99 (3.69) *(Ra)*

(Mole ratio of PET:cyclohexanone-1:4; Catalyst amount:0.3g; Reaction temperature:110°C; Solvent: Toluene; Reaction Time: 6h; F: Fresh catalyst; Rg: Regenerated catalyst; Ra: Reactivated catalyst; Yields refer to the isolated pure products)

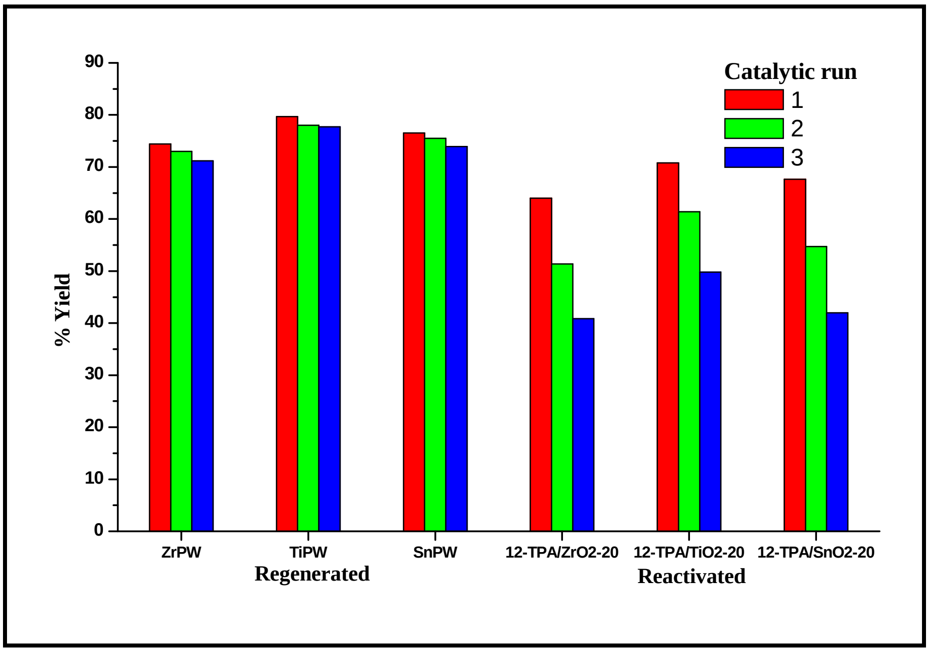


Figure 6.5 *Comparison of % yields of diacetal derivative of cyclohexanone at optimized condition using M(IV)PWs and 12-TPA/M(IV)O$_2$-20.*

Table 6.6 *Synthesis of diacetal derivative of acetophenone at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Catalyst	**% Yield (TON) of acetophenone diacetal**		
	Catalytic Run		
	1	***2***	***3***
ZrPW	65.28 (6.70) *(F)*	63.56 (6.52) *(Rg)*	61.89 (6.35) *(Rg)*
TiPW	70.12 (7.19) *(F)*	68.56 (7.03) *(Rg)*	67.35 (6.91) *(Rg)*
SnPW	68.99 (7.08) *(F)*	67.19 (6.89) *(Rg)*	66.03 (6.77) *(Rg)*
12-TPA/ ZrO_2-20	60.82 (6.24) *(F)*	48.56 (4.98) *(Ra)*	32.40 (3.32) *(Ra)*
12-TPA/ TiO_2-20	64.81 (6.65) *(F)*	51.00 (5.23) *(Ra)*	40.49 (4.15) *(Ra)*
12-TPA/ SnO_2-20	63.49 (6.51) *(F)*	50.08 (5.14) *(Ra)*	37.00 (3.79) *(Ra)*

(Mole ratio of PET:acetophenone-1:4; Catalyst amount: 0.3g; Reaction temperature:110°C; Solvent: Toluene; Reaction Time: 8h; F: Fresh catalyst; Rg: Regenerated catalyst; Ra: Reactivated catalyst; Yields refer to the isolated pure products)

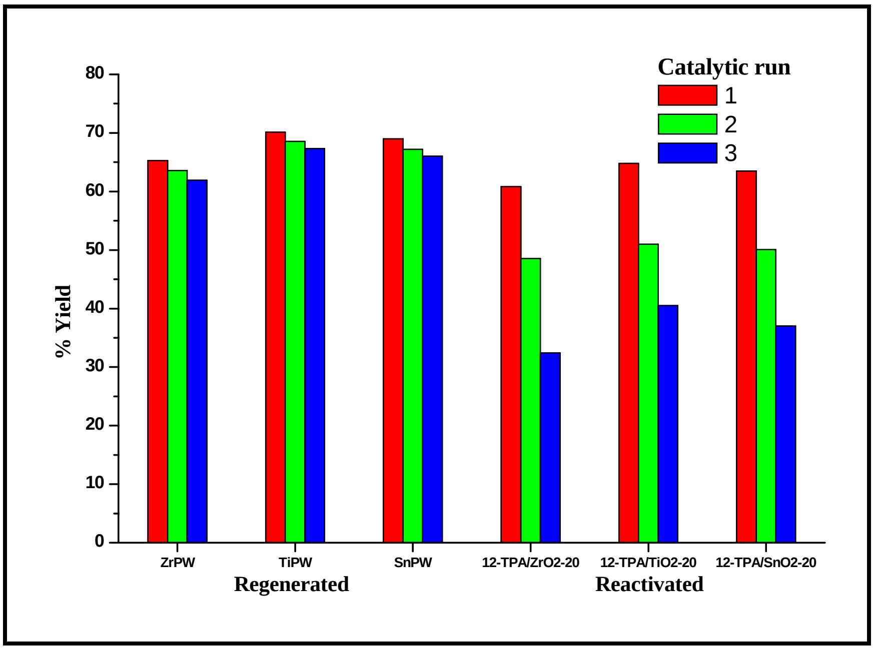


Figure 6.6 *Comparison of % yields of diacetal derivative of acetophenone at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Table 6.7 *Synthesis of diacetal derivative of benzophenone at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Catalyst	**% Yield (TON) of benzophenone diacetal**		
	Catalytic Run		
	1	***2***	***3***
ZrPW	54.19 (8.02) *(F)*	53.48 (7.91) *(Rg)*	50.89 (7.53) *(Rc)*
TiPW	62.00 (9.17) *(F)*	60.81 (8.99) *(Rg)*	59.02 (8.73) *(Rg)*
SnPW	57.35 (8.48) *(F)*	56.47 (8.35) *(Rg)*	55.11 (8.15) *(Rg)*
12-TPA/ ZrO_2-20	51.24 (7.58) *(F)*	39.78 (5.88) *(Ra)*	30.33 (4.48) *(Ra)*
12-TPA/ TiO_2-20	53.55 (7.92) *(F)*	41.30 (6.11) *(Ra)*	29.89 (4.42) *(Ra)*
12-TPA/ SnO_2-20	52.94 (7.83) *(F)*	40.06 (5.92) *(Ra)*	30.36 (4.49) *(Ra)*

(Mole ratio of PET:benzophenone-1:4; Catalyst amount:0.3g; Reaction temperature:110°C; Solvent: Toluene; Reaction Time: 8h; F: Fresh catalyst; Rg: Regenerated catalyst; Ra: Reactivated catalyst; Yields refer to the isolated pure products)

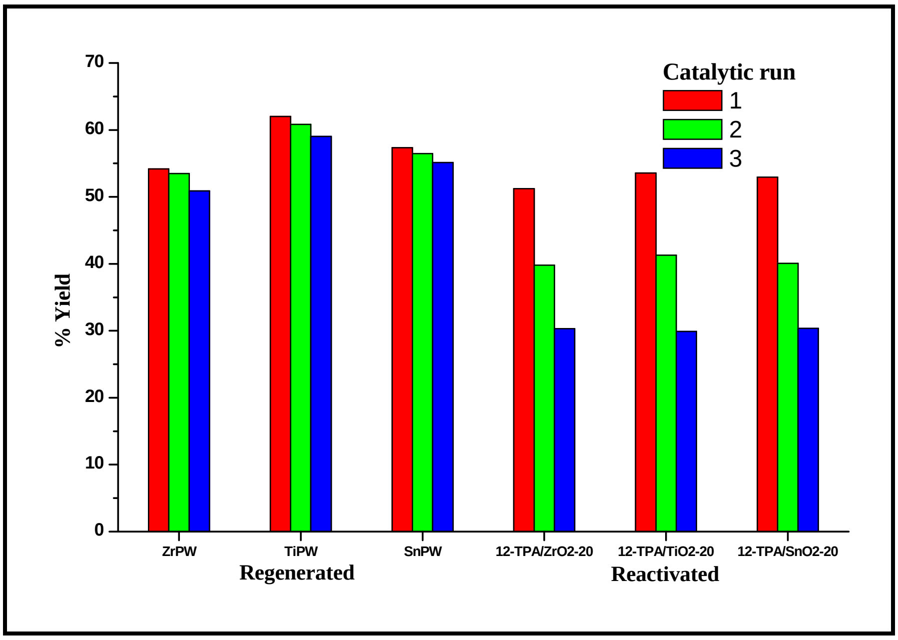


Figure 6.7 *Comparison of % yields of diacetal derivative of benzophenone at optimized condition using M(IV)PWs and 12-TPA/M(IV)O_2-20.*

Table 6.8 *Elemental analysis by EDX for fresh and spent ZrPW and 12-TPA/*ZrO_2*-20 in the synthesis of benzaldehyde diacetal.*

Reactants	**Materials**	**% by EDX analysis**			
		Zr	**P**	**W**	**O**
PET: Benzaldehyde	ZrPW (Fresh)	60.79	18.53	20.67	-
	ZrPW (Spent)	53.55	25.64	20.80	-
	12-TPA/ZrO_2-20 (Fresh)	28.75	0.11	3.44	67.70
	12-TPA/ZrO_2-20 (Spent)	14.28	0.83	1.97	82.92

(Mole ratio of PET:benzaldehyde-1:4; catalyst amount: 0.3g; reaction temperature: 110 °C; solvent: toluene; reaction time: 4h)

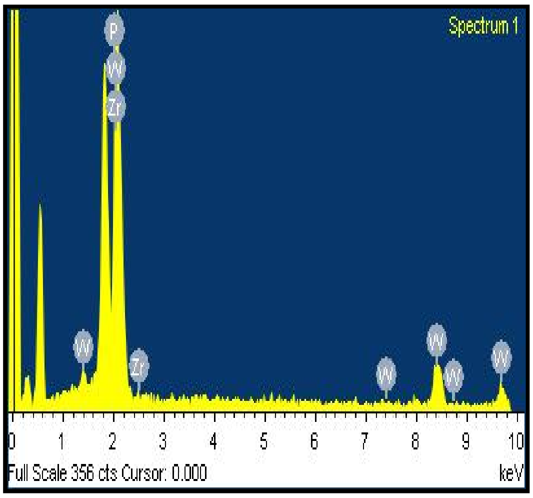


Figure 6.8 *EDX of fresh ZrPW*

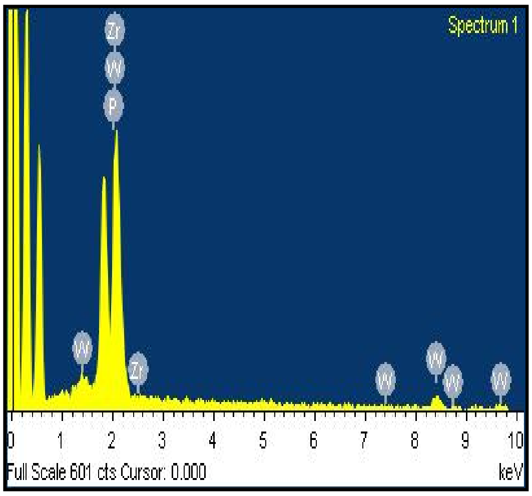


Figure 6.9 *EDX of spent ZrPW in the synthesis of benzaldehyde diacetal*

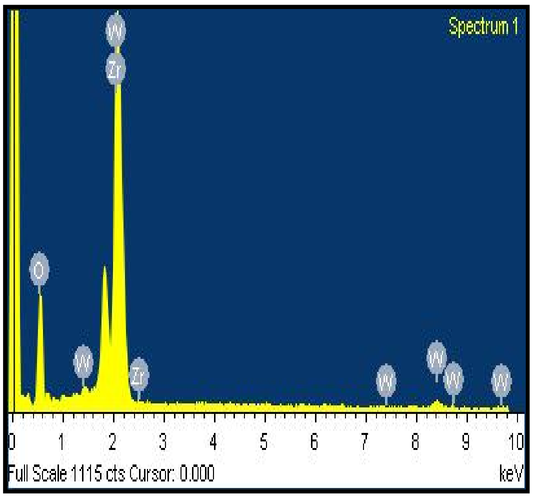


Figure 6.10 *EDX of fresh 12-TPA/*ZrO_2*-20*

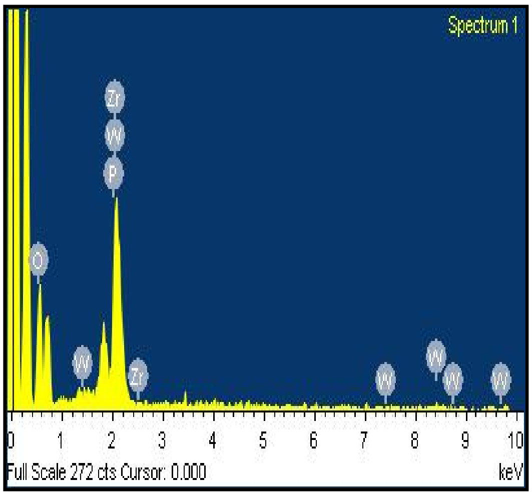
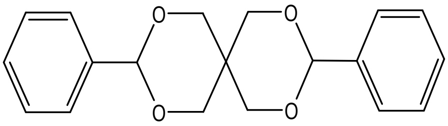
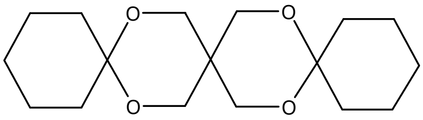
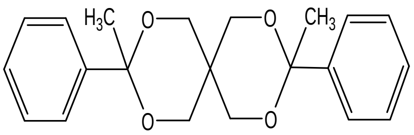
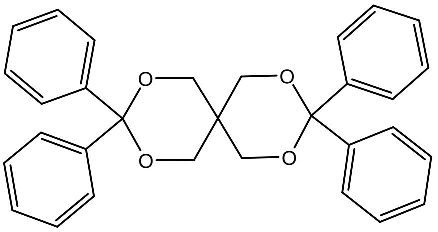


Figure 6.11 *EDX of spent 12-TPA/*ZrO_2*-20 in the synthesis of benzaldehyde diacetals*

Characterization of the products

The isolated products were characterized by FTIR spectroscopy and ^{1}H-NMR spectroscopy. Melting points are in good agreement with reported values [27] (Table 6.9).

Table 6.9 *Characterization of diacetal derivatives.*

Product formed	***Characterizations***	
 Diacetal derivative of benzaldehyde	**M.P. (^{o}C)**	155 -156
	IR *(υ_{max}/cm^{-1})*	2910 (CH), 2862 (CH), 1600 (C=C Aromatic), 1460 (C=C Aromatic), 1390 (CH), 1050 (C-O-C), 805 (C_6H_5), 710 (C_6H_5).
	^{1}H-NMR *(δH: 400 MHz; $CDCl_3$)*	3.51 (6H, m, $H_{ax,}$ H_{eq}), 4.70 (2H, d, *J*=11.7 Hz, 2 H_{eq}), 5.42 (2H, s, 2 × PhCH), 7.10–7.60 (10H, m, 2×Ph).
 Diacetal derivative of cyclohexanone	**M.P. (^{o}C)**	115-116
	IR *(υ_{max}/cm^{-1})*	2960 (CH), 2870 (CH), 1140 (C-O-C).
	^{1}H-NMR *(δH: 400 MHz; $CDCl_3$)*	1.4-1.7(20H, m,2×$(CH_2)_5$), 3-3.5 (8H, m, $(CH_2O)_4$).
 Diacetal derivative of acetophenone	**M.P. (^{o}C)**	146 -147
	IR *(υ_{max}/cm^{-1})*	2970 (CH), 2890 (CH), 1600 (C=C Aromatic), 1468 (C=C Aromatic), 1365 (CH), 1150 (C-O-C), 790 (C_6H_5), 700 (C_6H_5).
	^{1}H-NMR *(δH: 400 MHz; $CDCl_3$)*	1.51 (6H, s, 2 × Me), 3.15 (2H, dd, *J*=11.1 Hz, 2.4, 2×H_{eq}), 3.30 (2H, d, *J*= 11.1 Hz, 2×H_{ax}), 3.60 (2H, d, *J*= 11.7 Hz, 2×H_{ax}), 4.48 (2H, dd, *J*=11.7 Hz, 2×H_{eq}), 7.25-7.70 (10H, m, 2 × Ph).
 Diacetal derivative of benzophenone	**M.P. (^{o}C)**	160 -161
	IR *(υ_{max}/cm^{-1})*	2975 (CH), 2880 (CH), 1615 (C=C Aromatic), 1480 (C=C Aromatic), 1390 (CH), 1050 (C-O-C), 755 (C_6H_5), 770 (C_6H_5).
	^{1}H-NMR *(δH: 400 MHz; $CDCl_3$)*	3.6 (8H, s, $(CH_2O)_4$), 7.14–7.32 (20H, m,2×$(Ph)_2$).

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