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Friedel-Crafts alkylation and acylation of aromatic compounds under solvent free conditions using solid acid catalysts

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Abstract

Solid acid catalysts, M(IV) Phosphotungstates [M(IV)PWs], mixed materials of the class of TMBA (Tetravalent Metal Biantonic Acid) salts and 12-Tungstophosphoric acid (12-TPA) supported onto M(IV) Oxides [M(IV) = Zr, Ti, Sn] have been synthesized and their utility towards Friedel–Crafts alkylation and acylation reactions has been explored and compared. The catalysts have been characterized for elemental analysis by ICP-AES, TGA, FTIR, SEM, EDX, XRD, surface area (BET) and surface acidity (NH₃-TPD). Friedel–Crafts alkylation and acylation have been studied as model reactions under solvent free conditions wherein acetyl chloride is used for acylation of anisole/veratrole and benzyl chloride is used for alkylation of toluene. Reaction conditions have been optimized by varying parameters such as reaction time, reaction temperature, catalyst amount and mole ratio of the reagents. Highlighting features are selectivity of products under solvent free conditions and regeneration/reuse of catalysts without much loss in % yields.

Keywords: Solid acid catalyst; Phosphotungstates; Supported solid acid catalysts; Solvent free synthesis; Friedel Crafts Alkylation; Friedel Crafts Acylation.

1. Introduction

Friedel–Crafts reactions are among the most versatile methods used for the synthesis of substituted aromatic compounds [1]. Aromatic ketones are either valuable intermediates or end active ingredients in an extensive range of high-value added products, which include pharmaceuticals, agrochemicals, biocides, flavors, fragrances and fine chemicals [2].

Friedel–Crafts alkylation and acylation of aromatic hydrocarbons have been studied extensively using Lewis acid catalysts, such as, BF₃, AlCl₃, FeCl₃, TiCl₄ and protonic acid like HF, H₂SO₄ [3,4]. However, the use of conventional Lewis and mineral acid catalysts has lead to environmental problems, especially in large-scale production sites.

Heteropoly acids (HPAs) have proved to be the alternative for traditional acid catalysts due to both strong acidity and appropriate redox properties. The major disadvantage of HPAs, as catalyst lies in their low thermal stability, low surface area (1-10m²/g) and separation problems from reaction mixture. HPAs can be made eco-friendly, insoluble solid acids, with high thermal stability and high surface area by supporting them onto suitable supports. The support provides an opportunity for HPAs to be dispersed over a large surface area which increases catalytic activity [5]. In recent years alternate to existing solid acid catalysts, development of metal oxide supported catalysts, such as, zirconia supported heteropoly acid catalysts have gained importance, since these provide advantages over others like higher thermal stability, cost effective and eco-friendly systems for applications in large-scale productions [6].

During the last three decades, efforts have been made to replace the conventional catalysts with solid acid catalyst systems for Friedel–Crafts reactions. Among the solid acids reported, sulfated zirconia have been found to be highly active catalysts in many acid catalyzed reactions [7]. However, these catalysts suffer from the drawbacks, like poor thermal stability and tendency to form volatile sulfur compounds during catalysis. Further, regeneration by oxidation and leaching with water forming reactions, limit their applications in industry [8]. Similarly, zeolite H-beta and acid treated clays have been reported as replacement to the conventional Lewis acid catalysts for alkylation reactions and these also have some limitations [8]. Therefore, the need for an ideal solid acid catalyst is on.

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Tetravalent Metal Acid (TMA) salts are inorganic cation exchangers possessing general formula $M(IV)(HXO_4)_2 \cdot nH_2O$ [$M(IV) = Zr, Ti, Sn, Ce, Th$, etc. $X = P, W, Mo, As, Sb$, etc] where, H^+ of the structural hydroxyl groups are responsible for cation exchange, due to which TMA salts indicate good potential for application as solid acid catalysts, the acidic sites being Bronsted acid sites in nature^[9,10]. From our laboratory, TMA salts have been used as solid acid catalysts for esterification^[11-13], cyclodehydration^[14], ketalisation of ketones^[15], hydration of nitriles^[16], cyclodehydration of 1, n-diols^[17] and for synthesis of coumarin derivatives^[18].

When we used a mixed material of the class of Tetravalent Bimetallic acid (TBMA) salts such as Zirconium Titanium Phosphate (ZTP)^[13] (containing two different cations and an anion) and a mixed material of the class of Tetravalent Metal Bimetallic Acid (TMBA) salts (containing two different anions and a cation) such as Zr(IV) Phosphotungstate (ZrPW)^[19] as a solid acid catalyst, for synthesis of esters^[13] and coumarin derivatives^[19] respectively, enhanced catalytic activity was observed compared to their single salt counter parts.

In the present endeavour, $M(IV)$ Phosphotungstates [$M(IV)$ PWs], mixed materials of the class of TMBA salts such as Zirconium (IV) Phosphotungstate (ZrPW), Titanium (IV) Phosphotungstate (TiPW) and Tin (IV) Phosphotungstate (SnPW) possessing inherent acidity have been synthesized by sol-gel route. Looking to the potential utility of supported HPAs and for comparison of catalytic performance, we have supported 12-Tungstophosphoric acid (12-TPA) onto ZrO_2 , TiO_2 and SnO_2 by process of anchoring and calcination, resulting in 12-TPA/ ZrO_2 , 12-TPA/ TiO_2 and 12-TPA/ SnO_2 thereby inducing acidity in these oxides and additionally possess same components (i.e. Zr, Ti, Sn, P and W) as the TMBA salts. All synthesized materials have been characterized for elemental analysis by ICP-AES, TGA, FTIR, SEM, EDX, XRD, surface area (BET method) and surface acidity (NH_3 -TPD method). The potential utility of these materials as solid acid catalysts has been explored and compared by studying Friedel-Crafts alkylation and acylation as model reactions under solvent free conditions. Acetyl chloride is used as acylating agent for acylation of anisole and veratrole to selectively give 4-methoxy acetophenone (4-MA) and 3, 4-dimethoxy acetophenone (3, 4-DMA) whereas, benzyl chloride is used as alkylating agent for toluene to selectively give p-benzyl toluene (p-BT). Reaction conditions have been optimized varying parameters such as reaction time, reaction temperature, catalyst amount and mole ratio of the reagents including regeneration and reuse of catalysts. The catalytic activity of synthesized materials has been compared and correlated with acid properties of the materials.

2. Experimental

2.1 Synthesis of $M(IV)$ Phosphotungstates [$M(IV)$ PWs]

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

2.1.1 Synthesis of ZrPW (at optimized condition)

An aqueous mixture of $NaH_2PO_4 \cdot 2H_2O$ (0.1M, 50ml) and $Na_2WO_4 \cdot 2H_2O$ (0.1M, 50ml) was added dropwise (flow rate 1

$ml \cdot min^{-1}$) to an aqueous solution of $ZrOCl_2 \cdot 8H_2O$ (0.2M, 50ml) with continuous stirring for an hour at 70 °C. The gelatinous precipitates obtained was filtered, washed with double distilled water and dried at room temperature. The material was then broken down to the desired particle size (30-60 mesh) by grinding and sieving and acid treated by method reported earlier^[18]. This material was used for all studies.

2.1.2 Synthesis of TiPW (at optimized condition)

An aqueous mixture of $NaH_2PO_4 \cdot 2H_2O$ (0.1M, 50ml) and $Na_2WO_4 \cdot 2H_2O$ (0.1M, 50ml) was added dropwise (flow rate 1 $ml \cdot min^{-1}$) to a solution of $TiCl_4$ (0.2M, 50ml) (prepared in 10% W/V H_2SO_4 solution) with continuous stirring for an hour at room temperature. The gelatinous precipitates obtained are kept for ageing for 1h, then filtered and washed with double distilled water followed by drying at room temperature. The material was then broken down to the desired particle size (30-60 mesh) by grinding and sieving and acid treated by method reported earlier^[18]. This material was used for all studies.

2.1.3 Synthesis of SnPW (at optimized condition)

An aqueous mixture of $NaH_2PO_4 \cdot 2H_2O$ (0.1M, 50ml) and $Na_2WO_4 \cdot 2H_2O$ (0.1M, 50ml) was added dropwise (flow rate 1 $ml \cdot min^{-1}$) to a solution of $SnCl_4$ (0.1M, 100ml) (prepared in 0.1M HCl) with continuous stirring for an hour at room temperature. The gelatinous precipitates obtained are kept for ageing for 3h, then filtered and washed with double distilled water followed by drying at room temperature. The material was then broken down to the desired particle size (30-60 mesh) by grinding and sieving and acid treated by method reported earlier^[18]. This material was used for all studies.

2.2 Synthesis of 12-TPA supported Oxides (12-TPA/ ZrO_2 , 12-TPA/ TiO_2 , 12-TPA/ SnO_2)

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

2.3 Catalyst characterization

The ion exchange capacity (IEC)/protonating ability of $M(IV)$ PWs (possessing inherent acidity) was determined by measurement of Na^+ IEC using column method reported earlier^[20]. Chemical stability of all synthesized materials in various media such as acids (HCl, H_2SO_4 and HNO_3), bases (NaOH and KOH) and organic solvents (ethanol, benzene, acetone and acetic acid) was studied by taking 0.5 g of material in 50 ml of the particular medium and allowed to

stand for 24 h. The change in colour, weight, solubility, etc. was observed. Elemental analysis was performed on ICP-AES spectrometer (Thermo Scientific iCAP 6000 series). FTIR spectra was recorded using KBr pellet on Shimadzu (Model 8400S). Thermal analysis (TGA) was carried out on a Shimadzu (Model TGA 50) thermal analyzer at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. X-ray diffractogram ($2\theta = 10 - 80^{\circ}$) was obtained on X-ray diffractometer (Bruker AXS D8) with $\text{Cu-K}\alpha$ radiation with nickel filter. SEM and EDX of the sample were scanned on Jeol JSM-5610-SLV scanning electron microscope. Surface area measurement (by BET method) was carried out on Micromeritics Gemini at $-196\text{ }^{\circ}\text{C}$ using nitrogen adsorption isotherms. Surface acidity was determined on Micromeritics Chemisorb 2720, by a temperature programmed desorption of ammonia. The synthesized materials were preheated at $150\text{ }^{\circ}\text{C}$, $200\text{ }^{\circ}\text{C}$ and $700\text{ }^{\circ}\text{C}$. Ammonia was chemisorbed at $120\text{ }^{\circ}\text{C}$ and then desorption was carried out upto $700\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$.

2.4 Catalytic Activity

The reactions were carried out in a two necked 50 ml round bottomed flask equipped with a magnetic stirrer under heating in an oil bath. In a typical set up, a mixture of anisole or veratrole (10 mmol) and acetic anhydride (15 mmol) for acylation and toluene (10 mmol) and benzyl chloride (15 mmol) for alkylation, along with the catalyst (0.25 g) were taken in a round bottomed flask and stirred at $130\text{ }^{\circ}\text{C}$ for 5 h. The reactions were monitored by GC. After completion of

reaction, the catalyst was separated by decantation and reaction mixture was distilled to obtain the products 4-MA, 3, 4-DMA and p-BT.

2.5. Regeneration of catalyst

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

After separation of catalyst from reaction mixture by decantation, it is first refluxed in ethanol for 30 minutes to solubilise and remove adsorbed molecules, followed by drying at room temperature and acid treatment by method reported earlier [18]. This regeneration procedure was followed in subsequent recycle reaction for M (IV) PWs.

2.5.2. Regeneration of catalyst possessing induced acidity [12-TPA/M (IV) Oxides-20]

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

3. Results and Discussion

3.1. Catalyst characterization

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

Table 1: Elemental analysis by ICP-AES and EDX.

Materials	% by ICP-AES analysis			% by EDX analysis (atomic %)			
	M(IV)	P	W	M(IV)	P	W	O
ZrPW	Zr=26.88	4.96	25.37	Zr=60.79	18.53	20.67	-
TiPW	Ti=14.84	4.64	24.97	Ti=46.61	37.99	15.40	-
SnPW	Sn=36.82	4.67	29.41	Sn=59.33	23.31	17.37	-
12-TPA/ZrO ₂ -20	Zr=58.62	0.09	16.48	Zr=28.75	0.11	3.44	67.70
12-TPA/TiO ₂ -20	Ti=46.76	0.08	16.17	Ti=28.63	0.15	0.88	70.34
12-TPA/SnO ₂ -20	Sn=60.01	0.08	18.04	Sn=18.40	0.12	2.57	78.92

A study on the chemical stability of M (IV) PWs and 12-TPA/M (IV) Oxides-20 shows that these materials are stable in acid and organic solvent media, however not so stable in base

medium. The maximum tolerable limits for all synthesized materials have been presented in Table 2.

Table 2: Chemical stability data of M (IV) PWs and 12-TPA/M (IV) Oxides-20.

Materials	Chemical media	Maximum tolerable limits
M(IV)PWs	Acids	18N H ₂ SO ₄ , 16N HNO ₃ , 11.3N HCl
	Bases	5 N NaOH, 5 N KOH
	Organic Solvents	Ethanol, Benzene, Toluene, Acetone and Acetic acid
12-TPA/M(IV)Oxides-20	Acids	5N H ₂ SO ₄ , 16N HNO ₃ , 11.3N HCl
	Bases	3 N NaOH, 3 N KOH
	Organic Solvents	Ethanol, Benzene, Toluene, Acetone and Acetic acid

FTIR spectrum of M (IV) PWs (SM - Fig. 7) exhibits broad band in the region $\sim 3400\text{ cm}^{-1}$ which is attributed to asymmetric and symmetric $-\text{OH}$ stretching in all the samples. A medium band around $\sim 1635\text{ cm}^{-1}$ is attributed to P-O-H bending, indicating presence of structural $-\text{OH}$ protons contained in all samples. A band in the region $\sim 1083\text{ cm}^{-1}$ is attributed to the presence of P=O stretching in all samples. FTIR spectrum of 12-TPA/ZrO₂-20, 12-TPA/TiO₂-20 and 12-TPA/SnO₂-20 (SM - Fig. 8) exhibits peaks at $\sim 3450\text{ cm}^{-1}$, $\sim 1635\text{ cm}^{-1}$, $\sim 1083\text{ cm}^{-1}$, $\sim 987\text{ cm}^{-1}$, which corresponds to asymmetric and symmetric $-\text{OH}$ stretching, P-O-H bending, P=O stretching and W-O stretching respectively.

TGA thermogram (SM - Fig. 9) shows weight loss in the temperature range of $40 - 150\text{ }^{\circ}\text{C}$ for ZrPW, TiPW and SnPW to be 19.78%, 21.02% and 15.26% respectively, which corresponds to loss of surface moisture and hydrated water. Weight loss in the temperature range of $150\text{ }^{\circ}\text{C} - 650\text{ }^{\circ}\text{C}$ for ZrPW, TiPW and SnPW is found to be 7.25%, 4.28% and 6.04% respectively, which is probably due to the condensation of structural hydroxyl groups.

TGA thermograms of 12-TPA/ZrO₂-20, 12-TPA/TiO₂-20 and 12-TPA/SnO₂-20 (SM - Fig. 10) exhibit 0.9%, 0.4% and 1.4% weight loss in the temperature range of $30 - 150^{\circ}\text{C}$ which corresponds to the loss of surface moisture. Thereafter in the region $200-600^{\circ}\text{C}$ there is a negligible weight loss which

indicates fairly stable nature of the materials. SEM images (SM - Fig. 11-16) of all the synthesized materials exhibit irregular morphology. Absence of sharp peaks in X-ray diffractogram of M (IV) PWs (SM - Fig. 17) reveals the amorphous nature of M (IV) PWs. X-ray diffractogram of 12-TPA/ZrO₂-20 (SM - Fig. 18) shows intense and well defined characteristic diffraction peaks at 2θ values of 31.4, 35.2, 50.1, and 59.9 (JCPDS data card no. 17-923). X-ray diffractogram pattern of 12-TPA/TiO₂-20 (SM - Fig. 19) shows characteristic diffraction peaks at 2θ values of 25.2, 37.8, 48.0,

53.8, 55.0, 62.1 and 75.0 correspond to the crystal planes of (101), (004), (200), (105), (211), (213) and (215) respectively, indicates formation of anatase TiO₂ (JCPDS data card no. 21-1272). X-ray diffractogram pattern of 12-TPA/SnO₂-20 (SM - Fig. 20) shows characteristic diffraction peaks at 2θ values of 26.5, 33.8 and 51.8 correspond to the crystal planes of (110), (101) and (211) respectively, indicates formation tetragonal SnO₂ (JCPDS data card no. 41-1445).

Surface area values determined (by BET method) for all materials have been presented in Table 3.

Table 3: Surface area, surface acidity and IEC values for M (IV) PWs and 12-TPA/M (IV) Oxides-20.

Materials	Surface Area (BET method) (m ² /g)	Surface acidity (NH ₃ -TPD method)		IEC (meq./g)
		Preheating Temperature (°C)	Acidity (mmol/g)	
ZrPW	80.96	150	9.34	0.98
		200	6.05	0.76
		700	3.90	0.49
TiPW	86.48	150	11.05	2.97
		200	11.02	2.39
		700	8.28	1.07
SnPW	171.04	150	10.28	2.00
		200	7.54	1.64
		700	4.50	0.73
12-TPA/ZrO ₂ -20	33.90	150	1.07	-
		200	0.89	-
		700	0.17	-
12-TPA/TiO ₂ -20	60.50	150	2.03	-
		200	1.68	-
		700	0.27	-
12-TPA/SnO ₂ -20	139.54	150	1.42	-
		200	1.11	-
		700	0.22	-

3.2 Evaluation of acid property

Surface acidity for all the materials was determined by NH₃-TPD at 150 °C, 200 °C and 700 °C preheating temperatures (Fig. 1-6, Table 3). M (IV) PWs exhibit broad desorption peaks compared to 12-TPA/M (IV) Oxides-20, which is in accordance with the amorphous and crystalline nature of the materials respectively [18]. As already discussed earlier in the text, acidity in the M(IV)PWs is due to the presence of structural hydroxyl protons, H⁺ of the –OH being the Bronsted

acid sites. Further, surface acidity values of M (IV) PWs depend on the size and charge of the cation. Smaller size and higher charge of the cation indicates greater tendency to release a proton, i.e. H⁺ of the –OH groups present in M (IV) PWs. In the present study Zr⁴⁺, Ti⁴⁺ and Sn⁴⁺, all metal ions being tetravalent as well as bearing common anion PO₄³⁻ and WO₄²⁻, size of the cation (Zr⁴⁺-0.86 Å, Ti⁴⁺-0.74 Å, Sn⁴⁺-0.83 Å) seems to play a dominant role. Thus the acidity in the materials follows the order TiPW > SnPW > ZrPW.

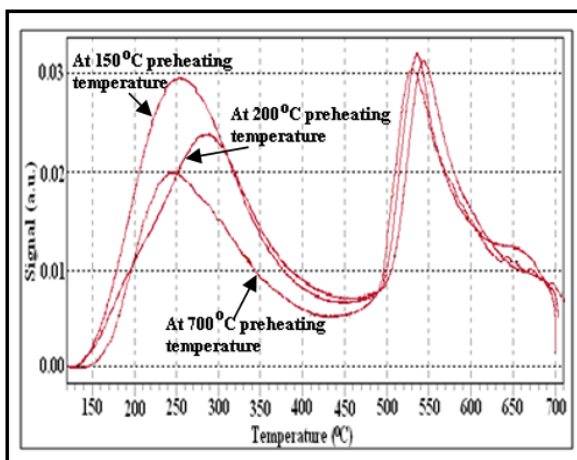


Fig 1: NH₃-TPD patterns of ZrPW

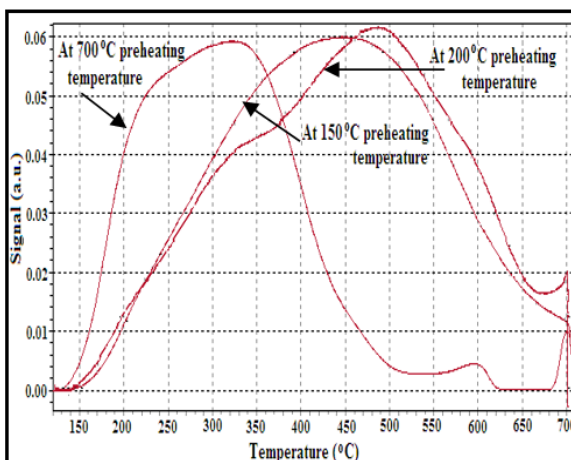
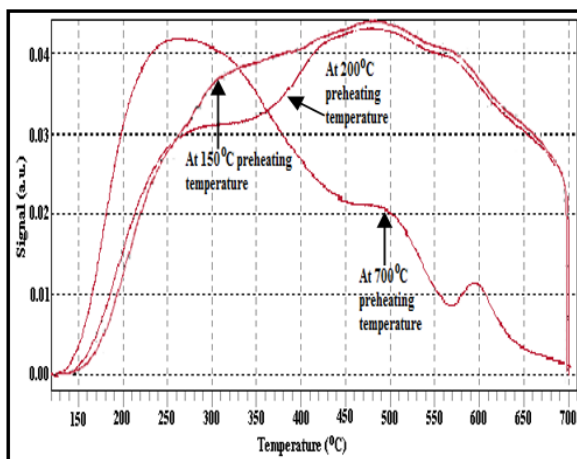
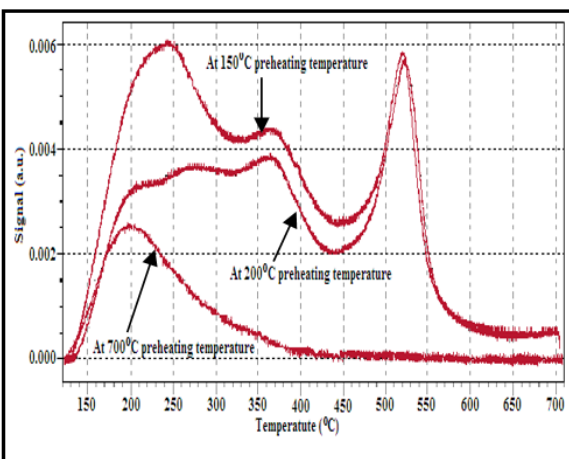
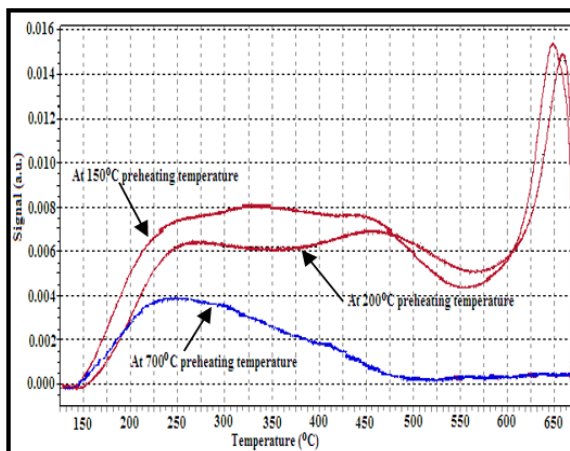
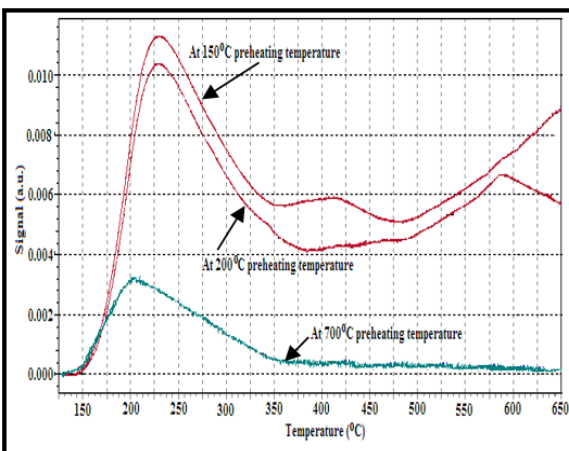


Fig 2: NH₃-TPD patterns of TiPW

Fig 3: NH₃-TPD patterns of SnPWFig 4: NH₃-TPD patterns of 12-TPA/ZrO₂-20Fig 5: NH₃-TPD patterns of 12-TPA/TiO₂-20Fig 6: NH₃-TPD patterns of 12-TPA/SnO₂-20

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

In case of 12-TPA supported catalysts, anchoring of 12-TPA onto the various oxides induces acidity into the oxides. A decrease in surface acidity for 12-TPA/M (IV) Oxides-20 with increasing preheating temperatures could be attributed to decomposition of 12-TPA into WO₃ crystallites [21].

3.3. Catalytic Activity

In the present study Friedel–Crafts reactions have been performed as described in experimental section. Firstly, reaction conditions were optimized using ZrPW and 12-TPA/ZrO₂-20 as solid acid catalyst for Friedel–Crafts alkylation of toluene with benzyl chloride and Friedel–Crafts acylation of anisole and veratrole with acetyl chloride by varying parameters such as reaction time, reaction temperature, catalyst amount and mole ratio of the reactants. The optimized reaction conditions are presented in **SM – Table 5**. Friedel–Crafts alkylation of toluene with benzyl chloride selectively gave p-BT. The effect of reaction time (2 h – 7 h) on the product yield in all cases was studied at 110 °C temperature with 1:1 mole ratio of toluene: benzyl chloride and 0.15 g of catalyst. The reaction reached equilibrium within 5 h. When reaction temperature is varied (110 °C and 140 °C),

there is significant increase in yield upto 130°C, after which decrease in yield is observed. With increasing catalyst amount, which was varied from 0.15 g to 0.35 g, yield increases probably due to increase in the number of acid sites. In all cases, optimum catalyst amount was taken as 0.25 g. The influence of mole ratio of reactants on product yield was studied using 0.25 g of catalyst at the refluxing temperature at optimized reaction time. The mole ratio toluene: benzyl chloride was varied as 1:1 to 1:2 and 2:1. In the present study, higher yield was observed with 1:1.5 mole ratio and taken as optimized mole ratio for acylation of anisole and veratrole with acetyl chloride.

It has been reported earlier that there is no significant effect of solvents in the acylation of anisole and veratrole and best results were obtained when aromatic ethers were used as self solvents [22]. In the present study therefore anisole and veratrole (aromatic ethers) have been used both as substrates and solvent and for this reason while optimizing reaction condition, concentration of only the acylating agent was varied. Thus, the Green Chemistry principle 5 which states that the “use of solvents should be made unnecessary whenever possible and when used, innocuous” is implemented.

At optimum condition, Friedel–Crafts alkylation of toluene with benzyl chloride [gave selectively p-benzyl toluene (p-BT)] and acylation of anisole/veratrole with acetyl chloride [gave selectively 4-methoxy acetophenone (4-MA) and 3, 4-dimethoxy acetophenone (3,4-DMA) respectively] was performed using ZrPW, TiPW, SnPW, 12-TPA/ZrO₂, 12-TPA/TiO₂ and 12-TPA/SnO₂ (reaction time: 5 h, reaction

temperature: 130 °C, catalyst amount: 0.25 g and mole ratio of substituted benzenes : benzyl chloride and acetyl chloride = 1:1.5) (Table 4).

When comparison is made between anisole and veratrole, the product yield is higher for veratrole (Table 4). The rate-determining step of the Friedel-Crafts acylation is the formation of the electrophilic intermediate (Scheme 1). The presence of an additional electron donating methoxy group in veratrole makes it a more active compound for electrophilic

substitution of acyl group in the para position than anisole due to an increased electron density at para position and resultant increased susceptibility for attack by the electrophile.

Regeneration and reusability for all the catalysts under study was conducted and results presented in Table 4. After each catalytic run, all the catalysts turn dark brown, probably due to the fact that reactant molecules get adsorbed on the surface of the catalysts.

Table 4: Friedel-Crafts alkylation of toluene with benzyl chloride and acylation of anisole/veratrole with acetyl chloride by using M (IV) PWs and 12-TPA/M (IV) Oxides.

Reactants	% Yield							
	Catalytic run	ZrPW	TiPW	SnPW	Catalytic run	12-TPA/ ZrO ₂	12-TPA/ TiO ₂	12-TPA/ SnO ₂
Toluene : Benzyl Chloride	1(F)	59.68	70.38	63.27				
	2(Rg)	58.32	69.00	60.08				
	3(Rg)	56.81	67.54	58.44				
Toluene : Benzyl Chloride	1(F)	59.68	70.38	63.27	1(F)	54.26	56.31	55.47
	2(Ru)	51.00	62.44	55.47	2(Ru)	42.18	44.01	43.00
	3(Ru)	40.84	54.12	44.56	3(Ru)	30.69	37.89	35.74
Anisole : Acetyl Chloride	1(F)	50.16	56.81	52.00	1(F)	44.19	48.87	46.00
	2(Rg)	48.99	55.08	50.76	2(Ru)	38.08	40.33	39.10
	3(Rg)	47.36	53.47	49.66	3(Ru)	29.46	31.88	30.69
Veratrole : Acetyl Chloride	1(F)	54.89	62.38	57.70	1(F)	48.43	52.89	50.17
	2(Rg)	53.00	61.46	55.00	2(Ru)	40.98	44.11	40.06
	3(Rg)	52.04	60.00	53.69	3(Ru)	31.13	35.00	32.63

(Reaction time: 5 h, Reaction temperature: 130°C, Catalyst amount: 0.25 g, Mole ratio of substituted benzenes: benzyl chloride/acetyl chloride = 1:1.5, F: Fresh, Rg: Regenerated, Ru: Reused)

In case of M (IV) PWs, after each subsequent run the catalysts were regenerated as described earlier in experimental section. It is observed that, on regeneration M (IV) PWs exhibit only a marginal decrease in yields upto three catalytic runs. However, when catalysts are reused, the decrease in % yields are much higher which is probably due to the deactivation of catalysts due to substrate molecules getting adsorbed on surface or also

entering interstices of the catalyst material [18]. Table 5 provides atomic wt. % of various components (Zr, P, W and O) for both fresh and spent catalysts (SM - Fig. 21 and 22) in case of synthesis of p-BT. Decrease in atomic wt. % of Zr in ZrPW and Zr and W in 12-TPA/ZrO₂-20 indicates leaching of ions which could be the probable reason for decrease in % yields of p-BT, 4-MA and 3,4-DMA.

Table 5: Elemental analysis by EDX for both fresh and spent ZrPW and 12-TPA/ZrO₂-20 in the synthesis of p-benzyl toluene.

Reactants	Materials	% by EDX analysis			
		Zr	P	W	O
Toluene: Benzyl chloride	ZrPW (Fresh)	60.79	18.53	20.67	-
	ZrPW (Spent)	50.56	27.06	22.38	-
	12-TPA/ZrO ₂ -20 (Fresh)	28.75	0.11	3.44	67.70
	12-TPA/ZrO ₂ -20 (Spent)	19.21	1.72	2.06	77.01

(Mole ratio of Toluene: Benzyl chloride -1:1.5; Catalysts amount - 0.25g;
Reaction temperature - 130 °C; Reaction Time- 5h)

It is reported that the mechanism for Friedel-Crafts alkylation and acylation over solid acid catalysts is the same as in case of homogeneous system where Lewis acid catalysts are used [23-25]. The proposed mechanism for the acylation and alkylation reaction (Scheme 1 and 2) on solid acid catalyst implies the formation of an adsorbed species by interaction of the acylating/alkylating agent with a Brønsted acid site [24-26] (acyl/alkyl cation). The Brønsted acid site generates an acyl carbonium ion, which in turn affects the electrophilic substitution. A higher density of acid sites increases number of acyl cations enhancing activity of the reaction.

Number and nature of surface acid sites play a predominant role in evaluating and correlating catalytic activity. Amongst M (IV) PWs performance of catalyst is found to be TiPW > SnPW > ZrPW whereas,

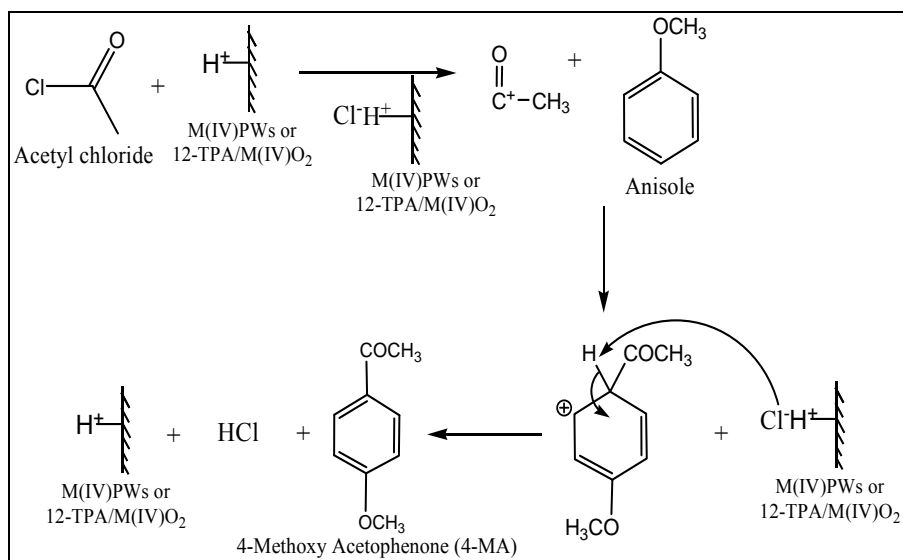
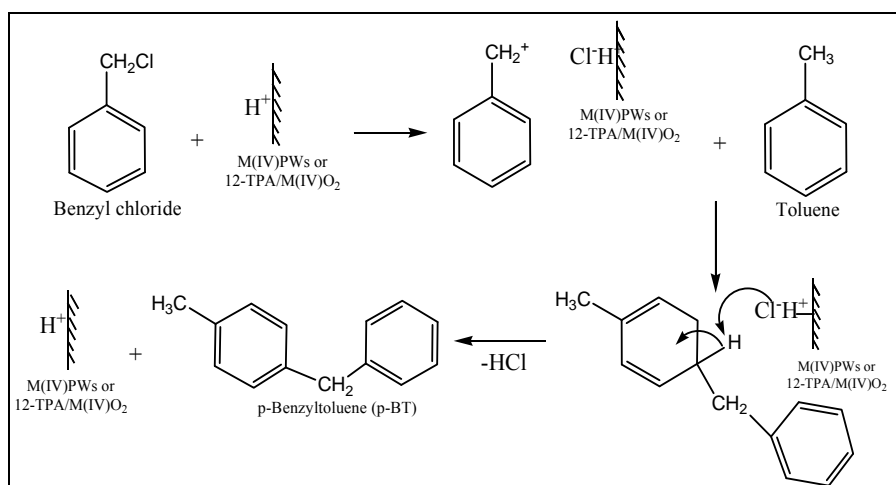
amongst 12-TPA/M(IV)Oxides-20, the order is found to be 12-TPA/TiO₂-20 > 12-TPA/SnO₂-20 > 12-TPA/ZrO₂-20 which could be attributed to increased surface acidity of these materials (Table 3). With reference to performance of catalysts, M (IV) PWs scores over 12-TPA/M (IV) Oxides-20 in terms of % yields of p-BT, 4-MA and 3, 4-DMA formed as well as reusability of catalysts.

Comparing catalyst efficiency/performance of M(IV)PWs, 12-TPA/M(IV)Oxides-20 with M(IV) phosphates and M(IV) tungstates of the class of TMA salts [M(IV) = Zr, Ti and Sn] (Table 6), it is observed that yields are higher in case of M(IV)PWs. Especially, TiPW works as the most efficient catalyst giving excellent yield for Friedel-Crafts alkylation of toluene with benzyl chloride to selectively give p-benzyl toluene.

Table 6: Comparison of % yield of p-benzyl toluene using TMA salts, TMBA salts [M (IV) PWs] and 12-TPA/M (IV) Oxides-20.

Catalyst Used	% yield
ZrP	49.30
ZrW	44.70
ZrPW	59.68
12-TPA/ZrO ₂ -20	54.26
TiP	57.00
TiW	50.00
TiPW	70.38
12-TPA/TiO ₂ -20	56.31
SnP	56.00
SnW	50.00
SnPW	63.27
12-TPA/SnO ₂ -20	55.47

(Mole ratio of Toluene: Benzyl chloride -1:1.5; Catalysts amount - 0.25g;
Reaction temperature - 130 °C; Reaction Time- 5h)

**Scheme 1:** Reaction mechanism of Friedel Crafts acylation of anisole using solid acid catalyst.**Scheme 2:** Reaction mechanism of Friedel Crafts alkylation of toluene using solid acid catalyst.

4. Conclusions

The work outlined herein reveals the promising use of both the types of solid acid catalysts with advantages of a solvent free synthesis, high selectivity of the products formed with no catalyst contamination, operational simplicity, mild reaction conditions, no acid waste generation, and possible regeneration and reuse of catalysts. Amongst the two types of catalysts

synthesized possessing same elemental composition, (i) M (IV) PWs (possessing inherent acidity) scores over (ii) 12-TPA/M (IV) Oxides-20 (possessing induced acidity) in terms of catalyst performance in Friedel-Crafts alkylation and acylation reactions. Finally, TiPW exhibiting the best performance has potential for commercialization.

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