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Research Paper

GREEN ROUTES TO SYNTHESIS OF ANTHRAQUINONE DERIVATIVES VIA FRIEDEL – CRAFTS REACTION UNDER SOLVENT FREE CONDITIONS USING SOLID ACID CATALYST

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The present study involves a simple one step green route to synthesis of anthraquinone derivatives via Friedel-Crafts reaction under solvent free conditions using solid acid catalysts. Two types of solid acid catalysts have been synthesized, characterized and their potential utility towards synthesis of anthraquinone derivatives has been explored and compared. M(IV)PWs [M(IV) = Zr, Ti and Sn, and PW = Phosphotungstate] mixed materials of the class of tetravalent metal bianionic acid (TMBA) salts have been synthesized by sol-gel route while 12-Tungstophosphoric acid (12-TPA) has been supported onto ZrO₂, TiO₂ and SnO₂ by process of anchoring and calcination to result in materials with similar elemental composition. The highlighting features are that the anthraquinone derivatives are obtained in a single step under solvent free conditions with good % yields with added advantages of regeneration and reuse of M(IV)PWs upto three catalytic runs without significant loss in % yields of the products formed.

Keywords: Solid acid catalyst, Friedel-Crafts reaction, Phosphotungstates, Anthraquinone, Sol-gel

INTRODUCTION

Tetravalent Metal Acid (TMA) salts are inorganic cation exchangers possessing general formula M(IV) (HXO₄)₂.nH₂O [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 Brønsted acid sites in nature (Bhaumik *et al.*, 2001; Slade *et al.*, 1997).

From our laboratory, TMA salts have been used as solid acid catalysts for esterification (Joshi *et al.*, 2008; Patel *et al.*, 2008; Thakkar *et al.*, 2009), cyclodehydration (Patel *et al.*, 2002), ketalisation of ketones (Patel *et al.*, 2003), hydration of nitriles (Patel *et al.*, 2003), cyclodehydration of 1,n-diols (Patel *et al.*, 2001) and for synthesis of coumarin derivatives (Joshi *et al.*, 2008).

When we used a mixed material of the class of tetravalent bimetallic acid (TBMA) salts such

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as zirconium titanium phosphate (ZTP) (Thakkar *et al.*, 2009) (containing two different cations and an anion) and a mixed material of the class of TMBA salts (containing two different anions and a cation) such as Zr(IV) phosphotungstate (ZrPW) (Ghodke *et al.*, 2013) as a solid acid catalyst, for synthesis of esters (Thakkar *et al.*, 2009) and coumarin derivatives (Ghodke *et al.*, 2013), respectively, enhanced catalytic activity was observed compared to their single salt counter parts.

Heteropoly acids (HPAs) have proved to be the alternative for traditional acid catalysts due to both strong acidity and appropriate redox properties. The major disadvantage of HPAs, as catalyst lies in their low thermal stability, low surface area (1-10 m²/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 (Khder *et al.*, 2013).

Anthraquinones and their derivatives are important members of the organic family, the structural unit often observed in some synthetic dyes and in many naturally occurring substances such as pigments, vitamins, and enzymes (Thomsan, 1957; Fieser *et al.* 1961; Fieser *et al.*, 1963). The quinone compounds occupy an important place among the different classes of anti-tumor agents (Valderrama *et al.*, 2006). The hydroxylated 9,10- anthraquinones exist widely in nature and are known to display various pharmacological activities (Shi *et al.*, 2001). Furthermore, the anthraquinones of the Rubiaceae family exhibit some interesting in vivo biological activities, such as anti-microbial (Sittie

et al., 1999), anti-fungal (Rath *et al.*, 1995), hypotensive, analgesic (Younos *et al.*, 1995), anti-malarial (Adwankar *et al.*, 1982; Kaumaglo *et al.*, 1992), anti-oxidant (Tripathi *et al.*, 1997), anti-leukemic and mutagenic functions (Chang *et al.*, 1995; Ismail *et al.*, 1997).

The conventional route to synthesis of anthraquinone derivatives involves two steps in which first step is the intramolecular condensation of o-arylbenzoic acids which is carried out in the presence of AlCl₃ or HF/BF₃ and the second step is the dehydration which is commonly catalyzed by concentrated H₂SO₄ or oleum (Fieser 1941), benzoyl chloride and concentrated sulfuric acid (Clar, 1948 and 1949), benzoyl chloride and zinc chloride (Clar, 1948) and polyphosphoric acid (Madje *et al.*, 2011).

A Friedel-Crafts reaction between phthalic anhydride and substituted benzenes in the presence of a eutectic mixture of aluminum chloride and sodium chloride (2:1) melt has been reported for the preparation of a variety of anthraquinones (Horii *et al.*, 1968). These methods however suffer from disadvantages such as long reaction times, use of toxic solvents, the reaction conditions are usually quite severe and some reagents are commercially not available and the desired product is afforded from two steps with low yields.

A few solid acid catalysts (Madje *et al.*, 2011; Singh *et al.*, 2005; Xu *et al.*, 2006; Xu *et al.*, 2005) have been reported for synthesis of anthraquinone derivatives with advantages such as ease of work up and high yields, however with disadvantages such as long reaction times, use of large amounts of catalyst and catalysts cannot be regenerated and reused. Therefore, the need for an ideal solid acid catalyst is on.

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 which possess induced acidity and same components (i.e., Zr, Ti, Sn, P and W) as the TMBA salts. All synthesized materials have been characterized for elemental analysis by ICP-AES, TGA, FTIR, SEM, EDX, XRD, surface area (BET method)

and surface acidity (NH_3 -TPD method). The potential utility of these materials as solid acid catalysts has been explored and compared by studying synthesis of anthraquinone derivatives via Friedel-Crafts reaction under solvent free conditions wherein substituted benzenes such as toluene, resorcinol, hydroquinone and nitrobenzene are treated with phthalic anhydride to give 2-methyl anthraquinone, 1, 3-dihydroxy anthraquinone, 1, 4-dihydroxy anthraquinone and 2-nitro anthraquinone, respectively. Parameters such as reaction time, reaction temperature, catalyst amount, and mole ratio of the reagents have been optimized including regeneration and reuse of catalysts. The catalytic activity of synthesized materials has been compared and correlated with acid properties of the materials.

Table 1: Optimization of Parameters for Synthesis of ZrPW

Parameters optimized	No.	Concentration (M)			Volume (mL)			Mole ratio	Temp. $\pm 2^\circ C$	Stirring Time (h)	Aging Time (h)	IEC meq/g
		Zr	P	W	Zr	P	W	Zr:P:W				
Concentration	1	0.1	0.1	0.1	50	50	50	1:1:1	30	1	15	0.56
	2	0.2	0.1	0.1	50	50	50	2:1:1	30	1	15	0.98
	3	0.2	0.1	0.2	50	50	50	2:1:2	30	1	15	0.44
	4	0.2	0.2	0.1	50	50	50	2:2:1	30	1	15	0.89
	5	0.1	0.2	0.2	50	50	50	1:2:2	30	1	15	0.38
Volume	6	0.1	0.1	0.1	100	50	50	2:1:1	30	1	15	1.08
	7	0.2	0.1	0.1	100	50	50	4:1:1	30	1	15	0.75
Aging Time	8	0.2	0.1	0.1	50	50	50	2:1:1	30	1	1	0.90
	9	0.2	0.1	0.1	50	50	50	2:1:1	30	1	3	0.92
	10	0.2	0.1	0.1	50	50	50	2:1:1	30	1	5	0.92
Temperature	11*	0.2	0.1	0.1	50	50	50	2:1:1	70	1	0	1.20
Stirring Time	12	0.2	0.1	0.1	50	50	50	2:1:1	70	2	0	1.18

Note: * Optimum condition for synthesis of ZrPW.

MATERIALS AND METHODS

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

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

Synthesis of ZrPW (at Optimized Condition)

An aqueous mixture of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (0.1 M, 50 mL) and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.1 M, 50 mL) was added dropwise (flow rate 1 mL/min) to an aqueous solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (0.2 M, 50 mL) 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 (Patel *et al.*, 2008). This material was used for all studies.

Synthesis of TiPW (at Optimized Condition)

An aqueous mixture of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (0.1 M, 50 mL) and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.1 M, 50 mL) was added drop wise (flow rate $1 \text{ mL}/\text{min}^{-1}$) to a

Table 2: Optimization of Parameters for Synthesis of TiPW

Parameters optimized	No.	Concentration (M)			Volume (mL)			Mole ratio	Temp. $\pm 2^\circ\text{C}$	Stirring Time (h)	Aging Time (h)	IEC meq/g
		Ti	P	W	Ti	P	W					
Concentration	1	0.1	0.1	0.1	50	50	50	1:1:1	30	1	15	3.06
	2	0.2	0.1	0.1	50	50	50	2:1:1	30	1	15	3.18
	3	0.2	0.1	0.2	50	50	50	2:1:2	30	1	15	2.27
	4	0.2	0.2	0.1	50	50	50	2:2:1	30	1	15	3.16
	5	0.1	0.2	0.2	50	50	50	1:2:2	30	1	15	2.60
Volume	6	0.1	0.1	0.1	100	50	50	2:1:1	30	1	15	3.45
	7	0.2	0.1	0.1	100	50	50	4:1:1	30	1	15	2.91
Aging Time	8*	0.2	0.1	0.1	50	50	50	2:1:1	30	1	1	3.48
	9	0.2	0.1	0.1	50	50	50	2:1:1	30	1	3	2.42
	10	0.2	0.1	0.1	50	50	50	2:1:1	30	1	5	2.75
Temperature	11	0.2	0.1	0.1	50	50	50	2:1:1	70	1	0	2.77
Stirring Time	12	0.2	0.1	0.1	50	50	50	2:1:1	70	2	1	3.28

Note: * Optimum condition for synthesis of TiPW.

Table 3: Optimization of Parameters for Synthesis of SnPW

Parameters optimized	No.	Concentration (M)			Volume (mL)			Mole ratio Sn:P:W	Temp. $\pm 2^\circ\text{C}$	Stirring Time (h)	Aging Time (h)	IEC meq/g
		Sn	P	W	Sn	P	W					
Concentration	1	0.1	0.1	0.1	50	50	50	1:1:1	30	1	15	1.93
	2	0.2	0.1	0.1	50	50	50	2:1:1	30	1	15	1.65
	3	0.2	0.1	0.2	50	50	50	2:1:2	30	1	15	1.40
	4	0.2	0.2	0.1	50	50	50	2:2:1	30	1	15	1.76
	5	0.1	0.2	0.2	50	50	50	1:2:2	30	1	15	1.83
Volume	6	0.1	0.1	0.1	100	50	50	2:1:1	30	1	15	1.99
	7	0.2	0.1	0.1	100	50	50	4:1:1	30	1	15	1.82
Aging Time	8	0.1	0.1	0.1	100	50	50	2:1:1	30	1	1	2.19
	9*	0.1	0.1	0.1	100	50	50	2:1:1	30	1	3	2.44
	10	0.1	0.1	0.1	100	50	50	2:1:1	30	1	5	2.30
Temperature	11	0.1	0.1	0.1	100	50	50	2:1:1	70	1	0	2.23
Stirring Time	12	0.1	0.1	0.1	100	50	50	2:1:1	30	2	1	2.38

Note: * Optimum condition for synthesis of SnPW.

solution of TiCl_4 (0.2 M, 50 mL) (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 1 h, 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 (Patel *et al.*, 2008). This material was used for all studies.

Synthesis of SnPW (at Optimized Condition)

An aqueous mixture of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (0.1 M, 50 mL) and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.1 M, 50 mL) was added drop wise (flow rate 1 mL/min) to a solution of SnCl_4 (0.1 M, 100 mL) (prepared in 0.1 M HCl)

with continuous stirring for an hour at room temperature. The gelatinous precipitates obtained are kept for ageing for 3 h, 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 (Patel *et al.*, 2008). This material was used for all studies.

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

For preparation of ZrO_2 , TiO_2 and SnO_2 , aqueous solutions of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (0.3 M, 100 mL), TiCl_4 (0.9 M, 100 mL) and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (0.3 M, 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 5 h. 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 3 h, 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 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.

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 (Waghmare *et al.*, 2008). Chemical stability of all synthesized materials in various media such as acids (HCl, H₂SO₄ and HNO₃), 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 color, 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°C·min⁻¹. X-ray diffractogram (2θ = 10 - 80°) was obtained on X-ray diffractometer (Bruker AXS D8) with Cu-K_α radiation with nickel filter. SEM and EDX of the sample were scanned on Jeol JSM-5610-SLV scanning electron microscope. Surface area measurement (by BET method) was carried out on Micromeritics Gemini at -196°C using nitrogen adsorption isotherms. Surface acidity was determined on Micromeritics Chemisorb 2720, by a temperature programmed desorption of ammonia. The synthesized materials were preheated at 150°C, 200°C and 700°C. Ammonia was chemisorbed at 120°C and then desorption was carried out upto 700°C at a heating rate of 10°C/min.

Catalytic Activity

In a typical reaction, a 25 mL round bottomed flask attached to a reflux condenser was used and charged with phthalic anhydride (1-1.2 mmol), substituted benzene (1-1.2 mmol), water (2 mL) and catalyst (0.15-0.35 g). The reaction mixture was stirred at particular temperature (110-140°C) in an oil bath for the appropriate time (0.5-4.0 h) and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was extracted with ethyl acetate (2×20 mL). The combined organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure and the crude product obtained was purified by recrystallization.

Regeneration of Catalyst

Regeneration of Catalyst Possessing Inherent Acidity [M(IV)PWs]

After separation of catalyst from reaction mixture by decantation, it is first refluxed in ethanol for 30 min to solubilize and remove adsorbed

molecules, followed by drying at room temperature and acid treatment by method reported earlier (Patel *et al.*, 2008). This regeneration procedure was followed in subsequent recycle reaction for M(IV)PWs.

Regeneration of Catalyst Possessing Induced Acidity [12-TPA/M(IV)Oxides-20]

After separation of catalyst from reaction mixture by decantation, it is first refluxed in ethanol for 30 minutes to solubilize and remove adsorbed molecules, followed by drying at 120°C for 3 h. This regeneration procedure was followed in

subsequent recycle reaction for 12-TPA/M(IV) oxides-20.

RESULTS AND DISCUSSION

Catalyst Characterization

Elemental analysis performed by ICP-AES for all the synthesized materials have been presented in Table 5, which is well supported by EDX analysis for all the materials (Table 5).

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

Table 4: Optimization of Loading of 12-TPA (wt.%) onto M(IV)Oxides

Materials	Surface Acidity (mmol/g)(at 700°C Preheating Temperature)
10 wt. % 12-TPA/ZrO ₂	0.113
20 wt. % 12-TPA/ZrO ₂	0.170
30 wt. % 12-TPA/ZrO ₂	0.121
10 wt. % 12-TPA/TiO ₂	0.195
20 wt. % 12-TPA/TiO ₂	0.270
30 wt. % 12-TPA/TiO ₂	0.214
10 wt. % 12-TPA/SnO ₂	0.150
20 wt. % 12-TPA/SnO ₂	0.220
30 wt. % 12-TPA/SnO ₂	0.201

Table 5: Elemental Analysis by ICP-AES and EDX

Materials	% by ICP-AES Analysis			% by EDX Analysis (Atomic %)			
	M(IV)	P	W	M(IV)	P	W	O
ZrPW	Zr=26.87	5.67	25.37	Zr=60.79	18.53	20.67	-
TiPW	Ti=17.24	9.24	23.36	Ti=46.61	37.99	15.40	-
SnPW	Sn=41.21	4.67	16.47	Sn=59.33	23.31	17.37	-
12-TPA/ZrO ₂ -20	Zr=79.14	0.26	21.79	Zr=28.75	0.11	3.44	67.70
12-TPA/TiO ₂ -20	Ti=81.44	0.25	20.40	Ti=28.63	0.15	0.88	70.34
12-TPA/SnO ₂ -20	Sn=76.22	0.23	22.76	Sn=18.40	0.12	2.57	78.92

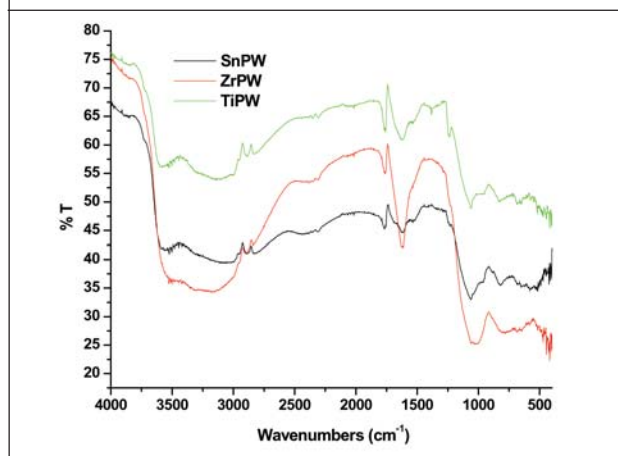
Table 6: Chemical stability data of M(IV)PWs and 12-TPA/M(IV) Oxides-20

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	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

media, however not so stable in base medium. The maximum tolerable limits for all synthesized materials have been presented in Table 6.

FTIR spectrum of M(IV)PWs (Figure 1) exhibits broad band in the region ~ 3400 cm⁻¹ which is attributed to asymmetric and symmetric –OH stretching in all the samples. A medium band around ~ 1635 cm⁻¹ is attributed to P-O-H bending, indicating presence of structural –OH protons

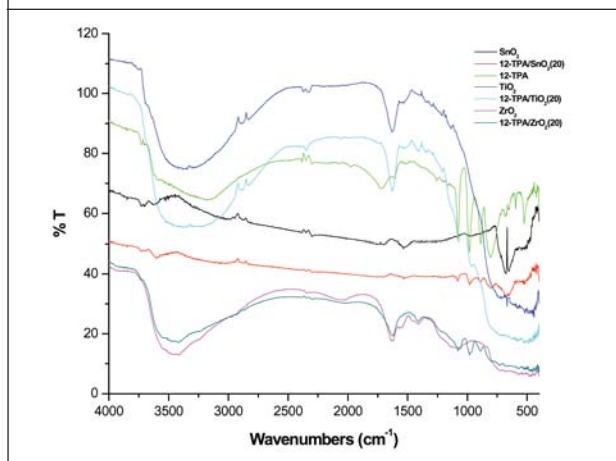
Figure 1: FTIR spectrum of M(IV)PWs



contained in all samples. A band in the region ~ 1083 cm⁻¹ is attributed to the presence of P=O stretching in all samples.

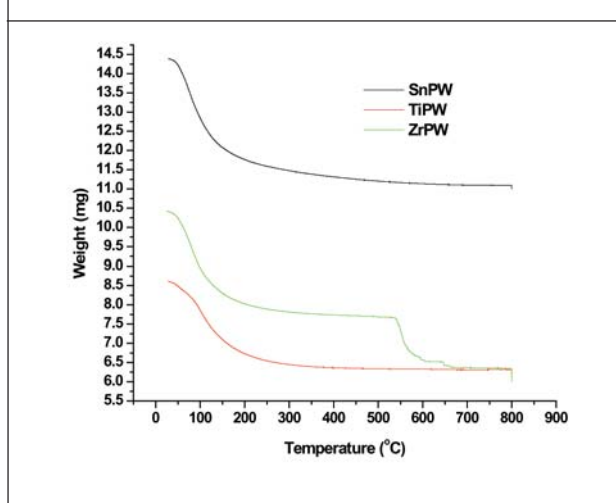
FTIR spectrum of 12-TPA/ZrO₂-20, 12-TPA/TiO₂-20 and 12-TPA/SnO₂-20 (Figure 2) exhibits peaks at ~3450 cm⁻¹, ~1635 cm⁻¹, ~1083 cm⁻¹, ~987 cm⁻¹, which corresponds to asymmetric

Figure 2: FTIR spectrum of 12-TPA/M(IV)Oxides-20



and symmetric –OH stretching, P-O-H bending, P=O stretching and W-O stretching respectively.

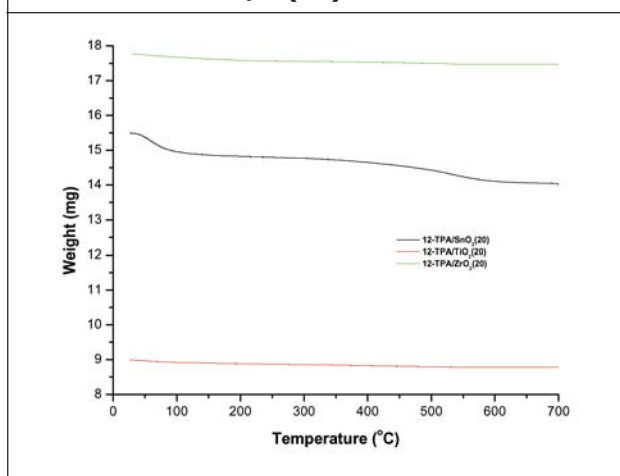
Figure 3: TGA plot of M(IV)PWs



TGA thermogram (Figure 3) shows weight loss in the temperature range of 40-150°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 150-650°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 (Figure 4) exhibit 0.9%, 0.4% and 1.4% weight loss in the temperature range of 30-150°C which corresponds to the loss of surface moisture. Thereafter in the region 200-600°C there is a

Figure 4: TGA plot of 12-TPA/M(IV)Oxides-20



negligible weight loss which indicates fairly stable nature of the materials.

SEM images (Figures 5 to 10) of all the synthesized materials exhibit irregular morphology. Absence of sharp peaks in X-ray diffractogram of M(IV)PWs (Figure 11) reveals the amorphous nature of M(IV)PWs.

X-ray diffractogram of 12-TPA/ZrO₂-20 (Figure 12) shows intense and well defined characteristic

Figure 5: SEM image of ZrPW

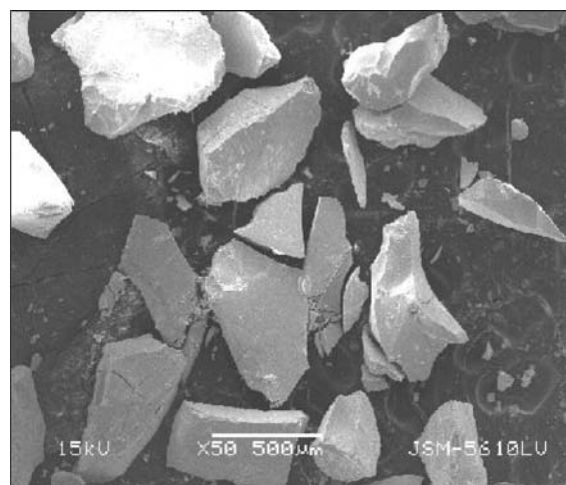


Figure 6: SEM image of TiPW

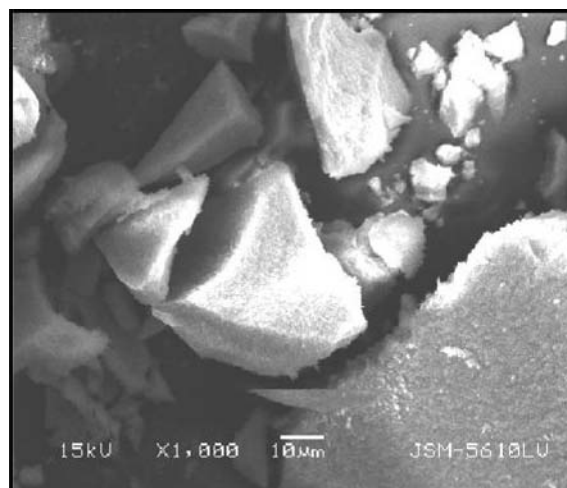


Figure 7: SEM image of SnPW

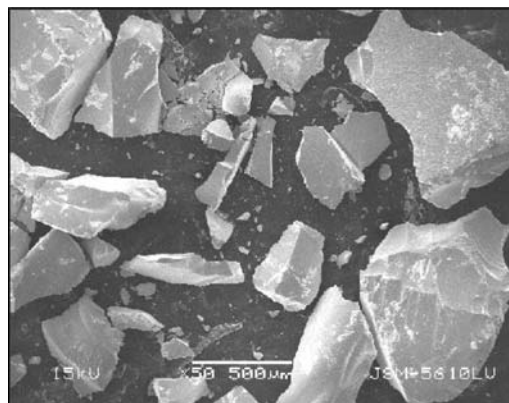


Figure 8: SEM image of 12-TPA/ZrO₂-20

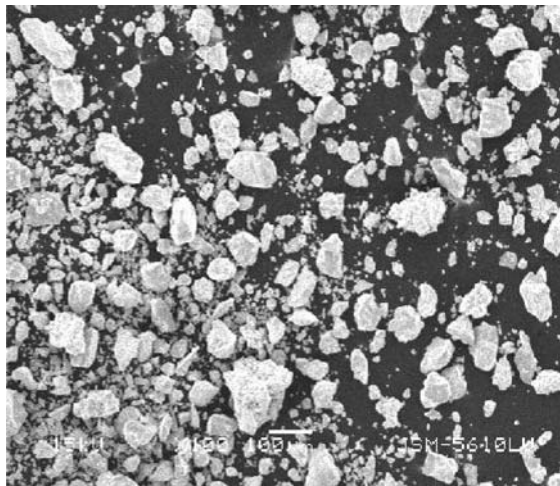


Figure 9: SEM image of 12-TPA/TiO₂-20

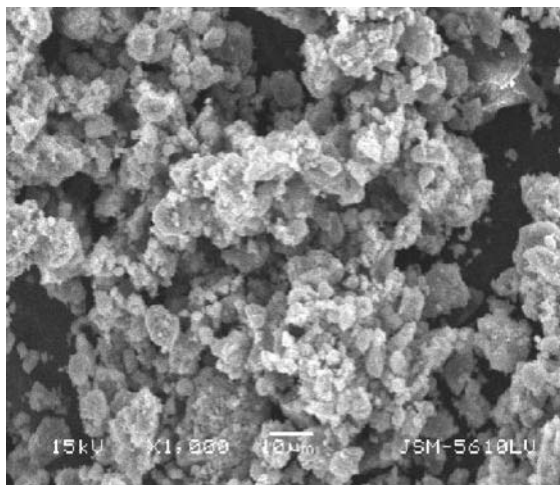


Figure 10: SEM image of 12-TPA/SnO₂-20

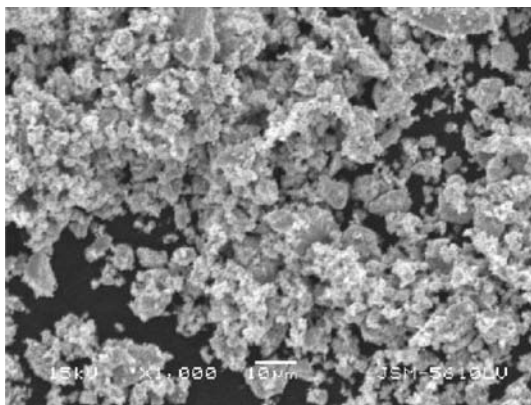


Figure 11: XRD patterns of M(IV)PWs

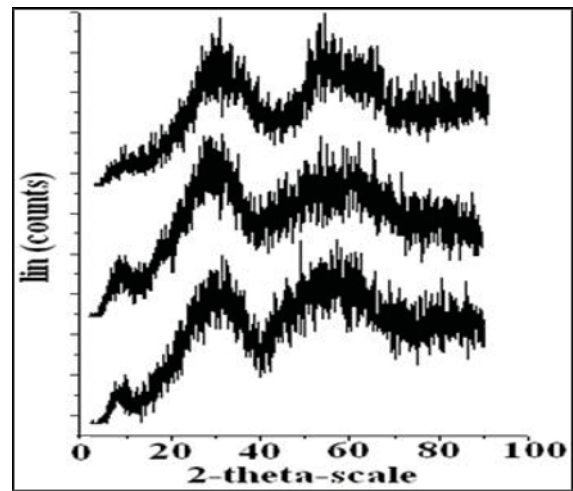
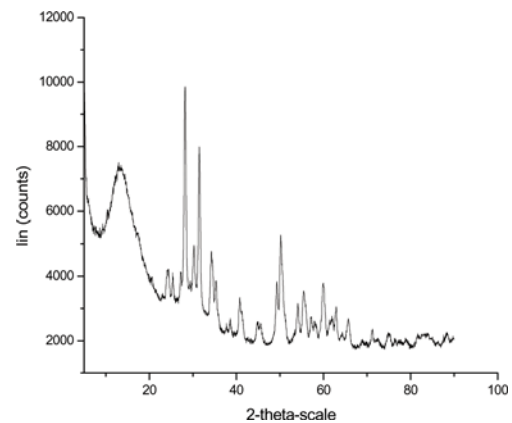
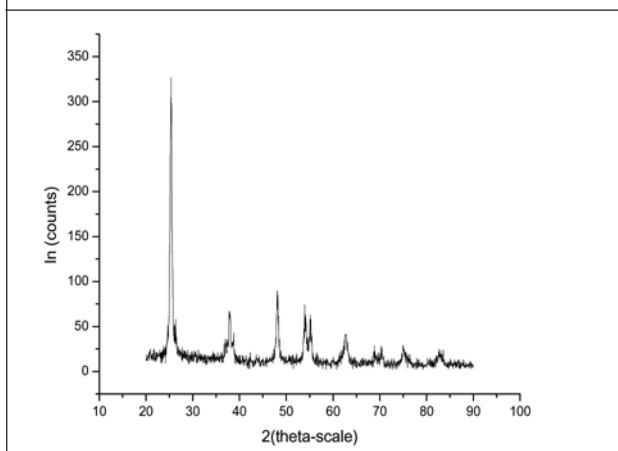


Figure 12: XRD pattern of 12-TPA/ZrO₂-20



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 (Figure 13) 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 (Figure 14) 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)

Figure 13: XRD pattern of 12-TPA/TiO₂-20

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 7.

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 (Figures 15 to 20, Table 7). M(IV)PWs exhibit broad desorption peaks compared to 12-TPA/M(IV)Oxides-20, which is in accordance with the amorphous and

Table 7: 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	-

Figure 14: XRD pattern of 12-TPA/SnO₂-20

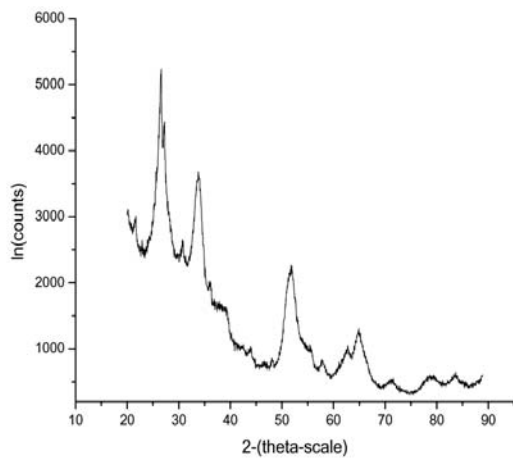


Figure 17: NH₃-TPD patterns of SnPW at different preheating temperatures

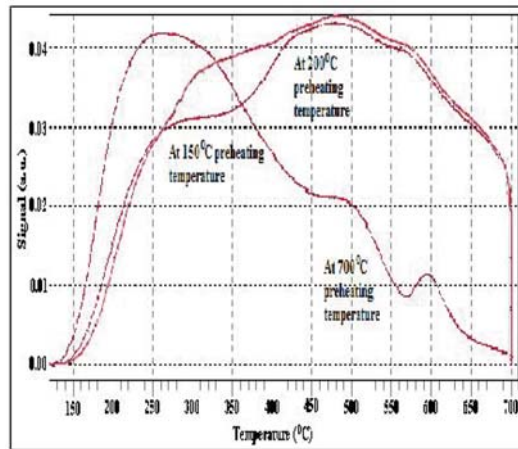


Figure 15: NH₃-TPD patterns of ZrPW at different preheating temperatures

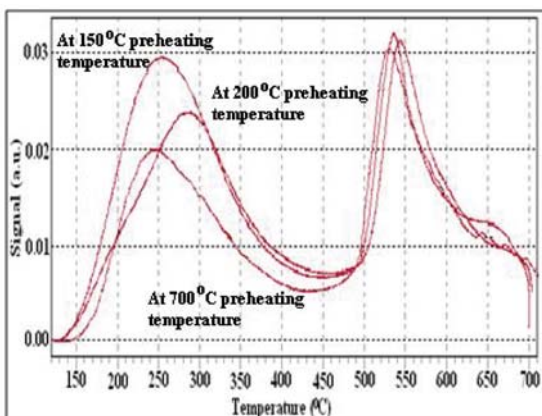


Figure 18: NH₃-TPD patterns of 12-TPA/ZrO₂-20 at different preheating temperatures

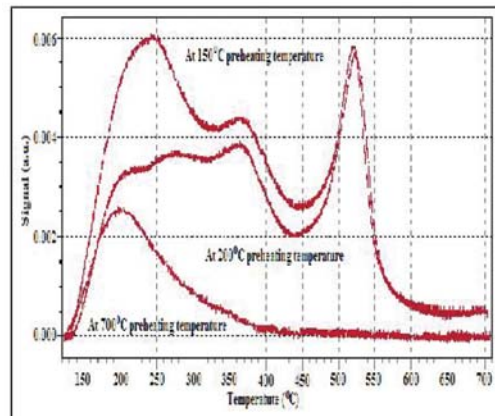


Figure 16: NH₃-TPD patterns of TiPW at different preheating temperatures

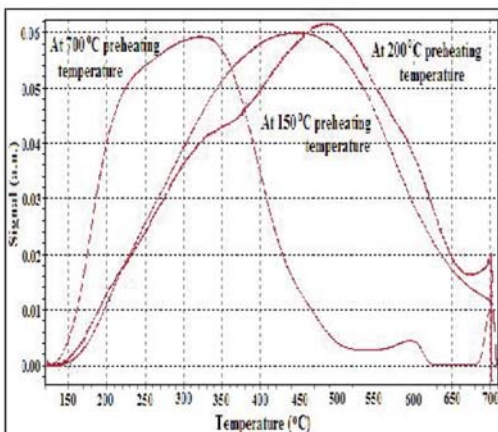


Figure 19: NH₃-TPD patterns of 12-TPA/TiO₂-20 at different preheating temperatures

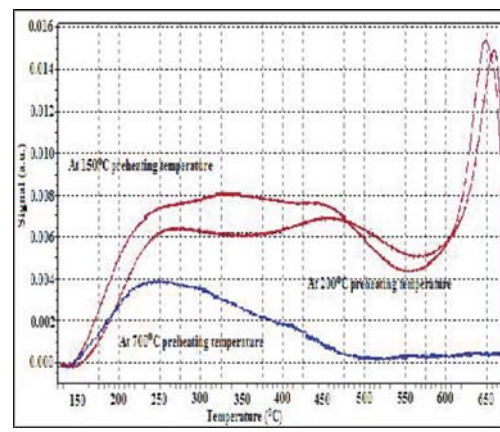
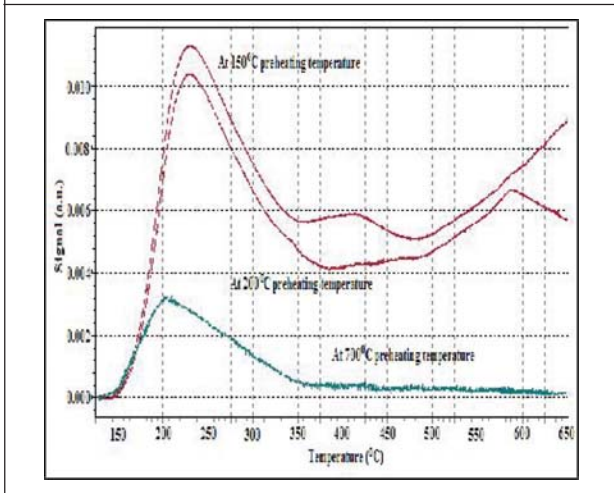


Figure 20: NH₃-TPD patterns of 12-TPA/SnO₂-20 at different preheating temperatures

crystalline nature of the materials respectively (Joshi *et al.*, 2008). 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 Brønsted 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. 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 7).

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 (Waghmare *et al.*, 2008).

Catalytic Activity

In the present study synthesis of anthraquinone derivatives via Friedel–Crafts reaction has been performed as described in experimental section. Firstly, reaction conditions were optimized using ZrPW and 12-TPA/ZrO₂-20 as solid acid catalyst for preparation of 2-methyl anthraquinone from toluene and phthalic anhydride by varying parameters such as reaction time, catalyst amount and initial mole ratio of the reactants. The optimized reaction conditions are presented in Table 8.

The effect of reaction time (0.5-4.0 h) on the product yield in all cases was studied at 120°C temperature with 1:1 mole ratio of toluene : phthalic anhydride and 0.15 g of catalyst. The reaction reached equilibrium within 3 h. When reaction temperature is varied (110°C and 140°C), there is no significant change in % yield. Therefore 120°C is optimized as reaction temperature. 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 0.3 g. 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 toluene : phthalic anhydride was varied as 1:1, 1.2:1 and 1:1.2. In the present study, higher % yield was observed with 1:1 mole ratio and taken as optimized mole ratio of substituted benzenes : phthalic anhydride.

Table 8: Optimization of Reaction Conditions for Preparation of Anthraquinone Derivative from Toluene and Phthalic Anhydride by Using ZrPW and 12-TPA/ZrO₂-20

Set No.	Reactants with their mole ratio	Catalyst Amount(g)	Reaction Time (h)	Reaction Temperature (°C)	% Yield	
					ZrPW	12-TPA/ZrO ₂
(A) Reaction time variation						
1	Toluene + Phthalic Anhydride(1:1)	0.15	0.5	120	8.7	6.5
2	Toluene + Phthalic Anhydride(1:1)	0.15	1.0	120	14.8	11.0
3	Toluene + Phthalic Anhydride(1:1)	0.15	1.5	120	27.3	25.6
4	Toluene + Phthalic Anhydride(1:1)	0.15	2.0	120	40.9	37.2
5	Toluene + Phthalic Anhydride(1:1)	0.15	2.5	120	51.7	46.1
6	Toluene + Phthalic Anhydride(1:1)	0.15	3.0	120	61.0	55.8
7	Toluene + Phthalic Anhydride(1:1)	0.15	3.5	120	61.1	55.8
8	Toluene + Phthalic Anhydride(1:1)	0.15	4.0	120	61.2	55.9
(B) Reaction temperature variation						
9	Toluene + Phthalic Anhydride(1:1)	0.15	3.0	110	50.3	41.1
10	Toluene + Phthalic Anhydride(1:1)	0.15	3.0	120	61.0	55.8
11	Toluene + Phthalic Anhydride(1:1)	0.15	3.0	130	57.8	50.4
12	Toluene + Phthalic Anhydride(1:1)	0.15	3.0	140	50.1	38.1
(C) Catalyst amount variation						
13	Toluene + Phthalic Anhydride(1:1)	0.15	3.0	120	61.0	55.8
14	Toluene + Phthalic Anhydride(1:1)	0.20	3.0	120	62.8	57.7
15	Toluene + Phthalic Anhydride(1:1)	0.25	3.0	120	64.9	60.0
16	Toluene + Phthalic Anhydride(1:1)	0.30	3.0	120	67.7	61.1
17	Toluene + Phthalic Anhydride(1:1)	0.35	3.0	120	67.8	61.1
(D) Mole ratio variation						
18	Toluene + Phthalic Anhydride(1:1)	0.30	3.0	120	67.8	61.1
19	Toluene + Phthalic Anhydride(1.2:1)	0.30	3.0	120	63.1	57.2
20	Toluene + Phthalic Anhydride(1:1.2)	0.30	3.0	120	40.3	35.1

At optimized condition, reaction of nitrobenzene, resorcinol and hydroquinone with phthalic anhydride was performed using TiPW, SnPW, 12-TPA/TiO₂ and 12-TPA/SnO₂ (reaction time: 3 h, reaction temperature: 120°C, catalyst amount: 0.3 g and mole ratio of substituted benzenes : phthalic anhydride = 1:1) (Table 8).

The % yield of products formed for all catalysts follows the order 1,4-dihydroxy anthraquinone > 1, 3-dihydroxy anthraquinone > 2-methyl anthraquinone > 2-nitro anthraquinone, which could be explained to be due to the presence of substituent (electron withdrawing/releasing nature

of functional groups) present on the benzene ring (Madje *et al.*, 2011; Naeimi *et al.*, 2008) (Table 9).

Regeneration and reusability for all the catalysts under study was conducted and results presented in Table 9. After each catalytic run, all the catalysts turn dark brown, probably due to the fact that reactant molecules get adsorbed on the surface of the catalysts. In case of M(IV)PWs, after each subsequent run the catalysts were regenerated as described earlier in experimental section. It is observed that, on regeneration M(IV)PWs exhibit only a marginal decrease in yields upto three catalytic runs. However, when catalysts are reused, the decrease in % 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 (Joshi *et al.*, 2008). Table 10 provides atomic wt. % of various components (Zr, P, W and O) for both fresh and spent catalysts in case of synthesis of 2-methyl anthraquinone. 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 anthraquinone derivatives.

The present study reveals the promising use of both types of solid acid catalysts, advantages being a solvent free single step reaction compared to the two step reaction in the

Table 9: Synthesis of Anthraquinone Derivatives from Substituted Benzene and Phthalic Anhydride by Using M(IV)PWs and 12-TPA/M(IV)Oxides-20

Reactants	% Yield							
	Catalytic run	ZrPW	TiPW	SnPW	Catalytic run	12-TPA/ ZrO ₂	12-TPA/ TiO ₂	12-TPA/ SnO ₂
Toluene:Phthalic Anhydride	1(F)	67.74	71.84	68.30	1(F)	61.11	66.40	62.90
	2(Rg)	66.00	70.11	67.08	2(Ru)	49.65	54.22	50.19
	2(Ru)	59.81	60.52	55.87				
	3(Rg)	64.07	67.95	65.17	3(Ru)	37.54	42.93	37.71
	3(Ru)	49.12	52.16	43.49				
Nitrobenzene:Phthalic Anhydride	1(F)	48.07	54.67	53.10	1(F)	40.08	42.38	40.54
	2(Rg)	46.32	53.90	52.23	2(Ru)	29.11	33.40	31.70
	3(Rg)	43.61	52.00	50.99	3(Ru)	17.80	21.00	20.51
Resorcinol:Phthalic Anhydride	1(F)	72.29	77.21	73.70	1(F)	67.17	70.77	68.44
	2(Rg)	71.37	76.03	71.84	2(Ru)	51.48	62.22	55.50
	3(Rg)	68.19	75.30	70.00	3(Ru)	40.33	48.51	41.17
Hydroquinone:Phthalic Anhydride	1(F)	74.00	79.11	77.09	1(F)	68.90	73.12	70.00
	2(Rg)	72.85	78.00	75.53	2(Ru)	54.00	63.09	58.29
	3(Rg)	69.33	75.42	72.67	3(Ru)	41.08	50.19	45.66

Note: Mole ratio of Substituted benzene/Phthalic anhydride -1:1; Catalysts amount -0.3g; Reaction temperature -120°C; Reaction Time: 3h; F: Fresh; Rg: Regenerated; Ru: Reused).

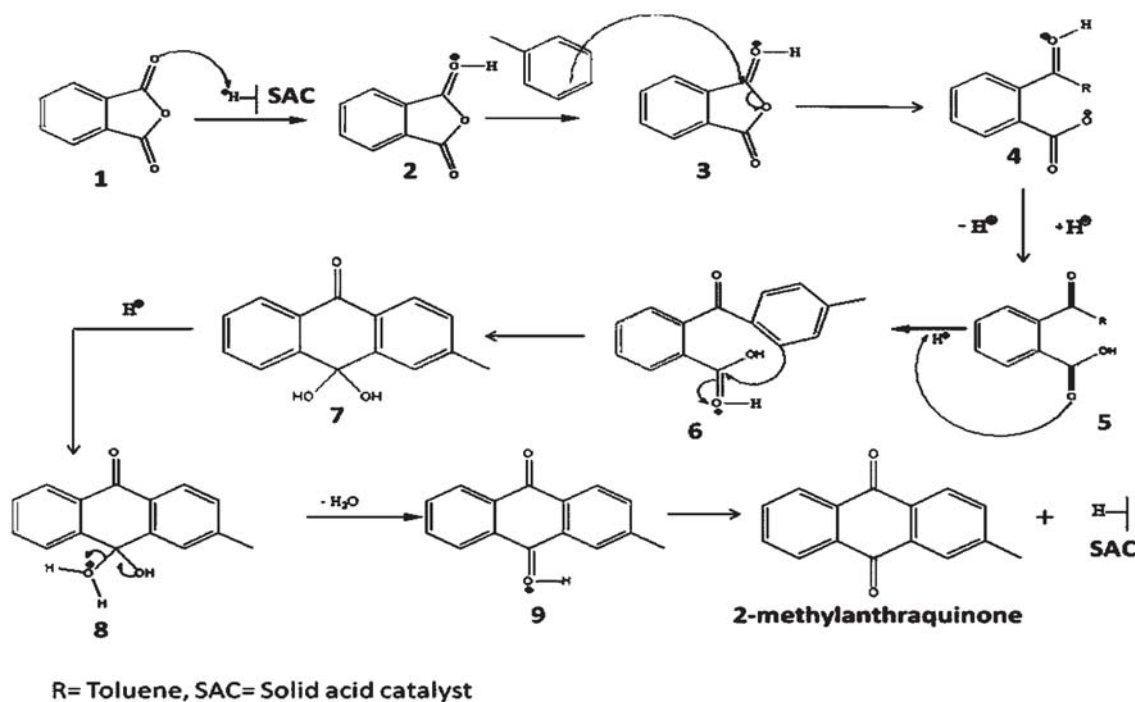
Table 10: Elemental analysis by EDX for both fresh and spent ZrPW and 12-TPA/ZrO₂-20 in the synthesis of 2-methyl anthraquinone

Reactants	Materials	% by EDX analysis			
		Zr	P	W	O
Toluene:Phthalic Anhydride	ZrPW (Fresh)	60.79	18.53	20.67	-
	ZrPW (Spent)	55.14	22.94	21.92	-
	12-TPA/ZrO ₂ -20 (Fresh)	28.75	0.11	3.44	67.70
	12-TPA/ZrO ₂ -20 (Spent)	17.09	1.58	0.51	80.82

Note: Mole ratio of Toluene:Phthalic anhydride -1:1; Catalysts amount - 0.3 g; Reaction temperature - 120 °C; Reaction Time- 4h.

conventional process (discussed earlier in the text), reusability of catalysts, mild reaction conditions, no acid waste generation and finally no catalyst contamination in the products formed. A possible mechanism for the Friedel-Crafts reaction for synthesis of 2-methyl anthraquinone by solid acid catalyst is presented in scheme 1.

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

Scheme 1: Proposed Mechanism for Synthesis of 2-methyl Anthraquinone Catalyzed by Solid Acid Catalyst

which could be attributed to increased surface acidity of these materials (Table 9). With reference to performance of catalysts, M(IV)PWs scores over 12-TPA/M(IV)Oxides-20 in terms of % yields of anthraquinone derivatives formed as well as reusability of catalysts.

Solid acid catalysts have been used earlier with good to excellent yields. When $B(HSO_4)_3$ is used the yields reported are very high (~92-96%) however, catalyst could not be reused (Madje *et al.*, 2011). The use of H-beta (22, 107 and 162) also reports high yields ~93-95%, however reaction temperatures were very high (250°C) and catalysts could not be reused (Xu *et al.*, 2006 and 2005). When K10 was used yields were comparable (~75-81%) to the present work, however with long reaction times (24 h) and catalyst could not be reused (Singh *et al.*, 2005).

Characterization of the Products

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

2-Methylantraquinone

$C_{15}H_{10}O_2$, yellow solid (melting point 178 °C);

IR (KBr, cm^{-1}): 2950 (w), 2900 (w), 1669 (s), 1593(s);

1H NMR (400 MHz, $CDCl_3$): δ 2.3–2.7 (3H,s), 7–8.3 (7H,m).

2-Nitroanthraquinone

$C_{14}H_7O_4N$, yellow solid (melting point 232 °C);

IR (KBr, cm^{-1}): 1670 (m), 1510 (s), 1390 (s);

1H NMR (400 MHz, $CDCl_3$): δ 7.3-7.8 (7H, m).

1,3-Dihydroxyanthraquinone

$C_{14}H_8O_4$, orange solid (melting point 268 °C);

IR (KBr, cm^{-1}): 3216 (s), 1660 (s), 1529 (s); 1434 (s);

1H NMR (400 MHz, $CDCl_3$): δ 6.6-7.3 (1H, s), 7.4 (1H, s), 7.8 (2H, s), 8.4 (2H, s), 12.2 (2H, s).

1, 4-Dihydroxyanthraquinone

$C_{14}H_8O_4$, red solid (melting point 196 °C);

IR (KBr, cm^{-1}): 2920 (w), 1630 (m), 1585 (m), 1450 (m);

1H NMR (400 MHz, $CDCl_3$): δ 7–7.5 (2H, s), 7.7–7.8 (2H, s), 8.0–8.3 (2H, s), 12.6–12.8 (2H, s).

CONCLUSION

The work outlined herein reveals the promising use of both the types of solid acid catalysts with advantages of a solvent free single step 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 the synthesis of anthraquinone derivatives. Finally, TiPW exhibiting the best performance has potential for commercialization.

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