A Comparative Study on Catalytic Activity of Solid Acid Catalysts towards Microwave Assisted Synthesis of Coumarin Derivatives

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Abstract: In the present endeavour, coumarin derivatives have been synthesized replacing the conventional catalyst with environment friendly solid acid catalysts. Two types of catalysts possessing similar elemental composition have been explored for their potential utility as solid acid catalyst. M(IV) Phosphotungstates which possess inherent acidity have been synthesized by sol-gel route, while in another case, acidity has been induced into M(IV) oxides, by process of anchoring and calcination, using 12-Tungstophosphoric acid (12-TPA) [M(IV) = Ti and Sn]. All the catalysts have been characterized for elemental analysis by ICP-AES, TGA, FTIR, SEM, EDX, XRD, surface area (by BET method) and surface acidity (by NH_3 -TPD method). The performance of these materials as solid acid catalysts has been explored by studying Pechmann condensation as a model reaction, wherein various phenols have been treated with methyl acetoacetate to give coumarins, under solvent free conditions using conventional and microwave heating. The synthesis conditions have been optimized by varying parameters such as reaction temperature, reaction time, catalyst amount and mole ratio of the reactants. The catalytic activity of synthesized materials has been compared and correlated with acid properties of the materials.

Keywords: Titanium(IV) Phosphotungstate, Tin(IV) Phosphotungstate, Supported solid acid catalysts, Microwave-assisted coumarin synthesis.

1. Introduction

Coumarins exhibit diverse applications [1],[2], Pechmann condensation being the most widely applied method for their synthesis. Pechmann condensation however uses traditional liquid acid catalysts such as sulfuric acid, trifluoroacetic acid, phosphorous pentoxide, ZrCl₄, TiCl₄, and ionic liquids, which require long reaction times, corrodes reactor, create by-products and salt waste due to acid neutralization [3].

Several solid acid catalysts [4]-[12] have been reported for synthesis of coumarin derivatives by Pechmann condensation with advantages such as they require short reaction time and these catalysts can be regenerated and reused, however, the major disadvantage is the requirement of a solvent medium for removal of azeotropic water [5],[6] along with poor yields of coumarins in some cases [4],[7].

Heteropoly acids (HPAs) have proved to be the alternative for traditional acid catalysts due to both strong acidity and appropriate redox properties. The major disadvantage of HPAs, as catalyst lies in their low thermal stability, low surface area $(1-10m^2/g)$ and separation problems from reaction mixture. HPAs can be made eco-friendly, insoluble solid acids, with high thermal stability and high surface area by supporting them onto suitable supports. The support provides an opportunity for HPAs to be dispersed over a large surface area which increases catalytic activity [13].

The use of microwave (MW) irradiation has been employed for a number of organic transformations to reduce the reaction time, rate enhancement and to increase selectivity and yields. The use of solid acid catalysts for MW assisted synthesis of coumarin is scarce. Tyagi et.al have reported MW assisted solvent free synthesis of coumarin derivatives using sulfated zirconia however with the disadvantage of leaching of sulfate ions during the course of the reaction [14]. The need for an ideal solid acid catalyst is on.

Tetravalent Metal Acid (TMA) salts are inorganic cation exchangers possessing general formula M(IV) $(HXO_4)_2.nH_2O$ [M(IV)=Zr, Ti, Sn, Ce, Th, etc. X=P, W, Mo, As, Sb, etc] where, H⁺ of the structural hydroxyl groups are responsible for cation exchange, due to which TMA salts indicate good potential for application as solid acid catalysts, the acidic sites being bronsted acid sites in nature [15],[16].

From our laboratory, TMA salts have been used as solid acid catalysts for esterification [17]-[19], cyclodehydration [20], ketalisation of ketones [21], hydration of nitriles [22], cyclodehyration of 1,n-diols [23] and for synthesis of coumarin derivatives [24].

When we used a mixed material of the class of Tetravalent Bimetallic acid (TBMA) salts such as Zirconium Titanium Phosphate (ZTP) [19] (containing two different cations and an anion) and a mixed material of the class of Tetravalent Metal Bianionic Acid (TMBA) salts (containing two different anions and a cation) such as Zr(IV) Phosphotungstate (ZrPW) [25] as a solid acid catalyst, for synthesis of esters and coumarin derivatives respectively, enhanced catalytic activity was observed compared to their single salt counter parts.

In the present endeavour, M(IV) Phosphotungstates [M(IV)PWs], mixed materials of the class of TMBA salts such as Ti(IV) Phosphotungstate (TiPW) and Sn(IV) Phosphotungstate (SnPW) possessing inherent acidity have been synthesized by sol-gel route. Looking to the potential utility of supported HPAs and for comparison of catalytic performance, we have supported 12-Tungstophosphoric acid (12-TPA) onto TiO₂ and SnO₂ by process of anchoring and

calcination, resulting in 12-TPA/TiO₂ and 12-TPA/SnO₂ which possess induced acidity and same components (i.e. 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 (NH₃-TPD method). The potential utility of synthesized materials as solid acid catalysts has been explored by studying Pechmann condensation as a model reaction, wherein phenols such as resorcinol (R), pyrogallol (Py), phloroglucinol (Ph), hydroquinone (Hq) and pnitrophenol (pNp) have been treated with methyl acetoacetate (MA) to give coumarin derivatives 7-hydroxy-4-methyl coumarin, 7,8-dihydroxy-4-methyl coumarin and 6-hydroxy-4-methyl 5,7-dihydroxy-4-methyl coumarin, coumarin and 6-nitro-4-methyl coumarin respectively, under solvent free conditions using conventional heating (CH) as well as microwave heating (MW). 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 (**SM - Tables 1 and 2**).

2.1.1 Synthesis of TiPW (at optimized condition)

An aqueous mixture of NaH₂PO₄.2H₂O (0.1M, 50ml) and Na₂WO₄.2H₂O (0.1M, 50ml) was added dropwise (flow rate 1 ml·min⁻¹) to a solution of TiCl₄ (0.2M, 50ml) (prepared in 10% W/V H₂SO₄ 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 [24]. This material was used for all studies.

2.1.2 Synthesis of SnPW (at optimized condition)

An aqueous mixture of NaH₂PO₄.2H₂O (0.1M, 50ml) and Na₂WO₄.2H₂O (0.1M, 50ml) was added dropwise (flow rate 1 ml·min⁻¹) to a solution of SnCl₄ (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 [24]. This material was used for all studies.

2.2 Synthesis of 12-TPA supported Oxides (12-TPA/TiO $_2$ and 12-TPA/SnO $_2)$

For preparation of TiO_2 and SnO_2 , aqueous solutions of $TiCl_4$ (0.9M, 100 ml) and $SnCl_4.5H_2O$ (0.3M, 100 ml) were

prepared to which liq. NH₃ (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. Amongst the different wt. % of 12-TPA loaded, 20 wt. % loading of 12-TPA onto oxides gives maximum surface acidity (SM - Table 3). 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) = 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 [26]. 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 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°C·min⁻¹ using an air as career gas. X-ray diffractogram ($2\theta = 10 - 80^\circ$) was obtained on X-ray diffractometer (Brucker AXS D8) with Cu-K $_{\alpha}$ radiation with nickel filter. SEM and EDX of the sample were scanned on Jeol JSM-5610-SLV scanning electron microscope. Surface area measurement (by BET method) was carried out on Micromeritics Gemini at -196°C using nitrogen adsorption isotherms. Surface acidity was determined on Micromeritics Chemisorb 2720, by a temperature programmed desorption of ammonia. The synthesized materials were preheated at 150°C, 200°C and 700°C. Ammonia was chemisorbed at 120°C and then desorption was carried out upto 700°C at a heating rate of 10°C/min.

2.4 Catalytic activity: Pechmann condensation

In a typical reaction, methyl acetoacetate (MA) (15mmol) (substrate as well as solvent) and phenols (10mmol) [resorcinol (R), pyrogallol (Py), phloroglucinol (Ph), hydroquinone (Hq) and p-nitrophenol (pNp)] was stirred with catalyst (0.20g) in 50 ml two necked round bottom flask at 130° C for 8 h. Using same conditions, the reactions were subjected to microwave irradiation (250W) at 130° C for 30 min. In both cases, after completion of reaction, the mixture got solidified within an hour on cooling.

The resulting solidified mixture (both cases) was dissolved in ethyl acetate (2 ml), and catalyst separated by filtration using a Buchner funnel. The filtrate, distilled under vacuum, yielded the crude product, which was purified by recrystallization. All synthesized coumarin derivatives were characterized for IR spectroscopy and melting point which are compared with the corresponding reported melting point [27]. Reaction parameters such as, mole ratio of reactants, amount of catalyst, reaction time and reaction temperature were optimized (**SM – Table 4**).

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 [24]. 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° 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. 1-4**).

	% by I	ICP-4	<i>AES</i>	% by EDX analysis (atomic			tomic
Materials	analysis			%)			
	M(IV)	Р	W	M(IV)	Р	W	0
TiPW (Fresh)	Ti:14.8	4.6	25.0	Ti:46.6	37.9	15.4	-
TiPW (Spent)	-	-	-	Ti:46.5	37.5	16.0	-
SnPW (Fresh)	Sn:36.8	4.7	29.4	Sn:59.3	23.3	17.4	-
SnPW (Spent)	-	-	-	Sn:53.6	28.7	17.8	-
12-TPA/	Ti-16 9	0.0	16.1	Ti-28 6	0.15	0.00	70.2
TiO ₂ -20(Fresh)	11.40.8	0.0	0.0 10.1 11.2	11.20.0	0.15	0.88	70.5
12-TPA/				Ti-26 5	0.23	1.02	723
TiO ₂ -20 (Spent)	-	11.2	11.20.3 0.23	1.02	12.5		
12-TPA/	Sp:60.0	0.0	18.0	Sp. 18 /	0.12	2 57	70.0
SnO ₂ -20 (Fresh)	511.00.0	11.00.0 0.0	18.0	511.10.4	0.12	2.57	79.0
12-TPA/		_	_	Sn.14.6	0.18	6.14	70.1
SnO ₂ -20 (Spent)	-	-	-	511.14.0	0.10	0.14	79.1

Table 1: Elemental analysis by ICP-AES and EDX

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

II A/WI(I V)OAIdeS-20.						
Materials	Chemical	Maximum tolerable limits				
	media					
	Acids	18N H ₂ SO ₄ , 16N HNO ₃ , 11.3N HCl				
M(IV)PWs	Bases	5 N NaOH, 5 N KOH				
101(17)1 (13	Organic	Ethanol, Benzene, Toluene, Acetone				
	Solvents	and Acetic acid				
12 TDA/	Acids	5N H ₂ SO ₄ , 16N HNO ₃ , 11.3N HCl				
M(IV)Oxides-	Bases	3 N NaOH, 3 N KOH				
	Organic	Ethanol, Benzene, Toluene, Acetone				
10	Solvents	and Acetic acid				

FTIR spectrum of M(IV)PWs (**SM - Fig. 5**) exhibits broad band in the region ~ 3400 cm^{-1} which is attributed to asymmetric and symmetric –OH stretching in all the samples. A medium band around ~ 1635 cm^{-1} is attributed to P-O-H bending, indicating presence of structural –OH protons contained in all samples. A band in the region ~ 1083 cm^{-1} is attributed to the presence of P=O stretching in all samples.

FTIR spectrum of 12-TPA/M(IV)Oxides-20 (**SM - Fig. 6**) exhibits peaks at ~3450 cm⁻¹, ~1635 cm⁻¹, ~1083 cm⁻¹, ~987 cm⁻¹, which corresponds to asymmetric and symmetric –OH stretching, P-O-H bending, P=O stretching and W-O stretching respectively.

TGA thermogram (**SM - Fig. 7**) shows weight loss in the temperature range of $40 - 150^{\circ}$ C for TiPW and SnPW to be 21.02% and 15.26% respectively, which corresponds to loss of surface moisture and hydrated water. Weight loss in the temperature range of 150° C - 650° C for TiPW and SnPW is found to be 4.28% and 6.04% respectively, which is probably due to the condensation of structural hydroxyl groups.

TGA thermograms of 12-TPA/TiO₂-20 and 12-TPA/SnO₂-20 (**SM - Fig. 8**) exhibit 0.4% and 1.4% weight loss in the temperature range of $30 - 150^{\circ}$ C which corresponds to the loss of surface moisture. Thereafter in the region 200-600°C there is a negligible weight loss which indicates fairly stable nature of the materials.

SEM images (SM - Fig. 9-12) of all the synthesized materials exhibit irregular morphology. Absence of sharp peaks in X-ray diffractogram of M(IV)PWs (SM - Fig. 13) reveals the amorphous nature of M(IV)PWs.

X-ray diffractogram pattern of 12-TPA/TiO₂-20 (**SM - Fig. 14**) shows characteristic diffraction peaks at 2 θ 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. 15**) shows characteristic diffraction peaks at 2 θ 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.

M(1V) P w s and $12-1$ PA/M(1V)Oxides-20.								
	Surface Area	Surface acidit						
	(BET method)	TPD meth	IEC					
Materials	(m^2/g)	Preheating	Acidity	IEC				
		Temperature	(mmol/	(meq./g)				
		(°C)	g)					
		150	11.05	2.97				
TiPW	86.5	200	11.02	2.39				
		700	8.28	1.07				
SnPW		150	10.28	2.00				
	171.0	200	7.54	1.64				
		700	4.50	0.73				
12 TDA/		150	2.03	-				
TiO ₂ -20	60.5	200	1.68	-				
		700	0.27	-				
10 770 4 /		150	1.42	-				
$\frac{12-1PA}{SnO}$ 20	139.5	200	1.11	-				
51102-20		700	0.22	-				

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

3.2 Evaluation of acid property

Surface acidity for all the materials was determined by NH_3 -TPD at 150°C, 200°C and 700°C preheating temperatures (Fig. 1-4, Table 3).



Figure 1: NH₃-TPD patterns of TiPW



Figure 2: NH₃-TPD patterns of SnPW



Figure 3: NH₃-TPD patterns of 12-TPA/TiO₂-20



Figure 4: NH₃-TPD patterns of 12-TPA/SnO₂-20

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 [24]. 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 Ti⁴⁺ and Sn⁴⁺, both the metal ions being tetravalent as well as bearing common anion PO₄³⁻ and WO_4^{2-} , size of the cation (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. 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 which also decreases with materials, 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

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Table 4: Pechmann condensation of phenols with methyl acetoacetate using M(IV)PWs and 12-TPA/M(IV)O2 at optimu	um
condition under conventional (CH) and microwave (MW) heating.	

Reactants	Mode of	% Yield							
Hea	Heating	Catalytic run	TiPW	SnPW	Catalytic run	12-TPA/TiO ₂	12-TPA/SnO ₂		
	СН	1(E)	69.4	62.5	1(E)	58.0	57.5		
	MW	1(F)	71.8	64.2	1(F)	60.9	58.9		
	СН	2(Ru)	61.8	54.3	2(Ru)	49.0	47.0		
	MW		63.4	56.1		51.0	49.0		
	CU		69.1	60.2		51.0	49.0		
D. MA	CH	2(Rg)	08.1	60.2		-			
K+MA	MW		70.2	62.3					
	СН	3(Ru)	52.9	47.1	3(Ru)	39.5	35.00		
	MW		55.1	49.2		41.4	39.2		
	СН		65.1	58.4					
	MW	3(Rg)	67.2	61.9		-			
	СН	1(E)	65.3	57.8	1(E)	52.6	50.7		
	MW	1(F)	65.0	56.7	1(F)	53.0	51.4		
D MA	СН	2(Rg)	64.6	56.0	2(Ru)	43.0	40.0		
Py+MA	MW		64.0	54.9		44.6	40.5		
	CH	3(R g)	63.0	54.2	3(Ru)	32.6	31.8		
	MW	5(Kg)	61.3	53.0	5(R u)	34.5	29.7		
Ph+MA	СН	1(F)	76.8	63.9	1(F)	60.1	58.9		
	MW	1(1)	77.0	66.7	1(1)	61.0	60.3		
	СН	2(Rg)	75.0	60.0	2(Ru)	49.3	48.1		
	MW	=(1-8)	75.8	64.1	-()	52.9	50.9		
	CH	3(Rg)	73.7	58.2	3(Ru)	40.8	38.0		
	MW	- (8/	74.0	63.0	- (43.9	40.1		
	CH	1(F)	78.2	70.2	1(F)	63.9	63.9		
	MW	. ,	79.9	72.9	. ,	64.0	65.2		
Hq+MA	CH	2(Rg)	73.5	69.1 70.0	2(Ru)	57.6	50.1		
_			70.2	/0.0	. ,	01.2	<u> </u>		
		3(Rg)	74.0	67.5	3(Ru)	40.2	40.1		
			50.0	45.0	1(F)	41.0	42.2		
	MW	1(F)	52.5	48.2		41.9	41.0		
	CH		483	43.4		36.9	29.1		
pNp+MA	MW	2(Rg)	51.0 42.7	2(Ru)	39.5	31.0			
	СН		47.1	40.6	3(Ru)	25.9	20.1		
	MW	- 3(Rg)	50.0	40.6		28.0	20.0		

(*R*:Resorcinol; *P*: Pyrogallol; *Ph*: Phloroglucinol; *Hq*: Hydroquinone; *pNp*: *p*-Nitrophenol; *MA*: Methyl acetoacetate; Mole ratio of Phenol:MA -1:1.5; Catalysts amount -0.2g; Reaction temperature -130°C; Reaction Time: 8h for CH and 30 min for MW; F:Fresh; Ru: Reused, Rg: Regenerated

preheating temperatures could be attributed to decomposition of 12-TPA into WO₃ crystallites [28].

3.3 Catalytic activity: Pechmann condensation

For Pechmann condensation of resorcinol with methyl acetoacetate reaction conditions were optimized using TiPW and SnPW (SM - Table 4). It is observed that, in both the cases yield increases with reaction time (2-10h) until equilibrium is reached within 8 h. For the same reaction time, in the both cases, yield increases with increase in catalyst amount (0.10-0.25g), since number of active sites per g of substrate increases. Reactions were studied in the temperature range (120°C-140°C). A maximum product yield is obtained with reaction temperature 130°C, beyond which product degradation is observed. Under MW irradiation it is observed that, yield increases with reaction time until equilibrium is reached within 30 min (SM - Table 4). It is observed that when the reaction time is further prolonged to 40 min, there is not much increase in % yield of coumarin derivative. Therefore, the reaction time 30 min was taken as optimum reaction time under MW. At optimized conditions (as in the case of resorcinol, **SM** – **Table 4**) yields of Pechmann condensation of other phenols using TiPW, SnPW, 12-TPA/TiO₂-20 and 12-TPA/SnO₂-20 under conventional (CH) and microwave (MW) heating have been presented in Table 4.

The reactivity of phloroglucinol with methyl acetoacetate was observed to be higher than pyrogallol due to two hydroxyl groups at *meta*-positions in phloroglucinol compared to one hydroxyl group in pyrogallol [24]. Presence of *meta*-hydroxy group strongly activates the substrates due to resonance effect. Further, low yield in case of p-nitrophenol may be due to the presence of electron withdrawing group (-NO₂) in p-nitrophenol.

Pechmann condensation proceeds through acid-catalyzed reactions. Therefore, Pechmann reaction depends strongly on

acidity of catalysts. Number and nature of surface acid sites play a predominant role in evaluating and correlating catalytic activity [24]. In all cases, yields are higher for M(IV)PWs (Table 4) which could be attributed to high surface area as well as high surface acidity of M(IV)PWs compared to 12-TPA/M(IV)Oxides-20 (Table 3).

Further, higher yields obtained under MW irradiation is probably due to the fact that the phenolic substrates and methyl acetoacetate being polar molecules, are microwave active and absorb the MW radiations rapidly and accelerate the rate of reaction. Formation of polar methanol (byproduct) also helps in absorption of MW radiation and thereby accelerating the reaction [14]. Table 4. Pechmann condensation of phenols with methyl acetoacetate using M(IV)PWs and 12-TPA/ $M(IV)O_2$ at optimum condition under conventional (CH) and microwave (MW) heating.

Regeneration and reusability for both the catalysts under study was conducted and results presented in Table 4. After each catalytic run, both the catalysts turn dark brown in each case, 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 catalyst was regenerated as described earlier in experimental section [24]. It is observed that, on regeneration M(IV)PWs exhibit only a marginal decrease in yields upto three catalytic runs. However, when M(IV)PWs were 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 [24]. The same reason could be forwarded in case of 12-TPA/M(IV)Oxides-20. Table 1 provides atomic wt. % of various components (Ti, Sn, P, W and O) for spent catalysts (SM Fig. 16 - 19) in case of synthesis of 7hydroxy-4-methyl coumarin. Decrease in atomic wt. % of M(IV), P or W in M(IV)PWs and 12-TPA/M(IV)Oxides-20 indicates leaching of ions (i.e. M(IV), P or W) which could be the probable reason for decrease in % yields of coumarins.

With reference to performance of catalysts M(IV)PWs scores over 12-TPA/M(IV)Oxides-20 in terms of % yields of coumarin derivatives formed as well as reusability of catalysts. It is observed that, M(IV)PWs (i.e. TiPW and SnPW) works as an efficient catalyst giving better yields (Table 5) for coumarin derivatives compared to TMA salts [24] (i.e. TiP, TiW, SnP and SnW) and TMBA salt [25] (i.e. ZrPW).

Table 5: Comparison of % yield of 7-hydroxy-4-methyl coumarin using TMA salts and TMBA salts.

Catalyst used	Substrates (mole ratio)	Catalyst amount (g)	Temperature (°C)	Time (h)	% yield			
TiP[24]	R:MA (1:1)	0.25	130	10	51.4			
TiW [24]	R:MA (1:1)	0.25	130	10	54.9			
SnP[24]	R:MA (1:1)	0.25	130	10	52.9			
SnW[24]	R:MA (1:1)	0.25	130	10	16.2			
ZrPW[25]	R:MA (1:1.5)	0.20	130	8	58.1			
TiPW*	R:MA (1:1.5)	0.20	130	8	69.4			
SnPW*	R:MA (1:1.5)	0.20	130	8	62.5			

(*Present work)

The Pechmann condensation proceeds through transesterification followed by intramolecular hydroalkylation and dehydration [29]-[31]. These three steps are acid catalyzed reactions. A possible mechanism for the Pechmann condensation of phenols and β -keto ester by solid acid catalysts has been proposed earlier [25].

3.4 Characterization of the products

The isolated products were characterized by melting point and FT-IR spectroscopy.

3.3a 7-Hydroxy-4-Methyl Coumarin

Melting point: 185-186°C; FT-IR (KBr): 3155 cm⁻¹, 1678 cm⁻¹, 1227 cm⁻¹, 1057 cm⁻¹, 974 cm⁻¹, 844 cm⁻¹, 748 cm⁻¹.

3.3b 7,8-Dihydroxy-4-Methyl Coumarin

Melting point: $244-245^{\circ}$ C; FT-IR (KBr): 3420 cm^{-1} , 1839 cm^{-1} , 1597 cm^{-1} , 1447 cm^{-1} , 1325 cm^{-1} , 1270 cm^{-1} , 1061 cm^{-1} , 901 cm^{-1} , 784 cm^{-1} , 515 cm^{-1} .

3.3c 5,7-Dihydroxy-4-Methyl Coumarin

Melting point: 283-284°C; FT-IR (KBr): 3447 cm⁻¹ 1865 cm⁻¹, 1660 cm⁻¹, 1618 cm⁻¹, 1530 cm⁻¹, 1456 cm⁻¹, 1160 cm⁻¹, 815 cm⁻¹, 750 cm⁻¹, 570 cm⁻¹.

3.3d 6-Hydroxy-4-Methyl Coumarin

Melting point: $165-166^{\circ}$ C; FT-IR (KBr): 3200 cm^{-1} , 1820 cm^{-1} , 1597 cm^{-1} , 1447 cm^{-1} , 1053 cm^{-1} , 832 cm^{-1} , 725 cm^{-1} , 575cm^{-1} .

3.3e 6-Nitro-4-Methyl Coumarin

Melting point: 149-150°C; FT-IR (KBr): 2920 cm⁻¹, 1788 cm⁻¹, 1567 cm⁻¹, 1440 cm⁻¹, 1325 cm⁻¹, 1250 cm⁻¹, 1061 cm⁻¹, 922 cm⁻¹, 854 cm⁻¹, 795 cm⁻¹.

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, 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 coumarin derivatives. Finally, TiPW exhibiting the best performance has potential for commercialization using MW heating wherein, reaction time is considerably reduced from several hours (8h) to few minutes (30min).

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