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Solvent free synthesis of coumarins using environment friendly solid acid catalysts

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ABSTRACT

Solid acid catalysts, ZrPW (Zirconium(IV) Phosphotungstate) and 12-TPA/ZrO_2 [12-Tungstophosphoric acid (12-TPA) supported onto ZrO_2] have been synthesized. The catalysts have been characterized for chemical stability, elemental analysis by ICP-AES, TGA, FTIR, SEM, EDX, XRD, surface area (BET) and surface acidity (NH_3-TPD). The performance of these materials as solid acid catalysts has been explored by studying Pechmann condensation as a model reaction, wherein phenols have been treated with methyl acetoacetate to give coumarins, under solvent free conditions using conventional heating as well as microwave heating. Catalytic activity of both the solid acid catalysts have been compared and correlated with surface properties of the materials.

1. Introduction

Coumarins are used as additives in food and cosmetics, optical brightening agents, dispersed fluorescent and laser dyes [1], exhibit useful and diverse biological activity and also serve as anticoagulant agents [2]. Synthetic routes to coumarins include Pechmann condensation, Perkin, Knoevenagel and Reformatsky reactions and by flash vacuum pyrolysis [3]. Pechmann condensation has been the most widely applied method for coumarin synthesis, since it proceeds from simple starting materials (phenol and β-keto ester) and gives good yields of coumarins with substitution in either pyrone or benzene ring or in both. However, Pechmann condensation utilizes various catalysts, such as sulfuric acid, trifluoroacetic acid, phosphorous pentoxide, $ZrCl_4$, $TiCl_4$, and ionic liquids, which require long reaction times, corrodes reactor, creates by-products and salt waste due to acid neutralization [4]. Use of heterogeneous solid acid catalysts would provide safer operating conditions, ease of product work up, reduction in equipment corrosion and minimization of waste production and above all the catalysts can be regenerated and reused. Therefore, there is a global effort to replace the conventional liquid acid catalysts by heterogeneous solid acid catalysts.

A number of solid acid catalysts have been reported for synthesis of coumarin derivatives. Hoefnagel et al. have reported the use of Amberlyst – 15, H-Beta and Filtrol as solid acid catalysts for synthesis of coumarin derivatives via Pechmann condensation and observed that, these catalysts though require short reaction times, require high reaction temperature and solvent medium for removal of azeotropic water [5]. When phosphotungstic acid was used, reaction time is short with good yields of coumarin, however the major disadvantage is that the catalyst cannot be regenerated and reused and requires the use of solvent [4]. Further, Laufer et al. have reported the use of Nafion resin supported over silica composite materials for synthesizing coumarin derivatives that gives good yields with short reaction times, but the catalyst regeneration and reuse studies have not been reported [6]. Palaniappan and Shekhar have reported the use of polyaniline supported catalytic systems for synthesizing 7-hydroxy-4-methyl coumarin under solvent free conditions but with poor yields of coumarin [7]. Gunnewegh et al. have reported Zeolite catalyzed synthesis of coumarin derivatives which requires short reaction times with regeneration and reuse of catalyst, however with requirement of solvent and gives low yields of coumarin derivatives [8]. Thus the need for an ideal solid acid catalyst is on.

Tetravalent Metal Acid (TMA) salts are inorganic cation exchangers possessing general formula $M(IV)(HXO_4)_2 \cdot nH_2O$[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

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potential for application as solid acid catalysts, the acidic sites being bronsted acid sites in nature [9,10]. Since, TMA salts are synthesized by sol–gel method, TMA salts with varying water content, composition and crystallinity can be obtained by varying several parameters such as mole ratio of reactants M:X (M = tetravalent metal, X = polyvalent anion), temperature of mixing, mode of mixing (metal salt solution to anion salt solution or vice versa), pH and rate of mixing. Variation in any of these parameters yields materials with different characteristics. The preparation procedure thus affects the structural hydroxyl groups, which is reflected in their performance as solid acid catalysts. Thus, the area of study of TMA salts is evergreen and much remains to be investigated.

From our laboratory, use of TMA salts as solid acid catalysts has been explored for esterification [11–13], cyclodehydration [14], ketalisation of ketones [15], hydration of nitriles [16] and cyclodehyration of 1,*n*-diols [17]. Synthesis of coumarin derivatives have been earlier reported by us using TMA salts as solid acid catalysts [18].

It has been earlier observed by us that, mixed materials of the class of tetravalent bimetallic acid (TBMA) salts i.e. Zirconium Titanium Phosphate (ZTP), used as solid acid catalyst, exhibits enhanced catalytic activity [13]. It was therefore thought of interest to explore the potential utility of mixed material of the class of Tetravalent Metal Bianionic Acid (TMBA) salts containing two different anions and a cation as solid acid catalyst with an aim to enhance surface acidity.

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 m^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 [19].

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 (SACs) for MW assisted synthesis of coumarin is scarce. Tyagi et al. have reported MW assisted solvent free synthesis of coumarin derivatives using sulfated zirconia which is also associated with the difficulty of leaching of sulfate ion during the course of reaction depriving reusability [20].

In the present endeavor, a mixed material Zirconium Phosphotungstate (ZrPW) of the class of TMBA salts containing two different anions and a cation, has been synthesized by sol–gel route. Another catalyst 12-Tungstophosphoric acid (12-TPA) supported on ZrO_2 (12-TPA/ZrO_2) possessing same component (i.e. Zr, P, and W), has been synthesized by process of anchoring and calcination [21]. Both the catalysts have been characterized for chemical stability, elemental analysis by ICP-AES, TGA, FTIR, SEM, EDX, XRD, surface area (BET) and surface acidity (NH_3-TPD) and their utility as solid acid catalysts has been explored by studying Pechmann condensation as a model reaction, wherein phenols have been treated with methyl acetoacetate to give coumarins, under solvent free conditions using conventional heating as well as microwave heating. Catalytic activity of both catalysts has been compared and correlated with surface properties of the materials.

2. Experimental

2.1. Synthesis of ZrPW

ZrPW was 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 have been presented in Table 1. We describe herewith the synthesis of ZrPW at optimized condition. An aqueous mixture of $NaH_2PO_4{\cdot}2H_2O$ (0.1 M, 50 ml) and $Na_2WO_4{\cdot}2H_2O$ (0.1 M, 50 ml) was added dropwise (flow rate 1 ml min^{-1}) to an aqueous solution of $ZrOCl_2{\cdot}8H_2O$ (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 [18]. This material was used for all studies.

2.2. Synthesis of 12-TPA/ZrO_2

10 g of $ZrOCl_2{\cdot}8H_2O$ was dissolved in 100 ml double distilled water followed by dropwise addition of liq. NH_3 (25%) with vigorous stirring. The pH of the solution was adjusted to 9.5. White precipitates obtained, was filtered and washed with conductivity water till removal of adhering ions which was first dried at 120 °C for 3 h, and then calcined at 550 °C for 5 h. For the preparation of 12-TPA supported catalyst, a series of aqueous solution of 10–30 wt.% of 12-TPA per gram of precalcined ZrO_2 was 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. This material was used for all studies.

2.3. Catalyst characterization

The solubility of ZrPW 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 ZrPW 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 ($2\theta = 10–80°$) was obtained on X-ray diffractometer (Brucker 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. Ammonia was chemisorbed at 120 °C and then desorption was carried out upto 700 °C at a heating rate of 10 °Cmin^{-1}.

2.4. Catalytic activity: Pechmann condensation

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

Table 1
Optimization of parameters for synthesis of ZrPW.

Parameters optimized	No	Concentration (M)			Volume (ml)			Mole ratio	Temp ± 2 °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[a]	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

[a] Optimum condition for synthesis of ZrPW.

Table 2
Solubility data of ZrPW (maximum tolerable limits).

Chemical media	Maximum tolerable limits
Acids	18N H_2SO_4, 16N HNO_3, 11.3N HCl
Bases	5N NaOH, 5N KOH
Organic solvents	Ethanol, benzene, toluene, acetone and acetic acid

synthesized coumarin derivatives were characterized for IR spectroscopy. Melting point (Tables 6 and 7) was compared with the corresponding reported melting point [22]. Reaction parameters such as, mole ratio of reactants, amount of catalyst, reaction time and reaction temperature were optimized.

For regeneration and reusability, the catalyst was refluxed in ethanol for half hour, washed with double distilled water and dried at room temperature. ZrPW was acid treated as described in catalyst synthesis whereas 12-TPA/ZrO_2 was dried in oven at 150 °C for 2 h and used.

3. Results and discussion

3.1. Catalyst characterization

A study on the solubility of ZrPW shows that it is stable in acid and organic solvent media. It is however not so stable in base medium. The maximum tolerable limits are presented in Table 2. Elemental analysis performed by ICP-AES for ZrPW shows Zr = 26.87%, P = 5.67% and W = 25.37%. The ratio of Zr:P:W was found to be 2:1:1. FTIR spectrum of ZrPW (Fig. 1) exhibits broad band in the region ~3400 cm^{-1} which is attributed to asymmetric and symmetric –OH stretching. A medium band around ~1635 cm^{-1} is attributed to P—O—H bending. These bands indicate the presence of structural –OH protons (bronsted sites) contained in ZrPW. A band in the region ~1083 cm^{-1} is attributed to the presence of P═O stretching. FTIR spectrum of 12-TPA/ZrO_2 (Fig. 2) 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 of ZrPW (Fig. 3) shows 19.78% weight loss in the temperature range of 40–150 °C which corresponds to loss of surface moisture and hydrated water. A 7.25% weight loss in the temperature range of 550–600 °C is attributed to condensation of structural hydroxyl groups. TGA thermogram of 12-TPA/ZrO_2 (Fig. 3) exhibits 0.9% weight loss in the temperature range of 30–180 °C which corresponds to the loss of surface moisture. SEM images (Figs. 4 and 5) of ZrPW and 12-TPA/ZrO_2 exhibits irregular morphology for both the catalysts.

EDX graph for ZrPW (Fig. 6) shows atomic % of Zr, P and W is found to be 60.79%, 18.53% and 20.67% respectively. EDX graph for 12-TPA/ZrO_2 (Fig. 7) shows atomic % of Zr, W and O is found to be 28.75%, 3.44% and 67.81% respectively. Absence of sharp peaks in X-ray diffractogram of ZrPW (Fig. 8) reveals the amorphous nature of ZrPW, while X-ray diffractogram pattern of 12-TPA/ZrO_2 (Fig. 8) shows intense and well defined characteristic diffraction peaks with *d* values of 2.84, 2.54, 1.81, and 1.54 Å (JCPDS data card no. 17-923). Surface area (BET method) for ZrPW and 12-TPA/ZrO_2 was found to be 80.96 m^2/g and 33.90 m^2/g respectively.

ZrPW exhibits broad desorption peaks (Fig. 9) at higher temperature (at ~240 °C and ~525 °C) compared to 12-TPA/ZrO_2 (at

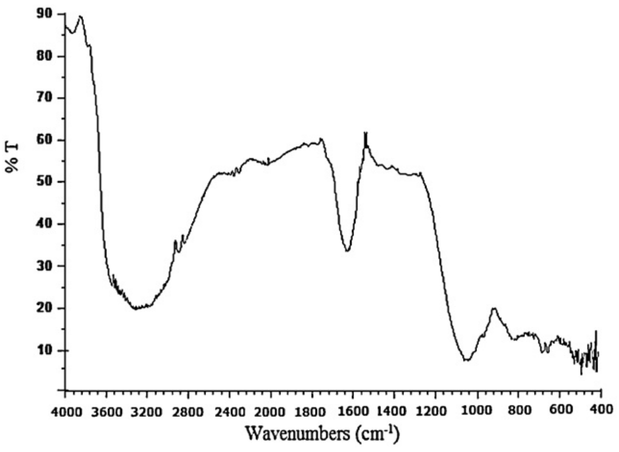


Fig. 1. FT-IR spectrum of ZrPW.

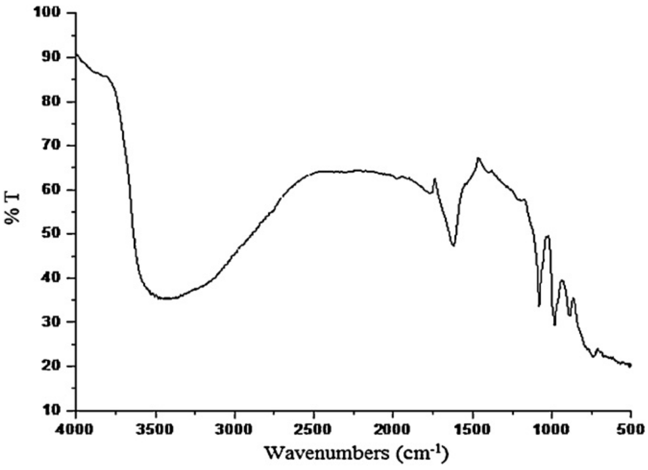


Fig. 2. FT-IR spectrum of 12-TPA/ZrO_2.

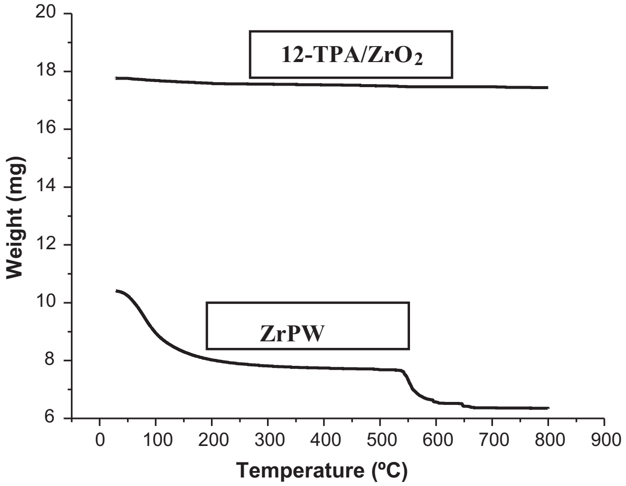


Fig. 3. TGA plot of ZrPW and 12-TPA/ZrO_2.

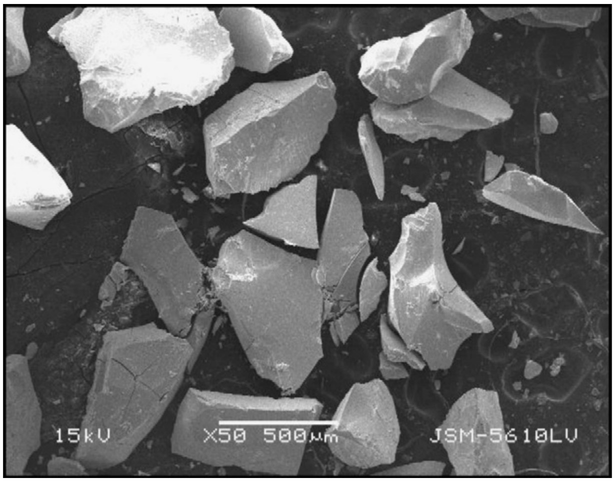


Fig. 4. SEM image of ZrPW.

~210 °C) (Fig. 10) indicating more as well as strong acid sites in ZrPW. Surface acidity for ZrPW and 12-TPA/ZrO_2 at 700 °C preheating temperature was found to be 3.93 mmol/g and 0.17 mmol/g respectively. Surface acidity for ZrPW at 150 °C and 200 °C preheating temperature (Fig. 11) was found to be 9.34 mmol/g and 6.05 mmol/g respectively, while surface acidity for 12-TPA/ZrO_2 at 150 °C and 200 °C preheating temperature (Fig. 12) was found to be 1.07 mmol/g and 0.89 mmol/g respectively. Decrease in surface acidity with increasing preheating temperatures could be attributed to condensation of structural hydroxyl groups as discussed above in thermal behavior of the material.

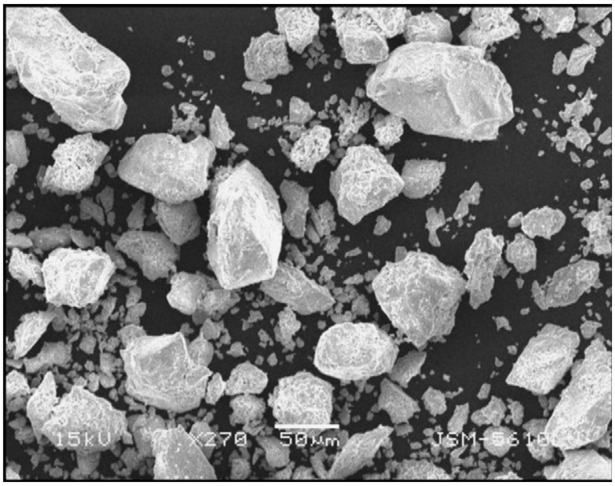


Fig. 5. SEM image of 12-TPA/ZrO_2.

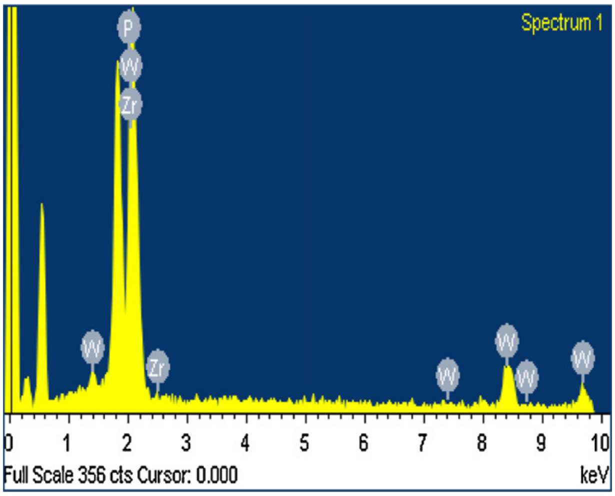


Fig. 6. EDX image of fresh ZrPW.

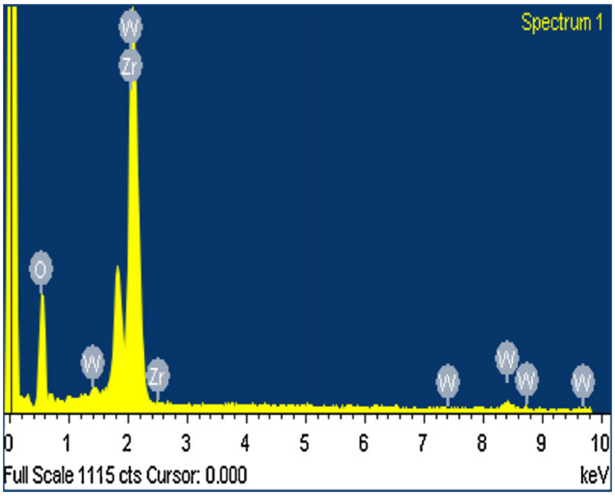


Fig. 7. EDX image of fresh 12-TPA/ZrO_2.

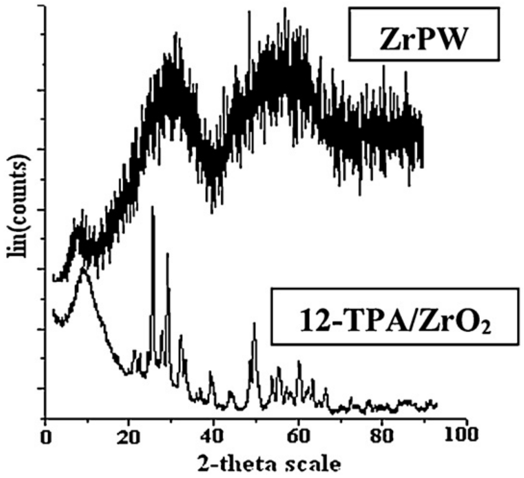


Fig. 8. XRD pattern of ZrPW and 12-TPA/ZrO_2.

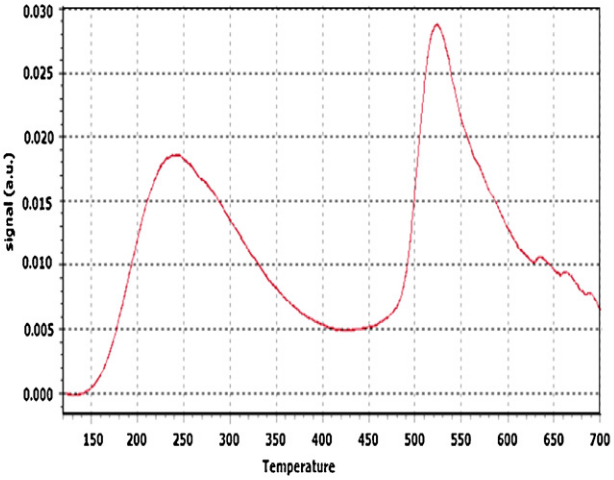


Fig. 9. NH_3-TPD pattern of ZrPW at 700 °C preheating temperature.

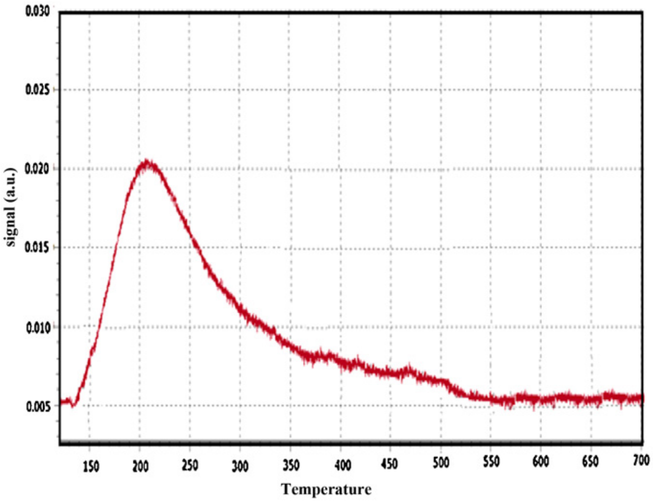


Fig. 10. NH_3-TPD pattern of 12-TPA/ZrO_2 at 700 °C preheating temperature.

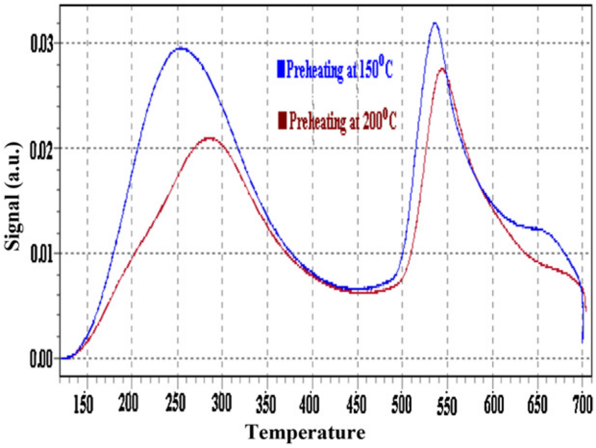


Fig. 11. NH_3-TPD patterns of ZrPW at 150 °C and 200 °C preheating temperature.

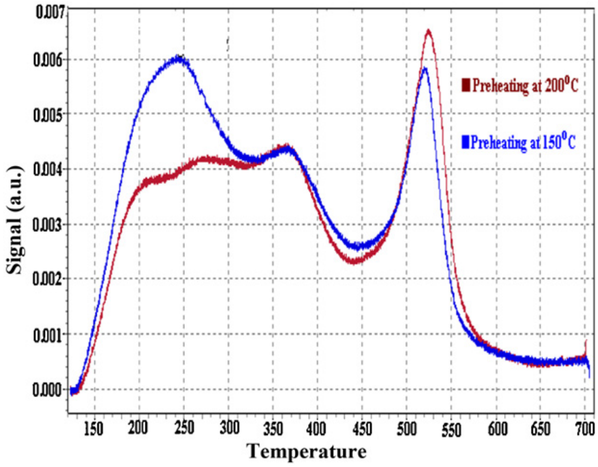


Fig. 12. NH_3-TPD patterns of 12-TPA/ZrO_2 at 150 °C and 200 °C preheating temperature.

Table 3
Optimization of reaction parameters for Pechmann condensation of resorcinol using ZrPW.

Reactants	Mole ratio	Amount of catalyst (g)	Reaction time (h)	Reaction temperature (°C)	% yield
R + MA	1:1	0.10	2	130	4.88
R + MA	1:1	0.10	4	130	12.55
R + MA	1:1	0.10	6	130	28.31
R + MA	1:1	0.10	8	130	43.90
R + MA	1:1	0.10	10	130	44.62
R + MA	1:1	0.10	8	120	40.14
R + MA	1:1	0.10	8	140	39.83
R + MA	1:1	0.15	8	130	51.69
R + MA	1:1	0.20	8	130	54.85
R + MA	1:1	0.25	8	130	56.48
R + MA	**1:1.5**	**0.20**	**8**	**130**	**58.12**
R + MA	1:2	0.20	8	130	50.41
R + MA	1.5:1	0.20	8	130	51.47
R + MA	2:1	0.20	8	130	48.32

Bold text indicates optimum condition for Pechmann condensation of resorcinol using ZrPW.

3.2. Catalytic activity: Pechmann condensation

In case of Pechmann condensation of resorcinol by conventional heating process using ZrPW, yield increases with reaction time until equilibrium is reached within 8 h (Table 3). For the same reaction time, yield increases with catalyst (ZrPW) amount, since number of active sites per g of substrate increases. A maximum product yield is obtained with reaction temperature 130 °C, beyond which product degradation is observed. In the present study, the catalytic activity increases as the wt.% of 12-TPA loaded onto ZrO_2 increases (Table 4). The material with 20 wt.% 12-TPA/ZrO_2 gives good yields of coumarin derivatives. Thus, for all studies 20 wt.% 12-TPA/ZrO_2 has been used [23,24].

Table 4
Optimization of amount of 12-TPA loading on ZrO_2 for Pechmann condensation of resorcinol with methyl acetoacetate.

Reactants	Catalyst used	% yield
R + MA	10 wt.% 12-TPA/ZrO_2	40.12%
R + MA	**20 wt.% 12-TPA/ZrO_2**	**57.01%**
R + MA	30 wt.% 12-TPA/ZrO_2	57.26%

Mole ratio of R:MA = 1:1.5; reaction temperature: 130 °C; reaction time: 8 h; amount of catalyst: 0.20 g.
Bold text indicates optimum condition for amount of 12-TPA loading on ZrO_2 for Pechmann condensation of resorcinol with methyl acetoacetate.

Table 5
Optimization of reaction time for Pechmann condensation of phenols using ZrPW under MW heating (250 W).

Reactants	Mole ratio	Amount of catalyst (g)	Reaction time (min)	Reaction temperature (°C)	% yield
R + MA	1:1.5	0.20	10	130	32.12
R + MA	1:1.5	0.20	20	130	49.83
R + MA	**1:1.5**	**0.20**	**30**	**130**	**61.82**
R + MA	1:1.5	0.20	40	130	61.90

Bold text indicates optimum reaction time for Pechmann condensation of phenols using ZrPW under MW heating (250 W).

Under MW irradiation it is observed that, yield increases with reaction time until equilibrium is reached within 30 min (Table 5). 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 (Table 5). 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 (by-product) also helps in absorption of MW radiation and thereby accelerating the reaction [20].

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 [20]. 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 (–NO_2) 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 [18]. In all cases, yields are higher for ZrPW which could be attributed to high surface area as well as high surface acidity of ZrPW compared to 12-TPA/ZrO_2 as is also indicative in NH_3-TPD patterns presented in Fig. 9 and 10. % yields of different coumarin derivatives at optimized condition, under conventional heating as well as by microwave heating using ZrPW and 12-TPA/ZrO_2 have been presented in Tables 6 and 7.

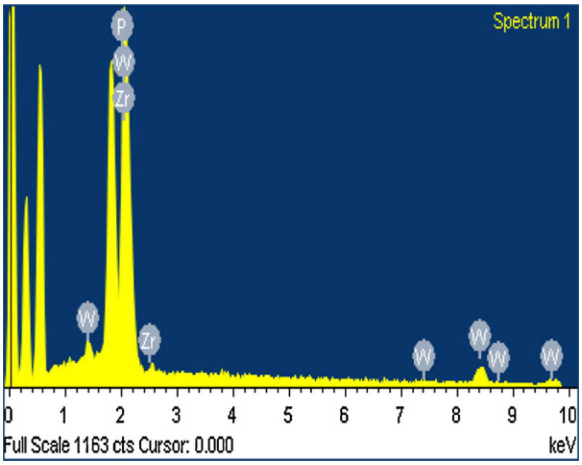


Fig. 13. EDX image of spent ZrPW.

Both the catalysts turn dark brown after each catalytic run during the course of the reaction, probably due to the fact that reactant molecules come onto surface of catalyst. Some molecules enter into reaction to give product while a few of them get adsorbed on surface, which is marked by change in color of catalysts. Reactant molecules are weakly adsorbed is evident from catalysts regaining its original color, when refluxed in ethanol as described in experimental section. It is observed that after every regeneration decreased yields are observed which is probably due to the deactivation of catalysts because of substrate molecules getting adsorbed on surface or also entering interstices of the catalyst material [18]. Further, EDX of spent ZrPW (Fig. 13) shows slight decrease in atomic % of Zr and W is found to be 54.26% and 20.19% respectively, while EDX of 12-TPA/ZrO_2 (Fig. 14) shows decrease in atomic % of Zr and

Table 6
Pechmann condensation of phenols using ZrPW and 12-TPA/ZrO_2 at optimum condition.

Reactants	Catalyst used	% yield	Melting point (°C)	Product formed
R + MA	ZrPW	58.12	185–186	7-Hydroxy-4-methyl coumarin
	12-TPA/ZrO_2	57.01		
Py + MA	ZrPW	54.22	244–245	7,8-Dihydroxy-4-methyl coumarin
	12-TPA/ZrO_2	48.45		
Ph + MA	ZrPW	61.00	283–284	5,7-Dihydroxy-4-methyl coumarin
	12-TPA/ZrO_2	58.37		
Hq + MA	ZrPW	64.48	165–166	6-Hydroxy-4-methyl coumarin
	12-TPA/ZrO_2	63.00		
pNp + MA	ZrPW	42.12	149–150	6-Nitro-4-methyl coumarin
	12-TPA/ZrO_2	38.18		

Mole ratio of phenol:MA = 1:1.5; reaction temperature: 130 °C; reaction time: 8 h; amount of catalyst: 0.20 g.

Table 7
Pechmann condensation of phenols using ZrPW and 12-TPA/ZrO_2 at optimized conditions under MW heating (250 W).

Reactants	Catalyst used	% yield	Melting point (°C)	Product formed
R + MA	ZrPW	61.82	185–186	7-Hydroxy-4-methyl coumarin
	12-TPA/ZrO_2	60.10		
Py + MA	ZrPW	53.68	244–245	7,8-Dihydroxy-4-methyl coumarin
	12-TPA/ZrO_2	49.82		
Ph + MA	ZrPW	61.73	283–284	5,7-Dihydroxy-4-methyl coumarin
	12-TPA/ZrO_2	60.19		
Hq + MA	ZrPW	66.37	165–166	6-Hydroxy-4-methyl coumarin
	12-TPA/ZrO_2	65.43		
pNp + MA	ZrPW	41.53	149–150	6-Nitro-4-methyl coumarin
	12-TPA/ZrO_2	40.68		

Mole ratio of phenol:MA = 1:1.5; reaction temperature: 130 °C; reaction time: 30 min; amount of catalyst: 0.20 g.

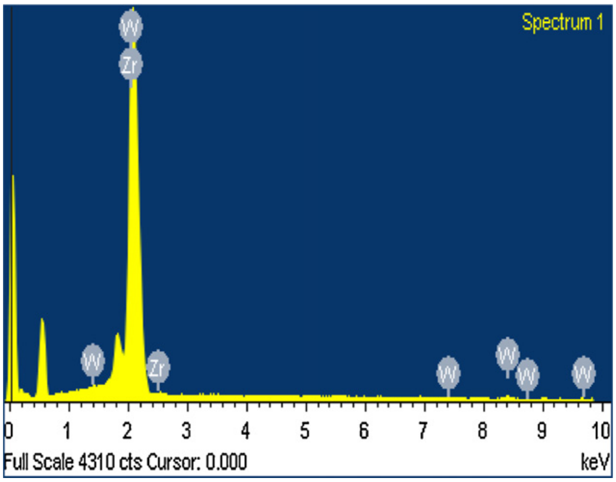


Fig. 14. EDX image of spent 12-TPA/ZrO_2.

W is found to be 26.12% and 2.81% respectively. Therefore, decrease in yield of coumarin derivatives may be due to the leaching of Zr and W. Results for reusability of both the catalysts in case of synthesis of 6-Hydroxy-4-Methyl coumarin at optimum condition have been presented in Table 8.

The Pechmann condensation proceeds through transesterification followed by intramolecular hydroalkylation and dehydration [25–27]. These three steps are acid catalyzed reactions. A possible mechanism for the Pechmann condensation of phenols and β-keto ester by solid acid catalysts is presented in Scheme 1, which is also proposed by other workers [7].

Table 8
Results for reusability of catalyst in case of synthesis of 6-hydroxy-4-methyl coumarin at optimum condition.

Catalyst used	Cycle no.	%Yield (conventional heating)	%Yield (MW heating)
ZrPW (with regeneration/acid treatment)	1	64.48	66.37
	2	63.12	65.81
	3	60.18	62.31
ZrPW (with out regeneration/acid treatment)	1	64.48	66.37
	2	56.21	55.28
	3	44.34	47.61
12-TPA/ZrO_2	1	63.00	65.43
	2	48.10	47.12
	3	39.81	38.36

3.3. *Characterization of the products*

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

3.3.1. *7-Hydroxy-4-methyl coumarin*

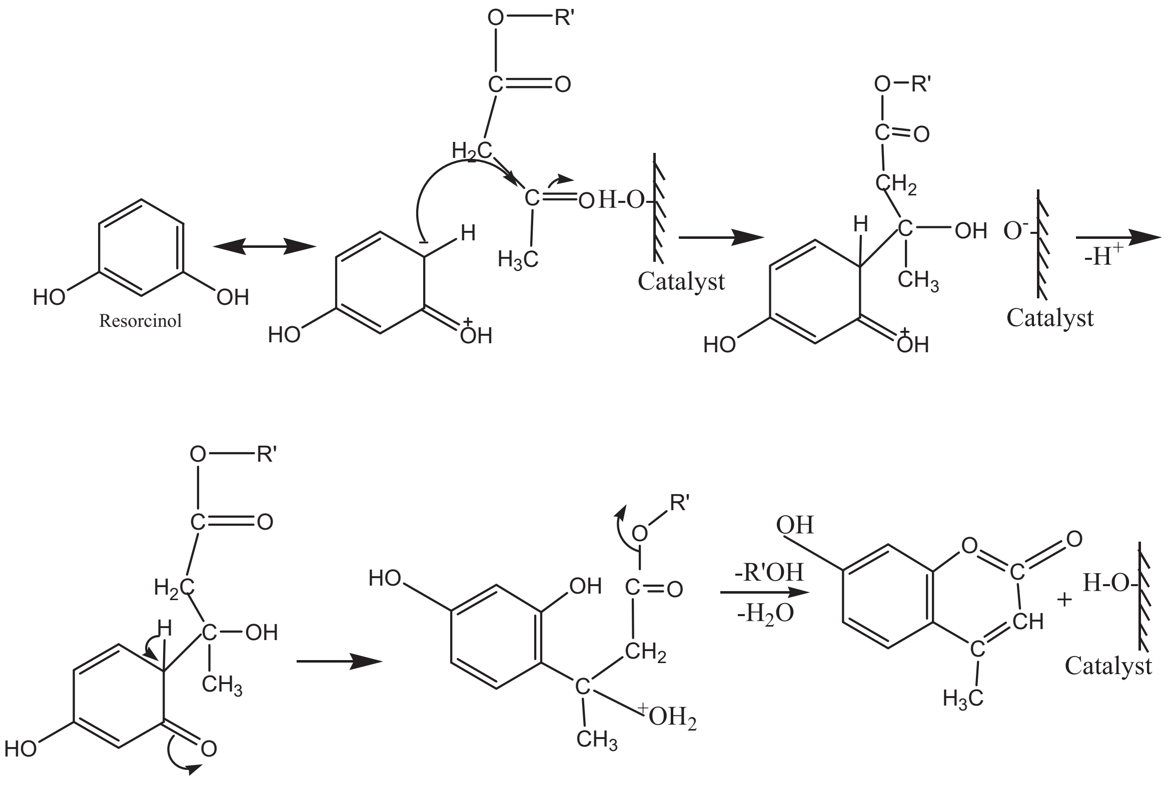
Melting point: 185–186 °C; FT-IR (KBr): 3155 cm^{-1}, 1678 cm^{-1}, 1227 cm^{-1}, 1057 cm^{-1}, 974 cm^{-1}, 844 cm^{-1}, 748 cm^{-1}.

3.3.2. *7,8-Dihydroxy-4-methyl coumarin*

Melting point: 244–245 °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}.

3.3.3. *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}.



Scheme 1. Possible mechanism for the Pechmann condensation of phenols and β-keto ester by solid acid catalysts.

3.3.4. 6-Hydroxy-4-methyl coumarin

Melting point: 165–166 °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}, 575 cm^{-1}.

3.3.5. 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 study reveals good performance of both the catalysts ZrPW and 12-TPA/ZrO_2 under conventional and MW assisted synthesis of coumarins, the highlighting feature being reduction of reaction time from several hours (8 h) to few minutes (30 min) under solvent free synthesis and MW conditions, besides advantages of operational simplicity, mild reaction conditions and environment friendly nature of the catalysts. Though both the catalysts can be regenerated and reused, ZrPW scores over 12-TPA/ZrO_2 where, yields go down considerably in subsequent cycles. Thus, ZrPW has potential for commercialization especially under microwave-assisted synthesis of coumarin derivatives.

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