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Ultrasound-assisted one-pot synthesis of substituted coumarins catalyzed by poly(4-vinylpyridinium) hydrogen sulfate as an efficient and reusable solid acid catalyst

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ABSTRACT

Poly(4-vinylpyridinium) hydrogen sulfate solid acid was found to be efficient catalyst for synthesis of substituted coumarins via Pechmann reaction using ultrasound irradiation at room temperature and neat condition in high yields with short reaction times. This methodology offers momentous improvements over various options for the synthesis of coumarins with regard to yield of products, simplicity in operation and green aspects by avoiding toxic catalysts and solvents. Further, the catalyst can be reused and recovered for several times.

1. Introduction

As a consequence of serious pollution problems, the adoption of "cleaner production" methods is an urgent priority. Four main approaches have recently been developed to synthesize compounds in an environmentally friendly manner [1,2]. One approach to increasing the environmental benign of a reaction is to conduct them under solvent-free conditions. While reaction yields will always be important, now, its *E* factor [3] and the volume productivity [4] are considered. The largest contribution to the magnitude of E factors comes from organic solvents. In industry, solvents are recycled whenever possible; however, recycling is rarely accomplished with complete efficiency.

Advantages of solvent-free reactions include reduced energy consumption, decreased reaction times; bring down handling costs due to simplification of experimental procedure and a considerable reduction in reactor size and, therefore, capital investment. These would be especially important during industrial production and have inspired a substantial research effort directed toward the development of solvent-free reactions [2,5–7].

Coumarin and its derivatives form an important class of benzopyrones found in nature. They are structural subunits in many complex natural products and have shown numerous biological activities, such as antitumor [8], anti-HIV (NNRTI) [9], antioxidation [10], tumor necrosis factor-a (TNF-a) inhibition [11], antimicrobial activity [12], serine protease inhibition [13] and anticancer activity [14]. Coumarins could be synthesized by various methods, such as Pechmann [15], Perkin [16], Knoevenagel [17], Reformatsky [18], Witting [19], Claisen [20] and flash vacuum pyrolysis reaction [21]. However, the Pechmann reaction is one of the simplest and direct methods for the synthesis of coumarins since it proceeds from very simple starting materials, namely, phenols and β-keto esters or unsaturated carboxylic acids utilizing various catalysts, mineral acids like sulfuric acid [9], trifluoroacetic acid [22], phosphorus pentoxide [23], Lewis acids such as $ZrCl_4$ [24], $TiCl_4$ [25], $InCl_3$ [26] and $BiCl_3$ [27]. In recent years, Lewis acids such as $AlCl_3$-nBPC, $Yb(OTf)_3$, GaI_3 and $Sm(NO_3)_3$ as well as acidic ionic liquid were employed to catalyze Pechmann reactions [28].

However, these catalysts have to be used in excess; for example, sulfuric acid in ten to twelve equivalents [15], trifluoroacetic acid in three to four equivalents [22] and phosphorous pentoxide is required in a fivefold excess [23]. Some of the Lewis acids such as $ZrCl_4$ are moisture sensitive, decomposes on storing and liberates corrosive HCl fumes [24] and require special care in handling and storage. Moreover, in some cases, mixtures of substituted phenols, β-keto esters and the acidic catalyst required to stand for a number of hours (depending on their reactivity) [29], high temperature (150 °C) [29]b, also microwave irradiation [30] and undesired side-products such as chromones, in addition to coumarins were isolated. Furthermore, metal triflates are highly expensive.

Also there have been some attempts to find alternative, environmentally benign synthesis routes. The use of heterogeneous

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acid catalysts offers advantages like ease of operation conditions, reduced equipment corrosion and minimized contamination of waste streams combined with reusability. Poly(4-vinylpyridine) supported sulfuric acid [30]b, Nafion-H [31], zeolite H-BEA, modified zirconia [32], Amberlyst 15 [33] and other solid acids have been employed as catalyst in the Pechmann reaction. In the case of Poly(4-vinylpyridine) supported sulfuric acid and Amberlyst-15, special equipment such as microwave oven was used for accelerating this reaction and the preparation of yttria–zirconia involved use of sulfuric acid at 500 °C. The neutral ionic liquids ([bmim]PF_6/$POCl_3$) was reported for the synthesis of 7-hydroxy-4-methylcoumarin, but it required hazardous $POCl_3$ [28e].

Microwave irradiation has also been used for coumarin synthesis via Pechmann reaction catalyzed by homogeneous liquid acids such as sulfuric acid, *p*-toluene sulfonic acid and ionic liquid [34–36]. However, sulfuric acid and *p*-toluene sulfonic acid are corrosive, hazardous and require careful handling in open chamber of domestic microwave system. The separation of ionic liquid catalyst to recover from reaction mixture by solvent extraction adds an extra step in synthesis.

Ultrasound irradiation has been established as a significant technique in synthetic organic chemistry [37–42]. Ultrasound-assisted has been used for the synthesis of 2-amino-4*H*-chromenes, coumarin thioglycopyranoside derivatives and hymecromone as insecticide intermediate [28,42–44]. Shorter reaction time is the main benefit of ultrasound-assisted reactions. Simple experimental procedure, high yields, improved selectivity and clean reaction of many ultrasound induced organic transformations offers additional convenience in the field of synthetic organic chemistry.

Poly(4-vinylpyridinium) hydrogen sulfate (PVPHS) is inexpensive, insensitive to air and requires no special care during its handling. The potential of this reagent for the chemoselective 1,1-diacetate protection and deprotection of aldehydes [45], the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes under conventional heating and ultrasound irradiation [46], synthesis of 12-aryl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-triones [47], the synthesis of coumarin derivatives under microwave irradiation [30b] has been recently explored.

With these considerations in mind, we decided to evaluate our solid acid catalyst for the Pechmann condensation under sonication and solvent-free conditions. To the best of our knowledge, the coupling of ultrasonic irradiation with solid phase catalyst PVPHS as an activator in Pechmann synthesis under solvent-free conditions is now reported by us for the first time.

2. Results and discussion

In continuation of our ongoing research program on the development of new catalyst and methods for organic transformations [48] and energy-saving procedures developed in our laboratory, in an earlier publication, we described Poly(4-vinylpyridinium) hydrogen sulfate (PVPHS) as efficient catalyst for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes under solvent-free conditions and ultrasound irradiation [46]. In here we wish to apply this protocol to the Pechmann synthesis (Scheme 1).

To optimize the reaction conditions, the reaction between resorcinol (110 mg, 1 mmol) and 0.25 mL ethyl acetoacetate (EAA) (260 mg, 2 mmol) was used as a model reaction. Before taking up the reaction using ultrasonic irradiation, it was tried out using different solvents such as toluene, methanol, ethanol and dichloromethane under reflux reaction conditions as well as solvent-free system at variety of temperature with PVPHS as the catalyst. The results are collected in Table 1.

Table 1
Effect of temperature, solvent, amount of catalyst on the synthesis of Coumarins.[a]

Entry	Amount of catalyst (mg)	Temperature (°C)	Solvent	Time (min)	Yield (%)[b]
1	–	60	Neat	6 h	Trace
2	10	Reflux	$C_6H_5CH_3$	60	72
3	10	Reflux	CH_3OH	60	66
4	10	Reflux	C_2H_5OH	60	68
5	10	Reflux	CH_2Cl_2	60	70
6	10	60	Neat	60	88
7	10	70	Neat	60	92
8	10	80	Neat	60	94
9	5	70	Neat	60	69

[a] Reaction conditions: resorcinol, 1.0 mmol; EAA, 1.2 mmol (with solvent) and 2.0 mmol (under solvent-free conditions).
[b] Determined by MS of the corresponding 7-hydroxy-4-methylcoumarin product.

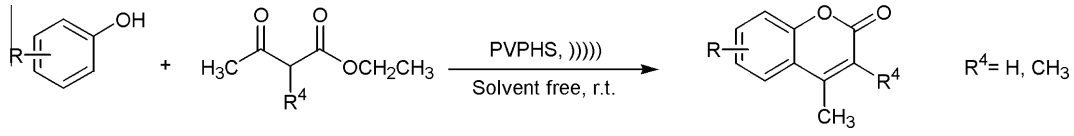
Table 2
Reaction of resorcinol and EAA in the presence of different amount of PVPHS at stirring at room temperature and ultrasonic irradiation under solvent-free conditions.[a]

Entry	Amonut of catalyst (mg)	Room temperature		Ultrasonic irradiation	
		Time (h)	Yield (%)[b]	Time (min)	Yield (%)[b]
1	–	6	Trace	60	44
2	5	2	32	15	86
3	10	2	48	5	96

[a] Reaction conditions: resorcinol, 1.0 mmol; EAA, 2.0 mmol.
[b] Determined by GC–MS of the corresponding 7-hydroxy-4-methylcoumarin product.

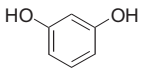
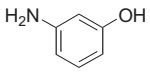
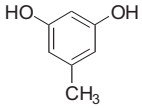
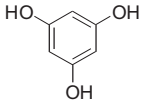
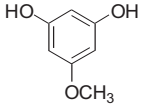
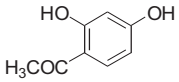
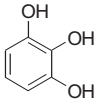
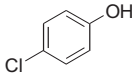
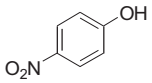
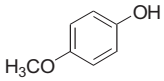
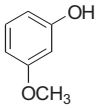
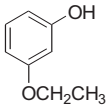
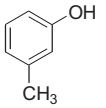
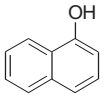
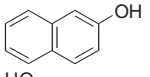
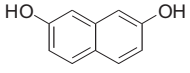
The resorcinol conversion increased with increase in temperature up to 80 °C and thereafter it attained steady state over the catalyst. There was no significant difference in conversion between 70 and 80 °C (Table 1, entries 6–8). The yield of 7-hydroxy-4-methylcoumarin decreased with decreasing of catalyst amount (Table 1, entry 9). Interestingly, no reaction took place in the absence of catalyst after 6 h of the reaction time (Table 1, entry 1). However, it was noticed that the best result was achievable under solvent-free conditions. The increased reactivity may be attributed to close contact of reactants in solvent-free condition where the dilution factor from solvent does not exist (viz. concentration effect). In some cases, the solid state organic reaction occurred more efficiently and more selectively than the solution reaction, since molecules in a crystal were arranged tightly and regularly [49].

In comparison with the stirring at room temperature, PVPHS employed under ultrasonic irradiation showed a more effective catalytic activity than the other in terms of yield and reaction time (Table 2, entries 2 and 3). Hence the ultrasonic irradiation which required only 5 min duration to complete reaction of resorcinol with EAA and the product yield was 96% is compared to the stirring at room temperature which have taken 120 min for reaction and yield was significantly less (48%) under solvent-free conditions



Scheme 1. The synthesis of substituted coumarins in presence PVPHS at room temperature under ultrasound irradiation and solvent-free conditions.

Table 3
Pechmann synthesis of various coumarins in the presence of PVPHS under ultrasonicirradiation.[a]

Entry	Phenol	β-Keto ester	Time (min)	Yield (%)[b]	Ref.
1		EAA MEAA	5 10	96 92	[54]
2		EAA	9	78	[55]
3		EAA	10	82	[56]
4		EAA MEAA	8 12	92 86	[54]
5		EAA MEAA	3 7	91 86	[57] [58]
6		EAA	10	89	[55]
7		EAA	12	78	[55]
8		EAA MEAA	8 14	90 86	[59] [58]
9		EAA	12	78	[55]
10		EAA	10	72	[60]
11		EAA	16	62	[57]
12		EAA	8	85	[59]
13		EAA	10	82	[28]
14		EAA	12	82	[61]
15		EAA	8	84	[62]
16		EAA	18	81	[54]
17		EAA	16	80	[55]
18		EAA	15	72[c]	[63]

[a] Reaction conditions: substrate, 1.0 mmol; EAA or MEAA, 2.0 mmol.
[b] Isolated yield.
[c] Obtained both a linear benzocoumarin (72%, m.p. 267 °C) and an angular benzocoumarin (14%, m.p. 276–277 °C) [63].

(Table 2, entry 3). However, in the absence of catalyst, the reaction yielded only trace and 44% of 7-hydroxy-4-methylcoumarin after 6 h and 60 min under stirring at room temperature and ultrasonic conditions, respectively (Table 2, entry 1). In the absence of solid acid, there is no solid phase, so this ultrasonic large acceleration is not related to additional effects of the liquid–solid systems. It can be explained that cavitational collapse in a liquid produces intense local heating, high pressures, and enormous heating and cooling rates. Therefore, acoustic cavitation provides a unique interaction of energy and matter, and ultrasonic irradiation of liquids causes high energy chemical reactions to occur.

It was clear that the ultrasound irradiation could accelerate Pechmann reaction. The following is expected to be plausible reason for the higher yields and shorter reaction times during ultrasonic irradiation. The chemical effects of ultrasounds have been attributed to implosive collapse of the cavitations period of the sound waves. The bubbles are generated at localized sites in the liquid mixture that contain small amounts of dissolved gases. When these bubbles burst, it results in high temperature and high pressure which facilitate the intermolecular reaction. When one of the phases is a solid, the ultrasonic irradiation has several additional enhancement effects, and this is especially useful when the solid acts as a catalyst [50]. When cavitation occurs near an extended solid acid catalyst surface, cavity collapse is non-spherical and drives high-speed jets of ethylacetoacetate (EAA) into the PVPHS surface. These jets and associated shock waves can cause substantial surface damage and expose fresh, highly heated surfaces. This fact increases the chances of interphase surface able to react [51].

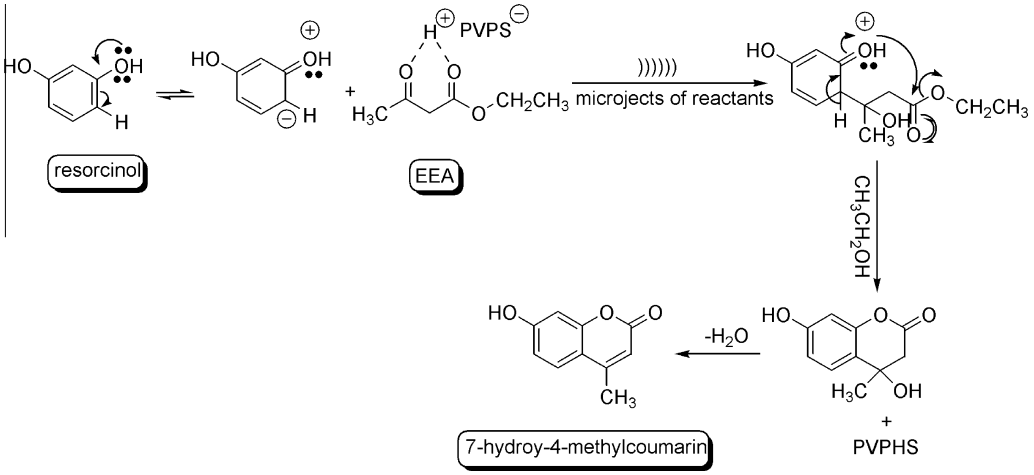
In order to evaluate the generality of the process, several diversified examples illustrating the present method for the synthesis of substituted coumarins was studied. The reaction of EAA with various phenols was carried out in the presence of PVPHS as catalyst under ultrasonic irradiation. The yields obtained were good to excellent and these results are illustrated in Table 3.

The shorter reaction times were observed for the reaction of phloroglucinol (Table 3, entry 5) with ethyl acetoacetate (EAA) and α-methyl ethyl acetoacetate (MEAA). This was mainly due to the presence of three hydroxyl groups that cooperated in activating the aromatic ring for hydroxyalkylation. The reactions of pyrogallol with EAA and MEAA (Table 3, entry 8) were slightly slower than that of the reactions of resorcinol and phloroglucinol presumably due to steric hindrance of hydroxyl groups. Substrates (Table 3, entries 1, 2, 4, 5 and 13) having electron-donating groups in the *para* position to the site of electrophilic substitution gave maximum yields under ultrasonic irradiation in a short reaction time. Moreover, the presence of electron-donating group in the *meta* position it decrease the further hydroxyalkylation site which leads to a lower rate of attack of nucleophile to electrophile. Phenol (Table 3, entry 9) required longer reaction duration, as no electron-donating group is present. Similarly, naphthols (Table 3, entries 16, 17) required long reaction times due to presence of another phenyl moiety. Alkoxyphenols (Table 3, entries 12–14) showed no detectable dealkylation under the reaction conditions. When the condensation of *meta*-aminophenol (Table 3, entry 2) with ethyl acetoacetate was carried out, the major product is the coumarin and only trace of quinoline was obtained [52]. A literature survey revealed that, resacetophenone (Table 3, entry 7) failed to react to give a coumarin derivative in the presence of sulfuric acid as the catalyst [53]. However, the reaction was observed under aluminium chloride catalysts [28], but required a temperature of 130 °C in nitrobenzene as the solvent. In contrast, the PVPHS furnished good yields of the product under ultrasonic irradiation. In all instances except two, coumarins are obtained. As exceptions, 2,7-dihydroxynaphthalene and 2-naphthol give a mixture of a linear and angular coumarin and a chromone. From these experiments, it is clearly demonstrated that the synthesis of coumarin derivatives using PVPHS under ultrasonic irradiation is indeed an effective method and is undoubtedly superior to other procedures with respect to reaction time, availability of catalyst, work-up procedure and yields.

Table 3 also compares the activities of various β-keto esters with various phenols. Reactivity order for β-keto esters was found to be EAA > MEAA (Table 3, entries 1, 4, 5 and 8). All products were characterized by comparison of their melting point, IR, ^{1}H NMR and mass spectra with those of authentic samples [28,54–63].

The possible mechanism for the synthesis of 7-hydroxy-4-methylcoumarin in the presence of PVPHS as a promoter under ultrasound irradiation is shown in Scheme 2. On the basis of this mechanism, the implosive collapse of the cavitations period of the sound waves generates the bubbles at localized sites in the liquid phase (EAA). When these bubbles burst, it results in high temperature and high pressure which facilitate the hydroxyalkylation reaction. When the catalyst is a solid, the ultrasonic irradiation has several additional enhancement effects [50]. The transesterification and dehydration occur concomitantly condensing together the two reactants at two sites to form coumarin product and regenerates PVPHS in the reaction.

We compared the obtained results (reaction conditions, time, isolated yield) with some of those reported in the literature (Ta-



Scheme 2. Proposed mechanism for Pechmann reaction of resorcinol with EAA at room temperature under ultrasonic irradiation.

Table 4
Comparison of our results with results obtained by other groups.

Entry	Catalyst	Reaction conditions	Time (h)	Yield (%)[a]	Ref.
1	p-TsOH	Neat/125 °C	4	89	[29]
2	PVPHS	Neat/MW (560 W)/65–70 °C	7 min	85	[30]b
3	Sulfamic acid	Neat/125 °C	8	93	[37]
4	$K_5CoW_{12}O_{40}.3H_2O$	Neat/125 °C	2	91	[52]
5	I2	Neat/90 °C	2.5	90	[53]
6	LiBr	Neat/130 °C	1	82	[54]
7	Amberlyst-15	Neat/125 °C	2	94	[55]
8	Cellulose sulfuric acid	Neat/110 °C	1.5	81	[56]
9	$SiO_2/H2SO_4$	Neat/120 °C	5 min	80	[58]
10	Zr-TMS-TFA-25	Neat/100 °C	9	88	[64]
11	Sulfate $Ce_xZr_{1-x}O_2$	Neat/120 °C	2.38	87	[65]
12	Nano-crystalline sulfate-Zr	Neat/MW (250 W)/150 °C	15 min	99	[66]
13	Mesoporous phosphate-Zr	Neat/160 °C	4	94	[67]
		Neat/MW (600 W)/160 °C	15	97	
14	$SiO_2/NaHSO_4$	CH_3CN/Reflux	1	95	[68]
15	PVPHS	Neat/70 °C	1	92	This work
		Neat/US (35 kHz, 200 W)	5 min	96	

[a] Isolated yield.

ble 4). As can be seen, our method was simpler, more efficient, and used no toxic solvents.

3. Experimental

3.1. Materials

Unless specified, all chemicals were analytical grade and purchased from Merck, Aldrich and Fluka Chemical Companies and used without further purification. Products were characterized by their physical constant and comparison with authentic samples. The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates.

3.2. Instrumentation

The IR spectra were recorded on a Perkin Elmer 781 Spectrophotometer using KBr pellets for solid and neat for liquid samples in the range of 4000–400 cm^{-1}. The UV spectra were recorded on an Agilent 8453 UV–vis spectrophotometer at room temperature. Mass spectra were recorded on a FINNIGAN MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. In all the cases the ^1H NMR spectra were recorded with Bruker Avance 400 or 300 MHz instrument using. ^{13}C NMR data were collected on Bruker Avance 100 or 75 MHz instrument. All chemical shifts are quoted in parts per million (ppm) relative to TMS using deuterated solvent. Microanalyses were performed on a Perkin–Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. Bandelin Sonorex (with a frequency of 35 kHz and a nominal power 200 W) ultrasonic bath was used for ultrasonic irradiation, built-in heating, 30–80 °C thermostatically adjustable. The reaction vessel placed inside the ultrasonic bath containing water.

3.3. General procedure for the preparation of coumarins

In a 25-mL batch reactor equipped with a distillation condenser the mixture of phenols (1.0 mmol), β-keto esters (2.0 mmol) and PVPHS (10 mg, 0.02 mmol) was stirred and irradiated with ultrasonic of low power (with a frequency of 35 kHz and a nominal power 200 W). The temperature of the reaction mixture started to rise. After 2 min of irradiation, the ultrasound source was switched off. Since the Pechmann reaction proved to be exothermic, the reaction mixture continued to rise in temperature. After completion of the reaction (monitored by TLC), ethanol was added to the reaction mixture and the catalyst was recovered by filtration. The filtrate was concentrated in vacuum, and the crude product was washed with water, dried and slowly recrystallized in ethanol or ethanol–water system. The melting point, IR, ^1H NMR and mass spectroscopic techniques were used to analyze the products and compared with the authentic samples.

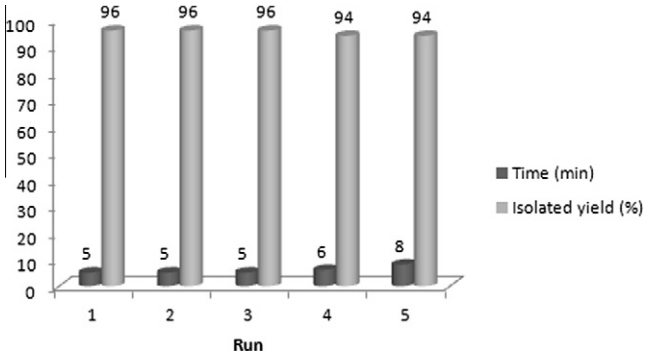


Fig. 1. Recovery and reuse of the catalyst on Pechmann reaction of resorcinol with EAA at room temperature under ultrasonic irradiation.

The recovered catalyst, after drying, was reused for four more consecutive pechmann reactions of resorcinol (1.0 mmol) and EAA (2.0 mmol) affording 96%, 96%, 94%, and 94% isolated yields, respectively, in 5, 5, 6, and 8 min (Fig. 1).

Of course, the SEM images of the fresh and recycled catalyst demonstrated a very interesting effect of ultrasonic irradiation on the surface morphology and particle size of solid acid catalyst (Fig. 2). Upper image is fresh catalyst and lower is recycled catalyst after first and 4th run of Pechmann reaction. High-velocity interparticle collisions caused by ultrasonic irradiation are responsible for the agglomeration of particles into extended aggregates. This process can effectively remove the inactive and passivating surface catalyst dramatically improves reaction rates. Scanning electron microscopy of the solid acid catalyst PVPHS showed likely that the origin of the observed rate enhancements comes from increased effective surface area and to a lesser extent from surface damage.

The SEM micrographs of recycled catalyst after first and 4th run showed that the structure of catalyst not changed noticeable (Fig. 2, lower images). Also the FTIR spectra of recycled catalyst

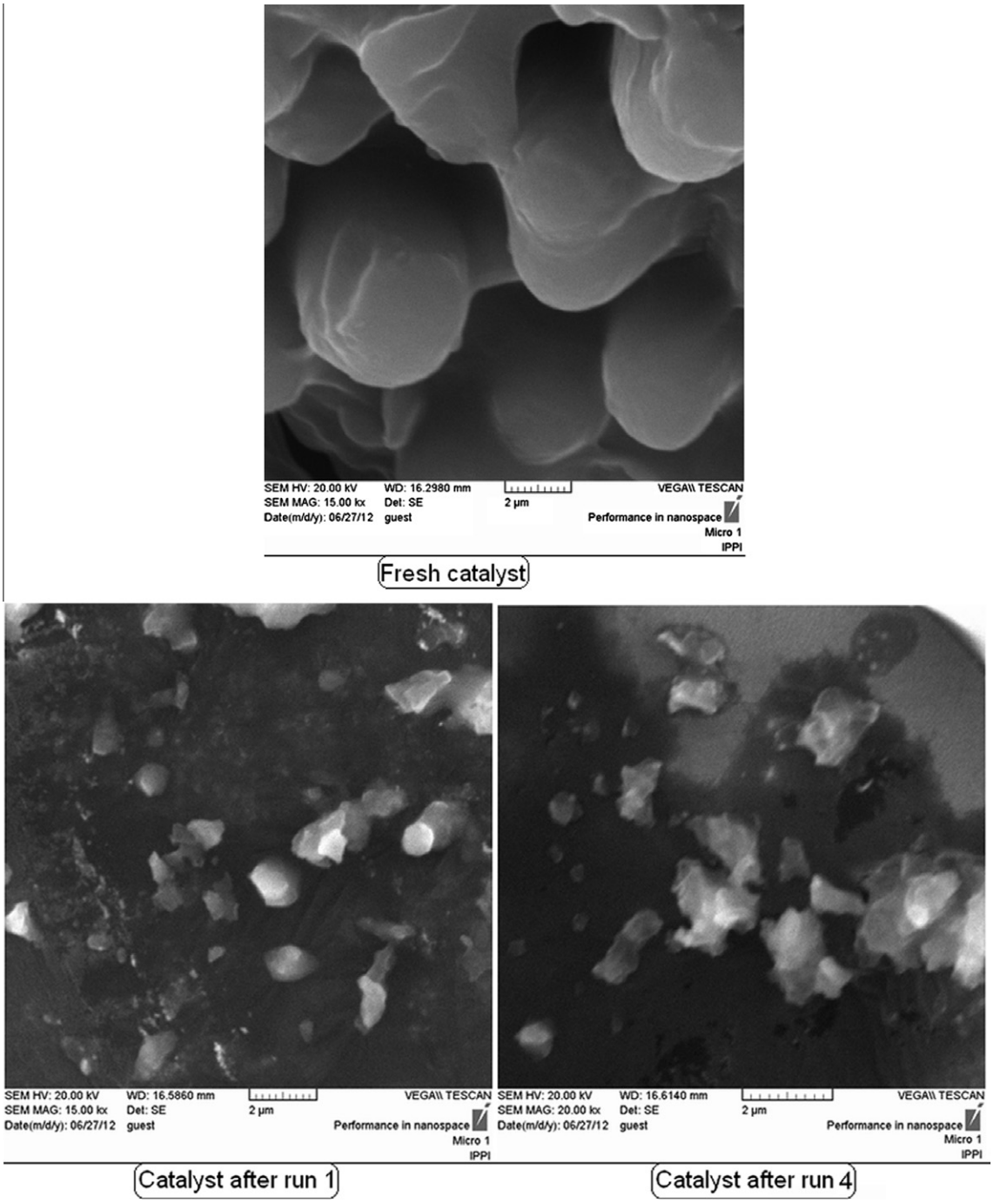


Fig. 2. SEM images of fresh PVPHS (upper image) and PVPHS after first and 4th runs of Pechmann reaction (lower images).

is same as after first and 4th run catalyst, therefore the composition of solid acid catalyst was not changed by ultrasonic irradiation.

3.4. The spectral data of selected compounds are below

7-Hydroxy-4-methylcoumarin (Table 3, entry 1): off-white powders, mp: 184–185 °C (ethanol) (lit. mp. 182–184 °C) [57]; IR (KBr): ν = 3450, 3028, 1675, 1585, 1400, 1230, 1054 cm^{-1}; ^1H NMR (300 MHz, DMSO-*d6*) δ = 2.24 (s, 3H, CH_3), 5.98 (s, 1H, ArH), 6.57 (s, 1H, ArH), 6.72 (d, J = 8.8 Hz, 1H, ArH), 7.46 (d, J = 8.8 Hz, 1H, ArH), 10.56 (brs, 1H, OH) ppm. MS (EI, 70 eV) m/z: 176 [M^+].

5-Hydroxy-3,4,7-trimethylcoumarin (Table 3, entry 4) white crystals, mp: 249–251 °C (ethanol) (lit. mp: 249 °C) [57]; IR (KBr): ν = 3216, 3028, 2986, 1675, 1620, 1283, 1120, 1062 cm^{-1}; ^1H NMR (300 MHz, DMSO-*d6*) δ = 2.04 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 6.57 (s, 2H, ArH), 10.32 (brs,1H, OH). MS (EI, 70 eV): m/z = 204 [M^+].

7,8-Benzo-4-methylcoumarin (Table 3, entry 16) white powders, mp: 155–156 °C (ethanol) (lit. mp: 153–154 °C); [57] IR (KBr): ν = 2920, 1675, 1615, 1561, 1285, 1167, 1056 cm^{-1}; ^1H NMR (400 MHz, DMSO-*d6*) δ = 2.56 (s, 3H, CH_3), 6.53 (s, 1H, ArH), 7.72–7.75 (m, 2H, ArH), 7.83 (d, J = 8.8 Hz, 1H, ArH), 7.90 (d, J = 8.8 Hz, 1H, ArH), 8.06–8.08 (m, 1H, ArH), 8.38–8.41 (m, 1H, ArH). MS (EI, 70 eV): m/z = 210 [M^+].

8-hydroxy-4-methyl-2H-naphtho[2,3-b]pyran-2-one (Table 3, entry 18) yellow powders, mp: 275–277 °C (ethanol/water) (lit. mp: 267 °C) [66]; IR (KBr) ν = 3360, 3031, 1705, 1564, 1238,

1062 cm^{-1}; ^1H NMR (400 MHz, DMSO-*d6*) δ = 2.46(s, 3H, CH_3), 6.30(s, 1H, ArH), 7.08 (dd, J = 8.8 and 1.8 Hz, 1H, ArH), 7.14 (d, J = 1.8 Hz, 1H, ArH), 7.54 (s, 1H, ArH), 7.88 (d, J = 8.8 Hz, 1H, ArH), 8.21 (s, 1H, ArH), 10.15 (brs, 1H, OH). MS (EI, 70 eV): m/z = 226 [M^+].

4. Conclusions

In conclusion, Pechmann synthesis of coumarins is efficiently catalyzed in the presence of PVPHS under ultrasound and solvent-free conditions. The methodology has several advantages such as: green aspects by avoiding toxic solvents, high reaction rates and excellent yields, no side reactions, ease of preparation and handling of the catalyst, effective recovering and reusability of the catalyst, use of inexpensive catalyst with lower loading and simple experimental procedure. The use of ultrasound offers some hope of activating less reactive, but also less costly, catalysts. Further work to explore this catalyst for the other organic transformations is in progress.

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