J IRAN CHEM SOC
DOI 10.1007/s13738-015-0687-8

ORIGINAL PAPER

Efficient synthesis of 4*H*-pyran derivatives using a polymeric catalyst based on PVP

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Received: 4 April 2015 / Accepted: 15 June 2015

Abstract A one-pot efficient method for the synthesis of 4*H*-pyran derivatives has been developed through a multi-component reaction of aldehydes, malononitrile, and 1,3-cyclic diketones using poly(vinylpyrrolidonium) hydrogen sulfate ([PVPH]HSO_4) as a heterogeneous and reusable catalyst. The synthesized polymeric catalyst has fully been characterized by Fourier transform infrared spectra, X-ray diffraction, scanning electron microscopy, thermal gravimetric analysis, Hammett acidity (H_0), and pH analysis, which expose of the polymeric catalyst. This procedure has the advantages of operational simplicity, mild conditions, easy work-up, short reaction times, high yields of the products, and reusability of the catalyst.

Keywords Poly(vinylpyrrolidone) · Poly(vinylpyrrolidonium) hydrogen sulfate ([PVPH]HSO_4) · 2-Amino-4*H*-pyran derivatives · Multi-component reactions

Introduction

Tetrahydrobenzo[*b*]pyrans and their derivatives are important class of heterocyclic compounds which have attracted the attention of chemists because of their wide range of useful biological and pharmacological properties, such as antitumor, anticancer, antibacterial, antioxidant, diuretic, and ant allergic [1–4] activities. These compounds can be used as pigments, fluorescence markers, photoactive materials, laser dyes, optical brighteners, potential calcium channel antagonists, and potent biodegradable agrochemicals, as synthons of natural compounds, and occur in a series of natural products [5–10].

Various types of methods including use of supported reagents [11–17], ionic liquids [18–20], nano-catalysts [21–25], and inorganic compounds [26–31] are reported for the preparation of the synthesis of these types of compounds.

In spite of their own merits, some of these methodologies suffer from one or more drawbacks such as use of toxic solvents, use of a large amounts of expensive or toxic catalysts, tedious work-up, unsatisfactory yields of products or long reaction times, and use of non-reusable catalysts. Therefore, introduction of efficient and economical methods that solve these drawbacks is still under consideration.

Cross-linked poly(vinylpyrrolidone) (PVP) is one of the most widely used polymeric supports for numerous reagents and catalysts because of its stability, commercial availability, reasonable high loading capacity, good physicochemical structure, and facile functionalization. In recent years and on the basis of these characteristics, various PVP-supported reagents have been designed to catalyze some of the organic reactions [32–38].

In 1997, Vaidyanathan et al. reported a new modified form of PVP which introduced as PVP-$(H_2SO_4)_n$ and Chehardoli and co-workers used this catalyst for the synthesis of nitro phenol derivatives [33, 34]. They proposed a structure for this reagent in which *N*-atom is protonated but did not provide any evidence to confirm their suggestion.

In continuation of our recently report on the application of a new PVP-based catalyst in the synthesis of xanthene derivatives [39], we were interested to study the applicability of poly(vinylpyrrolidonium) hydrogen sulfate in the promotion of the synthesis of 2*H*-indazolo[2,1-*b*] phthalazine-trione derivatives. Our studies on the structure

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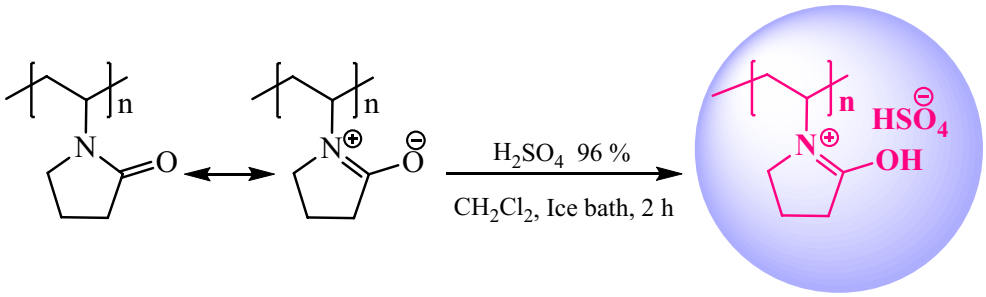
Published online: 29 June 2015



Scheme 1 Preparation of $[PVPH]HSO_4$

of the prepared reagent showed that the attributed structure by Chehardoli is incorrect and the reagent is not protected at *N*-atom and is actually protonated at *O*-atom. Herein we wish to report the results of this study and the results obtained from the preparation of 2*H*-indazolo[2,1-*b*] phthalazine-trione using this reagent as the catalyst.

Experimental

Materials

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. Cross-linked poly(vinylpyrrolidone) was purchased from BASF, the chemical company, Germany. All products were characterized by comparing their physical constants, and IR and NMR spectroscopy with authentic samples and those reported in the literature.

The FT-IR spectra were run on a VERTEX 70 Bruker company (Germany). Thermogravimetric analyses (TGA) were performed on TG/DTA6300 Sll-Nonotechnology company (Japan). Samples were heated from 25 to 800 °C at ramp 10 °C min^{-1} under N_2 atmosphere. Scanning electron microphotographs (SEM) were obtained on a SEM-Philips XL30. Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature on a Siemens D-500 X-ray diffractometer (Germany), using Ni-filtered Co-Kα radiation (λ = 0.15418 nm).

Catalyst preparation $[PVPH]HSO_4$

H_2SO_4 (0.55 mL, 96 %) was added to a suspension of powdered poly(vinylpyrrolidone) (1 g) [cross-linked poly(vinylpyrrolidone) with MW > 1,000,000] in 25 mL dry CH_2Cl_2 over a period of 15 min in an ice bath. After the addition was completed, the mixture was stirred for additional 2 h under the same conditions. Then the mixture was filtered and the solid residue was washed with diethyl ether (10 mL) and dried at 80 °C to afford $[PVPH]HSO_4$ as a pale yellow powder (Scheme 1).

General procedure for the synthesis of 4*H*-pyran derivatives

To a mixture of the aldehyde (1 mmol), dimedone or 1,3-cyclohexadione (1 mmol), and malononitrile (1.2 mmol) in H_2O:EtOH (7:3, 5 mL), $[PVPH]HSO_4$ (14 mg, 3.5 mol%) was added and the resulting mixture was stirred at 80 °C. After completion of the reaction [monitored by TLC: *n*-hexane: ethyl acetate (9:3)], the reaction mixture was cooled and filtered to separate the catalyst and product. After, warm EtOH (5 mL) was added to solve the product and filtrate to separate the catalyst. For further purification, products were recrystallized from ethanol.

Results and discussion

Catalyst characterization

FT-IR analysis

The infrared spectra of PVP and $[PVPH]HSO_4$ are shown in Fig. 1. As it can be seen, the modification of PVP to $[PVPH]HSO_4$ increased the number of vibrational modes and brought completely different FT-IR spectrum.

In the case of $[PVPH]HSO_4$, the broad band around 2600–3700 cm^{-1} can be attributed to the OH stretching of the HSO_4 groups. Additional bands at 1179, 1068, 882, and 579 cm^{-1} are assigned to the S=O asymmetric and symmetric stretching, S–OH bending, and symmetric S–O stretching vibrations, respectively [39]. Furthermore, in this spectra, the bands at 1431 (C–N) and 652 (N–C=O) cm^{-1} are disappeared, and a moderate absorption at 1644 cm^{-1} which can be related to the internal imine groups of the pendant rings of the polymer is appeared [39].

Powder X-ray diffraction

The XRD patterns of the PVP and $[PVPH]HSO_4$ samples are shown in Fig. 2. As shown in this figure, incorporation

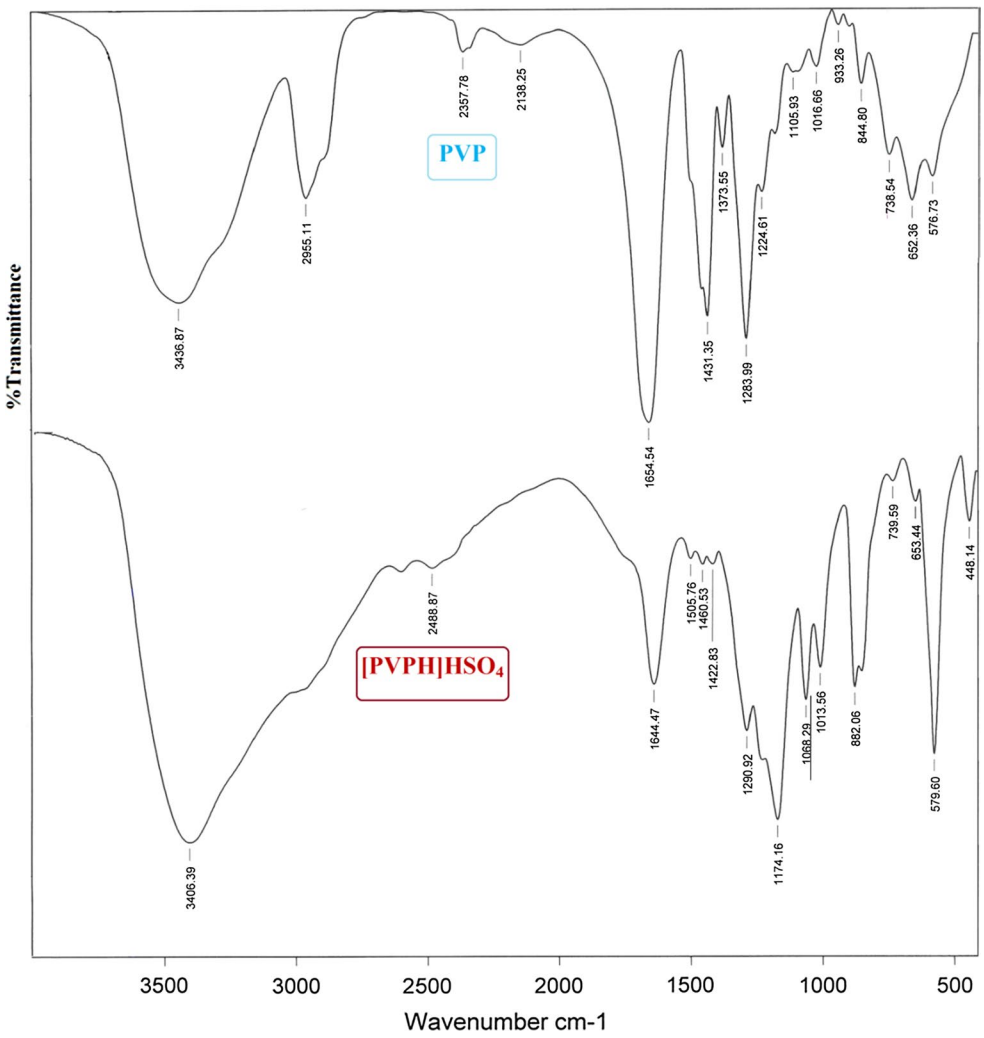


Fig. 1 FT-IR spectra of PVP and [PVPH]HSO_4

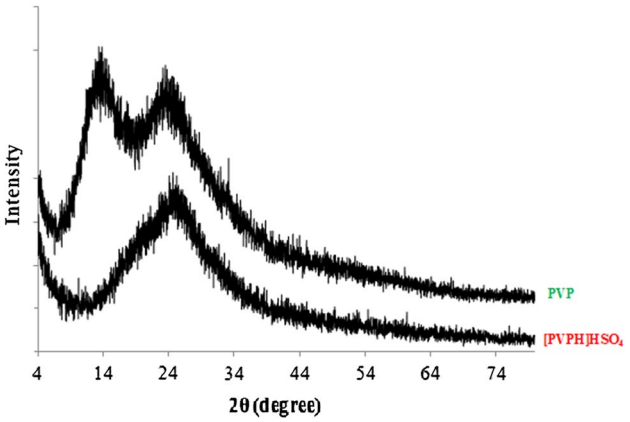


Fig. 2 XRD patterns of PVP and [PVPH]HSO_4

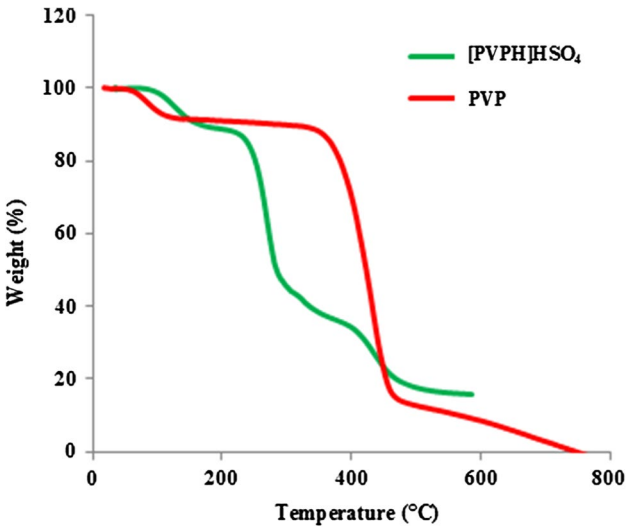


Fig. 3 TGA curves for PVP and [PVPH]HSO_4

of H_2SO_4 leads to some changes in the diffractogram of PVP. The PVP diffraction exhibits a diffused background pattern with two diffraction halos appeared around 2θ equal to 13 and 24 indicating that the polymer is amorphous [40]. After modification of PVP by H_2SO_4, the first peak (2θ around 13) is disappeared, and the broad peak at 2θ around 24 is slightly reduced. These observations imply that the crystallinity of PVP is decreased after reaction with H_2SO_4 [39].

Thermal analysis

The thermal stability of PVP and [PVPH]HSO_4 was determined by TGA curves, as shown in Fig. 3. The TGA curve of PVP displayed a weight loss below 120 °C which is corresponding to the loss of the physically adsorbed water and bonded H_2O within the gallery of PVP. The large proportion of polymer underwent degradation in the range of 370–430 °C. The TGA analysis of [PVPH]HSO_4 is completely different from PVP. The first weight loss which appeared at <120 °C attributed to the loss of moisture contents. In addition, this catalyst showed two major weight loss, the first weight loss occurs after 220 °C, which can be result of the thermal decomposition of the sulfonic groups [39], and the second weight loss appears after 400 °C. Therefore, the molecular decomposition of the catalyst occurred after 400 °C.

SEM analysis

The samples of PVP and [PVPH]HSO_4 were also analyzed by scanning electron microscopy (SEM) with various magnifications for determining the particle shape, surface morphology, and size distribution, as represented in Fig. 4. These images show that with chemical modification, the primary morphology of PVP was completely changed and the particles were aggregated. It should be noted that after the reaction of PVP with H_2SO_4, the polymer became swollen which increased the surface area of the catalyst and finally its catalytic activity.

pH analysis

To 12.5 mL of an aqueous solution of NaCl (1 M) with a primary pH 5.65, [PVPH]HSO_4 (0.25 g) was added and the resulting mixture was stirred for 2 h at room temperature after which the pH of the solution decreased to 1.30. This is equal to a loading of 2.5 mmol H^+/g of the catalyst [39].

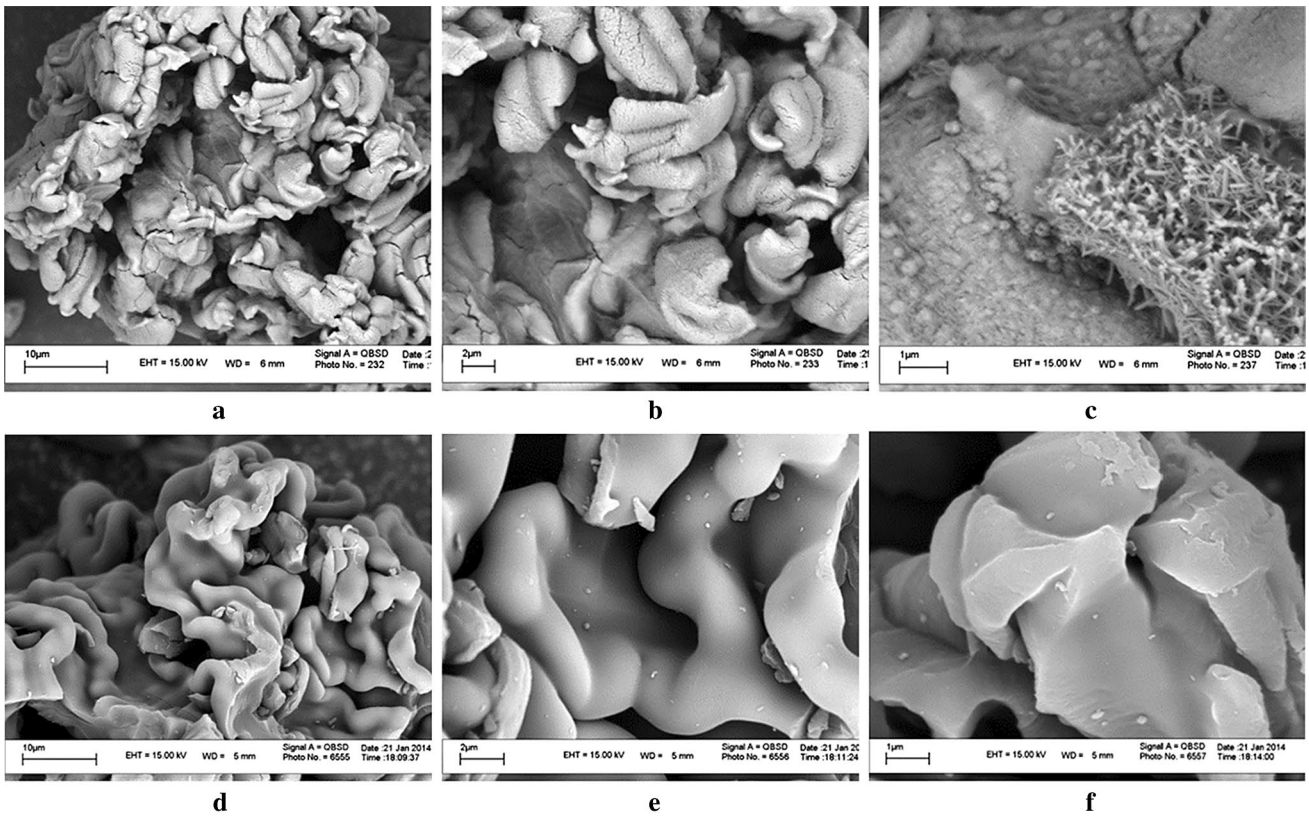


Fig. 4 SEM micrographs of [PVPH]HSO_4 (**a**–**c**) and PVP (**d**–**f**)

Hammett acidity

The Hammett acidity method is an effective way to the acidity strength of an acid in organic solvents, using UV–Vis technique [39]. The Hammett function is defined as

$$H_0 = pK(I)_{aq} + \log\left([I]_s / [IH^+]_s\right)$$

The pK $(I)_{aq}$is the pK_a value of aqueous solution of the indicator, and $[IH^+]_s$ and $[I]_s$ are the molar concentrations of protonated and unprotonated forms of the indicator in the solvent. According to Lambert–Beer's Law, the value of $[I]_s/[IH^+]_s$ can be determined and calculated through UV–Visible spectrum. For this purpose, 4-nitroaniline ($pK(I)_{aq}$ = 0.99) as the basic indicator and CCl_4 as the solvent were chosen. As can be seen in Fig. 5, the maximal absorbance of the unprotonated form of the indicator was observed at 330 nm in CCl_4. When $[PVPH]HSO_4$ as a catalyst was added to the indicator solution, the absorbance of the unprotonated form of the indicator decreased, which indicated that the indicator was partially in the form of $[IH^+]$. The obtained results are listed in Table 1.

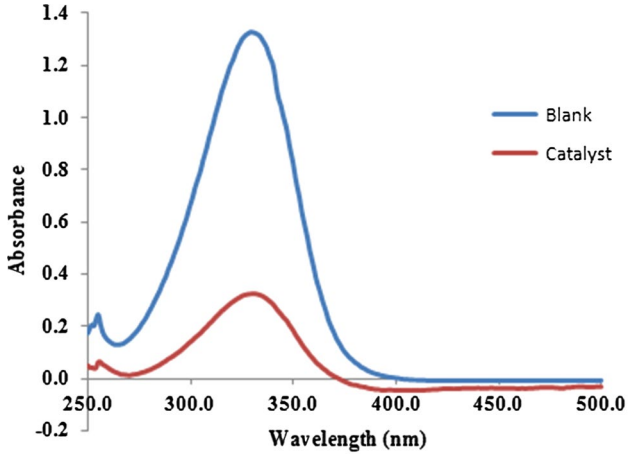


Fig. 5 Absorption spectra of 4-nitroaniline (Blank) and [PVPH]HSO_4(catalyst) in CCl_4

Table 1 Calculation of Hammett acidity function (H_0) for [PVPH]HSO_4

Entry	Catalyst	A_{max}	$[I]_s$ (%)	$[IH^+]_s$ (%)	H_0
1	–	1.329	100	0	–
2	$[PVPH]HSO_4$	0.326	24.52	75.48	0.502

Condition for UV–Visible spectrum measurement: solvent: CCl_4, indicator: 4-nitroaniline [$pK(I)_{aq}$ = 0.99], 1.44 × 10^{-4} mol/L (10 mL); catalyst: $[PVPH]HSO_4$ (10 mg), 25 °C

Catalytic activity

After preparation and characterization of $[PVPH]HSO_4$ and in continuation of our research program on the preparation and use of new catalysts in organic transformations [24, 39], we were interested to study the synthesis of 4*H*-pyran derivatives in the presence of this reagent as a new heterogeneous polymeric catalyst.

In order to optimize the reaction conditions, the reaction of 4-chlorobenzaldehyde, malononitrile, and dimedone as a model reaction was studied at different conditions and the results are tabulated in Table 2.

To illustrate the catalytic activity of $[PVPH]HSO_4$, in the controlled blank experiments, under the same reaction conditions, the model reaction was also carried out in the presence of PVP and H_2SO_4. The results showed that the

Table 2 Effect of temperature, and amounts of the catalyst and solvent in the promotion of the model reaction.[a]

Entry	Catalyst (mg)	Solvent	Time (min)	Yields (%) [b]	Temperature (°C)
1	14 (3.5 mol%)	EtOH	70	91	80
2	14	H_2O	120	50	80
3	14	H_2O:EtOH(3:7)	55	90	80
4	14	H_2O:EtOH(1:1)	30	92	80
5	14	H_2O:EtOH(7:3)	12	96	80
6	14	Solvent-free	13	93 [c]	80
7	14	H_2O:EtOH(7:3)	60	30	r.t.
8	14	H_2O:EtOH(7:3)	42	90	50
9	14	H_2O:EtOH(7:3)	13	96	100
10	8 (2 mol%)	H_2O:EtOH(7:3)	22	91	80
11	20 (5 mol%)	H_2O:EtOH(7:3)	23	95	80
12	25 (6.25 mol%)	H_2O:EtOH(7:3)	39	92	80

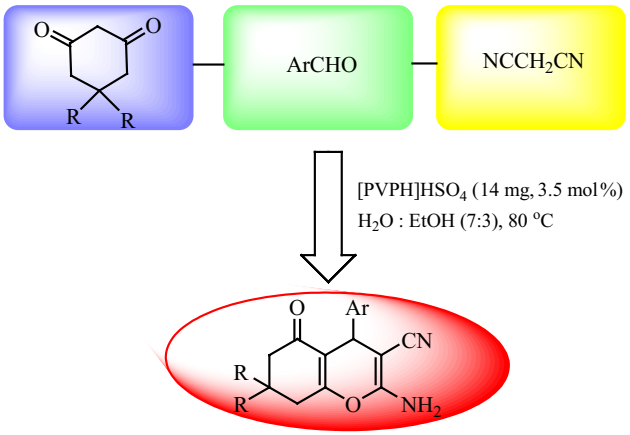
[a] Reaction conditions: 4-chlorobenzaldehyde (1 mmol); malononitrile (1.2 mmol); and dimedone (1 mmol)

[b] GC yield

[c] Xanthene derivative is obtained

Table 3 Reaction of 4-chlorobenzaldehyde with malononitrile and dimedone in the presence of PVP, H_2SO_4, and [PVPH]HSO_4 under optimized conditions

Entry	Reagent (amounts of the reagent)	Time (min)	Yield (%)
1	PVP (14 mg)	120	Trace
2	H_2SO_4 (2.5 mmol)	120	Trace
3	[PVPH]HSO_4 (14 mg, 3.5 mol%)	12	96



Scheme 2 Synthesis of 2-amino-4*H*-pyran derivatives in the presence of [PVPH]HSO

model reaction catalyzed by PVP and H_2SO_4 led to smaller amounts of the products during longer reaction times (Table 3).

On the basis of these studies, the best reaction conditions are selected as shown in Scheme 2.

It should be noted that in the absence of solvent, only the xanthene derivatives were obtained as the products of the reaction (Table 2, entry 6). Also, no significant increase in the yields of the products was observed when the reaction temperature was raised from 80 to 100 °C (Table 2, entry 9). Similarly, the use of higher amounts of the catalyst did not improve the reaction yield (Table 2, entries 11, 12).

After optimization of the reaction conditions, efficiency of this procedure was examined using different types of aldehydes and the results are summarized in Table 4. In all cases, various substituted aromatic aldehydes, containing electron-donating or electron-withdrawing groups, were reacted successfully and gave the corresponding products in high yields during short reaction times. However, aromatic aldehydes with electron-donating groups needed longer reaction times to provide high yields of the corresponding products.

Further, the scope of this one-pot reaction was extended by replacing 1,3-cyclohexadione with dimedone under the same reaction conditions as described above, and the corresponding products were obtained in good yields during acceptable reaction times (Table 4, entries 15–21).

It is important to note that some of the reactions were also tested in larger scales without any difficulty by using only 14 mg (3.5 mol%) of the catalyst. For example, the reaction of 4-chlorobenzaldehyde (Table 4, entry 3, 3 mmol) was investigated in the presence of 3.5 mol% of the catalyst. The reaction was completed within 15 min and the desired product was obtained in 95 % yield.

Finally and in order to show the excellent catalytic activity of this catalyst in comparison with the previously reported ones, we compared the results of the synthesis of 4*H*-pyran derivative of benzaldehyde in the presence of [PVPH]HSO_4 and other reagents with respect to the amounts of the used catalysts, reaction times, yields of the products, and reusability of the catalysts (Table 5).

It should be mentioned that although in some of these cases, the compared reaction is completed in the presence of lower amounts of the catalysts (Table 5, entries 1, 5, 8), these methods suffer from difficulty and/or use of expensive starting materials in the preparation of the catalyst.

In the separate study, we have also compared the stability of [PVPH]HSO_4 with *o*-sulfonated poly(vinylpyrrolidonium) chloride ([PVP-SO_3H]Cl) and find that our new catalyst is very stable in the presence of moisture, so that even after several days, it is not destroyed and its color is not changed at all (Fig. 6).

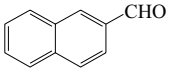
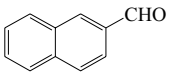
Reusability of the catalyst

In the next step, the reusability of the catalyst was investigated with the model reaction under the optimized conditions. After the separation of the product, the catalyst was washed with diethyl ether, dried, and reused for the same reaction. This process was carried out over six runs and all reactions led to the desired products with high efficiency (Fig. 7).

Conclusion

In conclusion, we have developed a simple and effective method for the synthesis of biologically and pharmacologically active 4*H*-pyran derivatives using [PVPH]HSO_4 as a heterogeneous catalyst in appropriate times with excellent yields. This catalytic system offers advantages such as mild reaction conditions, short reaction times, high yields of the

Table 4 Synthesis of 2-amino -4*H*-pyran derivatives using $[PVPH]HSO_4$ as the catalyst

Entry	Aldehyde	R	Time (min)	Yield(%)[a]	M.P. (°C)		
					Observed	Reported	Ref.
1	C_6H_5CHO	Me	10	96	230–232	227–229	[41]
2	4-FC_6H_4CHO	Me	11	96	202–204	200–203	[16]
3	4-ClC_6H_4CHO	Me	12	96	211–213	213–215	[41]
4	2-ClC_6H_4CHO	Me	15	94	214–216	214–215	[42]
5	4-BrC_6H_4CHO	Me	12	93	206–209	206–208	[41]
6	4-$CH_3OC_6H_4CHO$	Me	23	95	193–195	197–199	[41]
7	4-HOC_6H_4CHO	Me	54	93	200–203	206–208	[41]
8	4-$(CH_3)_2NC_6H_4CHO$	Me	25	89	213–215	210–212	[42]
9	4-$CH_3C_6H_4CHO$	Me	20	94	220–222	216–218	[41]
10	4-CNC_6H_4CHO	Me	24	93	224–226	226–228	[16]
11	4-$NO_2C_6H_4CHO$	Me	13	97	177–179	179–180	[42]
12	3-$NO_2C_6H_4CHO$	Me	13	96	212–214	207–210	[41]
13	PhCH=CHCHO	Me	16	88	180–183	182–184	[42]
14		Me	28	90	258–260	258–260	[14]
15	4-ClC_6H_4CHO	H	13	92	220–222	224–226	[14]
16	2-ClC_6H_4CHO	H	15	96	214–216	210–212	[14]
17	4-$CH_3C_6H_4CHO$	H	22	89	235–237	232–233	[14]
18	4-$CH_3OC_6H_4CHO$	H	28	91	188–190	190–192	[43]
19	4-$NO_2C_6H_4CHO$	H	14	89	230–232	234–236	[14]
20	4-CNC_6H_4CHO	H	22	88	235–237	234–236	[43]
21		H	35	90	253–255	254–255	[14]

Reaction conditions: aldehyde (1 mmol), malononitrile (1.2 mmol), dimedone or 1,3-cyclohexadione (1 mmol), catalyst (14 mg, 3.5 mol%), water:ethanol (7:3 = 5 mL), 80 °C

[a] Isolated yields

Table 5 Comparison of the results obtained for the synthesis of 4*H*-pyran derivative of benzaldehyde using $[PVPH]HSO_4$ with the other catalysts reported in the literature

Entry	Catalyst amount (mol%)	Solvent	Recovery	Time (min)	Yield (%)	Ref.
1	Fe_3O_4@SiO_2/DABCO (5 mg)	H_2O[a]	6	25	90	[44]
2	(SBPPSP) (4.3)	H_2O:EtOH	3	25	90	[45]
3	CA-SiO_2 (16)	H_2O:EtOH	–	17	93	[11]
4	Fe_3O_4/SiO_2-Met Nps (30 mg)	H_2O:EtOH	6	60	86	[25]
5	[γ-Fe_2O_3@Hap-$Si(CH_2)_3$ AMP)] (1.5)	H_2O	10	10	80	[15]
6	SO_4^{2-}/MCM-41(25 mg)	EtOH	3	50	86	[16]
7	PPA-SiO_2 (10 mg)	H_2O	3	13	80	[12]
8	SB-DABCO (6)	EtOH	15	35	96	[14]
9	SiO_2-Pr-SO_3H (3 mg)	H_2O	–	15	97	[17]
10	$[PVPH]HSO_4$ (14 mg, 3.5 mol%)	H_2O:EtOH[b]	6	10	96	This work

Reaction conditions: benzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1.2 mmol), reflux

[a] 80 °C

Fig. 6 Comparison of the stability and water adsorption of two forms of modified PVP

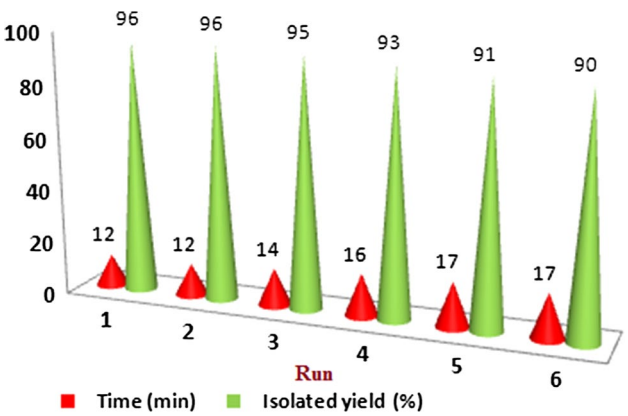


Fig. 7 Reusability of the $[PVPH]HSO_4$ in the preparation of 4*H*-pyran derivative of 4-chlorobenzaldehyde (Table 3, entry 3)

products, good reusability, and easy preparation of the catalyst which makes it a useful and attractive process for the preparation of these compounds.

Acknowledgments The authors are Grateful to the Research Council of the University of Guilan for partial support of this study.

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