TÜBİTAK

Turkish Journal of Chemistry

http://journals.tubitak.gov.tr/chem/

Research Article

Turk J Chem
(2013) 37: 756 – 764

doi:10.3906/kim-1206-28

Poly(4-vinylpyridine)-supported dual acidic ionic liquid: an environmentally friendly heterogeneous catalyst for the one-pot synthesis of 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols)

Kaveh PARVANAK BOROUJENI,* Pegah SHOJAEI
Department of Chemistry, Shahrekord University, Shahrekord, Iran

Received: 14.06.2012 • **Accepted:** 13.04.2013 • **Published Online:** 16.09.2013 • **Printed:** 21.10.2013

Abstract: A poly(4-vinylpyridine)-supported Brønsted ionic liquid was easily prepared from its starting materials and used as a novel, highly efficient, and reusable heterogeneous catalytic system for the synthesis of 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols) from the condensation reaction between aromatic aldehydes and 2 equivalents of 3-methyl-l-phenyl-5-pyrazolone.

Key words: 3-Methyl-l-phenyl-5-pyrazolone, aldehydes, ionic liquid, one-pot synthesis, heterogeneous catalysis

1. Introduction

Recently, various ionic liquids have attracted significant attention as an alternative reaction medium for homogeneous catalysis. One type is Brønsted acidic ionic liquids. These ionic liquids are of special importance because they possess simultaneously proton acidity and the characteristic properties of an ionic liquid.[1,2] Among them, SO_3H-functionalized ionic liquids with a hydrogen sulfate counteranion are of particular value as a class of dual acidic functionalized ionic liquids, because the existence of both SO_3H functional groups and hydrogen sulfate counteranions can enhance their catalytic acidities.[3–5] Thus, they are designed to replace traditional mineral liquid acids such as sulfuric acid and hydrochloric acid in chemical procedures. However, despite having widespread application in organic synthesis, most of them suffer from one or more of the following drawbacks: laborious work-up procedures, difficulty of recovery and recycling, disposal of spent catalyst, difficulty of handling, and corrosion problems. Thus, these shortcomings make them a prime target for heterogenization.[6–9]

2,4-Dihydro-3H-pyrazol-3-one derivatives including 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols) are known to possess a wide range of biological activities and are used as gastric secretion stimulatory,[10] anti-inflammatory,[11] antidepressant,[12] antibacterial,[13] antifilarial,[14] antitumor,[15] and antiviral agents.[16] Moreover, the corresponding 4,4'-(arylmethylene)bis(1H-pyrazol-5-ols) are used as insecticides,[17] pesticides,[18] dyestuffs,[19] and the chelating and extracting reagents for different metal ions.[20] One-pot tandem Knoevenagel-type condensation/Michael reaction between aromatic aldehydes with 2 equivalents of 3-methyl-l-phenyl-5-pyrazolone is one of the most pivotal preparation methods of 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols). In the absence of catalyst, this reaction is very slow (4–24 h in refluxing ethanol, benzene, or water and a further 24 h under ambient temperature) and the products are obtained in moderate yields.[21–23] Sodium dodecyl sulfate

*Correspondence: parvanak-ka@sci.sku.ac.ir

as a surfactant catalyst has been employed to accomplish this reaction in aqueous medium at 100 °C.[24] Furthermore, Elinson et al. utilized an electrocatalytic procedure for the preparation of 4,4'-(arylmethylene)bis(1H-pyrazol-5-ols).[25] In addition, ceric ammonium nitrate,[26] tetramethyl-tetra-3,4-pyridinoporphyrazinato copper (II) methyl sulfate,[27] silica-bonded S-sulfonic acid,[28] ([3-(3-silicapropyl)sulfanyl]propyl) ester,[29] silica sulfuric acid,[30] zanthan sulfuric acid,[31] and 3-aminopropylated silica gel[32] have been reported as catalysts for this reaction to date. Although these methods are suitable for certain synthetic conditions, there exist some drawbacks such as low yields, high reaction temperature, long reaction times, drastic reaction conditions, tedious work-up leading to the generation of large amounts of toxic waste, and the use of unrecyclable, hazardous, or difficult to handle catalysts. In view of this, there is a demand for clean processes utilizing ecofriendly and green catalysts for this useful reaction.

In a continuation of our work on the development of efficient and environmentally benign procedures using poly(vinylpyridine)-supported reagents and catalysts,[33] herein we report the synthesis of poly(4-vinylpyridine-*co*-1-sulfonic acid butyl-4-vinylpyridinium)hydrogen sulfate ($[P_4VPy\text{-}BuSO_3H]HSO_4$) from the reaction of poly(4-vinylpyridine) (P_4VPy, 2% divinylbenzene) with 1,4-butane sultone/H_2SO_4. $[P_4VPy\text{-}BuSO_3H]HSO_4$ was used as a dual acidic ionic liquid catalyst for the synthesis of 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols) by 2-component 1-pot tandem Knoevenagel-type condensation/Michael reaction between various aromatic aldehydes with 3-methyl-l-phenyl-5-pyrazolone.

2. Experimental

2.1. General

The chemicals were either prepared in our laboratory or were purchased from Merck and Fluka. Reaction monitoring and purity determination of the products were accomplished by GLC or TLC on silica-gel polygram $SILG/UV_{254}$ plates. Gas chromatography was recorded on a Shimadzu GC 14-A. IR spectra were obtained by a Shimadzu model 8300 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-300 spectrometer. A Leco sulfur analyzer was used for the measurement of sulfur in catalyst. Melting points were determined on a Fisher-Jones melting-point apparatus and are uncorrected. Thermal gravimetric analysis (TGA) was performed by a Stanton Redcraft STA-780 with a 20 °C/min heating rate in N_2. The shape and surface morphology of the samples were examined on a scanning electron microscope (SEM) (Hitachi S-3400N, Japan).

2.2. Synthesis of $[P_4VPy\text{-}BuSO_3H]HSO_4$

In a round bottomed flask (50 mL) equipped with a reflux condenser was added 1 g of the P_4VPy (2% DVB) to 1,4-butane sultone (1.5 mL) and the mixture was stirred at 100 °C for 30 h, filtered, washed with distilled water (20 mL), and dried at 80 °C overnight. Afterwards, H_2SO_4 (3 M, 5 mL) was added to the obtained resin and the mixture was stirred at room temperature for 2 h, filtered, washed with distilled water (20 mL), and dried at 80 °C overnight to give $[P_4VPy\text{-}BuSO_3H]HSO_4$.

2.3. Typical procedure for synthesis of 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols)

To a solution of an aldehyde (1 mmol), 3-methyl-l-phenyl-5-pyrazolone (2 mmol), and ethanol (3 mL) was added $[P_4VPy\text{-}BuSO_3H]HSO_4$ (0.1 mmol) and the resulting mixture was magnetically stirred under reflux

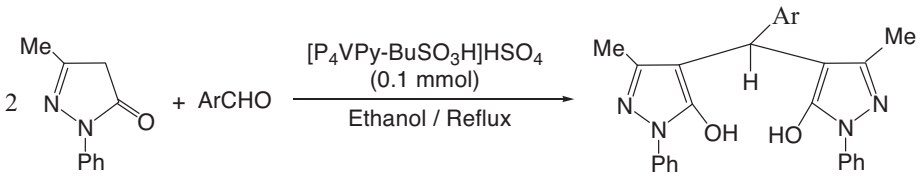
conditions. The progress of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was filtered off and washed with ethanol (2 × 5 mL), and the filtrate was concentrated on a rotary evaporator under reduced pressure to give the crude product. Whenever required, the products were purified by column chromatography on silica gel (n-hexane/EtOAc) or by recrystallization from ethanol.

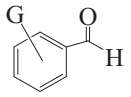
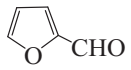
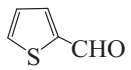
Representative spectral data of some of the obtained compounds are given below.

4,4'-(Phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table 1, entry 1a): IR (KBr, cm^{-1}): 3410, 3080, 2910, 2895, 1599, 1499, 1480, 1418, 1283, 1025, 739, 700; ^{1}H NMR (300 MHz, DMSO-d6): δ = 2.35 (6H, s), 4.99 (1H, s), 7.21–7.29 (7H, m), 7.47 (4H, t, J = 7.78 Hz), 7.72 (4H, d, J = 7.97 Hz), 13.99 (2H, br, OH).

4,4'-[(4-Chlorophenyl)methylene]bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table 1, entry 1d): IR (KBr, cm^{-1}): 3440, 3050, 2930, 2895, 1589, 1499, 1420, 1298, 8104, 749, 698; ^{1}H NMR (300 MHz, DMSO-d6): δ = 2.35 (6H, s), 4.99 (1H, s) 7.29, (4H, d, J = 8.10 Hz), 7.37 (2H, d, J = 7.90 Hz), 7.45 (4H, t, J = 7.01 Hz), 7.75 (4H, d, J = 7.50 Hz), 13.95 (2H, br, OH).

Table 1. Synthesis of 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols).



Entry	ArCHO	Time (h)	Yield (%)[a]	M.p. (°C) (Lit.[Ref])
1				
	a: G= H	0.7	95	171-173 (170-172[28])
	b: G= 4-CH_3	0.8	92	204-206 (202-204[28])
	c: G=4-OCH_3	0.9	92	177-179 (173-175[23])
	d : G= 4-Cl	0.8	95	216-218 (215-217[29])
	e : G= 2-Cl	0.9	92	235-237 (236-237[24])
	f: G= 4-OH	1	92	152-154 (149-150[23])
	g: G= 4-NO_2	0.6	97	226-228 (230-232[24])
	h: G= 4-CN	0.6	97	211-213 (210-212[29])
2		0.8	90	190-192 (189-190[26])
3		0.8	90	184-185 (181-183[28])

[a] Isolated yields. All products are known compounds and were identified by comparison of their physical and spectral data with those of the authentic samples.

4,4'-[(4-Nitrophenyl)methylene]bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table 1, entry 1g): IR (KBr, cm^{-1}): 3450, 3080, 2930, 2898, 1600, 1499, 1420, 1348, 749, 698; ^{1}H NMR (300 MHz, DMSO-d6):

δ = 2.41 (6H, s), 5.16 (1H, s), 7.29–7.32 (2H, m), 7.45 (4H, t, J = 6.91 Hz), 7.58 (2H, d, J = 8.01 Hz), 7.71–7.78 (4H, d, J = 7.51 Hz), 8.15 (2H, d, J = 8.01 Hz), 13.88 (2H, br, OH).

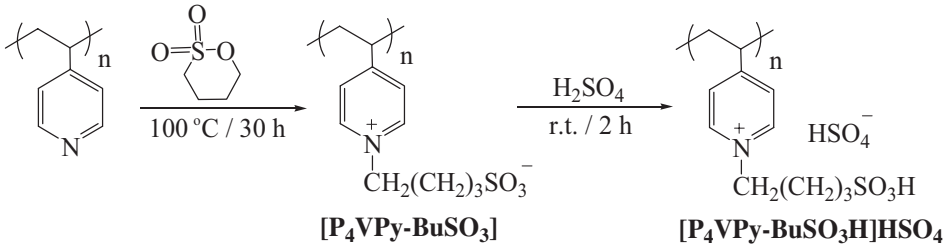
4,4'-[(4-Cyanophenyl)methylene]bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table 1, entry 1h): IR (KBr, cm^{-1}): 3430, 3098, 2928, 2895, 2238, 1595, 1499, 1420, 1299, 820, 760, 700; ^{1}H NMR (300 MHz, DMSO-d6): δ = 2.35 (6H, s), 5.11 (1H, s), 7.28 (2H, t, J = 7.37 Hz), 7.42 (4H, d, J = 7.88 Hz), 7.45–7.50 (6H, m), 7.79 (2H, d, J = 8.38 Hz), 13.91 (2H, br, OH).

4,4'-[(2-Furyl)methylene]bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table 1, entry 2): IR (KBr, cm^{-1}): 3430, 3090, 2930, 2895, 1595, 1498, 1418, 1288, 785, 698; ^{1}H NMR (300 MHz, DMSO-d6): δ = 2.36 (6H, s), 5.11 (1H, s), 6.14–6.19 (1H, m), 6.39–7.11 (1H, m), 7.28 (2H, t, J = 6.05 Hz), 7.48–7.56 (5H, m), 7.78 (4H, d, J = 8.06 Hz), 13.89 (2H, br, OH).

4,4'-[(2-Thienyl)methylene]bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table 1, entry 3): IR (KBr, cm^{-1}): 3430, 3086, 2930, 2895, 1599, 1498, 1420, 1300, 1289, 785, 700; ^{1}H NMR (300 MHz, DMSO-d6): δ = 2.38 (6H, s), 5.18 (1H, s), 6.79–6.83 (1H, m), 6.95–7.08 (1H, m), 7.29–7.33 (3H, m), 7.49 (4H, t, J = 7.88 Hz), 7.81 (4H, d, J = 7.88 Hz), 13.94 (2H, br, OH).

3. Results and discussion

The synthetic routes for $[P_4VPy\text{-}BuSO_3H]HSO_4$ are shown in Scheme 1. At the first stage, commercially available P_4VPy (2% DVB) reacted with 1,4-butane sultone to give poly(4-vinylpyridine-*co*-1-sulfonate butyl-4-vinylpyridinium) ($[P_4VPy\text{-}BuSO_3]$). The resulting pale yellow solid was analyzed by elemental analysis to quantify the percentage loading of the sulfonate moiety by measuring the sulfur content, giving 0.9 mmol sulfonate moiety per gram. In a second step, the $[P_4VPy\text{-}BuSO_3]$ was further treated with H_2SO_4 to form $[P_4VPy\text{-}BuSO_3H]HSO_4$ as a white cream solid. The acidic sites loading in $[P_4VPy\text{-}BuSO_3H]HSO_4$ obtained by means of acid–base titration was found to be 1.7 mmol/g.



Scheme 1. Synthesis of $[P_4VPy\text{-}BuSO_3H]HSO_4$.

For comparison, FT-IR spectra of the P_4VPy and $[P_4VPy\text{-}BuSO_3H]HSO_4$ are presented in Figure 1. As can be seen in the spectrum of $[P_4VPy\text{-}BuSO_3H]HSO_4$, new peaks appeared at 1160, 1200, and 1220 cm^{-1}, which can be assigned to S=O stretching vibration.[9] A new peak also appeared at 1645 cm^{-1}, which is ascribed to the C-N (pyridine-CH_2-) bond absorption. This observation confirms the N-alkylation of the pyridine ring.

Figure 2 shows the TGA curves of P_4VPy and $[P_4VPy\text{-}BuSO_3H]HSO_4$. A weight loss was observed in each case at around 100 °C due to loss of moisture. In the case of $[P_4VPy\text{-}BuSO_3H]HSO_4$, the second weight loss started at about 200 °C, and is mainly assigned to the decomposition of alky-sulfonic acid groups and hydrogen sulfate counteranions. In TGA curves of P_4VPy and $[P_4VPy\text{-}BuSO_3H]HSO_4$ the last weight losses

were observed at about 350 °C and 420 °C, respectively, which are attributed to the degradation of polymer backbone.

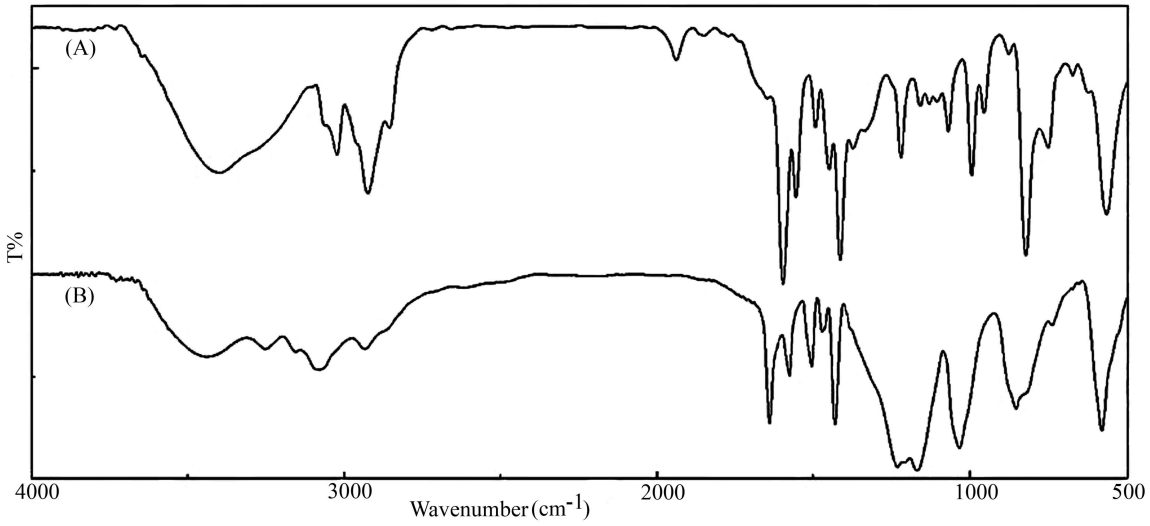


Figure 1. FT-IR spectra of (a) P_4VPy and (b) $[P_4VPy\text{-}BuSO_3H]HSO_4$.

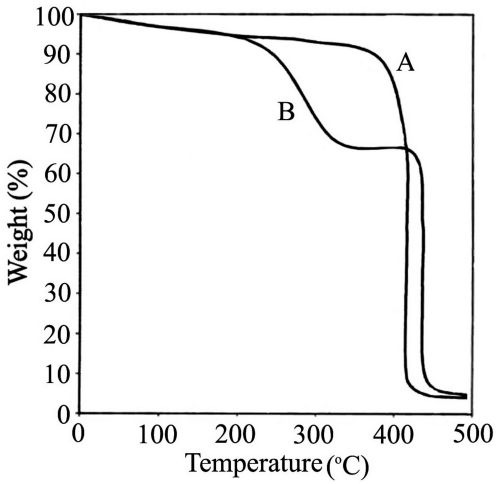


Figure 2. TGA curves of P_4VPy (a) and $[P_4VPy\text{-}BuSO_3H]HSO_4$ (b).

The SEM images of P_4VPy and $[P_4VPy\text{-}BuSO_3H]HSO_4$ are provided in Figure 3. From the image of P_4VPy, the surface of P_4VPy is somewhat coarse and irregular with many pores on the surface, whereas the SEM photograph of $[P_4VPy\text{-}BuSO_3H]HSO_4$ shows that with chemical modification the primary structure of P_4VPy was changed and the polymer support survived the sequence of functionalization steps.

In order to explore the catalytic activity of $[P_4VPy\text{-}BuSO_3H]HSO_4$, we studied the condensation reaction of aromatic aldehydes with 3-methyl-l-phenyl-5-pyrazolone (Table 1). The best results in terms of yield as well as reaction time were obtained by refluxing ethanol, which proved to be the solvent of choice among the other organic solvents. The optimum molar ratio of $[P_4VPy\text{-}BuSO_3H]HSO_4$ to aldehyde was found to be 0.1:1. Various types of substituted benzaldehydes (entries 1a–h) reacted with 3-methyl-l-phenyl-5-pyrazolone to give

the corresponding 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols). It was pleasing to observe that even acid sensitive aldehydes, such as 2-furyl and 2-thienyl carbaldehyde, were smoothly converted into the corresponding products, a conversion that is otherwise problematic in the presence of strong acid catalysts (entries 2 and 3). As shown in Table 1 (entry 1), the aromatic aldehydes with electron-withdrawing groups reacted faster than the aromatic aldehydes with electron-releasing groups. This observation can be rationalized on the basis of the mechanistic details of the reaction (Scheme 2). An aldehyde was first activated by $[P_4VPy\text{-}BuSO_3H]HSO_4$. Nucleophilic addition of 3-methyl-l-phenyl-5-pyrazolone to activated aldehyde was followed by the loss of H_2O generated benzylidene intermediate (I), which was further activated by $[P_4VPy\text{-}BuSO_3H]HSO_4$. Then the 1,4-nucleophilic addition of a second molecule of 3-methyl-l-phenyl-5-pyrazolone on activated intermediate I, in the Michael addition fashion, afforded the synthesis of 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols). The electron-withdrawing groups substituted on aromatic aldehyde in intermediate I increase the rate of the 1,4-nucleophilic addition reaction because the alkene LUMO is at lower energy in their presence compared with electron-donating groups.[34]

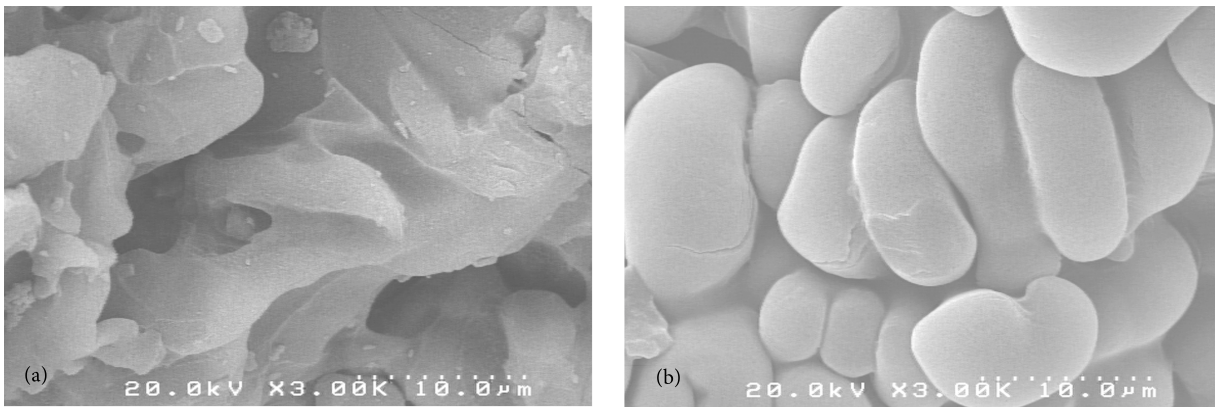
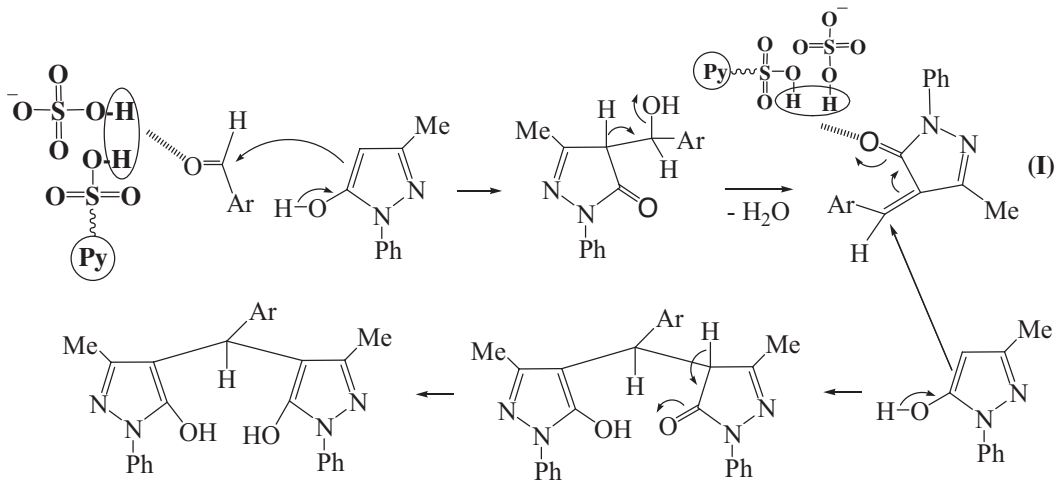


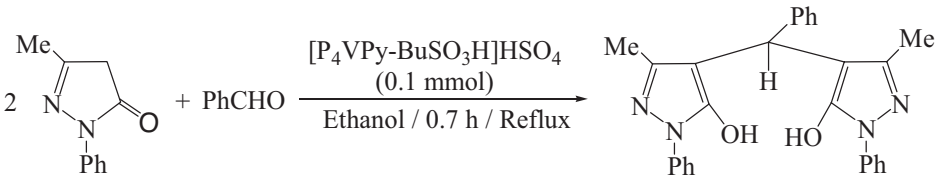
Figure 3. SEM photographs of P_4VPy (a) and $[P_4VPy\text{-}BuSO_3H]HSO_4$ (b).



Scheme 2. Suggested mechanism for the preparation of 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols) catalyzed by $[P_4VPy\text{-}BuSO_3H]HSO_4$.

In order to confirm the true heterogeneity of the catalytic systems (i.e. the absence of leaching of the acidic sites into the reaction mixture), $[P_4VPy\text{-}BuSO_3H]HSO_4$ was added to ethanol and the mixture was stirred for 2 h under reflux conditions. Then the catalyst was filtered off and the filtrate was analyzed for its acid content, which showed a negligible release of the acidic sites. The filtrate was found to be inactive for the condensation of 3-methyl-l-phenyl-5-pyrazolone with aldehydes. These observations indicate that $[P_4VPy\text{-}BuSO_3H]HSO_4$ is stable under the reaction conditions, and there is no leaching of acid moieties during reactions.

$[P_4VPy\text{-}BuSO_3H]HSO_4$ recovered after a reaction can be washed with ethanol and used again at least 5 times without any noticeable loss of catalytic activity (Scheme 3).



Run No.	1	2	3	4	5
Isolated Yield (%)	95	93	92	90	90

Scheme 3. Recyclability of $[P_4VPy\text{-}BuSO_3H]HSO_4$ in the preparation of 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols).

A comparison of the efficiency of $[P_4VPy\text{-}BuSO_3H]HSO_4$ catalyst with some of those reported in the literature is given in Table 2. As seen, in addition to having the general advantages attributed to solid catalysts, $[P_4VPy\text{-}BuSO_3H]HSO_4$ has good efficiency compared to many of those reported catalysts in the condensation of benzaldehyde with 2 equivalents of 3-methyl-l-phenyl-5-pyrazolone.

Table 2. Comparison of the efficiencies of a number of different reported catalysts with that of $[P_4VPy\text{-}BuSO_3H]HSO_4$ in the condensation of benzaldehyde with 2 equivalents of 3-methyl-l-phenyl-5-pyrazolone.

Entry	Cat./Solv./Temp.	Time (h)	Yield (%)
1	Sodium dodecyl sulfate/H_2O/Reflux	1	86.8[24]
2	Ceric ammonium nitrate/H_2O/r.t.	0.25	92[26]
3	[Cu(3,4-tmtppa)]$(MeSO_4)_4$/H_2O/90 °C	0.50	95[27]
4	Silica-bonded S-sulfonic acid/EtOH/Reflux	2	80[28]
5	[3-(3-Silicapropyl)sulfanyl]propyl)ester/EtOH/Reflux	3	90[29]
6	Silica sulfuric acid/EtOH/H_2O/70 °C	1	93[30]
7	Zanthan sulfuric acid/EtOH/Reflux	0.25	95[31]
8	3-Aminopropylated silica gel/CH_3CN/r.t.	0.16	98[32]
9	$[P_4VPy\text{-}BuSO_3H]HSO_4$/EtOH/Reflux	0.70	95

4. Conclusion

We synthesized $[P_4VPy\text{-}BuSO_3H]HSO_4$ as a novel heterogeneous acid catalyst that favorably combines the properties of ionic liquids and the advantages of solid supports. This solid catalyst can act as an efficient catalyst for the synthesis of 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols). The significant advantages of this methodology are high yields, short reaction times, simple work-up procedure, and easy preparation and

handling of the catalyst. In addition, the use of this catalyst resulted in a reduction in the unwanted and hazardous waste that is produced during conventional homogeneous processes. Finally, this solid catalyst can be recovered unchanged and used again.

Acknowledgment

The authors thank the Research Council of Shahrekord University for its partial support of this work.

References

1. Hallett, J. P., Welton T. *Chem. Rev.* **2011**, *111*, 3508–3576.
2. Wilkes, J. S. *J. Mol. Catal. A: Chem.* **2004**, *214*, 11–17.
3. Liu, X. M.; Liu, M.; Guo, X. W.; Zhou, J. X. *Catal. Commun.* **2008**, *9*, 1–7.
4. Wang, Y. Y.; Gong, X.; Wang, Z.; Dai, L. Y. *J. Mol. Catal. A: Chem.* **2010**, *322*, 7–16.
5. Hajipour, A. R.; Ghayeb, Y.; Sheikhan, N. S.; Ruoho, A. E. *Tetrahedron Lett.* **2009**, *50*, 5649–5651.
6. Chrobok, A.; Baj, S.; Pudło, W.; Jarzębski, A. *Appl. Catal. A: Gen.* **2009**, 366, 22–28.
7. Amarasekara, A. S.; Owereh, O. S. *Catal. Commun.* **2010**, *11*, 1072–1075.
8. Kotadia, D. A.; Soni, S. S. *J. Mol. Catal. A: Chem.* **2012**, *353–354*, 44–49.
9. Zang, Q. H.; Luo, J.; Wei, Y. *Green Chem.* **2010**, *12*, 2246–2254.
10. Rosiere, C. E.; Grossman, M. I. *Science* **1951**, *113*, 651.
11. Sugiura, S.; Ohno, S.; Ohtani, O.; Izumi, K.; Kitamikado, T.; Asai, H.; Kato, K. *J. Med. Chem.* **1977**, *20*, 80–85.
12. Bailey, D. M.; Hansen, P. E.; Hlavac, A. G.; Baizman, E. R.; Pearl, J.; Defelice, A. F.; Feigenson, M. E. *J. Med. Chem.* **1985**, *28*, 256–260.
13. Mahajan, R. N.; Havaldar, F. H.; Fernandes, P. S. *J. Indian Chem. Soc.* **1991**, *68*, 245–246.
14. Chauhan, P. M. S.; Singh, S.; Chatterjee, R. K. *Indian J. Chem., Sect. B* **1993**, *32*, 858–861.
15. Manfredini, S.; Bazzanini, R.; Baraldi. P. G.; Bonora, M.; Marangoni, M.; Simoni, D.; Pani, A.; Scintu, F.; Pinna, E.; Pisano, L.; La Colla, P. *Anticancer Drug Des.* **1996**, *11*, 193–204.
16. Sujatha, K.; Shanthi, G.; Selvam, N. P.; Manoharan, S.; Perumal, P. T.; Rajendran, M. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 4501–4503.
17. Lubs, H. A., Ed.; *The Chemistry of Synthetic Dyes and Pigments*; American Chemical Society, Washington, DC, 1970.
18. Londershausen, M. *Pestic. Sci.* **1996**, *48*, 269–292.
19. Garnovskii, A. D.; Uraev, A. I.; Minkin, V. I. *Arkivoc* **2004**, *iii*, 29–41.
20. Sivaprasad, G.; Perumal, P. T.; Prabavathy, V. R.; Mathivanan, N. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 6302–6305.
21. Pavlov, P. T.; Goleneva, A. F.; Lesnov, A. E.; Prokhorova, T. S. *Pharm. Chem. J. (Engl. Trans.)*, **1998**, *32*, 370–372.
22. Buzykin, B. I.; Lonshchakova, T. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Trans.)*, **1971**, 2224–2226.
23. Tale, N. P.; Tiwari, G. B.; Karade, N. N. *Chin. Chem. Lett.* **2011**, *22*, 1415–1418.
24. Wang, W.; Wang, S.-X.; Qin, X.-Y. Li, J.-T. *Synth. Commun.* **2005**, *35*, 1263–1269.
25. Elinson, M. N.; Dorofeev, A. S.; Nasybullin, R. F.; Nikishin, G. I. *Synthesis* **2008**, *12*, 1933–1937.
26. Sujatha, K.; Shanthi, G.; Selvam, N. P.; Manoharan, S. S.; Perumal, P. T.; Rajendran, M. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 4501–4503.
27. Sobhani, S.; Safaei, E.; Hasaninejad, A. R.; Rezazadeh, S. *J. Organomet. Chem.* **2009**, *18*, 3027–3031.

28. Niknam, K.; Saberi, D.; Sadegheyan, M.; Deris, A. *Tetrahedron Lett.* **2010**, *51*, 692–694.
29. Tayebi, S.; Baghernejadi, M.; Saberi, D.; Niknam, K. *Chin. J. Catal.* **2011**, *32*, 1477–1483.
30. Niknam, K.; Mirzadeh, S. *Synth. Commun.* **2011**, *41*, 2403–2413.
31. Suresh Kuarm, B.; Rajitha, B. *Synth. Commun.* **2012**, *42*, 2382–2387.
32. Sobhani, S.; Hasaninejad, A. R.; Faal Maleki, M.; Pakdin Parizi, Z. *Synth. Commun.* **2012**, *42*, 2245–2255.
33. Tamami, B.; Parvanak Boroujeni, K. *Iran. Polym. J.* **2009**, *18*, 191–206.
34. Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*, University Science Books, California, 2006.