IRANIAN JOURNAL OF CATALYSIS



Compiled by Seyedeh Zahra Dalil Heirati

Seyedeh Zahra Dalil Heirati was born in Rasht, Guilan, I. R. Iran (1982). She completed her B.Sc. in pure chemistry from Razi University, Kermanshah (2004). She received her M.Sc. degree in organic chemistry from the University of Guilan (2009). She is currently working towards her Ph.D. under the supervision of Prof. Farhad Shirini and Prof. Abdollah Fallah Shojaei at the University of Guilan. Her current researches focus on the development of new catalysts and synthetic methodologies.

College of chemistry, University of Guilan, Rasht 41335-19141, Iran.

E-mail: s.z.dalilheirati@gmail.com



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

Replacement of conventional, toxic and polluting Brönsted and *Lewis* acidic catalysts with eco-friendly reusable solid acid catalysts is an essential requirement in the development of green chemistry. Solid acid catalysts due to having all factors which are important in industry such as ease of the product separation, and recycling of the catalyst, and also environmental compatibility can be replaced with conventional Brönsted and Lewis acid catalysts [1]. The combination of high efficiency of the catalyst with its easy separation from the reaction products and the possibility of recycling is one of the key goals in the design of a new catalyst. Cross-linked polymers with providing the above mentioned requirements can play an important and useful role in chemistry.

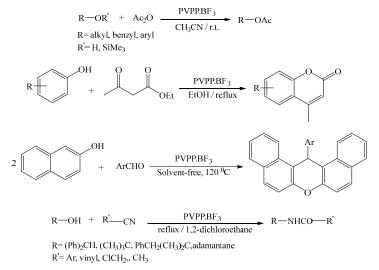
Cross-linked poly(vinylpyrrolidone) (PVP) is heterogeneous and polymeric support that has been widely used in the preparation of numerous reagents and catalysts because of its commercial availability, stability, reasonable high loading capacity, good physicochemical structure facile and functionalization. Beside various applications in industry such as stabilizer, sugar coating and film coating [2], this polymer can be an attractive support to immobilize mineral acids because of the basic nature of its pyridyl group. Therefore, recent applications of poly(vinylpyrrolidone) as a reagent support have been extensively investigated [3,4]. In this spotlight we have a brief review on the applications of the modified poly(vinylpyrrolidone) in the promotion of some of the important organic transformations.

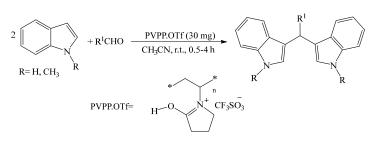
(A) Mokhtary et al. published several papers on the application of the poly(vinylpolypyrrolidone)-bound boron trifluoride (PVPP-BF₃) as efficient, noncorrosive, and stable solid catalyst in some organic reactions such as the acylation of alcohols, phenols and trimethylsilyl ethers with acetic anhydride [5], the synthesis of coumarins via Pechmann condensations of phenols with ethyl acetoacetate [6], the synthesis of 14-aryl-14H-dibenzo [a,j] xanthenes and bis(naphthalen-2-yl-sulfane) derivatives [7], and preparing amides by the reaction of nitriles with benzhydrol and tertiary alcohols via Ritter reaction [8]. Excellent yields, easy work-up and reusability and stability of the catalyst are some advantages of this method.

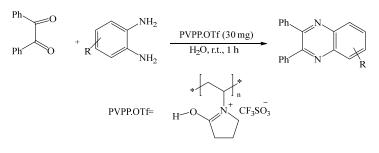
(B) Poly(vinylpolypyrrolidone)-supported triflic acid (PVPP.OTf) reported by Khaksar et al. was used as a simple, environmentally friendly and efficient catalyst for the synthesis of bis-indolyl methane derivatives by the reaction of indole or *N*-methyl indole with aldehydes [9]. Some advantages of this catalyst are short reaction times, ease of the product isolation/purification, no side reactions, low costs and simplicity in the process and handling.

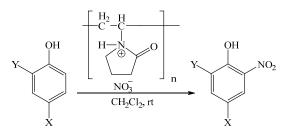
(C) Poly(vinylpolypyrrolidone)-supported triflic acid (PVPP.OTf) was found to be useful as a recyclable heterogeneous catalyst for the rapid and efficient synthesis of quinoxaline derivatives. Operational simplicity, wide substrate scope, and high yields are the advantages of this procedure [10].

(D) Nitration of the substituted phenols is reported by Nikoorazm et al. in dichloromethane at room temperature using supported nitric acid on poly(vinylpyrrolidone) efficient. as an environmentally friendly, mild nitrating agent. The methodology has some advantages such as mild and heterogeneous conditions, simple preparation of the supported nitrating agent, inexpensive and environmentally catalyst, and easy workup [11].







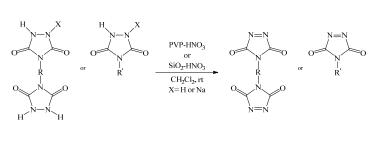


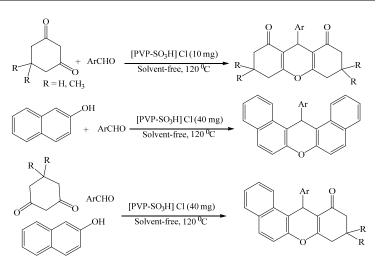
(E) Ghorbani-Choghamarani et al. described an efficient and heterogenous method for the selective oxidation of urazoles and bis-urazoles to the corresponding triazolinediones by supported nitric acid on silica gel (SiO₂-HNO₃) and / or poly(vinylpyrrolidone) (PVP-HNO₃). This method offers the advantages of shorter reaction times, high selectivity, nontoxicity, cost-effective reagent or catalyst, and easy workup [12].

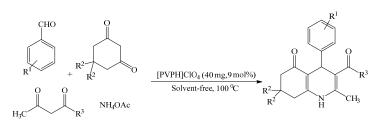
(F) Shirini et al. reported the synthesis of xanthene derivatives including 1,8-dioxooctahydroxanthenes, 14-aryl-14*H*-dibenzo[a,j] xanthenes, and 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones using O-Sulfonated poly(4-vinylpyrrolidonium) chloride [PVP-SO₃H] Cl as a polymeric solid acid catalyst. High reaction rates, no side reactions, ease of the preparation and handling of the catalyst, simple experimental procedure, use of inexpensive and reusable catalyst with lower loading and solvent free conditions makes this method superior [13].

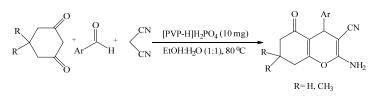
(G) Abedini et al. described a green approach for the promotion of the synthesis of Hantzsch products using poly(vinylpyrrolidinium) perchlorate {[PVPH]ClO4} as a new modified polymeric catalyst. Easy preparation of the catalyst, short reaction times, and high to excellent yields, simple and easy work-up procedure and reusability of the catalyst are notable advantages of this method [14].

(H) Very recently Shirini et al. introduced a novel Brönsted solid acid named poly(vinylpyrrolidonium) hydrogen phosphate ($[PVP-H]H_2PO_4$) as a highly efficient, heterogeneous, and reusable catalyst for the preparation of 2-amino-3-cyano-5-oxo-5,6,7,8-tetrahydro-4*H*-benzopyrans using aldehydes, dimedone, and malononitrile. This catalityc system shows significant improvements with regard to product yield and reaction time [15].









References

- [1] T. Okuhara, Chem. Rev.102 (2002) 3641-3665.
- [2] H. Folttmann, A. Quadir, Drug Del. Tech. 8 (2008) 22-27.
- [3] G. Chehardoli, M.A. Zolfigol, S.B. Azimi and E. Alizadeh, Chin. Chem. Lett. 22 (2011) 827-830.
- [4] A. Ghorbani-Choghamarani, H.Goudarziafshar, P. Zamani, Chin. Chem. Lett. 22 (2011) 1207–1210.
- [5] M. Mokhtary, M. Qandalee, F. Najafizadeh, C.R. Chim. 15 (2012) 389–393.
- [6] M. Mokhtary, F. Najafizadeh, C.R. Chim. 15 (2012) 530-532.
- [7] M. Mokhtary, S. Refahati, Dyes Pigm. 99 (2013) 378-381.
- [8] M.M. Lakouraj, M. Mokhtary, Monatsh. Chem. 140 (2009) 53–56.

- [9] S. Khaksar, M. Tajbakhsh, M. Gholami, C.R. Chim. 17 (2014) 30–34.
- [10] S. Khaksar, M. Tajbakhsh, M. Gholami, F. Rostamnezhad, Chin. Chem. Lett. 25 (2014) 1287-1290.
- [11] M. Nikoorazm, A. Ghorbani-Choghamarani, H. Goudarziafshar, Sci. Iran. C 18 (2011) 1353– 1355.
- [12] A. Ghorbani-Choghamarani, Z. Chenani, S. Mallakpour, Synth. Commun. 39 (2009) 4264-4270.
- [13] F. Shirini, P. Najafi Moghadam, S. Moayedi, M. Seddighi, RSC Adv. 4 (2014) 38581–38588.
- [14] M. Abedini, F. Shirini, M. Mousapour, Res. Chem. Intermed. 42 (2016) 2303-2315.
- [15] F. Shirini, O. Goli-Jolodar, M. Akbari, M. Seddighi, Res. Chem. Intermed. 42 (2016) 4733-4749.