Polyvinyl Pyridine as a Novel Solid Heterogeneous, Recyclable Catalyst for aza-Michael Reaction

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Abstract: Polyvinyl pyridine (PVP) is prepared by radical polymerization of 4-vinyl pyridine. PVP was used as a heterogeneous basic catalyst for the aza-Michael reaction of secondary amines and carbamates with α,β-unsaturated esters, cyanides and ketones to obtain the corresponding adducts in excellent yields (70–90%).

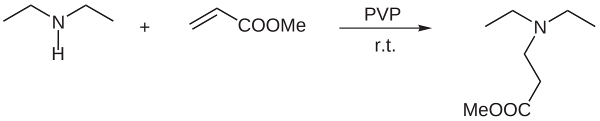
Key words: polyvinyl pyridine, aza-Michael reaction, heterogeneous solid base

Heterogeneous catalysts have many advantages over their homogeneous counterparts and hence are the focus of intense research activity. Though extensive work has been carried out on acidic heterogeneous catalysis the work on basic heterogeneous catalysis has yet to build momentum. This is due in part to various of such catalysts being easily deactivated when exposed to air through CO_2 poisoning (oxides of alkali and alkaline earth metals).

Among the methods for preparing β-amino carbonyl compounds, the aza-Michael reaction of nitrogen nucleophiles with α,β-unsaturated compounds is very commonly used.[1] Catalysts reported for this reaction include lanthanide triflates, $FeCl_3$, $InCl_3$, $CeCl_3$/NaI, platinum-group metal complexes and other Lewis acids.[2] However, these catalysts are not active for the aza-Michael reaction of carbamates, due to the low nucleophilicity of the of the carbamate nitrogen. Only a few catalysts such as, $FeCl_3·6H_2O/Me_3SiCl$, arylphosphines/Me_3SiCl,[3] Nafion®, SAC-13 perfluorinated resin sulfonic acid[4] and some transition-metal salts in their higher valency state[5] have been reported to catalyze such additions. Very recently we reported that Sn exchanged zeolite Hβ as an efficient catalyst for the one-pot synthesis of carbamates from amines,[6] but no heterogeneous basic polymer catalyst has yet been reported for this reaction.

Polymers have been used as catalyst supports for many years.[7] Polyvinyl pyridine (PVP) is a solid basic material, which can be prepared easily by radical polymerization of 4-vinylpyridine and has been used for preparation of supported catalysts/reagents in organic transformations.[8] However, to date, it has not been used as a heterogeneous basic catalyst. This prompted us to consider PVP as a solid heterogeneous catalyst for the aza-Michael reaction of various secondary amines as well as carbamates with compounds containing electron-deficient double bonds.

The PVP used in this study was soluble in methanol and chloroform but insoluble in most other solvents. The polymer was prepared in powder form by radical polymerization of 4-vinyl pyridine.[9] It was not cross-linked and its molecular weight was found to be in the range of 2.6–$3.0·10^5$ with a PDI of 1.5. The reaction of diethylamine with methyl acrylate in the presence of 5% by weight of PVP proceeded at room temperature within 2 hours and give 90% of the adduct (Scheme 1).[10] The PVP was recycled three times further and 88%, 85%, 80% yields were obtained in the subsequent reactions (Table 1).



Scheme 1 Michael reaction of diethylamine with methyl acrylate in the presence of PVP

Even bulky amines (entries 2nd and 9th) underwent smooth addition. Under the same conditions, carbamates also underwent reaction to give excellent yields of adducts.

In conclusion, we have demonstrated that the conjugate addition of compounds containing activated double bonds with secondary amines as well as with less nucleophilic carbamates can take place at room temperature, in the presence of PVP, to give high yields of the adducts. No solvent was needed and the catalyst is recyclable.

Acknowledgment

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References and Notes

(1) Jung, M. E. In *Comprehensive Organic Synthesis*, Vol. 4; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, **1991**, 30.
(2) (a) Kawatsuraand, M.; Hartwig, J. W. *Organometallics* **2001**, *20*, 1960. (b) Shriwastava, N.; Banik, B. K. *J. Org. Chem.* **2003**, *68*, 2109. (c) Bartoli, G.; Basco, M.; Marcantoni, E.; Petrini, M.; Sambri, L.; Torregiani, E. *J. Org. Chem.* **2001**, *66*, 9052. (d) Nakama, K.; Seki, S.; Kanemasa, S. *Tetrahedron Lett.* **2001**, *42*, 6719.
(3) Xu, L. W.; Xia, C. G. *Tetrahedron Lett.* **2004**, *45*, 4507.
(4) Wabnitz, T. C.; Yu, J. Q.; Spencer, J. B. *Synlett* **2003**, 1070.
(5) Kobayashi, S.; Kakumoto, K.; Sugiua, M. *Org. Lett.* **2002**, *4*, 1319.

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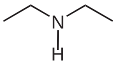
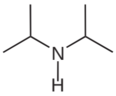
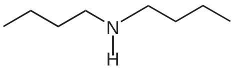
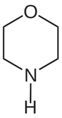
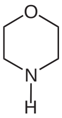
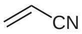
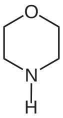
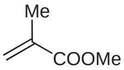
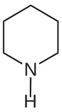
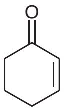
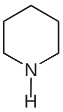
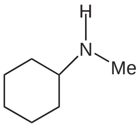
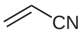
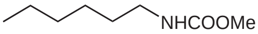
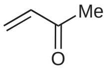
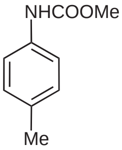
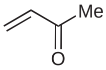
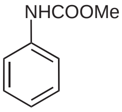
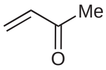
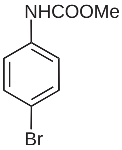
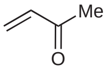
Table 1 Aza-Michael Reaction of Secondary Amines and Carbamates with Various Michael Acceptors[a]

Substrate	Donor	Acceptor	Time (h)	Yield (%)[b]
1			2	90
2			8	75
3			6	70
4			1	90
5			1	88
6			4	75
7			4	75
8			1	90
9			4	80
10			8	80
11			8	80
12			8	81
13			8	77

[a] Reaction conditions: donor = 5 mmol, acceptor = 5.5 mmol, catalyst = 5 wt% of substrate, temp = 30 °C.

[b] Isolated yield: all compounds were well characterized by ^{1}H NMR and IR spectroscopy.

(6) Raje, V. P.; Bhat, R. P.; Samant, S. D. *Tetrahedron Lett.* **2005**, *45*, 835.

(7) (a) Hodge, P. *Ind. Eng. Chem. Res.* **2005**, *44*, 8542.
(b) Akelah, A.; Sherrington, D. C. *Polymer* **24**, 1369.

(8) (a) Shan-Xin, Y.; Zha-Yang; Hecheng, X. *Huaxue Bianjbu, HEHUEZ* **1988**, 1005 (Chinese) (b) Brunelet, T.; Gelbord, G.; Geyot, A. *Polym. Bull.* **1985**, *5*, 145. (c) Tabacovic, R.; Tabacovic, I. *React. Funct. Polym.* **1999**, *39*, 263.
(d) Alcantara, R.; Canoira, L.; Guilherme-Joao, P.; Rodriguez, J. G.; Alcantara, E. *React. Kinet. Catal. Lett.* **2004**, *83*, 105.

(9) Matsuzaki, K.; Matsubara, T.; Kanai, T. *J. Polym. Sci.* **1977**, *15*, 1573.

(10) **General Reaction Procedure.**
To the amine or carbamate (5 mmol) and Michael acceptor (5.5 mmol) was added PVP (5% by weight on the basis of amine/carbamate). The reaction mixture was stirred at r.t. until complete conversion of the starting material. The reaction mixture was filtered and the catalyst washed with Et_2O. The crude product was purified by column chromatography. All products were characterized by ^1H NMR and IR spectroscopy.