



Aza-Michael-type addition reaction catalysed by a supported ionic liquid phase incorporating an anionic heteropoly acid



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ABSTRACT

In this work, we have obtained substituted amines under mild conditions in good yields using the Aza-Michael-type addition of various amines to vinyl compounds catalysed by a supported ionic liquid incorporating an anionic heteropoly acid. Different catalysts, including Lewis acids, Brønsted acids and heteropoly acids were investigated in which heteropoly acids having dual Brønsted and Lewis acid characteristics were excellent catalysts. The ionic liquid incorporating a polytungstate anion supported on magnetic diatomaceous earth as a magnetically separable heterogeneous catalyst offered the best results in terms of yield. The solid nanocatalyst was easily removed with a magnet.

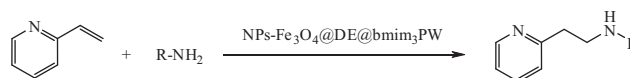
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The Aza-Michael-type addition has been catalysed by many different acids and bases; however side reactions often occur.¹ Therefore, efficient approaches are needed for the development of mild catalysts for the Aza-Michael-type addition. A number of alternative methodologies using catalysts such as metallic oxides,² transition metals,³ lanthanides,⁴ perchloric acid,⁵ silica gel,⁶ cyclodextrin,⁷ organometallics,⁸ ionic liquids,⁹ solvent free conditions¹⁰ and water as a solvent without any catalyst¹¹ have been reported. Recently, immobilization of homogeneous catalysts to develop heterogeneous catalysts has seen increased importance. Despite the fact that immobilized catalysts have various benefits over typical catalysts, the recovery and separation of these catalysts are quite difficult. In order to deal with this challenge, the use of magnetic nanocatalysts is one of the most attractive and applicable alternatives. These nanocatalysts can be recovered from the reaction mixture by employing an external magnetic field. Polytungstic acid, a heteropoly acid (HPA), is an active catalyst for various reactions.¹² It is an excellent catalyst due to its high acidic power and thermal stability.¹³ More recently, ionic liquids (IL) incorporating anionic heteropoly acid derivatives have been studied as catalysts.¹⁴ Herein, a supported IL strategy has been applied for the immobilization of a Keggin phosphotungstate anion on magnetic diatomaceous earth (DE) as a support $\text{Fe}_3\text{O}_4\text{@DE@bmim}_3\text{PW}$ and its use as an efficient and environmen-

tally-friendly catalyst for the Aza-Michael-type addition of amines to vinyl compounds at ambient temperature is reported (Scheme 1).

Experiments were performed to find the best conditions for the Aza-Michael-type addition of 2-vinyl pyridine and aniline as a model reaction. In the absence of catalyst the reaction did not occur (Table 1, entry 1). Different catalysts including Lewis acids (Table 1, entries 2–4), Brønsted acids (Table 1, entries 5–7) and heteropoly acids (Table 1, entries 8–11) were then examined. Among the various acids, heteropoly acids (HPAs) were excellent catalysts in the reaction of 2-vinyl pyridine and aniline. These catalysts have dual Brønsted and Lewis acid characteristics and promote the reaction of 2-vinyl pyridine. The activity of HPAs as a catalyst is controlled by the amount of Lewis-acid sites on the surface. Among the examined heteropoly acids, the best results were obtained using phosphotungstic acid (Table 1, entries 10 and 11). It seems that the addition of phosphotungstic acid could provide more active Lewis acid sites for the activation of 2-vinyl pyridine in the Aza-Michael-type reaction. Higher reaction rates were also observed with ILs possessing high dielectric constants.

In order to immobilize the polytungstate anion (PW), a supported IL strategy was applied. For this purpose, an IL



Scheme 1. Addition of amines to 2-vinyl pyridine using $\text{Fe}_3\text{O}_4\text{@DE@bmim}_3\text{PW}$.

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Table 1
Reaction of 2-vinylpyridine with aniline using various catalysts^a

Entry	Catalyst	Time (h)	Yield ^b (%)
1	—	24	—
2	FeCl ₃ ·6H ₂ O	4	43
3	FeCl ₂ ·4H ₂ O	4	35
4	NPs-Fe ₃ O ₄	4	45
5	H ₂ SO ₄	4	55
6	H ₃ PO ₄	4	32
7	CH ₃ COOH	4	35
8	H ₃ PMo ₁₂ O ₄₀	4	65
9	H ₄ SiW ₁₂ O ₄₀	4	72
10	H ₃ PW ₁₂ O ₄₀	4	90
11	H ₃ PW ₁₂ O ₄₀	2	85

^a Reaction conditions: 2-vinylpyridine (0.54 mL, 5 mmol, 1 equiv), aniline (0.46 mL, 5 mmol, 1 equiv), catalyst (3 mol %), CH₂Cl₂ (5 mL), rt.

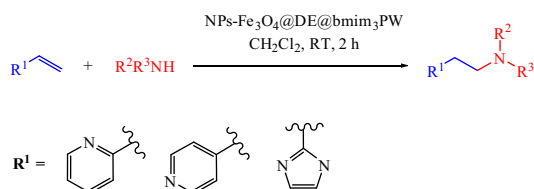
^b Isolated yield.

Table 2
IL catalysed reaction of 2-vinylpyridine (A) with aniline (B)^a

Entry	Catalyst	Mole ratio (A/B)	Time (h)	Yield ^b (%)
1	[bmim]Cl ⁻	1:2	4	Trace
2	NPs-Fe ₃ O ₄ @DE@[bmim]Cl ⁻	1:2	4	65
3	NPs-Fe ₃ O ₄ @DE@[bmim]Cl ⁻	1:1	4	50
4	bmim ₃ PW	1:2	4	81
5	bmim ₃ PW	1:1	4	75
6	NPs-Fe ₃ O ₄ @DE@bmim ₃ PW (1)	1:1	4	93
7	NPs-Fe ₃ O ₄ @DE@bmim ₃ PW (1)	1:1	2	90

^a Reactions conditions: CH₂Cl₂ (5 mL), catalyst (3 mol %), rt.

^b Isolated yield.

**Scheme 2.** Aza-Michael-type addition of various amines to vinyl compounds.**Table 3**
Catalytic Aza-Michael-type addition of various amines to vinyl compounds

Entry	Amine	Product ^a	Yield ^b (%)	
1			1a	95
			1b	95
			1c	95
2	MeNH ₂ (40% aq)		2a	91
			2b	94
			2c	83

(continued on next page)

incorporating the anionic polytungstate (bmim₃PW) was prepared in which the polytungstate anion (PW) was exchanged with Cl⁻ in 1-butyl-3-methylimidazolium chloride ([bmim]Cl⁻).¹⁵ In the next step, the IL was supported on magnetic diatomaceous earth (DE) to produce NPs-Fe₃O₄@DE@bmim₃PW (**1**).¹⁶ The catalytic performance of the supported catalyst **1** for the direct addition of alkylamines to 2-vinyl pyridine was more remarkable than the ionic liquid or NPs-Fe₃O₄@DE individually (Table 2). The best results were obtained when equimolar amounts of amines and 2-vinyl pyridine were used in the presence of **1** as the catalyst (Table 2, entries 6 and 7). The synthesized alkylamine was easily isolated in good yield and purity by filtration of the precipitated solid after evaporation. The paramagnetic nanoparticles could be easily removed with a magnet before evaporation of the solvent.

The presented method was shown to be applicable for the Aza-Michael-type addition using a wide range of amines, such as highly nucleophilic primary alkylamines and deactivated anilines, to vinyl compounds such as 4-vinyl pyridine, 2-vinyl imidazole and 2-vinyl pyridine (Scheme 2, Table 3).¹⁷ As shown in Table 3, the Aza-Michael-type addition of amines provided the products with high yields. Presumably, this is due to vinyl activation by the vicinal nitrogen.

The reusability of catalyst **1** was investigated in the reaction of 2-vinylpyridine with aniline. In order to evaluate the stability and recyclability, the catalyst was recovered by applying a magnetic field and the collected solid was washed with THF, dried at 50 °C for 6 h and reused in the next reaction. The catalyst was used for 5 reactions without any significant decrease in activity. Although there is a possibility of IL leakage into the liquid phase, due to the relatively strong interactions between the polar ionic liquid phase and outer surfaces of the solid support this leakage is minimized. Therefore, the catalyst activity remains without any significant reduction in activity.

In this Letter, the effect of different catalysts on the Aza-Michael-type addition reaction was investigated. Among the various catalysts used, the best results were achieved using the IL bmim₃PW which was physically supported on magnetic diatomaceous earth furnishing a magnetically separable catalyst. The activity may be due to a synergistic effect of the ionic liquid incorporating the polytungstate anion and the magnetic solid support. In conclusion, a simple and mild procedure for the Aza-Michael-type addition of various amines to activated vinyl

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