



Feature article

Efficient and reusable ionic liquid stabilized magnetic cobalt nanoparticles as catalysts for aza- and thia-Michael reactions

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1. Introduction

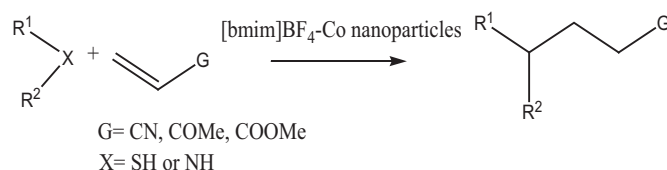
There are several reports of aza- and thia-Michael reactions that can be performed under mild reaction conditions (normally at room temperature for a few minutes/hours). Catalysts employed in such reactions include sulfated zirconia [1], silica-supported Lewis acids [2], polystyrene-sulfonic acid [3], Si–Cu core-shell nanoparticles [4], ionic liquids [5] and related acidic surfactants [6,7] and more recently by a ferrite-anchored glutathione catalyst [8]. Uncatalyzed intramolecular cyclization of hydroxyl/amino chalcones as well as aza-Michael addition has also been reported to be promoted in polyethylene glycol (PEG-400), but requires relatively longer reaction times to achieve reasonable yields [9]. Supported metal catalysts such as Co(II) complex supported on SBA-15 as reusable catalyst for aza- and thia-Michael reactions is highly efficient, but suffers from reduced active surface sites on metal due to the presence of chemically bound solid support [10].

The longer reaction time in most of the recyclable heterogeneous catalysts mentioned above, including nano-based catalysts and supported metal based catalysts is because of the low catalytic surface area. Consequently, these catalysts suffer from reduced activity after one or two cycles. Additionally, it is difficult to separate the catalyst.

Magnetic nano-materials have been used in the field of catalysis and other areas, such as medicine, drug delivery and remediation [11,12]. They can be easily synthesized and enhanced/tuned by post-synthetic surface modifications [13]. In view of their nano-size, the contact between reactants and catalyst increases dramatically thus mimicking

the homogeneous catalysts. They offer an added advantage of being magnetically separable, thereby eliminating the requirement of catalyst filtration after completion of the reaction [14]. Additionally, magnetically recyclable nanocatalysts have high catalytic activity and can be recycled easily [8].

Green chemistry emphasizes the development of environmentally benign chemical processes and technologies [15]. In the past, cerium(IV) ammonium nitrate has been used to catalyze aza-Michael addition of amines to α,β -unsaturated electrophiles [16]. Recently, it has been shown that cobalt nanoparticles (Co NPs) can be used as catalysts offering great opportunities for a wide range of applications in organic synthesis and chemical manufacturing processes. We hypothesized that it may be possible to use ionic liquid stabilized magnetically recyclable cobalt nanoparticles as catalyst for aza-Michael and thia-Michael addition reactions. The presence of a thin film of stabilizer i.e., hydrophilic room temperature ionic liquid [bmim]BF₄ on the surface of magnetic nanoparticles, would help to protect the catalytically active sites, allowing them to be reused multiple times with negligible loss of activity.



Scheme 1. Aza- and thia-Michael addition reaction catalyzed by [bmim]BF₄ stabilized cobalt nanoparticles.

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2. Results and discussion

Solventless catalysis of aza- and thia-Michael additions under mild conditions (at room temperature and under atmospheric conditions) was carried out in the presence of magnetic cobalt nanoparticles stabilized in ionic liquid. Products in quantitative yields were obtained

rapidly. When bare non-stabilized cobalt nanoparticles (in the absence of ionic liquids) was used, 1 mol of phenylthiol reacted with 1 mol of vinylmethylketone to give around ~8% yield in an hour. Moreover, recyclability was a serious issue as particles underwent degradation after the first cycle. However, when cobalt nanoparticles (30 ± 5 nm, 0.1 mmol) stabilized with ionic liquid [bmim]BF₄ were isolated and

Table 1
Synthesis of aza-Michael adducts using recyclable cobalt nanoparticles.^a

Entry	Michael donor	Michael acceptor	Product ^b	Time (min)	Yield (%)
1.1.1				30	96
1.1.2				40	95
1.1.3				45	94
1.1.4				75	87
1.1.5				28	96
1.1.6				30	97
1.1.7				40	96
1.1.8				60	88
1.1.9				25	98
1.1.10				28	90
1.1.11				35	87
1.1.12				58	84
1.1.13				28	95
1.1.14				30	94
1.1.15				40	92
1.1.16				70	89

^a Reaction condition: 1 mmol of amine 1 mmol of activated α,β -unsaturated compound (Michael acceptor) stirred together in the presence of 5 mol% of stabilized cobalt nanoparticles.

^b Isolated products characterized using FT-IR, TLC, ¹H and ¹³C NMR.

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