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Graphical Abstract

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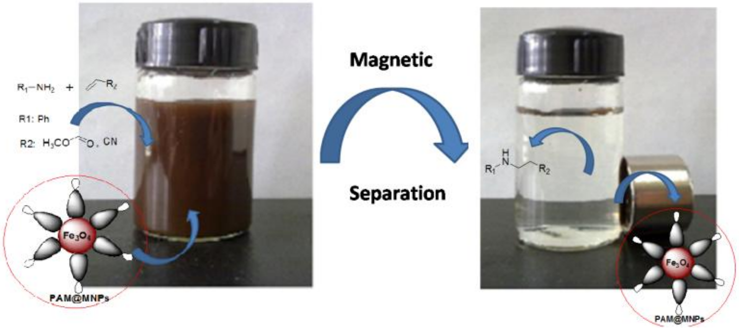

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Polymer coated magnetically separable organocatalyst for C-N bond formation *via* aza-Michael addition

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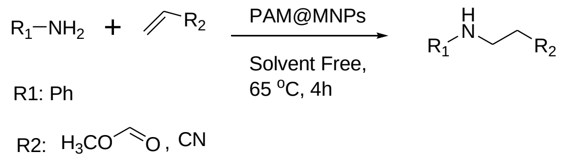
ABSTRACT

A polyacrylamide coated magnetite (PAM@MNP) catalyst was synthesized by following a two step approach involving the reaction of magnetite (Fe_3O_4) particles with coupling agent 3-(trimethoxysilyl)propyl methacrylate followed by grafting of acrylamide and subsequent polymerization via surface initiated radical polymerization technique. The synthesized organocatalyst was used for one-pot aza-Michael addition reaction of amines with electron deficient alkenes to give β-amino carbonyls. The magnetic properties of the synthesized organocatalyst provide it a facile recovery by external magnet which eliminates the problems arising during catalyst separation by conventional filtration.

Development of organocatalysts for organic transformations is an area of current research interest as they do not contain toxic metallic components and are considered to be green, readily accessible and highly efficient[1-5]. Organocatalysts generally possess higher stability thereby simplifying handling and storage and the reactions can be carried out under non-inert reaction conditions such as in air[6-12].Organocatalysts are simple organic compounds which show higher solubility in most of the organic solvents; thus, the separation of the organocatalyst from reaction mixtures and its recycling is a challenging task. One of the most promising approaches to overcome such limitations is the immobilization or heterogenization of homogeneous organocatalyst to a suitable support matrix, which makes the catalyst easily recoverable and recyclable. Recently, magnetic nanoparticles have emerged to be promising, robust, easily available support materials for preparing the heterogeneous catalysts[13-16] owing to their magnetic properties and large surface area. The prime advantage of using magnetic nanoparticles as support is the facile recovery of catalyst using an external magnet which solves the problem associated with catalyst loss during the filtration at the end of the reaction[17-18]. Furthermore, magnetic nanoparticles can be easily functionalized with various coupling agents, which can provide a strong chemical interaction between the organocatalyst and the metallic support to prevent the leaching of the catalyst during the reaction. Thus, magnetically separable organocatalysts have emerged to be efficient, robust, and feasible substitutes to conventional metal based catalysts for organic transformations. In addition, the nano-size of MNPs provides efficient interaction between catalyst and reactant molecules, which provides a way to bridge the gap between homogeneous and heterogeneous catalysts. So far, magnetically separable organocatalysts have been used for various organic transformations such as enantioselective C–C, C–N, C–O bond formation[19], Diels–Alder[20,21], Baylis–Hilman [22,23], Mannich[24,25-27], Michael[28,29], Friedel–Crafts alkylation[30], oxidation[31,32] and carbohydrate synthesis[33].

Among the great variety of organocatalytic transformations, aza-Michael addition occupy a very important position and has received widespread attention for accessing a variety of synthetically useful building blocks for the synthesis of bioactive natural compounds[34-37]. This reaction involves the interaction between α,β-unsaturated carbonyl compounds as Michael acceptors and amines as Michael donors through the hydrogen bonding between the carbonyl oxygen atom and the amine NH proton. Thus, the amine donor should be electron rich in nature. Owing to this reason, in general the reaction rates are faster with aliphatic amines compared to those of aromatic amines and very electron deficient amines such as 4-nitroaniline did not react due to the decrease in nucleophilicity of the nitrogen atom of 4-nitroaniline[38]. During the past decade, a number of efficient organocatalysts both homogeneous as well as immobilized have been developed for facile recovery and recycling for aza-Michael addition reactions. Furthermore, advanced strategies, for example using light[39], microwave[40-42] and ultrasonic irradiation[43] have also been explored in the literature. Although extensive research has been carried out with organocatalysts for C-N bond formation through aza-Michael addition, the use of magnetic nanoparticles immobilized organocatalyst is rarely known. To the best of our knowledge there is only one report is known on the use of magnetic nano-organocatalyst for aza-Michael addition[40]. In this report, magnetic nano-particles have been coated with glutathione *via* post grafting method using ultrasonication. Furthermore, the developed nano-organocatalyst has been used for aza-Michael reaction at higher temperature (140 °C) under microwave irradiation using water as reaction media.

Herein, we report, a simple, cost effective and efficient synthesis of magnetite functionalized polyacrylamide (PAM@Fe_3O_4), a magnetically recoverable organocatalyst for aza-Michael reaction under solvent less conditions (Scheme 1).

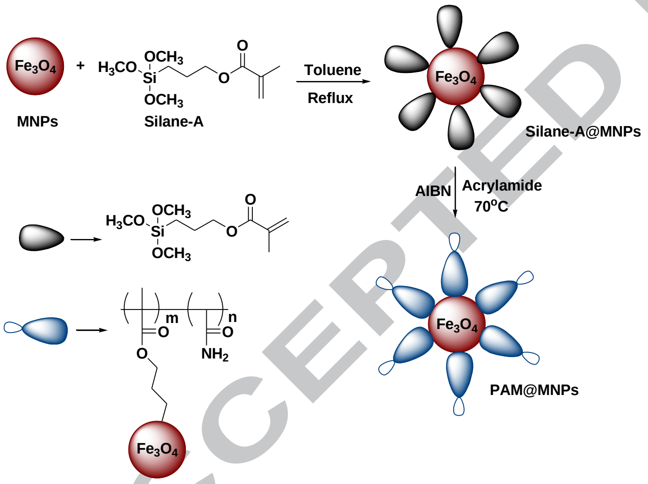


Scheme 1: PAM@MNP-catalyzed aza-Michael addition

Synthesis and characterization of the catalyst

Preparation of polyacrylamide coated magnetic nanoparticles, PAM@MNPs

The process for synthesis of polyacrylamide coated magnetic nanoparticles is shown in Scheme 2, Fe_3O_4 magnetic nanoparticles (MNPs) were synthesized by a chemical co-precipitation of Fe^{2+} and Fe^{3+} ions under alkaline condition. After that the MNPs were functionalized with 3-trimethoxysilylpropyl methacrylate (silane-A) to afford vinyl groups which were subsequently subjected to surface initiated polymerization with acrylamide to get the desired polyacrylamide coated MNPs (PAM@MNPs). The un-grafted homopolymers/ oligomers were separated via repeated washings with ethanol.



Scheme 2: Synthesis of polyacrylamide coated magnetic nanoparticles (PAM@MNPs)

Figure 1 shows the FT-IR spectra of pure Fe3O4, silane-A functionalized Fe_3O_4 and PAM@ MNPs, respectively. FT-IR spectrum of Fe_3O_4 (Fig. 1a) showed characteristic peaks at 574 and 1384 cm^{-1} respectively which are attributed to the bending vibration mode of Fe–O and stretching mode of Fe–O. The peak at 3415 cm^{-1} is due to the –OH groups presented on the surface of Fe_3O_4 nanoparticles[44-45]. The IR spectrum of silane-A functionalized Fe_3O_4 (Fig. 1b) exhibited absorption peaks at 1710 and 1644 cm^{-1} related to the stretching vibration of C=O and C=C bonds, respectively. The absorption peaks appeared at 1411 and 2910 cm^{-1} attributed to Si-O bond and asymmetric stretching vibration of CH_2 groups, respectively. Other peaks appearing at ~1,100 attributed to the vibrational modes involving the bridging oxygen atoms in Si-O bonds. All these peaks revealed the successful functionalization and existence of vinyl groups onto the surface of magnetite. In Figure 1c, shows the characteristic bands of bending vibration of N–H bond (1630 cm^{-1}) and stretching vibration of N–H bond (V^{as}_{N-H} ,3400 cm^{-1}; V^{s}_{N-H} , 3170 cm^{-1}), respectively[46]. Comparison of all three FTIR spectra clearly indicated the successful functionalization of MNPs with polyacrylamide.

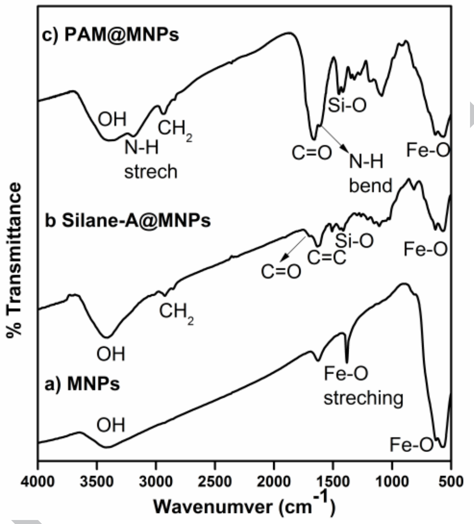
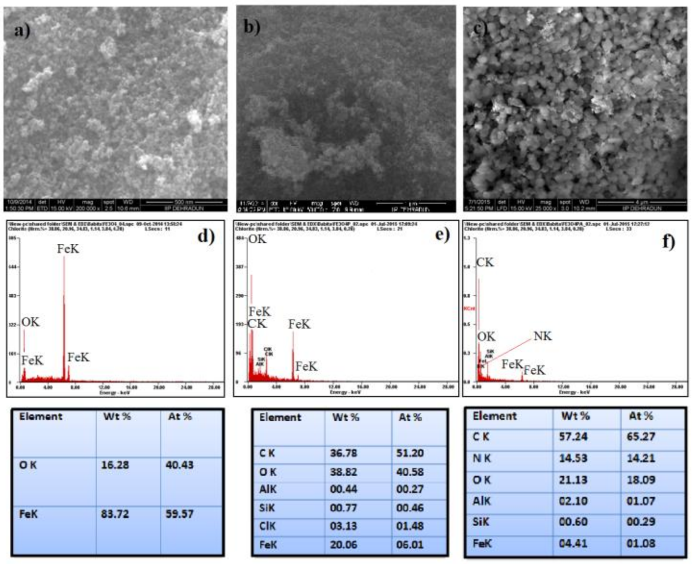


Fig. 1:FT-IR spectra of: a) neat MNPs; b) silane-A@MNPs; c) PAM@MNPs

The surface morphology of pure Fe_3O_4 (MNP), silane-A functionalized Fe_3O_4 and polyacrylamide coated Fe_3O_4 nanoparticles were determined by FE-SEM as shown in figure 2. The FE-SEM image of Fe_3O_4 confirmed that the particles are nearly spherical in shape with size ranging from 50–100 nm (Fig. 2a). However, in the case of the silane-A functionalized Fe_3O_4 NPs, the morphology was found to be slightly changed from spherical to agglomerated cluster type structure (Fig. 2b). However, after coating with PAM, clearly spherical shaped nanoparticles were observed, without having any agglomeration (Fig. 2c). Furthermore, the EDX pattern of all three materials indicated the presence of desired elements which further confirmed the successful formation of PAM coated magnetic NPs (Fig. 2d-f).



Element	Wt %	At %
O K	16.28	40.43
FeK	83.72	59.57

Element	Wt %	At %
C K	36.78	51.20
O K	38.82	40.58
AlK	00.44	00.27
SiK	00.77	00.46
ClK	03.13	01.48
FeK	20.06	06.01

Element	Wt %	At %
C K	57.24	65.27
N K	14.53	14.21
O K	21.13	18.09
AlK	02.10	01.07
SiK	00.60	00.29
FeK	04.41	01.08

Fig. 2: SEM images of: a) Fe_3O_4 nanoparticles; b) silane-A@MNPs; c) PAM@MNPs and EDX of: d) Fe_3O_4 nanoparticles; e) silane-A@MNPs; f) PAM@MNPs

The XRD diffraction pattern of pure Fe_3O_4 is in well agreement with the reported standard pattern of crystalline magnetite (Figure 3a)[47-48]. The characteristic diffraction peaks at (220), (311), (400), (422), and (511) revealed the inverse cubic spinel structure of Fe_3O_4 and well matched with JCPDS card No. 65–3107. Similarly these characteristic peaks also appeared in silane-A functionalized Fe_3O_4 and polyacrylamide functionalised Fe_3O_4, confirmed the presence of the magnetic core (Figure 3b, c). However, the peak broadening in case of PAM@Fe_3O_4, may be assumed to be due to the presence of amorphous polymer coating.

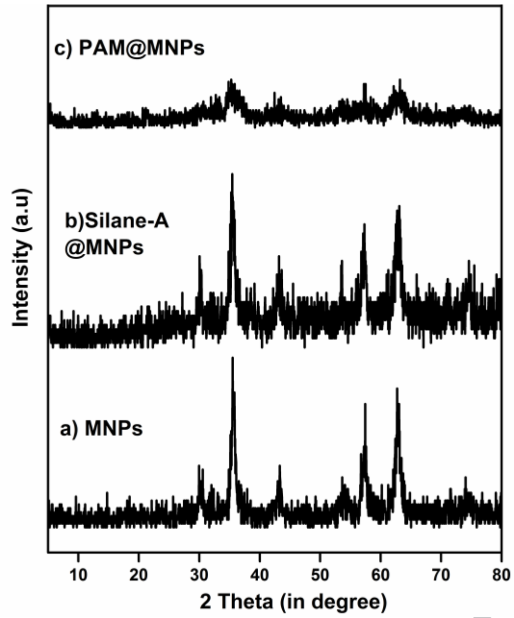


Fig. 3: XRD diffractogram of: a) Fe_3O_4 nanoparticles; b) silane-A@MNPs; c) PAM@MNPs

Thermal stabilities of the synthesized materials were determined by thermogravimetric analysis (TGA)[49] as shown in Fig. 4. In neat Fe_3O_4, a small amount of weight loss between 100-200 °C is assumed due to the evaporation of the adsorbed water molecules. In Figure 4b, the major weight loss between 250-300 °C is attributed to the loss of silane-A functionalities presented on the support of MNPs. In Figure 4c, sharp decrease in weight loss between 200 and 650 ◦C was observed as compared to neat Fe_3O_4 NPs and silane-A@MNPs. The initial weight loss below 140 °C can be attributed to the evaporation of water molecules in the polymer matrix. The major and sharp weight loss between 200-650 °C was attributed to the decomposition of the grafted polymer and other organic components, which were presented on the surface of MNPs.

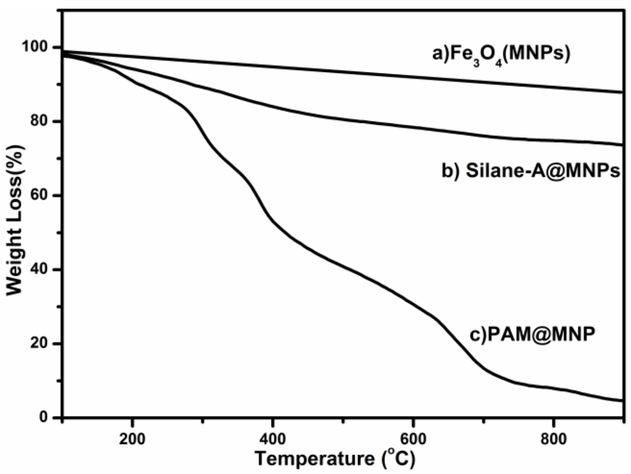


Fig. 4: TGA thermogram of: a) Fe_3O_4 NPs; b) silane-A@MNPs; c) PAM@MNPs

Catalytic activity

After the successful synthesis and characterization of the polyacrylamide coated magnetic nanoparticles (PAM@Fe_3O_4), we decided to explore its catalytic potential for aza-Michael reaction (Scheme 1). At first, reaction conditions were optimized by choosing aniline and methyl acrylate as the representative substrates for aza-Michael reaction. The results are summarized in Table 1. The reaction was first conducted in various solvents in order to choose an optimum reaction medium for the reaction. In toluene at 65 °C, the reaction was found to be slow and afforded poor conversion (Table1, entry 1). Similarly, poor conversion was observed in polar aprotic solvents such as acetonitrile and dichloromethane (Table1, entry 2, 3). Polar protic solvents such as water and ethanol provided better conversion (Table1, entry 4, 5); however solvent less condition was found to be best, which further makes the developed protocol benign from environmental viewpoints. The reaction was found to be slow at room temperature; however the conversion increased with temperature and at 65 °C it was obtained maximum. Further increase in temperature did not influence the reaction to any significant extent (Table1, entry 6). Similarly, 100 mg catalyst was found to be optimum for this reaction and further increase in catalyst amount did not provide any significant improvement (Table1, entry 7). Based on these optimization experiments, we have chosen 65 °C as optimum reaction temperature, 100 mg catalyst amount under solvent less condition. Next, we compared the catalytic activity of the PAM@MNPs with neat MNPs under identical conditions. The reaction with neat MNPs was found to be very slow and provided only 30% yield of the desired product (Table 1, entry 7). This is due to the agglomeration of the bare MNPs which is in well agreement with the suggested literature reports[40,50]. Furthermore, during the recycling experiment with recovered neat MNPs, the catalytic activity was found to be nil which again confirmed the deactivation of the MNPs due to their agglomeration tendency (Table 1, entry 7).

Table 1: Results of the optimization experiments^{a}

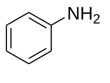
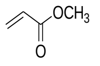
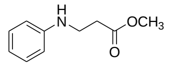
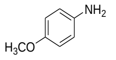
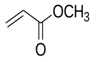
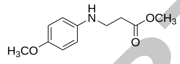
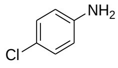
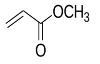
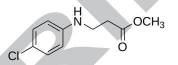
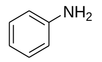
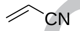
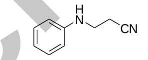
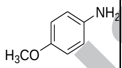
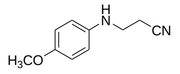
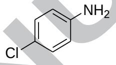
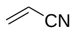
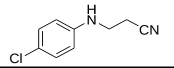
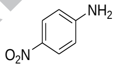
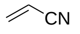
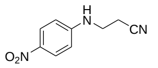
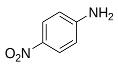
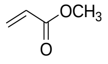
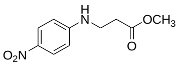
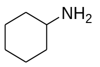
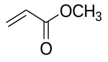
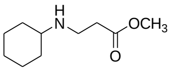
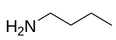
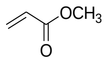
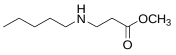
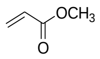
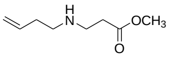
Entry	Solvent	Yield (%)^{b}
1	Toluene	50
2	Dichloromethane	60
3	Acetonitrile	45
4	Water	75
5	Ethanol	70
6	Without solvent	85^{a}, 20^{c}, 50^{d},92^{e}
7	Without solvent	-^{f}, 65^{g} 90^{h}, 30^{i}, -^{j}

^{a}Reaction conditions: aniline (1 mmol) , methy1 acrylate (1.5 mmol), and catalyst (100 mg), solvent (2 ml), 65°C for 4h; ^{b}Isolated yield; ^{c}at room temperature, at ^{d}50 °C, at ^{e}75 °C; ^{f}without catalyst, ^{g}using 50 mg of catalyst, ^{h}150 mg catalyst was used, ^{i}using neat MNPs as catalyst, ^{j}recycling experiment using recovered neat MNPs as catalyst.

Deploying the above optimized reaction conditions, the scope of this catalyst was then investigated for aza-Michael reaction using a variety of substrates and the results are summarized in Table 2. In general aromatic amines were found to be less reactive (Table 2, entry 1-8) as compared to aliphatic ones (Table 2, entry 10-11). However, aromatic amines carrying either electron-donating or electron withdrawing substituents were successfully reacted with unsaturated olefins to produce their corresponding Michael adducts in moderate to higher yields. However, very electron deficient amines such as 4-nitroaniline did not react even after prolonged reaction time, which is due to the decrease in nucleophilicity of the nitrogen atom (Table 2, entry 7,8). Alicyclic amine such as cyclohexylamine also reacted smoothly under the described conditions and afforded moderate product yield (Table 2, entry 9). Furthermore, the reaction rate with aliphatic amines such as 1-butylamine and allylamine was found be faster as compared to aromatic amines and afforded higher product yield in comparatively lower reaction time (Table 2, entry 10,11).

In the previously known report[40], magnetic nano-particles have been coated with glutathione using post grafting method using ultrasonication. In this case the covalent attachment of organocatalyst on MNPs is not very much confirmed which may hamper the long term stability of organocatalyst due to leaching However, in the present study, the MNPs were initially functionalized by silane-A linker to have covalent immobilization of acrylamide followed by its polymerization to get the leach proof stable catalyst. Also, in the previous report, the magnetic organocatalyst has been used at higher temperature (140 °C) under microwave irradiation using water as reaction media. In contrast, in the present study, the reaction has been carried out at lower temperature i.e. 65 °C under solvent less conditions. These benefits of the present study establish its superiority over the existing report.

Table 2: PAM@MNP catalyzed aza-Michael addition of under solvent-free condition^{a}

Entry	Amine	Michael acceptor	Product	T/ (h)	Yield (%)b
1.				4	85
2.				5	80
3.				4.5	72
4.				7	76
5.				3	75
6.				6	82
7.				10	-
8.				12	-
9.				4.5	84
10.				3.5	90
11.	$CH_2=CHCH_2NH_2$			3.5	87

^{a}Reaction conditions: amine (1 mmol), alkene (1.5 mmol), and PAM@MNPs (100 mg) at 65 °C; ^{b}Isolated yield; ^{c}using bare MNPs as catalyst; ^{d}recycling experiment using recovered MNPs as catalyst

Further, we evaluated the recycling of the recovered PAM@MNPs organocatalyst for aza-Michael addition of aniline with methyl acrylate as representative substrates. After completion of the reaction the catalyst could easily be separated with the help of an external magnet as shown in Figure 5.

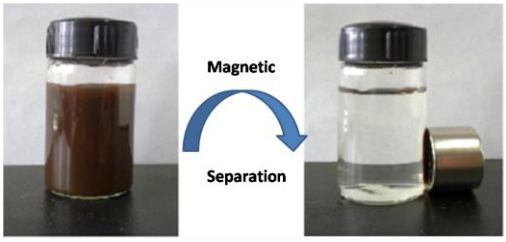


Fig. 5: Separation of catalyst using external magnet

The recovered catalyst was washed with methanol, dried and reused for subsequent runs under described optimized reaction conditions. The recyclability of the catalyst was checked for five runs. In all experiments the reaction time and yield of desired product remained almost similar as shown in Figure 6, establishing the efficient recycling of the catalyst.

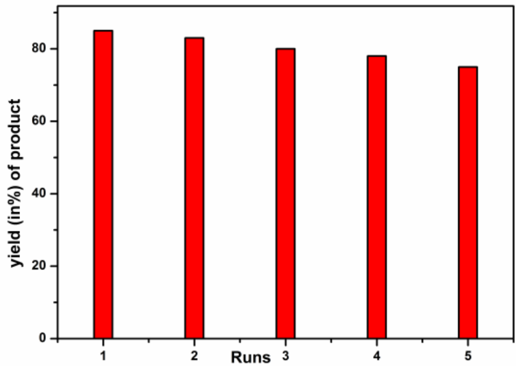


Fig. 6: Results of recycling experiment

Conclusion

A novel magnetically separable organocatalyst i.e. polyacrylamide coated magnetic nanoparticles was synthesized by following a simple two step strategy involving functionalization of MNPs followed by surface initiated polymerization. The catalyst showed excellent activity for aza-Michael reaction under solvent-less conditions. Importantly, after completion of the reaction, the catalyst could readily be recovered by simple magnetic influence of external magnet. The recovered organocatalyst could be reused for several runs without any significant loss in activity. We believe that this novel concept of magnetically separable organocatalysts will help in fulfilling the gap between homogeneous and heterogeneous organocatalysis and will provide the economically viable and environmentally benign protocols for organic transformations.

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References and notes

Synthesis of Fe_3O_4 nanoparticles (MNPs)

The Fe_3O_4 magnetic nanoparticles were synthesized by co-precipitation of Fe(II) and Fe(III) solutions under alkaline conditions by following the procedure reported elsewhere. In brief 1.99 g (10 mmol) of $FeCl_2.4H_2O$ and 3.24 g (12 mmol) of $FeCl_3.6H_2O$ were dissolved in 50 mL of distilled water. A separate solution of NH_4OH was made by dissolving 30 mL NH_4OH (25% ammonia) in 50 mL of distilled water. Both the solutions in the beaker were allowed to stir for about half an hour, to achieve uniform mixing. After that NH_4OH solution was added drop wise into the first solution till a pH of 9 is obtained. The obtained solution was stirred continuously that generates magnetic nanoparticles. The obtained precipitates were separate with the help of external magnet and washed with distilled water and ethanol and dried at 100 ºC overnight then grinded. Finally the black coloured MNPs were obtained.

Preparation of silane A-modified MNPs (Silane-A@MNPs)

In a typical synthesis, 2 g of Fe_3O_4 nanoparticles were dispersed in 30 mL toluene by sonication for about 1 h, and then 4mL of 3-(trimethoxysilyl) propylmethacrylate (silane-A) is added under the inert atmosphere. The reaction mixture was stirred for 24 h under refluxing condition. Afterwards, the silane A-functionalized Fe_3O_4 nanoparticles obtained were separated by magnet, washed with ethanol, water and then dried in a vacuum oven at 80 °C overnight.

Synthesis of polyacrylamide coated Fe_3O_4 nanoparticles (PAM@MNPs)

Surface-initiated radical polymerization was performed to functionalize silane A-modified Fe_3O_4 nanopartocles with polyacrylamide. In a typical procedure, 1 g of silane A-modified Fe_3O_4 nanoparticles, 0.02 g of AIBN, 30 mL of ethanol and 10 mL of distilled water were all put together in a three necked round bottom flask and sonicate it for 30 min to get uniform dispersion and then heated at 70°C, with constant stirring under inert atmosphere. Then 1g acrylamide dispersed in 20 mL ethanol and 10 mL distilled water was added drop wise to the above reaction mixture and again stirred for 4h in inert atmosphere. Finally the resultant product was collected by magnetic separation, washed with ethanol several times, and dried at 80°C in a vacuum oven.

General Procedure for the Synthesis of aza-michael product

Aniline (1 mmol), methyl acrylate (1.5 mmol) and catalyst (100 mg) were placed into a round bottom flask and stirred at $60\ ^{o}C$ for 4 h. The progress of the reaction was monitored with thin-layer chromatography (TLC). After completion of the reaction, the reaction mixture was cooled to room temperature and the catalyst was recovered by external magnet. The reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography. Conversion of the substrates and selectivity of the products was determined by GCMS. The recovered catalyst was dried at 50 °C for 2 h and can be reused for recycling experiments.

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Highlights of the Research

- Polymer coated magnetically separable organocatalyst for C-N bond formation
- Prior Functionalization of MNPs for covalent immobilization of polyacrylamide.
- Synthesized organocatalyst was used for C-N bond formation via aza-Michael addition
- Magnetic organocatalyst was easily recovered by influence of the external magnet.
- Magnetic organocatalyst provided consistent activity for several runs.