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Cross-linked poly (dimethylaminoethyl acrylamide) coated magnetic nanoparticles: A high loaded, retrievable, and stable basic catalyst for water-medium synthesis of benzopyranes

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ABSTRACT

A novel heterogeneous catalyst has been synthesized based on distillation-precipitation polymerization of methyl acrylate onto the modified magnetic nanoparticles followed by amidation of methyl ester groups by *N,N*-dimethylethylenediamine. The resulting poly(dimethylaminoethyl acrylamide) coated magnetic nanoparticles (MNP@PDMA) catalyst characterized using an array of sophisticated analytical techniques including FTIR, TGA, SEM, TEM, CHN, vibrating sample magnetometer (VSM), and XRD analysis. The resulting heterogeneous base catalyst allowed the performance of domino Knoevenagel condensation/Michael addition/cycloaddition reactions for the water-medium synthesis of 4*H*-benzo[*b*]pyranes in excellent yields. Multilayer and polymeric identity of coated material on the surface of magnetic nanoparticle provides many catalytic unite resulted in high loading level and high stability of catalyst. Straightforward magnetic separation and recycling of catalyst for up to 5 runs is possible without significant loss of efficiency.

Keywords: Heterogeneous catalysis, supported catalysis, polymer, nanostructures, immobilization, Michael addition, multicomponent reactions.

1. Introduction

However, application of homogeneous catalysts in organic synthesis have advantages such as accessibility of all catalytic site, tuning the chemo-, regio-, and enantioselectivity, good yield and easy optimization of catalytic systems by modification of ligands and metals, they suffer from important drawbacks such as instability, deactivation, difficult recovery and recycling of the catalyst.[1,2] Therefore, heterogenization of homogeneous catalysts is an applicable way to overcome these problems. Commonly, heterogenization carried out by supporting of homogeneous catalysts onto the surface of insoluble organic and inorganic solids such as cross-linked polymers,[3,4] mesoporous silica,[5,6] magnetic nanoparticles[7-9] and zeolites.[10]

Recently, magnetic supported catalysts have attracted great attention in organic synthesis as heterogeneous catalysis.[7-9,11] Surface modification followed by supporting of a catalyst onto the magnetic nanoparticles is an elegant way to bridge the gap between heterogeneous and homogeneous catalysis. The most highlight aspect of magnetic nanoparticles is their easy separation from the reaction mixture by application of an external permanent magnet. This made magnetic nanoparticles a promising alternative to other heterogeneous catalysts especially porous/mesoporous systems which most of them require a filtration or centrifugation step or a tedious workup of the reaction mixture for recovering the catalyst.[12,13] Magnetic nanoparticles have also good stability, easy synthesis and functionalization and high surface area, as well as low toxicity and price.[14-16] To date, many homogenous catalysts have been immobilized onto the magnetic nanoparticles via different surface functionalization.[11]

Although these heterogeneous catalysts are widely used in organic synthesis, they are in most cases not as active and selective as their homogeneous counterparts.[17] A great proportion of these catalysts are deep inside the supporting material and thus reactants have limited access to the catalytic sites.[18] It also is obvious that the number of catalytic units is low, compared to the large surface of magnetic nanoparticles (low loading) led to the using of larger amount of catalyst.[19-21] Surface functionalization of magnetic nanoparticles with various polymer grafting methods is a good choice to overcome these limits.[22-24] The surface-grafted polymers not only efficiently improve the solubility of the magnetic nanoparticles in different solvents but also endow the particles a series of functionalities for various applications. This also provides the advantage that more catalytic units can be grafted to the surface of magnetic nanoparticles and thus provides higher catalyst loading. Accordingly, different types of polymers with various topological structures, including linear,[25] brush,[26] hyper-branched[27] and dendrimer[27-29] have been used for polymeric functionalization of magnetic nanoparticles.

In our present work, we report the development of a novel heterogeneous organocatalyst combining the unique properties of magnetic nanoparticle and a cross-linked basic polymer. The broad applicability of ensuing catalyst was probed through a library synthesis of 2-amino-4*H*-benzo[*b*]pyranes.

4*H*-benzo[*b*]pyranes have a wide range of biological activities and are widely distributed in nature. They have also diverse pharmacological properties and some significance application in the design of new therapeutic agents.[30,31] The conventional reported method for synthesis of 4*H*-benzo[*b*]pyranes is using organic solvents such as DMF or acetic acid under reflux temperature.[32] Several homogeneous or heterogeneous basic or acidic catalysts have been used for this reaction.[31,33,36-39]

However in most of these methods catalysts cannot be recycled and a large volume of solvent is needed for product separation. In addition, they have one or more of other disadvantages such as using equivalent or high wt% value of catalyst, toxicity of catalyst, centrifuging or filtration methods for catalyst recovery, long reaction times, reflux condition, inert atmosphere, non-green solvents, and high overall cost of reagents. Thus new routes for the synthesis of 4*H*-benzo[*b*]pyranes have attracted considerable attention in the search for new and rapid methods to access them.

2. Experimental

2.1. Reagents and analysis

Ferric chloride hexahydrate ($FeCl_3.6H_2O$), ammonia (25%), ferrous chloride tetrahydrate ($FeCl_2.4H_2O$), 3-(trimethoxysilyl)propylmethacrylate (MPS), *N,N*-dimethylethylenediamine and methylenebisacrylamide (MBA) were obtained from Merck without further purification. 2,2'-Azobisisobutyronitrile (AIBN, Kanto, 97%) was recrystallized from ethanol and methyl acrylate (Sigma-Aldrich) was distilled before use.

Thin layer chromatography (TLC) was performed with silica gel 60 F254 plates and UV light was used for visualization. FT-IR spectra of samples were taken using an ABB Bomem MB-100 FT-IR spectrophotometer. NMR spectra were recorded on a Brucker NMR 500 MHz instrument. Thermogravimetric analysis (TGA) was acquired under a nitrogen atmosphere with a TGA Q 50 thermo-gravimetric analyzer. Transmission electron microscopy (TEM) images were taken with a TOPCON-002B electron microscope. The magnetic property of catalyst was measured by a VSM Model 7400.

2.2. Synthesis of modified magnetic nanoparticles (MNP@MPS)

The magnetic Fe_3O_4 nanoparticles were prepared by chemical co-precipitation method. An iron salt solution was obtained by mixing 13.6 g $FeCl_3.6H_2O$ and 5 g $FeCl_2.4H_2O$ in 500 mL deionized water under nitrogen at room temperature. By dropwise addition of NH_3 solution, pH was adjusted to 12. A black precipitate was formed after continuously stirring for 1 h. The precipitate was magnetically separated and washed four times with deionized water and two times with ethanol and was dried under vacuum at 50°C overnight.

The resulted Fe_3O_4 nanoparticles (3 g) were ultrasonically suspended in 400 mL of ethanol/water mixture (4:1) and pH of solution was adjusted on 9 by adding ammonium solution. Tetraethyl orthosilicate (TEOS, 15 mL) was dropwise added to the solution at 50 °C in the presence of a constant nitrogen flow. The mixture was stirred for 6 h. Then silica coated nanoparticles were magnetically separated and washed three times with deionized water and two times with ethanol. The final dark brown product (MNP) was dried at 50 °C under vacuum for 24 h.

Afterward, 1 g MNP were dispersed in 40 mL of a 4/1 mixture of ethanol/water, then 2 mL of ammonium hydroxide 25% solution was added. Then, an excess amount (10 mmol per 1 g of MNP) of the MPS was added dropwise over a period of 10 min, and the reaction mixture was stirred at 50 °C for 48 h. The modified MNP@MPS were magnetically separated and washed three times with methanol to remove any excess of reagent and salts.

2.3. Synthesis of catalyst

500 mg of MNP@MPS nanoparticles were dispersed by ultrasonic in 200 mL methanol in a 500 mL single-necked flask for 10 min. Then, a mixture of 2 g methyl acrylate, 500 mg of MBA, and 70 mg of AIBN were added to the flask to initiate the polymerization. The mixture was completely deoxygenated by bubbling purified argon for 30 min. The flask submerged in a heating oil bath attached with a fractionating column, Liebig condenser, and a receiver. The reaction mixture was heated from ambient temperature to the boiling state within 1 h and the

reaction was ended after about 100 mL of methanol was distilled from the reaction mixture within 5 h. The obtained cross-linked poly(methylacrylate) coated MNP (MNP@PMA) were collected by magnetic separation and washed two times with water and three times with methanol to eliminate excess reactants and few generated co-polymer microspheres.

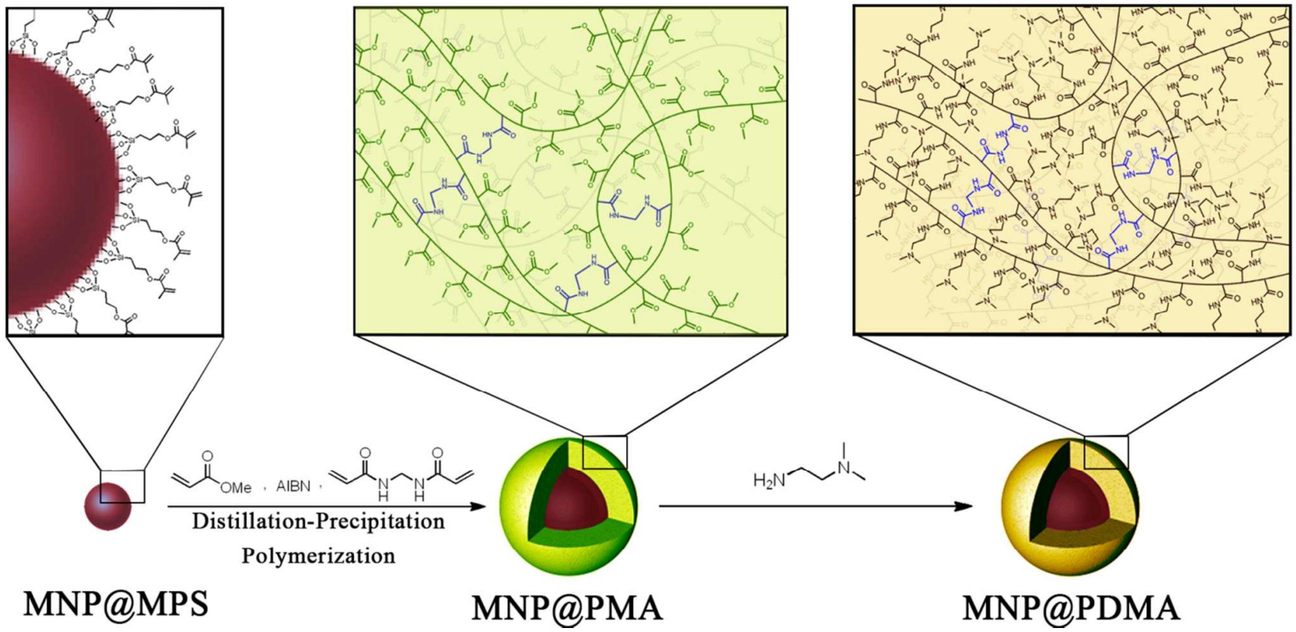
500 mg of MNP@PMA nanoparticles were dispersed by ultrasonic in 20 mL methanol in a 50 mL single-necked flask for 10 min. Then, 15 mL *N*,*N*-dimethylethylenediamine was added and mixture was stirred at 60 °C until the stretching vibration bond of carbonyl of poly(methylacrylate) disappeared (about 48 h). The final catalyst poly(dimethylaminoethyl) acrylamide coated MNP (MNP@PDMA) was magnetically separated and washed three times with methanol to remove any excess of reagent and then dried at 60 °C for 12 h.

2.4. General procedure for synthesis of 4H-benzo[b]pyranes

In a 10 mL round bottom flask, aldehyde (1 mmol), malononitrile (1.2 mmol), water (2 mL), and MNP@PDMA (25 mg, 4 mol%) was added and the mixture was stirred for 5 min at room temperature. Then, dimedone (1 mmol) was added to the flask and the mixture was vigorously stirred for an appropriate time monitored by TLC until all starting materials were fully disappeared. The reaction mixture diluted with hot ethylacetate. Then, the catalyst was magnetically separated and washed two times with methanol and dried under vacuum. The organic layer was concentrated under vacuum and the resulting solid products were recrystallized from ethanol.

3. Result and discussion

Schematic illustration of catalyst synthesis is shown in Scheme 1. The first step involves the synthesis of dark brown MNPs by the co-precipitation technique based on a reported method [34]. Silica coating of Fe_3O_4 surface by TEOS increases its stability against heat and harsh reagents. Coating of 3-methacryloxypropyltrimethoxy-silane (MPS) onto the MNPs gives two important results including easier polymerization on the surface of magnetic nanoparticles due to the presence of methacrylate groups and covalent attachment of copolymers to the surface of MNP. Without MPS modification, only a minor part of the magnetic nanoparticles can be coated with a complete layer of polymer chains instead of all of them.[35] The synthesis of MNP@PMA was performed via distillation-precipitation polymerization method without any surfactant with MNP@MPS as the seed, methyl acrylate as monomer, MBA as cross-linker, and AIBN as initiator in methanol. Since cross-linked polymers are not soluble in the methanol, they will continuously precipitate from the solution and attach to the surface of the MNPs to form a robust shell through the simultaneous distillation of the solvent. This surfactant-less method leads to the formation of a multilayer polymeric shell around MNPs. In the final step, reaction of esteric groups with *N*,*N*-dimethylethylenediamine provides the desired MNP@PDMA catalyst. The tertiary amine groups on the surface of catalyst can act as basic catalyst (Scheme 1).



Scheme 1. Synthesis of catalyst MNP@PDMA

The identity of catalyst was characterized using an array of sophisticated analytical techniques. Fig. 1 shows the FT-IR spectra of Fe_3O_4@SiO_2 (MNP) (a), MNP@MPS (b), MNP@PMA (c), and MNP@PDMA (d), respectively. Fig. 1a shows stretching vibrations of Fe-O and Si-O at 582 and 1083 cm^{-1}, respectively. Coating of MPS onto the MNP confirmed by observed peaks at 2929, 1707, and 1404 cm^{-1} in Fig. 1b which are attributed to C-H, esteric C=O, and C=C bonds, respectively. The FTIR spectrum of MNP@PMA (Fig. 1c) shows a strong vibration bond in 1735 cm^{-1} associated to esteric C=O of poly(methylacrylate). Conversion of CO_2Me groups of polymer shell to $CONH(CH_2)_2N(Me)_2$ and formation of final catalyst are confirmed by appearance of amidic C=O bond at 1638 cm^{-1} and elimination of esteric C=O peak in the FTIR spectrum of MNP@PDMA in Fig. 1d compared to Fig. 1c.

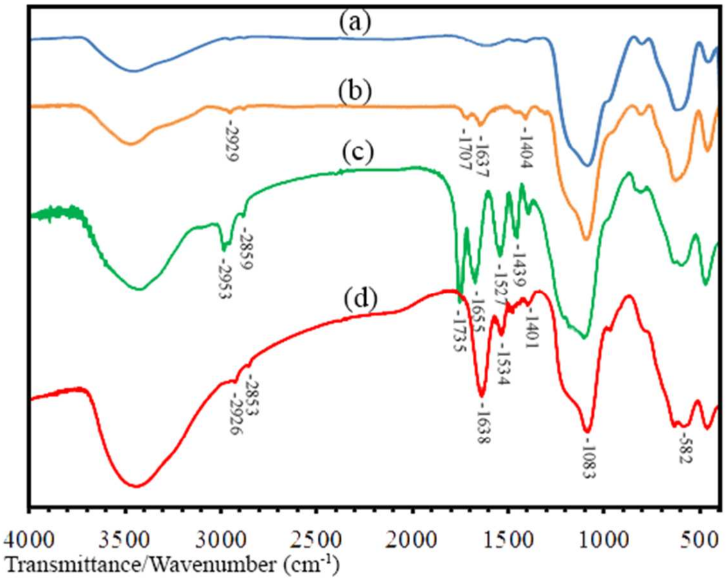


Fig. 1. FT-IR spectra of MNP (a), MNP@MPS (b), MNP@PMA (c) and MNP@PDMA (d)

The presence as well as the degree of crystallinity of magnetic iron oxide (Fe_3O_4) in synthesized MNP@PDMA was obtained from X-Ray diffraction (XRD) patterns (Fig. 2). According to the XRD pattern of standard Fe_3O_4 sample (JCPDS file No. 19-0629), pattern of MNP@PDMA is completely match with the pure Fe_3O_4, confirming the presence of Fe_3O_4 and denotes that all modifications did not change the Fe_3O_4 phase. The broad peak at 2θ=20 is corresponded to the amorphous silica phase in the catalyst structure.

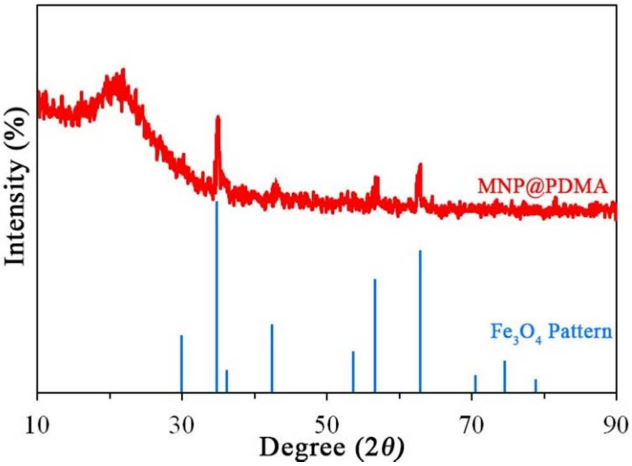


Fig. 2. XRD diffraction patterns of the catalyst MNP@PDMA

The magnetization curves of bare Fe_3O_4 nanoparticles and MNP@PMDA catalyst are shown in Fig. 3a and b, respectively. It can be seen that the Fe_3O_4 and MNP@PDMA particles are superparamagnetic with magnetic saturation (MS) values of about 64.1 and 24.6 emu g^{-1}, respectively. The 39.5 emu/g diminution of saturation magnetization was attributable to the presence of SiO_2/PDMA shell on Fe_3O_4 particles. However, the level of catalyst magnetizations is still sufficient to strongly response to an external magnet thorough catalyst recovering (Fig. 3, inserted image).

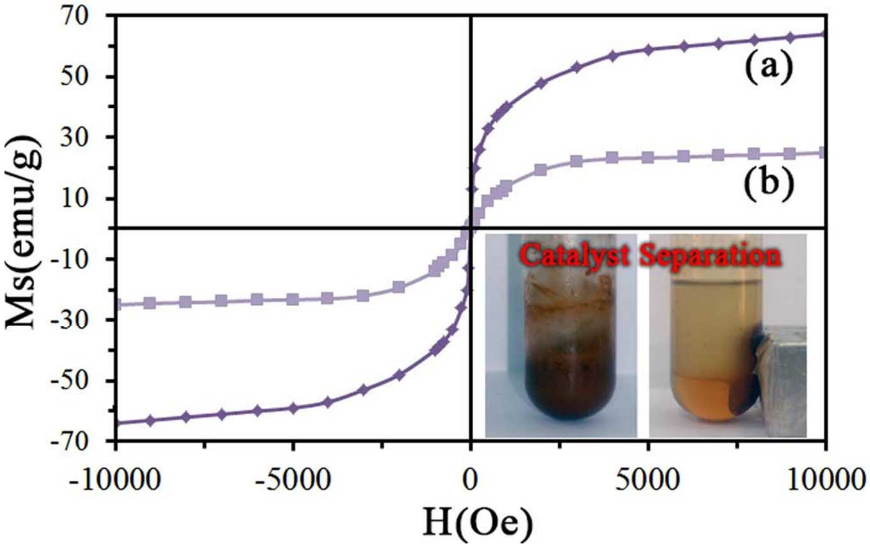


Fig. 3. VSM curves for Fe_3O_4 (a), MNP@PDMA (b) and magnetic recovery of catalyst (inserted image)

The thermogravimetric analysis (TGA) of the magnetic nanocatalyst MNP@PDMA as well as MNP@MPS and MNP@PMA were performed over the range of temperature 25-900 °C (Fig. 4a-c). As shown in Fig. 4a-c, weight loss within 150 °C was completely attributed to the loss of adsorbed water molecules on the surface of nanostructure materials. TGA curve of MNP@MPS (Fig 4a) shows a weight loss at 250 °C attributed to the loss of propylmethacrylate. From this weight loss (4.1 wt %) it is calculated that the loading of MPS bounded to the MNP surface was 0.32 mmol g^{-1}. The TGA curve of MNP@PMA (Fig. 4b) shows an increased weight loss (21.5 wt %) due to the loss of PMA shell. MNP@PDMA loses 29 % of its weight at 220°C (Fig. 4c), corresponded to the cross-linked poly(dimethylaminoethyl) acrylamide. Since, both of MNP@PMA and MNP@PDMA contain monomer and cross-linker, calculation of accurate loading amount of $-CO_2Me$ or $-NMe_2$ based on TGA curves is not possible.

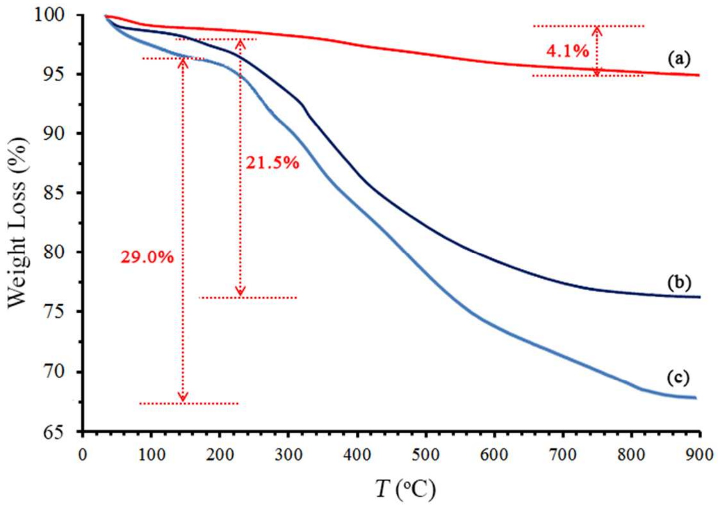


Fig. 4. TGA carves of (a) MNP@MPS, (b) MNP@PMA, and (c) MNP@PDMA

The loading amount of basic NMe_2 groups on the surface of catalyst was calculated by back titration method. 50 mg MNP@PDMA was dispersed in water and an excess amount of HCl (0.5 *M*) was added. The mixture was stirred for 3 h until neutralization of all amine groups on the surface of catalyst. Then the catalyst was magnetically separated. The excess amount of HCl in remaining solution was tittered by NaOH (0.1 *M*) in the presence of phenolphthalein. The loading amount of NMe_2 on the surface of MNP@PDMA was found 1.58 mmol/g.

All results of elemental analysis for MNP@MPS, MNP@PMA and MNP@PDMA are showed in Table 1. The loading amount of MPS on the surface of MNP@MPS was calculated about 0.38 mmol/g based on C atom which is in good agreement with TGA data. Since the only source of N atom in MNP@PMA is the nitrogen of cross-linker (plus 0.09% in entry 1), the content of MBA in MNP@PMA can be calculated based on N atom. It was found that the loading amount of MBA in MNP@PMA is about 0.28 mmol/g which means 4.3 wt% of MNP@PMA. The loading amount of CO_2Me groups is also calculated based on C content of

MNP@PMA after subtracting the C content of MBA (%$C_{for\ MBA}$=2.35 wt%). As shown in Table 1 (entry 3), the nitrogen content of MNP@PDMA is increased due to the conversion of PMA to PDMA on the catalyst surface. Since the cross-linker content of MNP@PMA and MNP@PDMA is almost the same, the loading amount of *N*,*N*-dimethylaminoethyl acrylamide in PDMA and subsequently basic NMe_2 group in MNP@PDMA can be calculated. Regarding to the N content of MNP@PMA (0.87-0.09=0.78%), corresponded to MBA, it can be calculated that N content of *N*,*N*-dimethylaminoethyl acrylamide in PDMA is 4.18% (5.05-0.78-0.09=4.18%), which is equal to 1.49 mmol/g of *N*,*N*-dimethylaminoethyl acrylamide or NMe_2. These results are in good agreement with the loading amount calculating from titration.

Table 1

The results of CHN analysis for MNP@MPS, MNP@PMA and MNP@PDMA

Entry	Sample	C(%)	H(%)	N(%)	Loading (mmol/g)
1	MNP@MPS	3.19	0.62	0.09	0.38[a]
2	MNP@PMA	13.27	1.97	0.87	For MBA 0.28[b] For CO_2Me 1.61[c]
3	MNP@PDMA	18.15	3.09	5.05	For NMe_2 1.49[d]
4	Recycled MNP@PDMA	17.63	2.94	4.86	For NMe_2 1.43[d]

[a] Based on carbon atom.

[b] Based on nitrogen atom.

[c] Based on carbon atom after subtracting the %C of MBA. %C of MBA can calculate from the loading amount of MBA (0.28 mmol/g) which is 2.35%.

[d] Based on nitrogen atom after subtracting the %N of MBA which is 0.78% (0.87-0.09=0.78%).

The morphology of the MNP@PDMA was also investigated by TEM and SEM (Fig. 5a and b, respectively). The TEM image of MNP@PDMA catalyst confirms the nanometer size of the catalyst and shows that dark MNPs with 5-10 nm diameters are encapsulated by grey polymer layers. The SEM and TEM images of MNP@PDMA show that MNPs are entrapped by polymer shells.

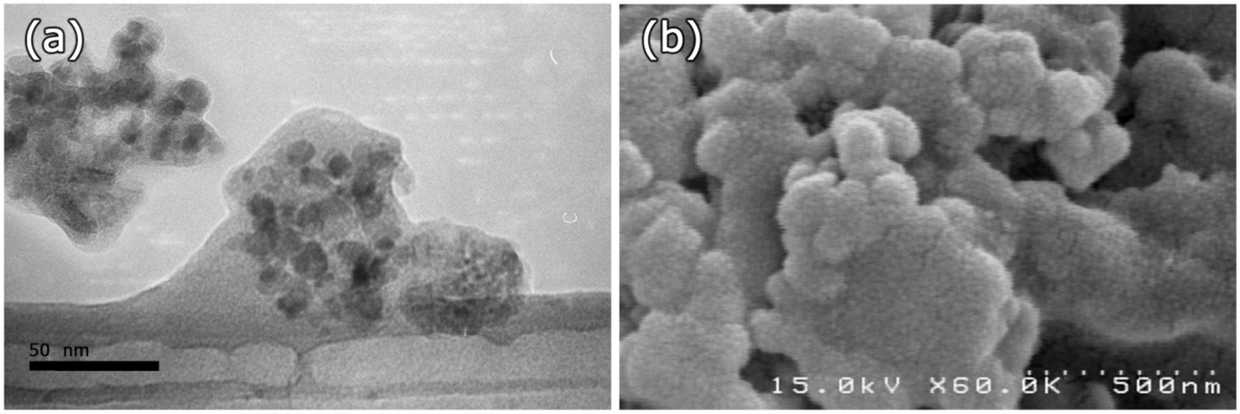


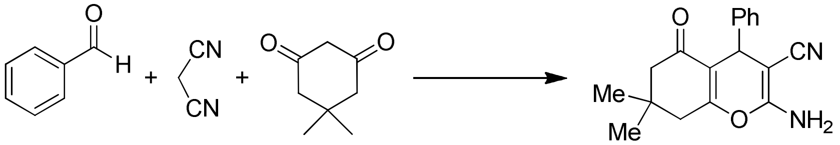
Fig. 5. TEM (a) and SEM (b) images of MNP@PDMA

To evaluate catalytic performance and efficiency of MNP@PDMA, we selected the one-pot reaction of benzaldehyde, malononitrile and dimedone for the synthesis of 2-amino-4*H*-benzo[*b*]pyrane as a base-catalyzed model reaction.

The reaction of benzaldehyde, malononitrile and dimedone without catalyst under solvent-free or using water as solvent at 80°C gives only a trace amount of 4-*H*-benzo[*b*]pyrane in 60 min (Table 2, Entry 1,2). Thus our first investigation focused on the optimization of solvent and temperature in the presence of enough catalyst (Table 2). It was found that the simultaneous presence of solvent and catalyst has a key role. The reaction gives trace amount of product without solvent even with 10 mol% catalyst. Optimization of solvent and temperature in the presence of enough catalyst showed that H_2O is the best medium for the reaction at room temperature. Then, the amount of catalyst optimized in H_2O as solvent at room temperature for the model reaction. As indicates in Table 2, maximum yield of 4*H*-benzo[*b*]pyrane was obtained using 25 mg catalyst (4 mol%) after 25 min at room temperature (Entry 14). The lower amount of catalyst dramatically decreased the yield of reaction even with increasing time or temperature (Entries 13,16).

Table 2

Optimization of solvent and temperature and catalyst amount for the synthesis of amino 4-*H*-benzo[*b*]pyrane[a]



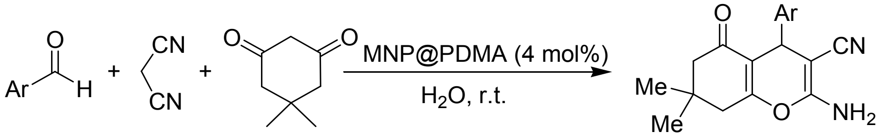
Entry	MNP@PDMA (mol%)	Solvent	*T* (°C)	Time (min)	Yield (%)[b]
1	-	Solvent-free	80	60	Trace
2	-	H_2O	80	60	15
3	10	Solvent-free	r.t	60	20
4	10	EtOH	r.t	60	60
5	10	EtOH:H_2O (1:1)	r.t	60	84
6	10	H_2O	r.t	60	94
7	10	H_2O	50	40	94
8	10	CH_3CN	50	60	80
9	10	CH_2Cl_2	r.t	60	21
10	10	H_2O	r.t	10	85
11	6	H_2O	r.t	10	80
12	4	H_2O	r.t	10	77
13	3	H_2O	r.t	10	59
14	4	H_2O	r.t	25	95
15	3	H_2O	r.t	30	75
16	3	H_2O	60	30	84

[a] Reaction condition: benzaldehyde (1 mmol), malononitrile (1.2 mmol), dimedone (1 mmol), solvent (3 mL), loading of amine groups in MNP@PDMA (1.58 mmol/g).
[b] Isolated yield.

Thus, the reaction of benzaldehyde, malononitrile, and dimedone proceeds well at room temperature in the presence of 4 mol% catalyst and H_2O as solvent via Aldol condensation/Michael addition/interamolecular cycloaddtion sequences and produces corresponding 4*H*-benzo[*b*]pyrane within 25 minutes with 95% yield.

With the optimized reaction conditions, we examined the generality of the supported MNP@PDMA catalyst for the synthesis of 4*H*-benzo[*b*]pyranes using different types of aldehydes. As seen in Table 3, various aldehydes such as aldehydes carrying electron-withdrawing groups (Entries 1-9), weak and strong electron-donating group (Entries 9-14, 18), conjugated aldehyde (Entry 15) and 1,4-dialdehyde (Entry 16) were also reacted and gave good yields of products. However, in the presence of 4 mol% MNP@PDMA, the reaction time for highly deactivated aldehydes increased. In a scale-up experiment, we examined the reaction between benzaldehyde, malononitrile and dimedone as a model reaction under optimized conditions in 10 mmol scale. The yield of scale-up reaction did not change. This demonstrated that catalyst performance in a scale-up process is as good as in a 1 mmol scale reaction.

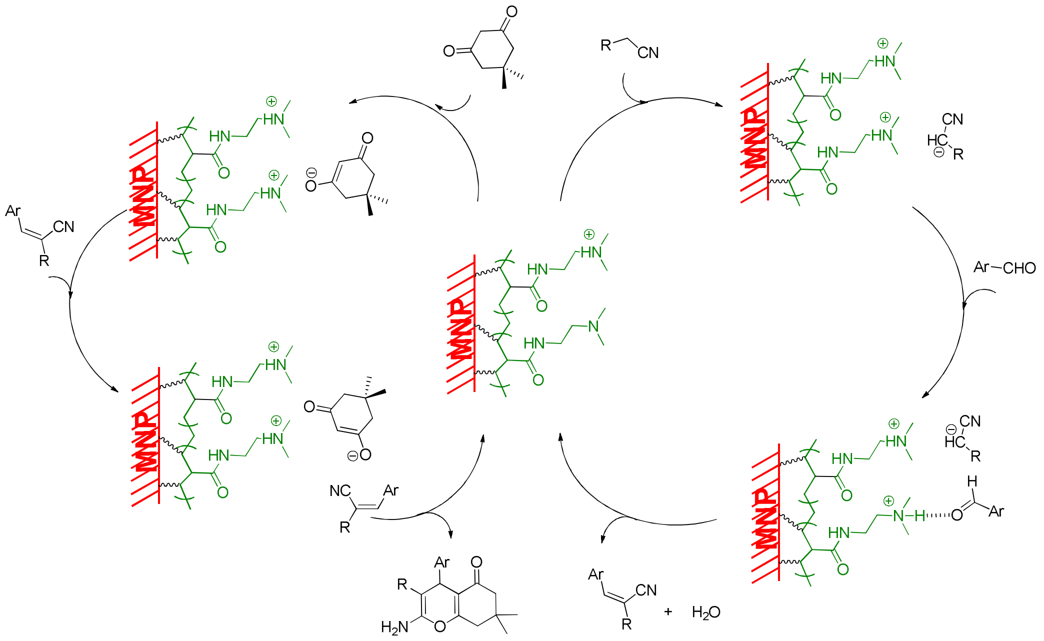
Table 3
Synthesis of 2-amino-4*H*-benzo[*b*]pyranes under optimized condition[a]



Entry	Ar	Time (min)	Yield (%)[b]
1	2-NO_2-Ph	12	91
2	3-NO_2-Ph	10	95
3	4-NO_2-Ph	10	96
4	4-Cl-Ph	13	92
5	2-Cl-Ph	10	90
6	2,4-di(Cl)Ph	15	92
7	4-(CN)-Ph	21	89
8	Ph	25	95
9	4-Me-Ph	25	89
10	2-(OH)-Ph	31	80
11	4-(OH)-Ph	33	86
12	2-(OMe)-Ph	35	75
13	4-(OMe)-Ph	45	86
14	4-(NMe2)-Ph	40	81
15	PhCH=CH-	41	88
16	Furfural	30	90
18	Vanilline	45	84
19	4-(CHO)-Ph	32	87

[a] Reaction condition: aldehyde (1 mmol), malononitrile (1.2 mmol), dimedone (1 mmol), H_2O (3 mL), MNP@PDMA (25 mg, 4 mol%), room temperature.
[b] Isolated yield.

Although we have not established the mechanism the catalytic reaction in an experimental manner, a possible explanation is proposed in Scheme 1. It is notable that the heterogeneous basic catalyst is partially protonated in H_2O.



Scheme 2. Plausible mechanism for synthesis of product through basic site of catalyst

The recyclability of MNP@PDMA was investigated in the synthesis of 4*H*-benzo[*b*]pyranes by choosing the reaction between benzaldehyde, malononitrile and dimedone as model reaction. Reaction was repeated for five times and after each cycle, catalyst was magnetically separated, washed and dried for next run. The results indicate that no significant loss of catalyst activity was observed and the yield of product remains up to 90 % (Fig. 6). It is notable that the amount of remaining catalyst after 5 runs was measured 21 mg. Also the CHN analysis shows that the catalyst content after five cycles did not change so much (Table 1, Entry 4). These results show that catalyst is stable under reaction condition and no significant leaching occurs.

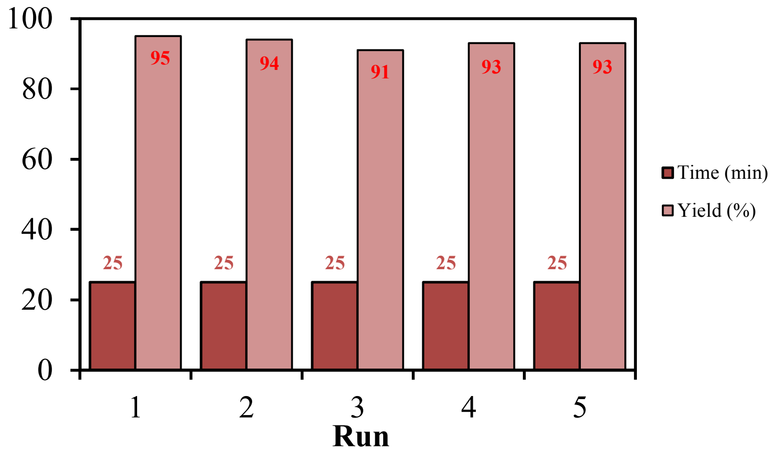


Fig. 6. Recycling experiment

To determine whether our reaction using MNP@PDMA actually occurs through a heterogeneous catalytic process, the following experiment was carried out. The model reaction was performed under optimized condition (Table 2, entry 14), and the MNP@PDMA catalyst was completely removed from the reaction mixture by an external magnet after 10 min. Then, the reaction was allowed to stir for 6 hours (Fig. 7) and it was found that no further production of 4*H*-benzo[*b*]pyrane was observed. Moreover, titration analysis of recycled catalyst showed that the loading amount of NMe_2 did not significantly change (1.51 mmol/g). These results can rule out any contribution of leached amine into the reaction medium, and confirms that the observed catalyst is completely heterogeneous.

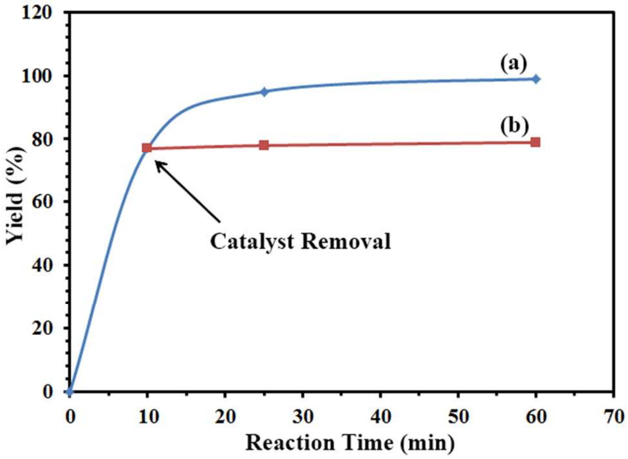


Fig. 7. Leaching experiment. (a) reaction in the presence of catalyst and (b) reaction after removal of catalyst.

Table 4 summarizes the advantages of MNP@PDMA compared to the most recent reported heterogeneous catalyst for the synthesis of 2-amino-4*H*-benzo[*b*]pyranes. As seen, present protocol and catalyst have the advantages of magnetic recyclability, high loading level of active catalyst site, using of low weight percent of catalyst and high product yield.

Table 4

Comparison of reaction conditions and catalyst efficiency of MNP@PDMA with the most recent reported catalyst for the synthesis of 2-Amino-4*H*-benzo[*b*]pyranes.

Catalyst	Magnetic recoverable	Catalyst loading [a] (mmol/g)/mg /mol%	Solvent	*T* (°C)	Time (min)[b]	Yield (%)[b]	Ref
MNP@PDMA	Yes	1.58/ 25/ 4	H_2O	r.t.	25	95	This work
Amino-β-cyclodextrin	NO	-/ 125/ 9	None	r.t.	1	95	[31]
Fe_3O_4@SiO_2/DABCO	Yes	-/ 50/ -	H_2O	80	25	90	[39]
SB-DABCO	NO	1/ 60/ 6	EtOH	r.t.	35	96	[36]
Salep-*g*-PMAPTAH	NO	3/ 2/ 0.5	H_2O	r.t.	15	93	[33]
(SB-DBU)Cl	NO	0.45/ 110/ 5	EtOH	r.t.	35	94	[37]
Nano γ-Fe_2O_3	Yes	-/ 16 / 10	H_2O	r.t.	300	95	[38]

[a] For 1 mmol scale.
[b] For benzaldehyde.

4. Conclusion

Generally, we have developed a novel and efficient heterogeneous basic catalyst in which cross-linked poly(dimethylaminoethyl) acrylamide coated on the modified MNPs by the distillation-precipitation polymerization method. The resulted catalyst proved to be an effective magnetic catalyst for green synthesis of 2-amino-4*H*-benzo[*b*]pyranes in excellent yields. High loading level, high stability, high efficiency at room temperature in water medium, easy magnetic recyclability and reusability, short reaction time, and excellent yields and easy separation of product are the most important aspects of the present catalyst and protocol. Moreover, we developed a novel method for synthesis of magnetic catalysts with high loading level and good stability which can be a good candidate for laboratory and industrial applications.

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Cross-linked poly (dimethylaminoethyl acrylamide) coated magnetic nanoparticles: A high loaded, retrievable, and stable basic catalyst for water-medium synthesis of benzopyranes

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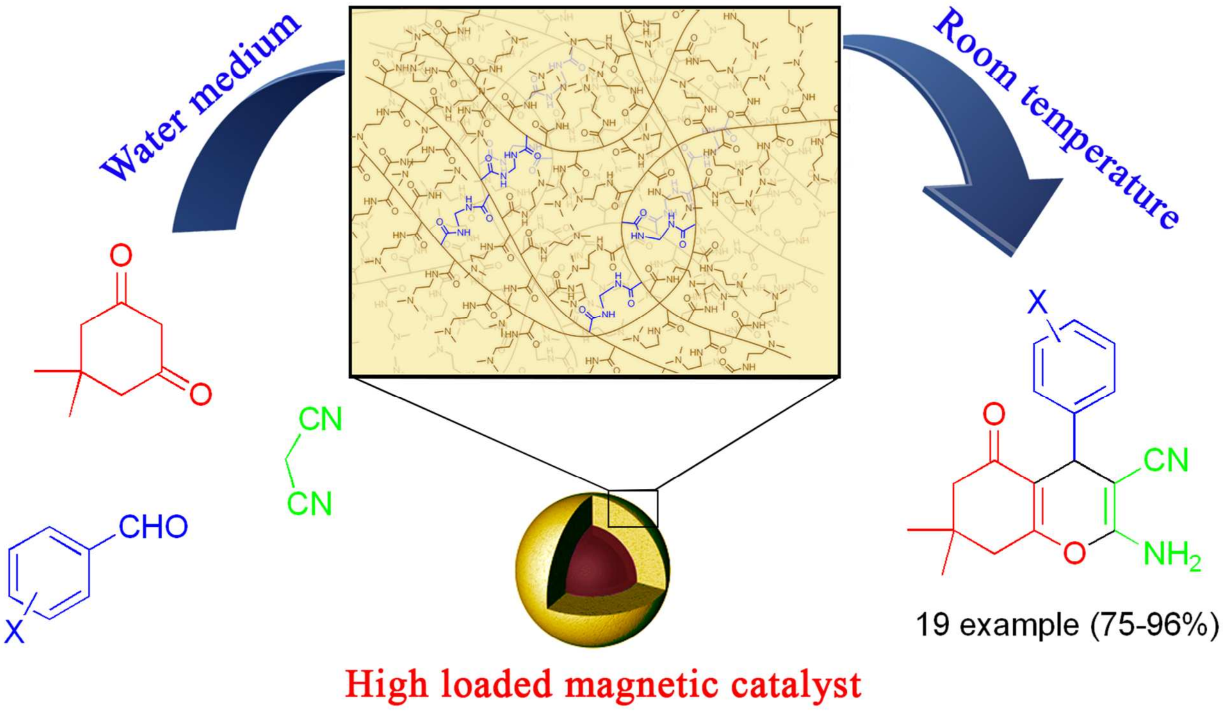

A high loaded basic magnetic catalyst was synthesized by distillation-precipitation-polymerization method. The catalyst shows high activity in water medium for the synthesis of 4*H*-benzopyrans.