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Piperidine and Piperazine Immobilized on Iron Oxide Nanoparticles as Magnetically Recyclable Heterogeneous Catalysts for One-Pot Synthesis of β-Phosphonomalonates

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Abstract Piperidine and piperazine immobilized on silica-coated γ-Fe_2O_3 magnetic nanoparticles were synthesized as new supported bases via the reaction of chloro-functionalized γ-Fe_2O_3@SiO_2 with piperidine and piperazine, respectively. The resulting bases were employed as magnetically recyclable heterogeneous catalysts for the efficient one-pot three-component synthesis of β-phosphonomalonates. The catalysts were easily separated from the reaction mixture by using a magnet and recycled for five times without significant loss of the catalytic activity.

Keywords Magnetic nanoparticles · Piperidine · Piperazine · Heterogeneous catalyst · β-Phosphonomalonates

1 Introduction

Among the organophosphorous compounds, phosphonate derivatives are important key intermediates in biochemical processes due to their wide biological applications as enzyme inhibitors, metabolic probes, peptide mimetics, antibiotics, and pharmacological agents [1–4]. These vast applications have made the development of a number of methods for the synthesis of phosphonates. A versatile and powerful tool for the synthesis of phosphonates is direct P–C bond formation such as Arbuzov reaction [5, 6]. Another significant existing route for P–C bond formation involves the addition of a phosphorous nucleophile to an electron-deficient alkene (phospha-Michael addition) [7–18]. These protocols proceeded through two-pot procedure in which P–C and C–C bonds formation occurred in separate steps. Ethylenediamine diacetate [19], diethylamine [20], 1,5,7-triazabicyclo[4.4.0]dec-5-ene [21], iron doped carbon nanotube [22] and clay supported heteropoly acid [23] are the catalysts which have been reported for the one-pot synthesis of β-phosphonomalonates. We have also recently used ionic liquids [5-hydroxypentylammonium acetate (5-HPAA) and 2-hydroxyethylammonium acetate-SiO_2 (2-HEAA-SiO_2)], iodine, micellar solution of sodium stearate, *n*-propylsulfonated γ-Fe_2O_3 (NPS-γ-Fe_2O_3) and γ-Fe_2O_3@SiO_2-La$(OTf)_2$ for this purpose [24–29]. Although, the reported methods are valuable, they suffer from one or more of the following drawbacks: tedious work-up procedures, requiring ultrasound irradiation or heat, and using expensive, unrecyclable and toxic catalysts or solvents. So, it is still preferable to follow an eco-friendly procedure that applies an efficient and reusable catalyst for the one-pot synthesis of β-phosphonomalonates.

Piperidine and piperazine are known as organic bases, which are used as conventional active catalysts for the synthesis of organic compounds [30–33]. Despite the high catalytic activity of piperidine and piperazine, their separation from homogeneous reaction mixtures requires neutralization by acidic conditions, which lead to worthless ammonium salts. Harmful effect of acidic work-up can be removed by immobilization of piperidine and piperazine onto solid supports to obtain heterogeneous catalysts. Both

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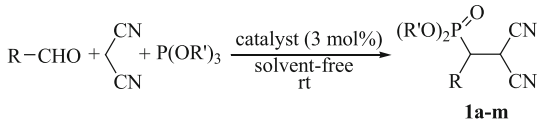
organic polymers like resins [34, 35] and inorganic matrices such as silica [36–39] have been employed as solid supports for this purpose. However, although the supported catalysts can be recovered by filtration or centrifugation methods, these techniques are energy and time consuming and may cause loss of the catalyst during the separation process. The use of magnetic nanoparticles (MNPs) as supporting materials offers a solution to this problem [40, 41]. MNPs are easily separated by an external magnet. Magnetic separation of MNPs is simple, economical and promising for industrial applications. This type of separation is also typically more effective than filtration or centrifugation as it prevents loss of the catalyst. In this view, we have recently focused our efforts on the development of new heterogeneous catalysts based on magnetic nanoparticles [28, 29, 42–45]. Following these studies, herein, we report the synthesis of piperidine and piperazine immobilized on silica-coated γ-Fe_2O_3 MNPs (piperidine-MNPs and piperazine-MNPs) as new heterogeneous bases (Scheme 1).

To investigate the catalytic activity of piperidine-MNPs and piperazine-MNPs in organic reactions, we have used them as magnetically recyclable heterogeneous basic catalysts for the synthesis of β-phosphonomalonates via one-pot three-component reaction of aldehydes, malononitrile and trialkyl phosphites. The catalysts could be readily separated from the reaction mixture by using an external magnet. This kind of separation removes the need of filtration and facilitates recycling of the catalysts (Scheme 2).



Scheme 2 Synthesis of β-phosphonomalonates in the presence of piperidine-MNPs or piperazine-MNPs

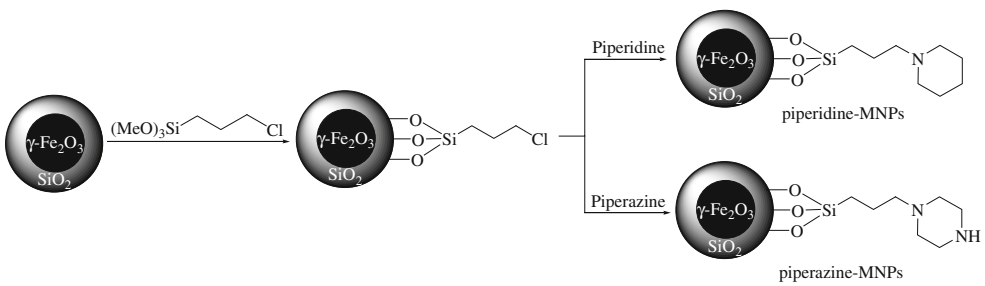
2 Experimental

2.1 General

Chemicals were purchased from Merck Chemical Company. NMR spectra were recorded on a Bruker Avance DPX-250 and 400 using deutrated $CDCl_3$ as solvent and TMS as internal standard. The purity of the products and the progress of the reactions were accomplished by TLC on silica-gel polygram SILG/UV254 plates. Transmission electron microscopy analysis was performed using TEM microscope (Philips CM 10-H-100 kV). FT-IR spectra were recorded on a Shimadzu Fourier transform infrared spectrophotometer (FT-IR-8300). Thermo gravimetric analysis (TGA) was performed using a Shimadzu thermo gravimetric analyzer (TG-50). Elemental analysis was carried out on a Costech 4010 CHNS elemental analyzer. Mass spectra were recorded on a Shimadzu GCMS-QP5050A. The morphology of the products was determined by using Hitachi Japan, model s4160 scanning electron microscopy (SEM) at accelerating voltage of 15 kV. Power X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu K_α ($\lambda = 0.154$ nm) radiation.

2.2 Synthesis of γ-Fe_2O_3@SiO_2

The γ-Fe_2O_3 nanoparticles were synthesized by a reported chemical co-precipitation technique [46–48]. $FeCl_2{\cdot}4H_2O$ (3.98 g) and $FeCl_3{\cdot}6H_2O$ (6.50 g) were dissolved in deionized water (60 mL) under Ar atmosphere at room temperature. A NH_4OH solution (0.6 M, 400 mL) was then added drop wise (drop rate = 1 mL min^{-1}) to the stirring mixture at room temperature to reach the pH of the reaction solution to 11. The resulting black dispersion was continuously stirred for 1 h at room temperature and then heated to reflux for 1 h to yield a brown dispersion. The magnetic nanoparticles were then purified by a repeated centrifugation (3,000–6,000 rpm, 20 min), decantation and redispersion cycle three times. The as-synthesized sample was heated in air at 2 °C min^{-1} up to 200 °C and then kept in



Scheme 1 Synthesis of piperidine-MNPs and piperazine-MNPs

the furnace for 3 h to give a reddish-brown powder. Concentrated solution of ammonia (3.5 mL) was then added to the dispersed γ-Fe_2O_3 nanoparticles (3.5 g) in deionized water (40 mL)/ethanol (160 mL) and the resulting mixture was stirred at 40 °C for 30 min. Subsequently, tetraethyl orthosilicate (TEOS, 2.0 mL) was charged to the reaction vessel and the mixture was continuously stirred at 40 °C for 24 h. The silica-coated nanoparticles (γ-Fe_2O_3@SiO_2) were collected by a permanent magnet followed by washing three times with EtOH and diethyl ether and dried at 100 °C in vacuum for 24 h.

2.3 Synthesis of Chloro-Functionalized γ-Fe_2O_3@SiO_2

A mixture of γ-Fe_2O_3@SiO_2 (2.0 g) in dry toluene (40 mL) was sonicated for 45 min. 3-Chloropropyl trimethoxysilane (0.5 mL) was added to the dispersed γ-Fe_2O_3@SiO_2 in toluene and slowly heated to 105 °C. The reaction mixture was stirred at this temperature for 20 h. The resulting chloro-functionalized γ-Fe_2O_3@SiO_2 was separated by an external magnet and washed three times with diethyl ether and CH_2Cl_2, and dried under vacuum. The loading amount of Cl atom was 0.4 mmol per gram catalyst based on elemental analysis and TGA.

2.4 Synthesis of Piperidine-MNPs and Piperazine-MNPs

Piperidine or piperazine (0.1 g) was added to chloro-functionalized γ-Fe_2O_3@SiO_2 (1.7 g) in dry toluene (15 mL), and the mixture was stirred for 6 h. The resulting solid material was separated by an external magnet, washed with diethyl ether and CH_2Cl_2, and dried at room temperature in vacuum to afford piperidine-MNPs or piperazine-MNPs.

2.5 Synthesis of β-Phosphonomalonates in the Presence of Piperidine-MNPs or Piperazine-MNPs

Piperidine-MNPs (3 mol %, 0.083 g) or piperazine-MNPs (3 mol %, 0.120 g) was added to a stirred mixture of aldehyde (1 mmol), malononitrile (1 mmol) and trialkyl phosphite (1 mmol). The reaction mixture was stirred at room temperature for the appropriate time (Table 2). EtOH (10 mL) was added to the reaction mixture. The catalyst was separated by an external magnet, washed with EtOH, dried and reused for a consecutive run under the same reaction conditions. Solvent of the remaining solution was evaporated under reduced pressure to give the crude products. The pure products were obtained by chromatography on silica gel eluted with *n*-hexane:EtOAc (1:2).

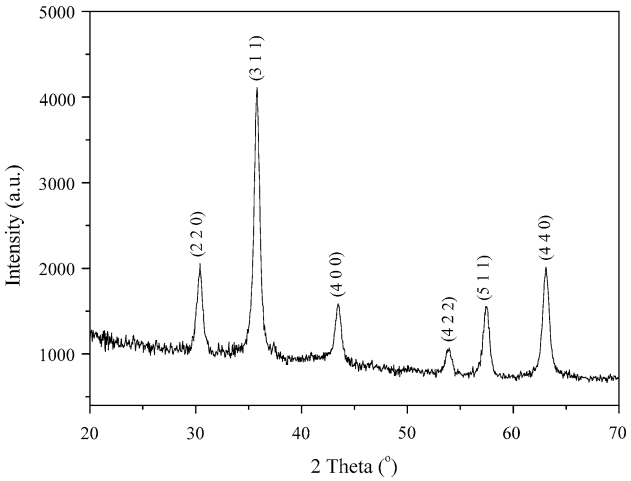


Fig. 1 XRD pattern of γ-Fe_2O_3 MNPs

3 Results and Discussion

3.1 Synthesis and Characterization of Piperidine-MNPs and Piperazine-MNPs

At first, γ-Fe_2O_3 nanoparticles were synthesized by a reported chemical co-precipitation technique of ferric and ferrous ions in alkali solution followed by thermal treatment [46–48]. Figure 1 shows the XRD pattern of γ-Fe_2O_3 MNPs. The observed diffraction patterns have a good agreement with the cubic structure of maghemite (JCPDS file No 04-0755), a unit cell dimension of 8.35 Å and the space group of P4132 (213). The average crystallite size was calculated to be 13.1 nm using the Scherrer equation in which $K = 0.9$ and $\lambda = 0.154$ nm.

γ-Fe_2O_3 MNPs suspension was sonicated in an alkaline solution of tetraethyl orthosilicate (TEOS) to obtain MNPs coated by silica. The shell of silica not only improves the dispersibility but also provides suitable sites (Si–OH groups) for further surface functionalization. The resulting silica-coated γ-Fe_2O_3 MNPs (γ-Fe_2O_3@SiO_2) were then allowed to react with (3-chloropropyl)trimethoxysilane in toluene under reflux conditions to give chloro-functionalized silica-coated γ-Fe_2O_3. Piperidine-MNPs and piperazine-MNPs were obtained by the reaction of chloro-functionalized silica-coated γ-Fe_2O_3 with excess amount of piperidine and piperazine, respectively. The synthesized piperidine-MNPs and piperazine-MNPs were characterized by SEM, TEM, FT-IR, TGA and elemental analysis.

SEM images of piperidine-MNPs and piperazine-MNPs were showed uniformity and spherical morphology of MNPs (Fig. 2). The particle size distribution of piperidine-MNPs and piperazine-MNPs were evaluated using TEM (Fig. 3). The mean diameter of nanoparticles was 14 nm.

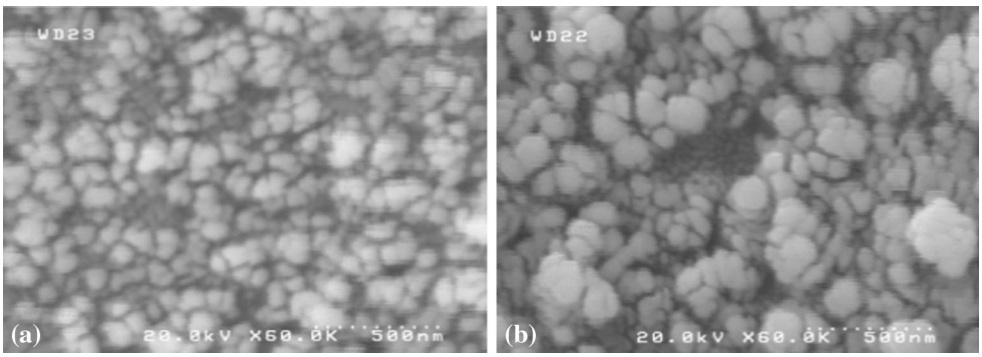


Fig. 2 SEM of **a** piperidine-MNPs and **b** piperazine-MNPs

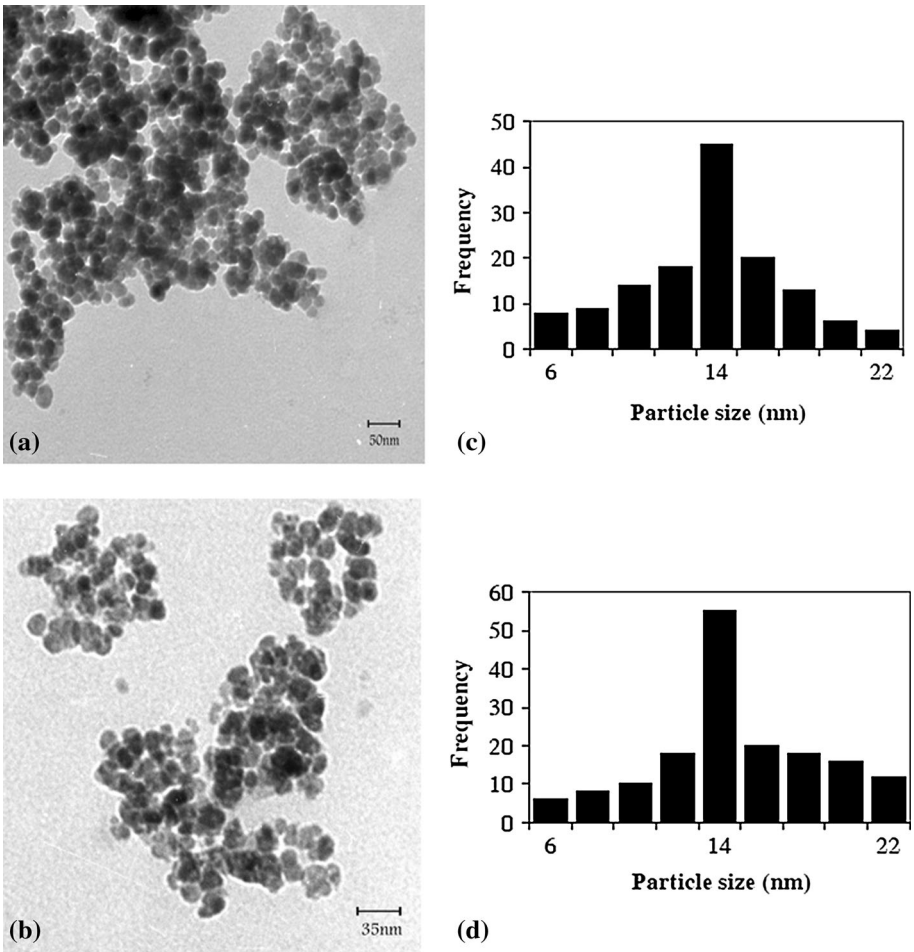


Fig. 3 **a** TEM of piperidine-MNPs, **b** TEM of piperazine-MNPs, **c** particle size distribution histogram of piperidine-MNPs and **d** particle size distribution histogram of piperazine-MNPs

FT-IR spectra of γ-Fe_2O_3, γ-Fe_2O_3@SiO_2, piperidine-MNPs and piperazine-MNPs (Fig. 4) were showed broad bands at around 550–650 cm^{-1}, which were attributed to Fe–O vibrations [49]. In the spectra of γ-Fe_2O_3@SiO_2, piperidine-MNPs and piperazine-MNPs, the Si–O-Si stretching modes of silica shell can be observed as a strong broad peak at about 1,099–1,220 cm^{-1} [50]. In the spectra of piperidine-MNPs and piperazine-MNPs, a typical band at about 2,960 cm^{-1} was attributed to C–H stretching vibrations of alkyl chains. An absorption band at 3,461 cm^{-1} was observed in the spectrum of piperazine-MNPs which was related to the stretching vibration of N–H bonds. These results indicated that piperidine and piperazine were successfully grafted onto the γ-Fe_2O_3@SiO_2 MNPs.

The thermal stability of piperidine-MNPs and piperazine-MNPs were investigated by thermogravimetric analysis (TGA) (Fig. 5). TG curve of piperidine-MNPs

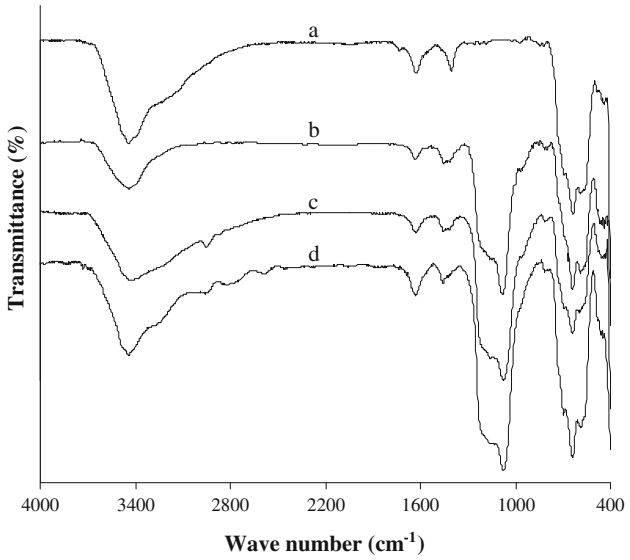


Fig. 4 FT-IR spectra of **a** γ-Fe_2O_3, **b** γ-Fe_2O_3@SiO_2, **c** piperidine-MNPs and **d** piperazine-MNPs

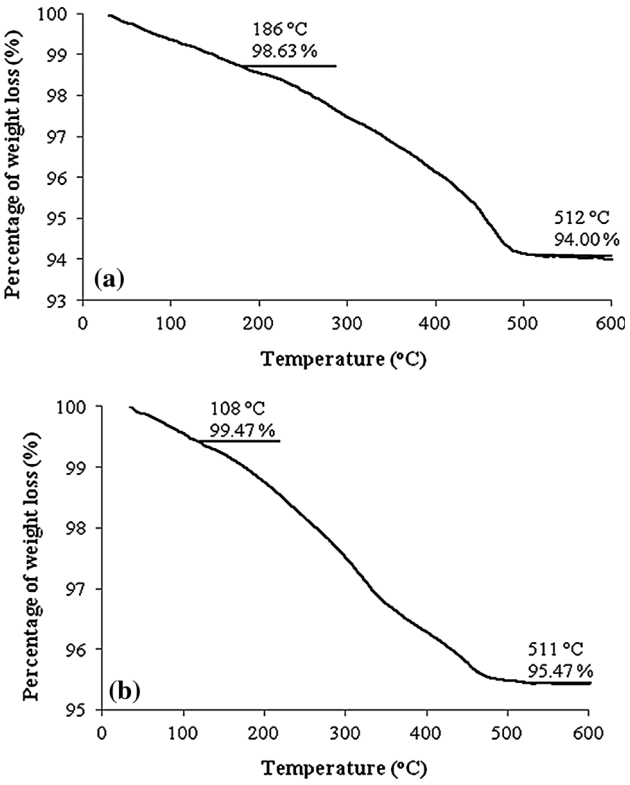


Fig. 5 TGA of **a** piperidine-MNPs and **b** piperazine-MNPs

showed the weight loss around 180 °C, which was related to the adsorbed water molecules on the support. The organic parts were decomposed completely in the temperature range of 195–496 °C. According to the TGA, the amount of piperidine supported on γ-Fe_2O_3@SiO_2 was evaluated to be 0.36 mmol g^{-1}. These results were in agreement with those obtained by elemental analysis (C = 3.46 % and N = 0.51 %). As shown in the TG curve of piperazine-MNPs (Fig. 5b), the weight loss around 105 °C was attributed to the loss of adsorbed water molecules. Complete loss of organic moiety was seen in the temperature range from 108 to 511 °C. Using TG curve, the amount of piperazine supported on γ-Fe_2O_3 was calculated to be 0.25 mmol g^{-1}. The loading amount of piperazine on γ-Fe_2O_3 was also quantified via elemental analysis and it was 0.25 mmol g^{-1} based on carbon and nitrogen content (C = 2.13 % and N = 0.71 %).

Table 1 One-pot reaction of benzaldehyde, malononitrile and triethyl posphite under different conditions[a]

Entry	Catalyst (mol %)	Solvent	Time	Yield[b] (%)
1	Piperidine-MNPs (1)	–	3 h	72
2	Piperidine-MNPs (3)	–	15 min	91
3	Piperidine-MNPs (5)	–	15 min	91
4	Piperazine-MNPs (1)	–	3 h	69
5	Piperazine-MNPs (3)	–	10 min	90
6	Piperazine-MNPs (5)	–	10 min	91
7	Piperidine-MNPs (3)	H_2O	24 h	62
8	Piperidine-MNPs (3)	EtOH	24 h	69
9	Piperidine-MNPs (3)	*n*-Hexane	24 h	42
10	Piperidine-MNPs (3)	CH_3CN	24 h	70
11	Piperidine-MNPs (3)	Toluene	24 h	74
12	Piperazine-MNPs (3)	H_2O	24 h	55
13	Piperazine-MNPs (3)	EtOH	24 h	64
14	Piperazine-MNPs (3)	*n*-Hexane	24 h	51
15	Piperazine-MNPs (3)	CH_3CN	24 h	67
16	Piperazine-MNPs (3)	Toluene	24 h	78
17	–	–	24 h	62
18	γ-Fe_2O_3 (0.083 g)	–	24 h	60
19	γ-Fe_2O_3@SiO_2 (0.083 g)	–	24 h	61
20	Piperidine (3)	–	10 min	92
21	Piperazine (3)	–	10 min	91

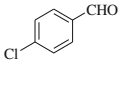
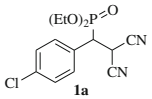
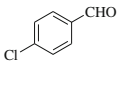
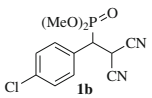
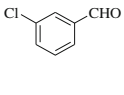
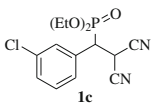
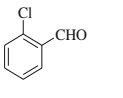
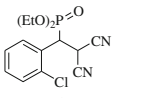
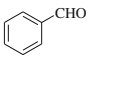
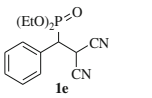
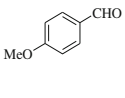
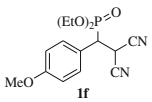
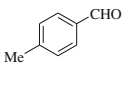
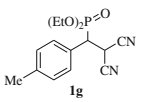
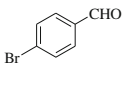
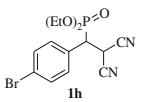
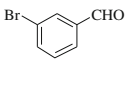
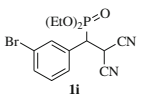
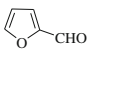
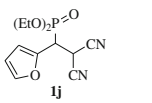
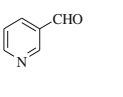
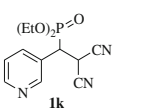
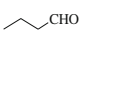
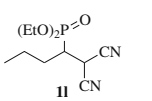
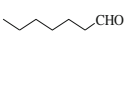
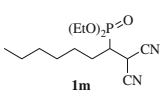
[a] Reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol), triethyl phosphite (1 mmol), room temperature

[b] Isolated yield

3.2 Synthesis of β-Phosphonomalonates Catalyzed by Piperidine-MNPs and Piperazine-MNPs

As part of our attempts orientated to the development of new methods for the synthesis of phosphonate derivatives [51–54], we have recently introduced acidic or neutral conditions for the one-pot synthesis of β-phosphonomalonates [24–29]. Herein, we have studied the application of piperidine-MNPs and piperazine-MNPs as magnetically

Table 2 Synthesis of β-phosphonomalonates in the presence of piperidine-MNPs or piperazine-MNPs[a]

Entry	Aldehyde	Product	Catalyst			
			piperidine-MNPs		piperazine-MNPs	
			Time (min)	Yield (%)[b]	Time (min)	Yield (%)[b]
1		 **1a**	15	85	15	91
2		 **1b**	15	83	20	89
3		 **1c**	15	75	15	75
4		 **1d**	20	75	20	80
5		 **1e**	15	91	10	90
6		 **1f**	5	82	5	81
7		 **1g**	15	83	5	82
8		 **1h**	5	74	5	85
9		 **1i**	30	83	15	81
10		 **1j**	60	79	50	82
11		 **1k**	5	94	5	96
12		 **1l**	15	76	15	75
13		 **1m**	25	72	25	74

[a] Reaction conditions: aldehyde (1 mmol), malononitrile (1 mmol), trialkyl phosphite (1 mmol), catalyst (3 mol %), room temperature

[b] Isolated yield

recyclable heterogeneous basic catalysts for the one-pot three-component synthesis of β-phosphonomalonates.

At first, the reaction of benzaldehyde, malononitrile and triethyl phosphite was chosen as a model reaction to optimize the reaction conditions such as molar ratio of the catalyst and solvent (Table 1, entries 1–16). It was found that the best yield of the product was obtained at room temperature under solvent-free conditions in the presence of 3 mol % of piperidine-MNPs or piperazine-MNPs (Table 1, entries 2 and 5). In order to show the role of the catalyst, similar reactions in the absence of the catalyst and in the presence of γ-Fe_2O_3 and γ-Fe_2O_3@SiO_2 were also examined. Under these conditions, the reactions led to the formation of the desired product in 60–62 % yields after a long reaction time (Table 1, entries 17–19). The role of piperidine and piperazine as non-supported bases were also studied in the reaction of benzaldehyde, malononitrile and triethyl phosphite (Table 1, entries 20 and 21). The results showed that the catalytic activity of piperidine and piperazine did not change after their supporting on the surface of MNPs.

To establish the generality of this method, the synthesis of various β-phosphonomalonates was studied using malononitile, different aldehydes and trialkyl phosphites under optimized reaction conditions (Table 2).

As the results of Table 2 indicate, β-phosphonomalonates **1a** and **1b** were generated in high yields from the reaction of 4-chlorobenzaldehyde and malononitrile with triethyl and trimethyl phosphite, respectively (Table 2, entries 1 and 2). The reaction of various substituted benzaldehyde with malononitrile and triethyl phosphite were proceeded well and produced the corresponding products **1c-i** in good to high yields (Table 2, entries 3–9). Interestingly, piperidine-MNPs and piperazine-MNPs efficiently promoted the synthesis of β-phosphonomalonates using acid-sensitive aldehydes such as furfural and pyridine-3-carbaldehyde without polymerization or decomposition (Table 2, entries 10 and 11). These catalysts were also applied successfully for the synthesis of β-phosphonomalonates from the reaction of triethyl phosphite and malononitrile with aliphatic aldehydes (Table 2, entries 12 and 13).

To show the special catalytic behaviour of piperidine-MNPs and piperazine-MNPs in the synthesis of β-phosphonomalonates, the reaction of benzaldehyde, malononitrile and triethyl phosphite was performed in the presence of a catalytic amount of metal oxides (ZnO, CuO, Sb_2O_3, SnO_2, HgO, PbO, MoO_3, ZrO_2, MgO and CaO), basic catalysts {aminopropylated silica (AP-SiO_2) [54] and γ-Fe_2O_3-pyridine based catalyst [43] }, BrØnsted acids ($HClO_4$-SiO_2 and $H_3PMo_{12}O_{40}$), ionic liquids (5-HPAA and 2-HEAA-SiO_2), iodine and sodium stearate (Table 3). As is evident from Table 3, piperidine-MNPs and piperazine-MNPs were the most effective catalysts for this purpose leading to the formation of β-phosphonomalonate **1e** in high yield in a short reaction time.

Table 3 Comparison of the catalytic activity of piperidine-MNPs and piperazine-MNPs with various catalysts for the synthesis of β-phosphonomalonate **1e**[a]

Entry	Catalyst	Time	Yield (%)[b]
1	ZnO	24 h	61
2	CuO	24 h	56
3	Sb_2O_3	24 h	54
4	SnO_2	24 h	50
5	HgO	24 h	63
6	PbO	24 h	59
7	MoO_3	24 h	51
8	ZrO_2	24 h	54
9	MgO	24 h	35
10	CaO	24 h	38
11	AP-SiO_2	24 h	41
12	γ-Fe_2O_3-pyridine based catalyst	24 h	50
13	$HClO_4$–SiO_2	24 h	52
14	$H_3PMo_{12}O_{40}$	24 h	56
15	5-HPAA	20 min	44
16	2-HEAA-SiO_2	15 min	30
17	I_2	24 h	31
18	Sodium stearate	24 h	43
19	Piperidine-MNPs	15 min	91
20	Piperazine-MNPs	10 min	90

[a] Reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol), triethyl phosphite (1 mmol), catalyst (3 mol %), solvent-free, room temperature

[b] Isolated yield

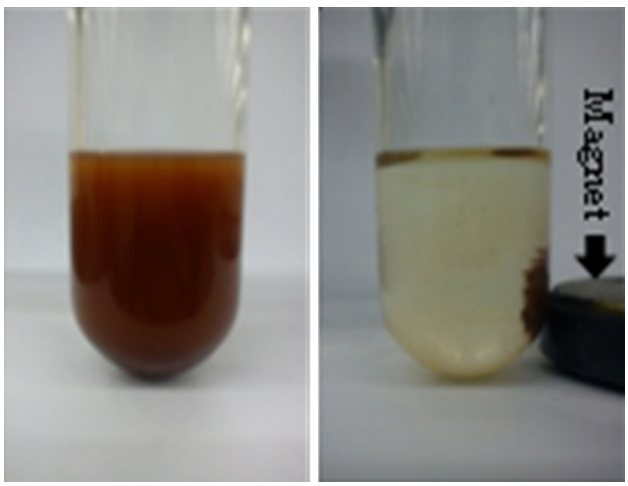


Fig. 6 Catalyst separation from the reaction mixture using an external magnet

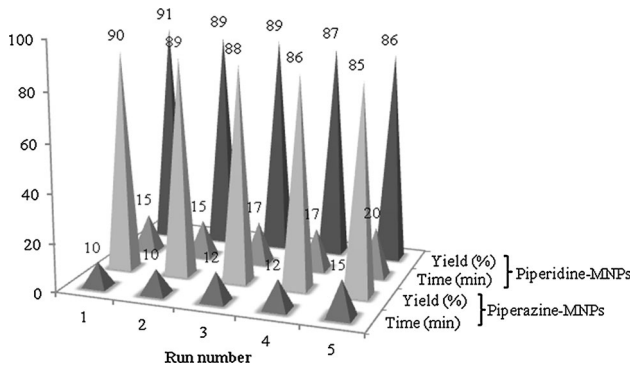


Fig. 7 Reusability of piperidine-MNPs and piperazine-MNPs for the synthesis of β-phosphonomalonate 1e

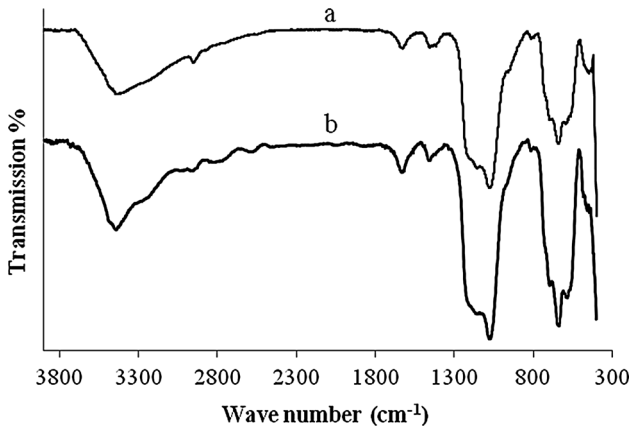


Fig. 9 FT-IR spectra of **a** piperidine-MNPs and **b** piperazine-MNPs after five times reuse

The recovery and reuse of a catalyst is highly preferable for a catalytic process. In this regard the recyclability of piperidine-MNPs and piperazine-MNPs was investigated in a model reaction of benzaldehyde, malononitrile and triethyl phosphite under optimized reaction conditions. After the reaction was completed, EtOH was added to the reaction mixture and the whole amount of the catalyst simply separated from the product by an external magnet (Fig. 6). The recovered catalyst was washed with EtOH, dried at room temperature and reused for five consecutive trials without loss of their catalytic activity (Fig. 7).

It is worth to note that the reusability test was stopped after five runs. Comparison of TEM images (Fig. 8) and FT-IR spectra (Fig. 9) of reused catalysts with those of the fresh catalysts (Fig. 3a, 3b, 4c and 4d) showed that the morphology and structure of piperidine-MNPs and piperazine-MNPs was remained intact after five recoveries. Furthermore, the loading amount of the catalysts after five times reuse was determined by elemental analysis, and found that 0.34 and 0.24 mmol g^{-1} of piperidine and piperazine were grafted onto MNPs. These results indicated that the catalysts were stable and could tolerate the present reaction conditions.

4 Conclusions

In conclusion, novel supported piperidine and piperazine onto silica coated γ-Fe_2O_3 magnetic nanoparticles were synthesized and characterized by different techniques. These solid bases were applied as magnetically recyclable heterogeneous catalysts for the one-pot three-component reaction of aldehydes, malononitrile and trialkyl phosphites. β-Phosphonomalonates were obtained using this protocol, in good to high yields at room temperature under solvent-free conditions. More importantly, the catalysts were easily separated by an external magnet and reused five times without significant loss of their catalytic activity.

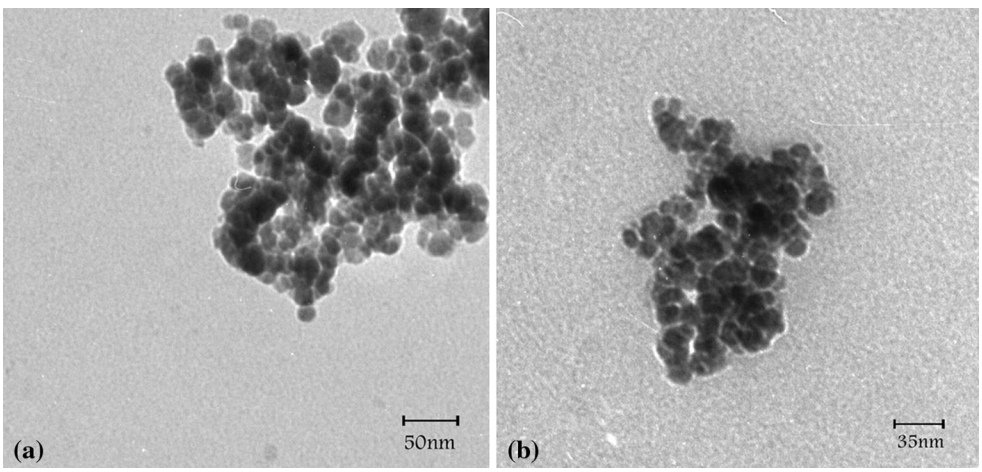


Fig. 8 TEM image of **a** piperidine-MNPs and **b** piperazine-MNPs after five times reuse

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