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ARTICLE TYPE

Lanthanum (III) triflate supported on nanomagnetic γ-Fe_2O_3: A new magnetically recyclable heterogeneous Lewis acid for the one-pot synthesis of β-phosphonomalonates

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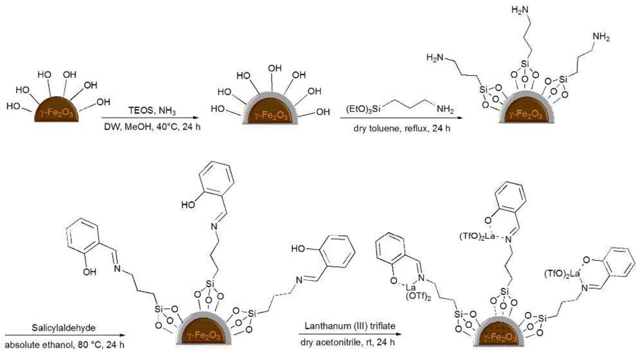
Lanthanum (III) triflate supported on nanomagnetic γ-Fe_2O_3 was synthesized and characterized by HRTEM, XRD, ICP, FT-IR, TGA and VSM. It was applied as a magnetically recyclable heterogeneous Lewis acid catalyst for the efficient one-pot synthesis of β-phosphonomalonates *via* tandem Knoevenagel-phospha-Michael reaction. The catalyst was easily separated from the reaction mixture by magnetic decantation using an external magnet and reused ten times.

Introduction

Within organophosphorous compounds, phosphonates are an important class of molecules. They have broad application in medicinal chemistry,[1] material chemistry,[2] and catalysis.[3] There are several methods for the synthesis of phosphonates. Among them, phospha-Michael addition has evoked remarkable attention by organic chemists.[4] These protocols proceed through two-pot procedure in which P-C and C-C bond formations occurred in separate steps. It is worth to note that scarce reports are available for the one-pot synthesis of β-phosphonomalonates *via* tandem Knoevenagel-phospha-Michael reaction.[4d,5] Even though, phospha-Michael addition could be proceed by these methods, most of the existing protocols suffer from limitations such as low yields, long reaction times, using hazardous organic solvents or unrecyclable catalysts and tedious work-up procedures leading to copious amount of toxic wastes. 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.

In the last two decades, rare earth metal triflates [RE$(OTf)_3$] including lanthanide triflates [Ln$(OTf)_3$] have been introduced as promising mild, powerful and selective Lewis acids for a variety of functional group transformations.[6] While most of Lewis acids are decomposed or deactivated in the presence of water or protic solvents, RE$(OTf)_3$ are quite stable in aqueous media[7] and can be recovered from the reaction mixture by aqueous extraction and reused.[8] As a consummate goal in industrial and economical catalyst development, immobilization of RE$(OTf)_3$ on solid supports affords improved recycling and facile use in synthetic schemes. Several techniques for the immobilization of these catalysts on insoluble matrixes such as organic polymers or inorganic materials have been developed.[9] These immobilized catalysts have been recycled without any loss of catalytic activity. However, while the embedded catalysts have very good activity, their recovery by filtration or centrifugation methods is time consuming and may cause loss of the catalyst. Therefore, there is a need for the design and preparation of new version of heterogeneous RE$(OTf)_3$ to circumvent this problem. One way to atain this goal is to immobilize these catalysts onto magnetic nanoparticles (MNPs) such as iron oxide. Supported catalysts on MNPs can be easily collected by using an external magnet without additional centrifugation or filtration of the sample. Magnetic separation of nanoparticles is simple, economical, and promising for industrial applications. To the best of our knowledge, synthesis of RE$(OTf)_3$ supported on MNPs have not yet been investigated.

To benefit the valuable applications of MNPs and unique properties of RE$(OTf)_3$ as Lewis acids, and in continues of our recent works on the development of new heterogeneous catalysts,[10] in this paper, we have synthesized lanthanum (III) triflate supported on γ-Fe_2O_3@SiO_2 [γ-Fe_2O_3@SiO_2-La$(OTf)_2$] as a new catalyst (Scheme 1). We have also used the synthesized γ-Fe_2O_3@SiO_2-La$(OTf)_2$ as a magnetically recyclable heterogeneous Lewis acid for the efficient one-pot synthesis of β-phosphonomalonates.



Scheme 1 Synthesis of γ-Fe_2O_3@SiO_2-La$(OTf)_2$.

Experimental

Chemicals were purchased from Merck Chemical Company. NMR spectra were recorded on a Bruker Avance DPX-250 and 400 in CDCl3 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. HRTEM analysis was performed using HRTEM microscope (Philips CM30). FT-IR spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrophotometer (FT-IR-8300). IR spectra were run on a Perkin Elmer 780 instrument. Mass spectra were recorded on a Shimadzu GCMS-QP5050A. Thermo gravimetric analysis (TGA) was performed using a Shimadzu thermo gravimetric analyser (TG-50). Power X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu Kα (λ = 0.154 nm) radiation. Room temperature magnetization isotherms were obtained using a vibrating sample magnetometer (VSM, LakeShore 7400). The content of La in the catalyst was determined by ICP-OES VISTA-PRO inductively coupled plasma analyzer.

Synthesis of γ-Fe_2O_3 MNPs

γ-Fe_2O_3 MNPs were synthesized by a reported chemical co-precipitation technique of ferric and ferrous ions in alkali solution with minor modifications.[11] $FeCl_2.4H_2O$ (1.99 g) and $FeCl_3.6H_2O$ (3.25 g) were dissolved in deionized water (30 mL) under Ar atmosphere at room temperature. A NH_4OH solution (0.6 M, 200 mL) was then added drop wise (drop rate = 1 $mL.min^{-1}$) to the stirring mixture at room temperature to reach the reaction pH 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 separated by an external magnet and washed with deionized water until it was neutralized. The as-synthesized sample was heated at 2 $^oC.min^{-1}$ up to 250 ^oC and then kept in the furnace for 3 h to give a reddish-brown powder.

Synthesis of silica-coated magnetite nanoparticles (γ-Fe_2O_3@SiO_2)[12]

The synthesized γ-Fe_2O_3 (3.5 g) was suspended in deionized water (40 mL)/ethanol (160 mL) and sonicated at 40 °C for 1 h. Concentrated solution of ammonia (3.5 mL) was added slowly to the sonicated mixture and 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.

Synthesis of aminopropylated γ-Fe_2O_3@SiO_2[13]

The prepared γ-Fe_2O_3@SiO_2 (3.5 g) was sonicated in dry toluene (50 mL) for 30 min. 3-Aminopropyltriethoxysilane (3.5 mL) was added to the dispersed γ-Fe_2O_3@SiO_2 in toluene under mechanical stirring, slowly heated to 105 °C and kept at this temperature for 24 h. The solid was separated by an external magnet, washed three times with ethanol and dried under vacuum.

Synthesis of Schiff base supported on γ-Fe_2O_3@SiO_2 (γ-Fe_2O_3@SiO_2-L)

The synthesized aminopropylated γ-Fe_2O_3@SiO_2 (3 g) was sonicated in absolute ethanol (50 mL) for 30 min. Salicylaldehyde (3 mL) was added slowly to the sonicated mixture and stirred at 80 °C for 24 h. The resulting mixture was cooled to room temprature. The solid was separated by an external magnet, washed with ethanol and dried at 50 °C in oven under vaccum.

Synthesis of γ-Fe_2O_3@SiO_2-La(OTf)$_2$

γ-Fe_2O_3@SiO_2-L (2 g) was sonicated in dry acetonitrile (30 mL) for 30 min. Lanthanum (III) triflate (0.5 g) was added to the dispersed mixture in acetonitrile under mechanical stirring. The reaction mixture was stirred at room temperature for 24 h. The solid was separated by an external magnet and washed three times with acetonitrile. It was then dried under vaccum at 90 °C overnight to furnish γ-Fe_2O_3@SiO_2-La(OTf)$_2$.

General procedure for the synthesis of β-phosphonomalonates

A mixture of aldehyde (1 mmol), malononitrile (1 mmol), triethyl phosphite (1 mmol) and γ-Fe_2O_3@SiO_2-La(OTf)$_2$ (0.08 g, 1 mol%) was stirred at room temperature for an appropriate time (Table 2). The reaction mixture was diluted with EtOAc. The catalyst was separated by an external magnet, washed with EtOAc, dried and re-used for a consecutive run under the same reaction conditions. Evaporation of the solvent of the filtrate under reduced pressure gave the crude products. The pure products (**1-14**) were isolated by chromatography on silica gel eluted with *n*-hexane:EtOAc (1:2).

Results and discussion

Catalyst synthesis and characterization

The synthetic procedure of γ-Fe_2O_3@SiO_2-La(OTf)$_2$ is outlined in Scheme 1. At first, γ-Fe_2O_3 MNPs were synthesized by a chemical co-precipitation technique of ferric and ferrous ions in alkali solution.[11] The magnetic nanoparticles were then allowed to react with an alkaline solution of tetraethyl orthosilicate (TEOS) to give γ-Fe_2O_3@SiO_2. The outer shell of silica not only improved the dispersibility but also provided suitable sites (Si-OH groups) for further surface functionalization. The resulting γ-Fe_2O_3@SiO_2 was then functionalized with 3-aminopropyltriethoxysilane followed by condensation with salicylaldehyde to give Schiff base supported on γ-Fe_2O_3@SiO_2 (γ-Fe_2O_3@SiO_2-L). Finally, the reaction of La(OTf)$_3$ with γ-Fe_2O_3@SiO_2-L in dry acetonitrile led to the formation of γ-Fe_2O_3@SiO_2-La(OTf)$_2$.
The size and structure of γ-Fe_2O_3@SiO_2-La(OTf)$_2$ were evaluated using high resolution transmission electron microscopy (HRTEM). HRTEM image demonstrated spherical-like shape for γ-Fe_2O_3@SiO_2-La(OTf)$_2$ with diameter of ca. 13 nm (Fig. 1). It also showed the core–shell structure of the particles and confirmed the presence of the silica shell, which has a uniform thickness of 2 nm (Fig. 1b).

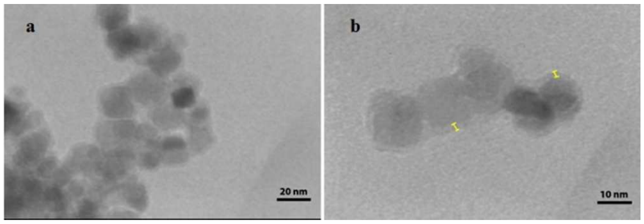


Fig. 1 HRTEM images of γ-Fe_2O_3@SiO_2-La(OTf)$_2$.

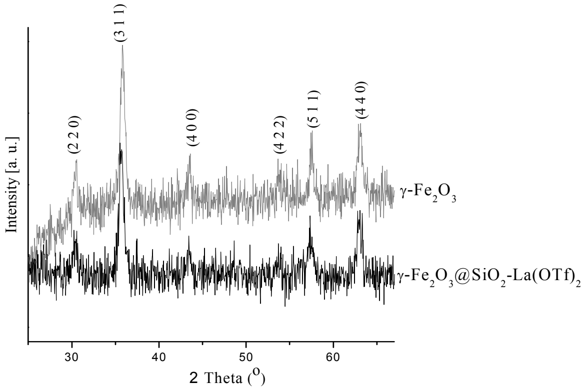


Fig. 2 XRD patterns of γ-Fe_2O_3 and γ-Fe_2O_3@SiO_2-La(OTf)$_2$.

The crystalline structure of γ-Fe_2O_3 and γ-Fe_2O_3@SiO_2-La(OTf)$_2$ were characterized by X-ray diffraction (XRD) (Fig. 2). The XRD pattern of γ-Fe_2O_3 showed characteristic peaks matched with those of standard γ-Fe_2O_3 nanoparticles (JCPDS file No 04-0755) with a unit cell dimension of 8.35 Å and space group of P4132 (213). The same set of characteristic peaks was observed in the XRD pattern of γ-Fe_2O_3@SiO_2-La(OTf)$_2$, which indicated the stability of the crystalline phase of nanoparticles during the subsequent surface modification. The deduced average size of γ-Fe_2O_3@SiO_2-La(OTf)$_2$ from Sherrer's formula was about 13.5 nm.

Thermogravimetric analysis (TGA) was used to study the thermal stability of the catalyst. The thermal behaviour of γ-Fe_2O_3@SiO_2-La(OTf)$_2$ is shown in Fig. 3. Two weight loss stages were observed in the TGA curve. The first region, which occurred below 147 °C was corresponded to the loss of trapped water from the catalyst. In the second stage, weight loss was about 8.3 wt%, which could be attributed to the loss of organic components attached to the surface. According to the TGA, the amount of organic components functionalized on γ-Fe_2O_3@SiO_2 calculated to be 0.13 mmol.g^{-1}. The ICP analysis showed that 0.12 mmol of lanthanum was anchored on 1.0 g of γ-Fe_2O_3@SiO_2-La(OTf)$_2$.

FT-IR spectra of γ-Fe_2O_3 and γ-Fe_2O_3@SiO_2-La(OTf)$_2$ are shown in Fig. 4. The band at around 620–650 cm^{-1} was assigned to the stretching vibrations of Fe-O bond in γ-Fe_2O_3 and γ-Fe_2O_3@SiO_2-La(OTf)$_2$. The intense band in the range of 1000-1300 cm^{-1} was related to the vibration of Si-O-Si bond. The peaks positioned at around 1500-1610 and 1660 cm^{-1} in the FT-IR spectrum of γ-Fe_2O_3@SiO_2-La(OTf)$_2$ were related to the stretching vibrations of C=C and C=N bonds, respectively. The band at 1440 cm^{-1} was assigned to the stretching vibration of S=O, which attributed to the sulfonate group of lanthanum (III) triflate loaded on MNPs. The strong and broad band in the range of 2800-3700 cm^{-1} corresponded to Si-OH groups and adsorbed water that overlapped with C-H stretching vibration of phenyl and CH_2 groups. A band at 1650 cm^{-1} in the spectra of γ-Fe_2O_3 and γ-Fe_2O_3@SiO_2-La(OTf)$_2$ was also due to the OH vibration of adsorbed water.

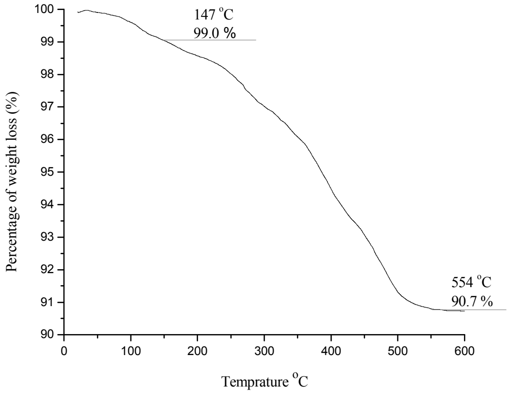


Fig. 3 TGA diagram of γ-Fe_2O_3@SiO_2-La(OTf)$_2$.

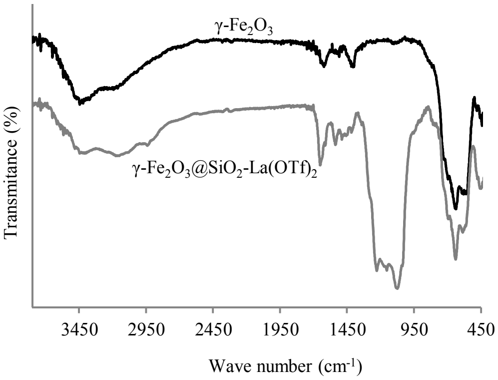


Fig. 4 FT-IR spectra of γ-Fe_2O_3 and γ-Fe_2O_3@SiO_2-La(OTf)$_2$.

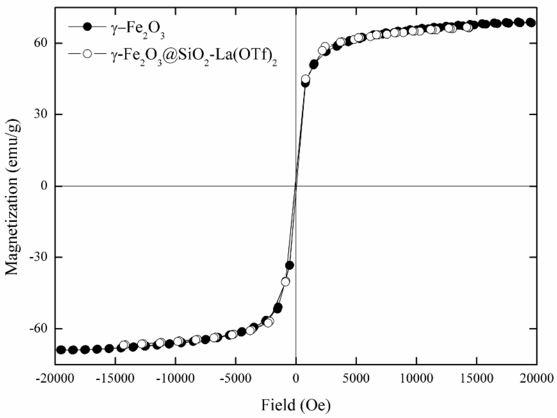


Fig. 5 Magnetization curves of γ-Fe_2O_3 and γ-Fe_2O_3@SiO_2-La(OTf)$_2$.

The magnetization curves of γ-Fe_2O_3 and γ-Fe_2O_3@SiO_2-La$(OTf)_2$ were measured at room temperature with a vibrating sample magnetometry (VSM). As shown in Figure 5, no reduced remanence and coercivity were detected, indicating both unmodified and La$(OTf)_2$-modified γ-Fe_2O_3 are superparamagnetic. The value of saturation magnetic moments of γ-Fe_2O_3 and γ-Fe_2O_3@SiO_2-La$(OTf)_2$ are 68.6 and 66.5 emu/g, respectively.

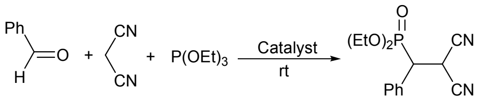
Evaluation of catalytic activity of γ-Fe_2O_3@SiO_2-La$(OTf)_2$ in the synthesis of β-phosphonomalonates *via* tandem Knoevenagel-phospha-Michael reaction

In continuous of our recent research programs on the development of novel methods for the synthesis of phosphonate derivatives,[10b-f,14] in this paper, we have studied the applicability of γ-Fe_2O_3@SiO_2-La$(OTf)_2$ as a new magnetically recyclable heterogeneous Lewis acid for the one-pot synthesis of β-phosphonomalonates directly from aldehydes, malononitrile and trialkyl phosphites.

At first, one-pot reaction of benzaldehyde, malononitrile and triethyl phosphite was chosen to optimize the reaction conditions such as solvents and molar ratio of the catalyst at room temperature (Table 1, Entries 1-6). We found that in the presence of 1 mol% of γ-Fe_2O_3@SiO_2-La$(OTf)_2$, the corresponding β-phosphonomalonate was obtained in the best yield at room temperature under solvent-free conditions (Entry 1). When 0.5 mol% of the catalyst was used, the yield of the desired product was decreased to 83% (Entry 6).

Table 1

One-pot reaction of benzaldehyde, malononitrile and triethyl posphite under different conditions.



Entry	Catalyst	Solvent	Time (h)	Yield[a] (%)
1	γ-Fe_2O_3@SiO_2-La$(OTf)_2$	-	1	91
2	γ-Fe_2O_3@SiO_2-La$(OTf)_2$	H_2O	1	42
3	γ-Fe_2O_3@SiO_2-La$(OTf)_2$	EtOH	1	76
4	γ-Fe_2O_3@SiO_2-La$(OTf)_2$	$CHCl_3$	1	78
5	γ-Fe_2O_3@SiO_2-La$(OTf)_2$	Toluene	1	67
6	γ-Fe_2O_3@SiO_2-La$(OTf)_2$[b]	-	1	83
7	-[c]	-	24	46
8	γ-Fe_2O_3[d]	-	1	62
9	Aminopropylated γ-Fe_2O_3@SiO_2[e]	-	1	66
10	La$(OTf)_3$	-	1	92

[a] Isolated yield, conditions: benzaldehyde (1 mmol), malononitrile (1 mmol), triethyl phosphite (1 mmol), catalyst (1 mol%, except for entries 6-9), room temperature.

[b] Catalyst = 0.5 mol%.

[c] No catalyst.

[d] Catalyst = 0.08 g

[e] Catalyst = 0.002 g (1 mol%, 0.6 mmol of amine was anchored on 1.0 g of catalyst).

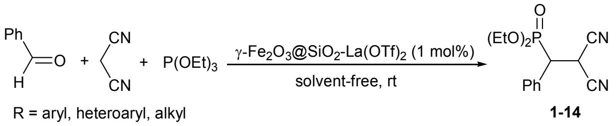
In order to show the role of the catalyst, similar reactions in the absence of the catalyst and in the presence of nanomagnetic γ-Fe_2O_3 and aminopropylated γ-Fe_2O_3@SiO_2 were also examined. These reactions led to the formation of the desired product in lower yields than that obtained in the presence of γ-Fe_2O_3@SiO_2-La$(OTf)_2$ (Entries 7-9). La$(OTf)_3$ catalyzed a similar reaction as well as γ-Fe_2O_3@SiO_2-La$(OTf)_2$ (Entry 10). This observation showed that the catalylic activity of La$(OTf)_3$ did not changed after its supporting on the surface of nanoparticls.

To confirm the generality of the present method, we next examined the reaction of a variety of aldehydes with malononitrile and triethyl phosphite under the optimized reaction conditions. The results of this study are depicted in Table 2.

As indicated in Table 2, reactions of benzaldehyde and different substituted benzaldehydes containing electron-donating and electron-withdrawing groups with malononitrile and triethyl phosphite proceeded well to give the corresponding β-phosphonomalonates in good to high yields (Entries 2-10). Acid-sensitive aldehydes such as pyridine-3-carbaldehyde and furan-2-carbaldehyde underwent successful tandem Knoevenagel-phospha-Michael reaction without any decomposition or polymerization (Entries 11, 12). This catalytic system was also successfully applied for the reaction of aliphatic aldehydes with malononitrile and triethyl phosphite and produced the desired products in good yields (Entries 13, 14).

Table 2

One-pot synthesis of different β-phosphonomalonates catalyzed by γ-Fe_2O_3@SiO_2-La$(OTf)_2$.



Entry	Carbonyl compound	Product	Time (h)	Yield[a] (%)
1	benzaldehyde	**1**	1	90
2	4-chlorobenzaldehyde	**2**	2	92
3	3-chlorobenzaldehyde	**3**	1	86
4	2-chlorobenzaldehyde	**4**	2	81
5	4-bromobenzaldehyde	**5**	1	87
6	3-bromobenzaldehyde	**6**	1	80
7	4-methoxybenzaldehyde	**7**	3	83
8	3-methoxybenzaldehyde	**8**	1	85
9	4-hydroxybenzaldehyde	**9**	1	89
10	4-methylbenzaldehyde	**10**	2	87
11	3-pyridincarbaldehyde	**11**	1	96
12	furfural	**12**	2	84
13	butyraldehyde	**13**	3	81[b]
14	heptanaldehyde	**14**	3	77[b]

[a] Isolated yield, conditions: aldehyde (1 mmol), malononitrile (1 mmol), triethyl phosphite (1 mmol), catalyst (0.08 g, 1 mol%), room temperature (except for entries 13,14), solvent-free conditions. All the products were characterized by spectroscopic methods and compared with the authentic samples (see supplementary material and references 4c,5b-e).

[b] Reaction temperature: 60 °C.

It is important to note that the magnetic property of γ-Fe_2O_3@SiO_2-La$(OTf)_2$ facilitates efficient recovery of the catalyst from the reaction mixture during work-up procedure. After performing the reaction of benzaldehyde, malononitrile and triethyl phosphite, EtOAc was added to the reaction mixture. The catalyst was separated by using an external magnet (Fig. 6), washed with EtOAc, dried 30 min at 100 °C and reused for ten runs (Fig. 7). Significant loss of the catalytic activity of the catalyst was not observed after five times reuse. The comparison of HRTEM images of used γ-Fe_2O_3@SiO_2-La$(OTf)_2$ (Fig. 8) with the fresh catalyst showed the fact that the morphology of the catalyst remained intact after five times recovering. FT-IR spectrum (Fig. 9) of the catalyst after ten times reuse was compared with that of the fresh catalyst (Fig. 4). In the FT-IR spectrum of used catalyst, besides the corresponding peaks to γ-Fe_2O_3@SiO_2-La$(OTf)_2$, bands at 835, 1078 and 2233 cm^{-1} were also observed. These peaks are related to P-O, P=O and CN bonds in the product (**1**) and showed that a gradual decrease in the catalytic activity of γ-Fe_2O_3@SiO_2-La$(OTf)_2$ during ten times reuse might be due to the catalyst poisoning by the product.

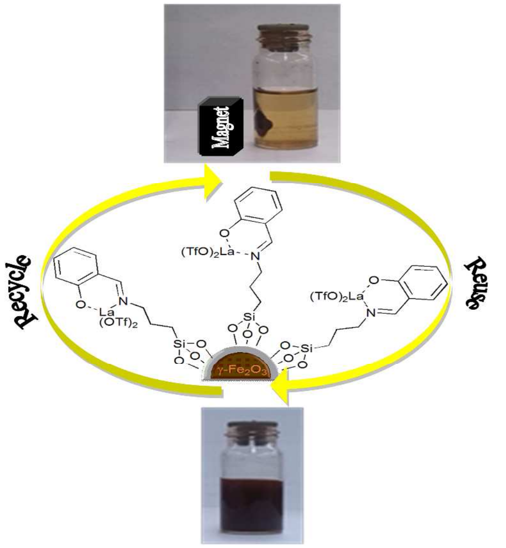


Fig. 6 Separation of γ-Fe_2O_3@SiO_2-La$(OTf)_2$ from the reaction mixture by an external magnet.

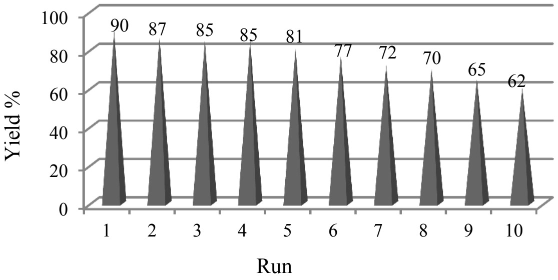


Fig. 7 Reusability of γ-Fe_2O_3@SiO_2-La$(OTf)_2$ as a magnetically recyclable heterogeneous catalyst for tandem Knoevenagel-phospha-Michael reaction of benzaldehyde, malononitrile and triethyl phosphite at room temperature after 1 h.

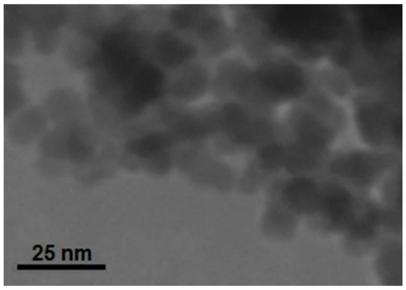


Fig. 8 HRTEM image after five times reuse of γ-Fe_2O_3@SiO_2-La$(OTf)_2$.

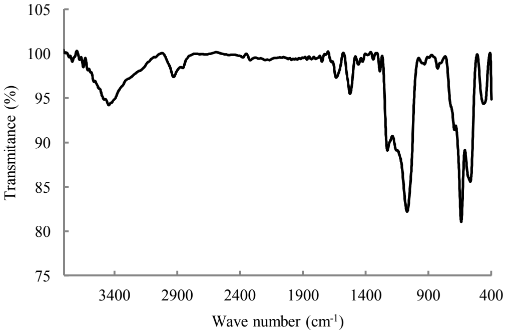
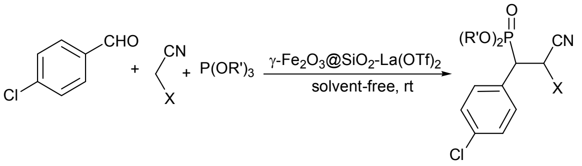


Fig. 9 FT-IR spectrum of γ-Fe_2O_3@SiO_2-La$(OTf)_2$ after ten times reuse.

Table 3
One-pot synthesis of β-phosphonomalonates from 4-chlorobenzaldehyde with different *in situ* generated Michael acceptors and trialkyl phosphites catalyzed by γ-Fe_2O_3@SiO_2-La$(OTf)_2$.



Entry	R′	X	Product	Time (h)	Yield[a] (%)
1	Et	CN	**2**	2	92
2	Me	CN	**15**	1	87
3	*iso*-Pr	CN	**16**	2	72
4	Et	CO_2Et	**17**	1	84[b]

[a] Isolated yield, 4-chlorobenzaldehyde (1 mmol), active methylene group (1 mmol), trialkyl phosphite (1 mmol), catalyst (0.08 g, 1 mol%), room temperature (except for entry 4), All the products were characterized by spectroscopic methods and compared with the authentic samples (see supplementary material and references 4c,5b-e,15).
[b] d.r. = 50:50, according to NMR, reaction temperature: 60 °C

The generality of the method was also evaluated for the one-pot synthesis of β-phosphonomalonates from different *in situ* generated Michael acceptors and trialkyl phosphites (Table 3). As it is obvious from Table 3, one-pot reaction of 4-chlorobenzaldehyde and malononitrile with various trialkyl phosphites gave the corresponding β-phosphonomalonates in 72-92% yields. In addition to malononitrile, ethyl 2-cyanoacetate as an *in situ* generated Michael acceptor was also examined to carry out the reaction with triethyl phosphite and the desired product was obtained in 84% yield (Entry 4).

Conclusion

In summary, in this paper, lanthanum (III) triflate supported on nanomagnetic γ-Fe_2O_3@SiO_2 was synthesized. It was successfully applied as a new magnetically recyclable heterogeneous Lewis acid for the one-pot synthesis of β-phosphonomalonates *via* tandem Knoevenagel-phospha-Michael reaction under solvent-free conditions. The catalyst was easily isolated from the reaction mixture by an external magnet and reused ten times.

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Notes and references

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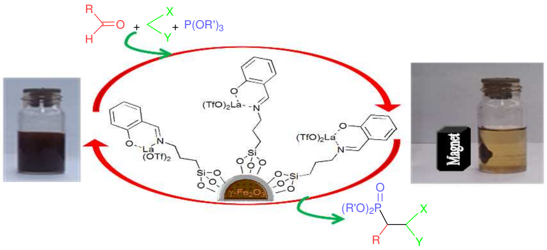

A new magnetically recyclable heterogeneous Lewis acid was synthesized and used for the one-pot synthesis of β-phosphonomalonates.