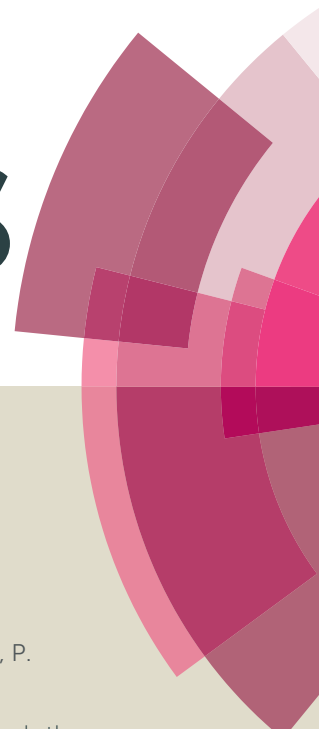


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# Ethylenediamine-functionalized Magnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2$ Nanoparticles: Cooperative Trifunctional Catalysis for Selective Synthesis of Nitroalkenes

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**Abstract** A magnetically separable trifunctional nanocatalyst  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  was synthesized and characterized by TEM, FT-IR, XRD, TGA, and EA. The designed nanocatalyst was found to be highly active for selective synthesis of nitroalkenes with nitromethane and aromatic aldehyde through cooperative trifunctional catalysis of primary amine, secondary amine and Si-OH groups on the surface of catalyst. Under the optimized conditions, various representative substrates were extended to obtain the corresponding products in a moderate or excellent yield. After reaction, the trifunctional nanocatalyst was easily recovered and recycled by applying an external magnet. In addition, a possible cooperative trifunctional catalysis mechanism was also proposed.

**Keywords:** Nitroalkenes, Magnetically recyclable nanocatalyst, Henry reaction, Cooperative trifunctional catalysis

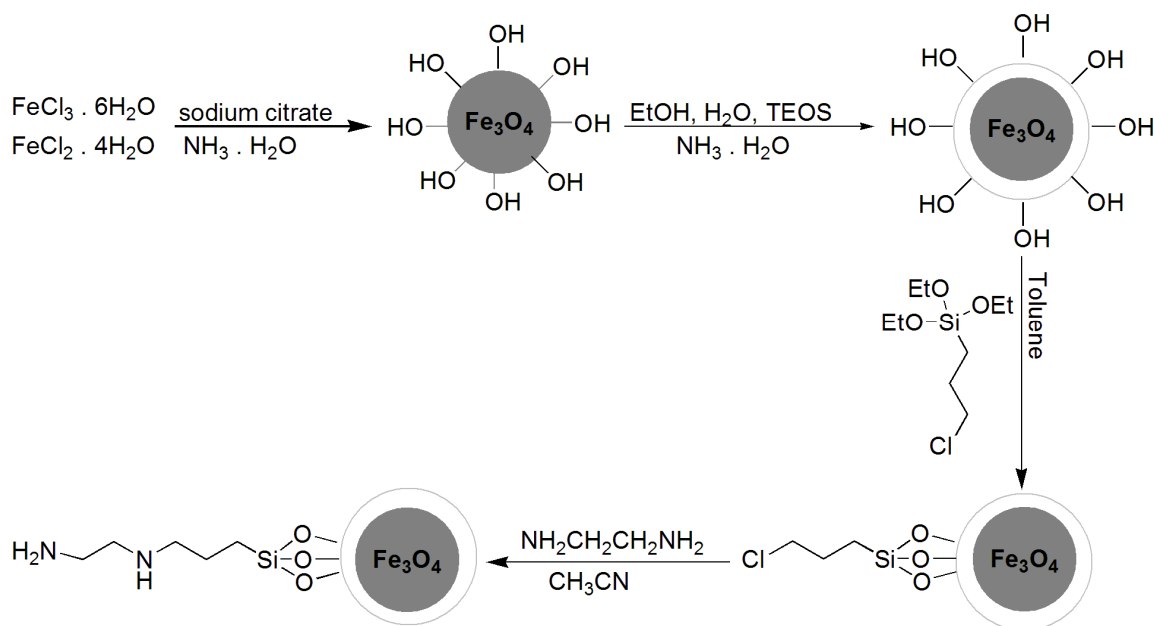
## 1 Introduction

Since the concept of monomolecular bifunctional catalyst for cooperative catalysis was first proposed in 2003 by Takemoto group<sup>1</sup>, both homogeneous and heterogeneous catalysts with molecular design and their application in organic transforms have become the focus of attention. The pursuit for green chemical process impels scientists and researchers to exploit more recoverable catalysts with multifunctional surface. The immobilization of homogeneous catalysts on solid supports has been considered as an efficient approach to realize catalyst recycling.<sup>2</sup> It is worth mentioning that the dispersion of most heterogeneous catalysts in reaction medium are poor.<sup>3,4</sup> Therefore, the catalytic activity of the heterogeneous catalyst will be inevitably affected compared to the corresponding homogeneous catalyst. Due to the large specific surface area and versatile surface, nanoparticles have attracted much attention for immobilization of homogeneous catalysts.<sup>5</sup> However, nanoparticles are difficult to separate by conventional filtration techniques.<sup>6</sup> Magnetic nanoparticles are a promising option.<sup>6</sup> As an ideal support, magnetic  $\text{Fe}_3\text{O}_4$  is non-toxic, easy to prepare, active for modification and functionalization.<sup>5</sup> From the point view of sustainable development, magnetically separable nanocatalysts with multifunctional surface are attracting researches' great attentions.

Nitroalkenes are versatile building blocks<sup>7</sup> because they have been widely used as substrates such as Michael addition<sup>1, 8</sup>, Friedel-Crafts alkylation<sup>9, 10</sup>, 1, 3-dipolar cycloaddition<sup>11, 12</sup> and domino reaction<sup>13</sup>. They have also been used as key precursors of different targets for scavengers of macrophage-generated oxidants<sup>14</sup>, antidepressant drug<sup>15</sup> and rat even human monoamine oxidase inhibitors<sup>16</sup>. The nitro group can be

converted into various functional groups.<sup>17, 18</sup> Several reports about nitroalkenes synthesis have been described.<sup>17-26</sup> The immobilization of amines on silica has received much attention due to the large specific surface area and good dispersion.<sup>19-23</sup> In these reports, few nanocatalysts have bifunctional even trifunctional active sites on their surfaces.<sup>21-22</sup> Additionally, conventional filtration and centrifuge for isolation of these silica-supported nanocatalysts from the reaction mixture is not so efficient.<sup>6</sup> Magnetic Fe<sub>3</sub>O<sub>4</sub>-supported catalysts with multifunctional surface not only can achieve simple and efficient separation but also can collaboratively accelerate a single reaction or enable one-pot reaction sequences.

With this background in mind, in this paper a magnetically separable trifunctional nanocatalyst (Scheme 1, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>) was prepared for cooperative catalytic synthesis of nitroalkenes under mild conditions without additional solvents. The reaction between nitromethane and aromatic aldehyde might experience a cooperative trifunctional catalytic process which was promoted by primary amine, secondary amine and Si-OH groups on the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>. Under the optimized conditions, various representative substrates were extended. After reaction the separation and recovery of magnetic Fe<sub>3</sub>O<sub>4</sub> supported catalysts could be achieved using an external magnet. Combined with the experimental data and literatures, possible reaction mechanism for selective synthesis of nitroalkenes through a trifunctional cooperative catalysis was proposed.<sup>17-19, 21, 22, 25-27</sup>



**Scheme 1** The synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>

## 2 Experimental Section

### 2.1 Materials

Ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), ferrous chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O), ammonia (25 wt %), trisodium citrate, acetonitrile (CH<sub>3</sub>CN), ethanediamine (NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, P. R. China). Toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>) was obtained from Tianjin Jiangtian Chemical Technology Co., Ltd. Absolute alcohol, nitromethane were supplied by Tianjin Real & Lead Chemical Co., Ltd. Tetraethyl orthosilicate (TEOS) was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. Chloropropyl triethoxysilane was purchased from Heowns Biochem Technologies LLC. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>) were dried with CaH<sub>2</sub>, distilled under reduced pressure and stored over molecular sieves. Other reagents, unless otherwise stated, were used as received for the

reaction without further purification. Deionized water was used for all experiments.

## 2.2 Analytical Methods

NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in  $\text{CDCl}_3$  using TMS as an internal standard. The morphology of the samples was observed on a Tecnai G2 F20 transmission electron microscopy (TEM). The content of nitrogen was determined by a Vario EL cube elemental analyzer. Thermogravimetric analysis (TGA) was measured with a STA 409 PC thermal analyzer (NETZSCH, Germany). Fourier transform infrared spectroscopy (FTIR) analysis was performed on a BIO-RAD FTS3000 IR Spectrum Scanner. The X-ray diffraction (XRD) spectra of the samples were measured using an X-ray diffractometer (BDX3300) with reference target: Cu Ka radiation ( $\lambda=1.54$  Å), voltage: 30 kV and current: 30 mA. The samples were measured from 10 to 90° (2 $\theta$ ) with steps of 4° min<sup>-1</sup>. Preparative TLC (20 cm × 20 cm) was performed on Silica Gel 60 F254.

## 2.3 Preparation of Fe<sub>3</sub>O<sub>4</sub> Magnetic Nanoparticles (Fe<sub>3</sub>O<sub>4</sub> MNPs)

The Fe<sub>3</sub>O<sub>4</sub> MNPs were prepared following the reported chemical co-precipitation methods with slight modification.<sup>28-30</sup> First, an oven-dried 500 mL, three-necked flask equipped with a Teflon coated mechanical stir bar, constant-voltage funnel was charged with ferric chloride hexahydrate (21.624 g, 0.08 mol), ferrous chloride tetrahydrate (8.419 g, > 0.04 mol) and sodium citrate dehydrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$  0.510 g) and then sealed tightly with a rubber septum. The flask was evacuated and backfilled with nitrogen three times under mechanical stirring. Then, 100 mL of distilled water was added *via* a dropping funnel under vigorous stirring. The mixture was heated to 60 °C and stirred for

30 min. Finally, 100 mL of aqueous solution containing (25 wt %) ammonium hydroxide 25 mL was added drop-wise to the above mixture, and it immediately turned black. The reaction mixture was heated to 80 °C and kept for 2 h and then allowed to cool to room temperature. The black products were obtained with the help of a magnet and washed with distilled water, ethanol 3 times respectively and then dried under vacuum at 50 °C.

#### 2.4 Synthesis of Aminopropyl Modified Silica Coated Fe<sub>3</sub>O<sub>4</sub> Magnetic Nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>)

Silica coated Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>) was synthesized according to the procedure reported in the previous literatures.<sup>28, 29, 31, 32</sup> Chloropropyl modified silica coated Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Cl) was synthesized according to the procedure reported in the previous literature.<sup>33</sup> The obtained Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Cl (3 g) was suspended in acetonitrile (200 mL) with sonication about 20 min. To the mixture, ethylenediamine (10 mL) was added drop-wise *via* a dropping funnel under mechanical stirring at nitrogen atmosphere and the reaction mixture was refluxed for 12 h. After cooling to room temperature, the resulted solid (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>) was separated magnetically and then washed with absolute ethanol several times and dried under vacuum at 50°C.

#### 2.5 General procedure for the synthesis of nitroalkenes

Typically, the reactions were carried out as follows: an oven-dried 25 mL flask was charged with Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> (0.1 g) and the aldehyde (0.3 mmol) in CH<sub>3</sub>NO<sub>2</sub> (5 mL). Then the mixture was stirred at 80 °C under air. After the reaction was completed, the solid catalyst was separated magnetically, washed with ethyl acetate and dichloromethane

3 times respectively. Combined the organic layer and dried with anhydrous  $\text{Na}_2\text{SO}_4$ , then the  $\text{Na}_2\text{SO}_4$  was filtered off. After removal of the solvent under reduced pressure, the crude product was purified by preparative TLC to give the pure nitroalkene.

## 2.6 Separation of the catalyst and recycling tests

After completion of the reaction, the solid catalyst was separated from the reaction mixture with the help of a magnet and washed with ethyl acetate and dichloromethane 3 times respectively. Without drying, the recovered catalyst was directly used in next run with new portions of reactants.

## 3 Results and Discussion

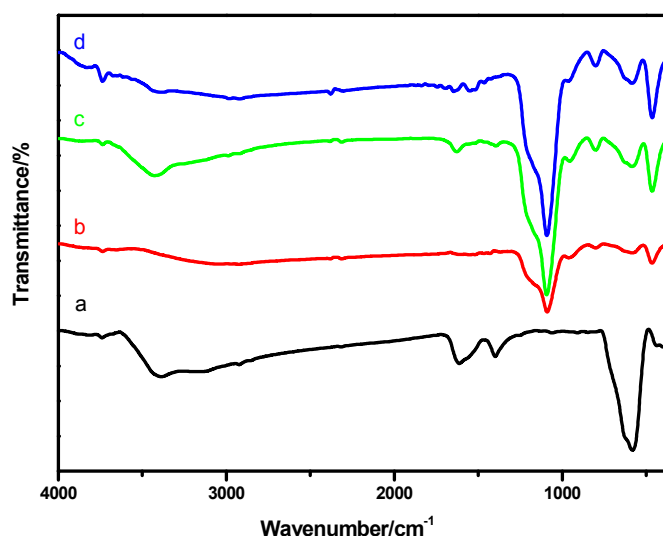
### 3.1 Synthesis and characterization of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$

Scheme 1 shows the sequence of events in the functionalization of  $\text{Fe}_3\text{O}_4$  MNPs with ethylenediamine. Firstly, the  $\text{Fe}_3\text{O}_4$  MNPs were prepared using reported chemical coprecipitation methods with slight modification. Secondly, the surface of  $\text{Fe}_3\text{O}_4$  MNPs was coated with a silica shell by the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in ethanol/ammonia mixture to yield  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ . Then treatment of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  with chloropropyl triethoxysilane obtained chloropropyl modified  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  ( $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Cl}$ ). Finally,  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  was synthesized *via* the substitution of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Cl}$  with excess of ethylenediamine. The content of nitrogen was determined to be 1.27 mmol/g by elemental analysis.

FTIR spectra of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Cl}$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  were shown in Figure 1. The strong adsorption peak at  $581\text{ cm}^{-1}$  corresponded to the characteristic vibration absorption peak of Fe-O bond. The peak at  $3386\text{ cm}^{-1}$  was assigned to the -OH



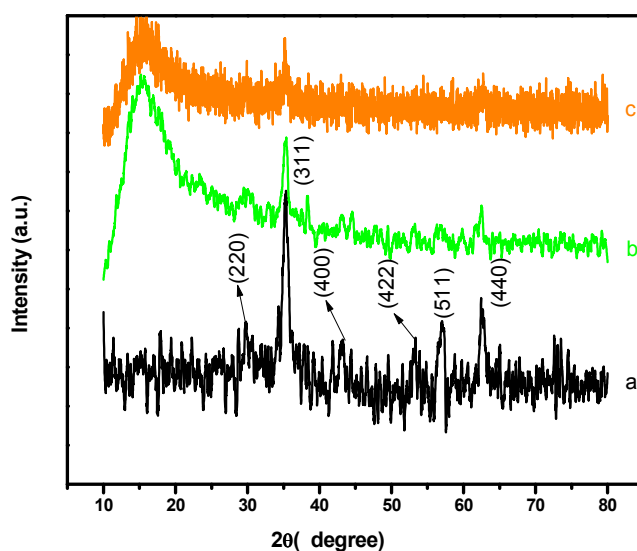
on the surface  $\text{Fe}_3\text{O}_4$  particles. The adsorption peaks located at  $1613$  and  $1398\text{ cm}^{-1}$  can be attributed to the stretching vibration of  $\text{C}=\text{O}$  and  $\text{C}-\text{O}$ , which indicates the presence of carboxyl groups on the surface of  $\text{Fe}_3\text{O}_4$  NPs. The new absorption peaks in Figure 1(b) at  $1089$ ,  $795$  and  $465\text{ cm}^{-1}$  were assigned to the  $\text{Si}-\text{O}-\text{Si}$ , the peaks at  $960$  and  $3736\text{ cm}^{-1}$  were assigned to  $\text{Si}-\text{OH}$  moieties. These indicate that the silica has been successfully coated on the surface of  $\text{Fe}_3\text{O}_4$  NPs. In Figure 1(c) and (d) the adsorption peaks at  $1459\text{ cm}^{-1}$  and  $2927\text{ cm}^{-1}$  were related to  $\text{C}-\text{H}$  stretching modes of the propyl groups. The absorption peaks at  $3421\text{ cm}^{-1}$  and  $1508\text{--}1551\text{ cm}^{-1}$  were assigned to the stretching vibration and bending vibration of  $\text{N}-\text{H}$ . These suggested that the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  was synthesized successfully.



**Fig. 1** FT-IR spectra of  $\text{Fe}_3\text{O}_4$  (a),  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (b),  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Cl}$  (c) and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  (d)

The crystalline structures of the  $\text{Fe}_3\text{O}_4$  particles,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  were

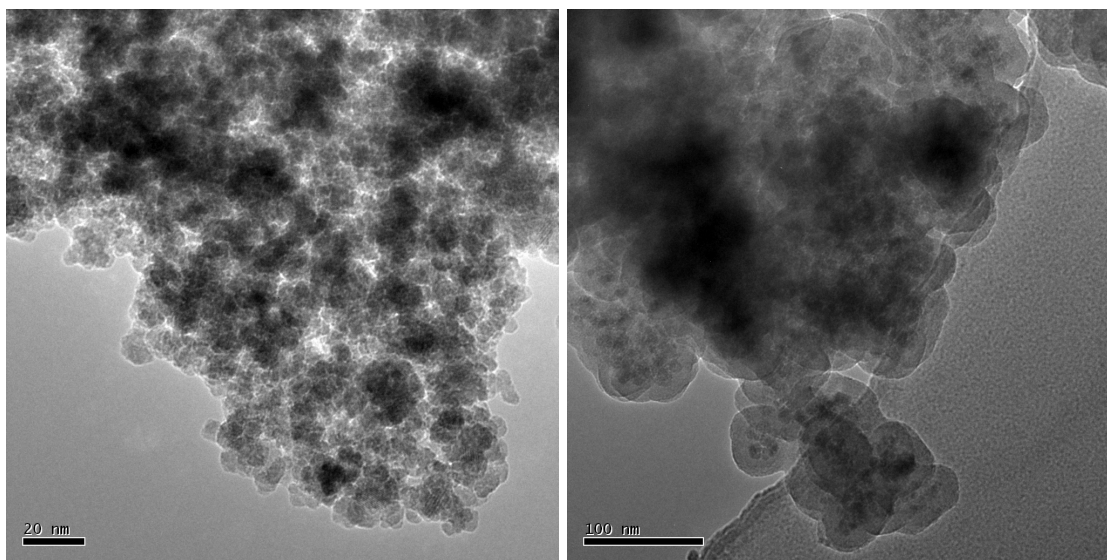
characterized by XRD and the results are shown in Figure 2. The experimentally obtained patterns were compared with the standard  $\text{Fe}_3\text{O}_4$  pattern (JCPDS (The Joint Committee on Powder Diffraction Standards) card no. 19-0629). The diffraction peaks at  $2\theta = 30.2^\circ$ ,  $35.4^\circ$ ,  $43.4^\circ$ ,  $53.1^\circ$ ,  $57.2^\circ$  and  $62.6^\circ$  correspond to the (220), (311), (400), (422), (511) and (440)  $\text{Fe}_3\text{O}_4$  lattice indices respectively.<sup>28-31</sup> These results prove that the  $\text{Fe}_3\text{O}_4$  obtained has highly crystalline cubic spinel structure. The XRD patterns of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (b) and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  (c) show an obvious diffusion peak at about  $15.3^\circ$  which is due to the effect of amorphous silica and organic groups.<sup>28, 31, 34, 35</sup> These results indicated that the surface of  $\text{Fe}_3\text{O}_4$  was coated with a silica shell successfully and  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  was successfully modified by organic groups.



**Fig. 2** XRD patterns of  $\text{Fe}_3\text{O}_4$  (a),  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (b) and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  (c)

The surface morphology and size of  $\text{Fe}_3\text{O}_4$  (a) and  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (b) were observed by transmission electron microscopy (TEM) as shown in Figure 3.

It can be seen that the  $\text{Fe}_3\text{O}_4$  particles are successfully packaged by silica. Although the presence of multinuclei  $\text{Fe}_3\text{O}_4$  cores embeded in  $\text{SiO}_2$  shell, this will not affect its application as a support in catalysis.<sup>3</sup>

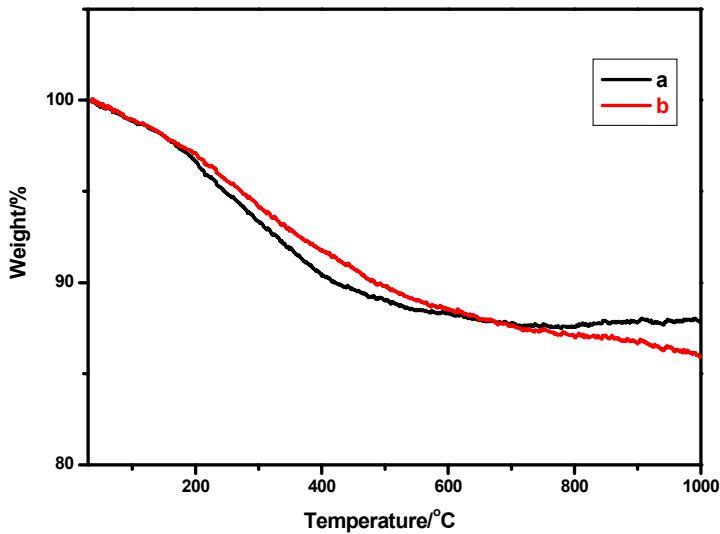


**Fig. 3** TEM images of  $\text{Fe}_3\text{O}_4$  (a) and  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (b)

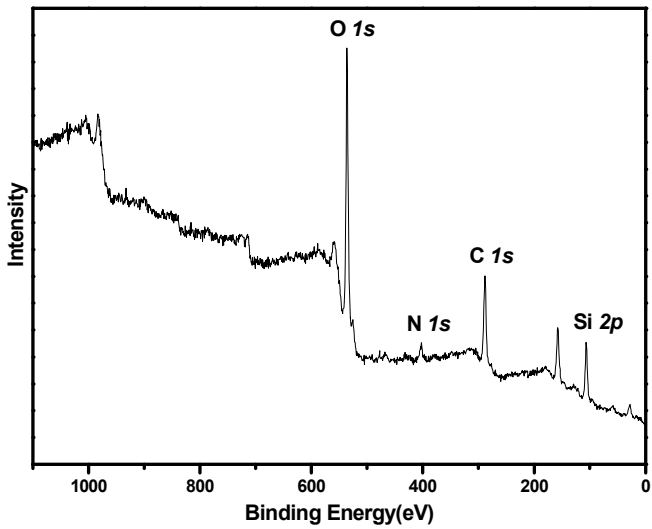
Thermogravimetric analysis was performed to evaluate the stability of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ , since the following reaction required heating in an aerobic condition. Figure 4 indicated the TG spectra of the fresh and spent catalyst recorded up to 1000 °C. As shown in Figure 4, when  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  was heated from room temperature to 80 °C, the loss of weight was only 0.7%, which proved that  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  was relatively stable as a catalyst in experimental conditions and it may be attributed to the bound water. Also, the decomposition of the surface organic groups of catalyst may contribute to the loss part as the small amount of nitrogen leaching occurred in recycled catalyst.

X-ray photoelectron spectrum of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  was shown in Figure 5. The O 1s

peak at 536.0eV and Si 2*p* peak at 106.4eV corresponded to the SiO<sub>2</sub>-type material. The C 1*s* peak at 284.7 eV and the N 1*s* peak at 399.6 eV confirmed that ethylenediamine was successfully grafted to the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>.<sup>33</sup>



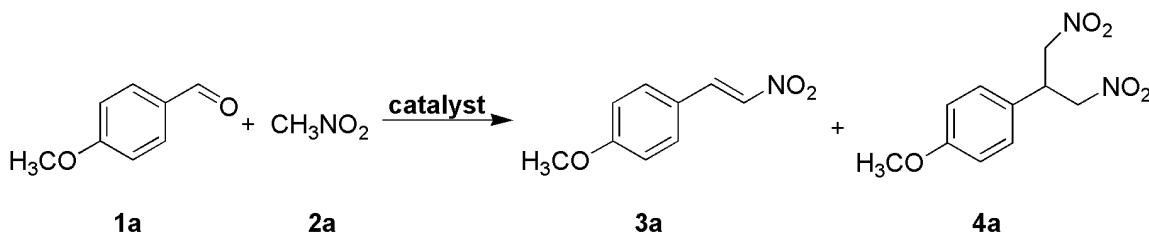
**Fig. 4** TGA spectra of the fresh (a) and spent (b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>



**Fig. 5** XPS spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>

### 3.2 Cooperative catalysis for selective synthesis of nitroalkenes

#### 3.2.1 Evaluation of its catalytic activity



**Scheme 2** Selective synthesis of nitroalkene in the presence of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$

**Table 1** Effect factors of cooperative catalysis for selective synthesis of nitroalkenes

Entry <sup>a</sup>	Amount of catalyst (g)	Time (h)	Temperature (°C)	Yield (%) <sup>b</sup>
1	0.050	4	80	55
2	0.075	4	80	68
3	0.100	4	80	97
4	0.125	4	80	98
5	0.150	4	80	>99
6	0.100	4	30	trace
7	0.100	4	60	69
8	0.100	2	80	65
9	0.100	3	80	87

<sup>a</sup> Reaction conditions: anisaldehyde (0.3 mmol) and nitromethane (5.0 mL), in air.

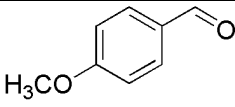
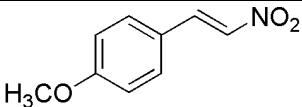
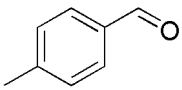
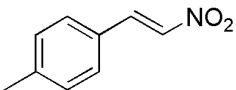
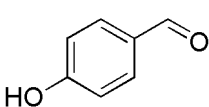
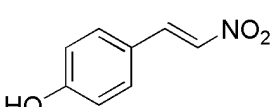
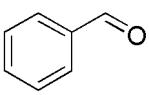
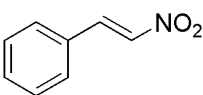
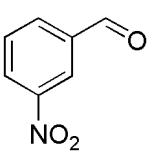
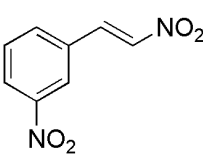
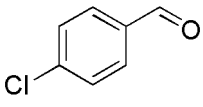
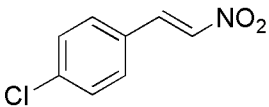
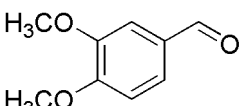
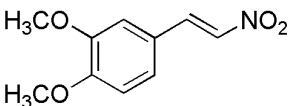
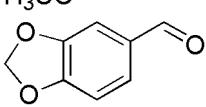
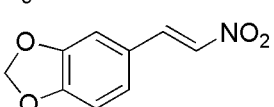
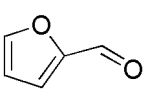
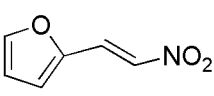
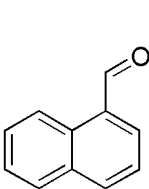
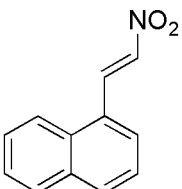
<sup>b</sup> Isolated yield based on aldehyde.

The catalytic activity of prepared  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  was tested for selective synthesis of nitroalkenes using anisaldehyde (0.3 mmol, **1a**) and nitromethane (5.0 mL, **2a**) as a model reaction without additional solvents (Scheme 2). A wide variety of reaction conditions such as the amount of catalyst, reaction time and temperature were investigated as shown in Table 1. The yield increased with the increase of the amount of

catalyst (Table 1, entries 1-3). However, no significant improvement of the yield was observed when the amount of catalyst increased from 0.100 g to 0.150 g. Therefore, 0.100 g  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  (Table 1, entry 3) was considered sufficient to catalyze the reaction. The optimized conditions were determined to be: anisaldehyde (0.3 mmol, **1a**), nitromethane (5.0 mL, **2a**) and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  (0.100 g) at 80 °C in air for 4h. The corresponding product **3a** was detected in 97% isolated yield.

Under the optimal conditions in Table 1, a range of representative aromatic aldehydes were applied to evaluate the scope of the reaction as shown in Table 2. The  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  catalyst was effective and selective toward most of the substrates. Both aldehydes bearing electron-rich and electron-withdrawing substituents on the aromatic rings reacting with nitromethane proceeded well and selectively gave the corresponding nitroalkenes in a moderate or excellent yield. However, the electron-withdrawing substituted aromatic aldehydes were slightly inferior to the electron-rich substituted aromatic aldehydes even under prolonged reaction times. As expected, the reaction between nitromethane and heterocyclic aromatic aldehyde was in a moderate yield.

**Table 2** The reaction between nitromethane and aromatic aldehydes.

Entry <sup>a</sup>	Aldehyde	Nitroalkene	Time (h)	Yield (%) <sup>b</sup>
1			<b>3a</b> 4	97
2			<b>3b</b> 4	95
3			<b>3c</b> 4	88
4			<b>3d</b> 4	97
5			<b>3e</b> 6	74
6			<b>3f</b> 6	87
7			<b>3g</b> 4	93
8			<b>3h</b> 4	89
9			<b>3i</b> 4	56
10			<b>3j</b> 4	97

<sup>a</sup> Unless otherwise specified, all the reactions were carried out using aromatic aldehydes or heterocyclic aromatic aldehyde (0.3 mmol), nitromethane (5.0 mL), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> (0.100 g), under 80 °C in air.

<sup>b</sup> Isolated yield based on aldehyde.

**Table 3** Reaction conditions for anisaldehyde and nitromethane using supported and unsupported amines

Entry <sup>a</sup>	Catalyst (g)	Time (h)	Yield (%) <sup>b</sup>
1	NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> (0.004 g)	4	63
2	NH(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> (0.010 g)	4	47
3	NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> (0.004 g) + NH(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> (0.010 g)	4	70
4	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @Cl (0.200 g)	4	trace
5	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @NH <sub>2</sub> (0.200 g)	4	95
6	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @NH <sub>2</sub> (0.200 g)	8	71 (26) <sup>c</sup>

<sup>a</sup> Reaction conditions: anisaldehyde (0.6 mmol) and nitromethane (5.0 mL), under 80 °C in air.

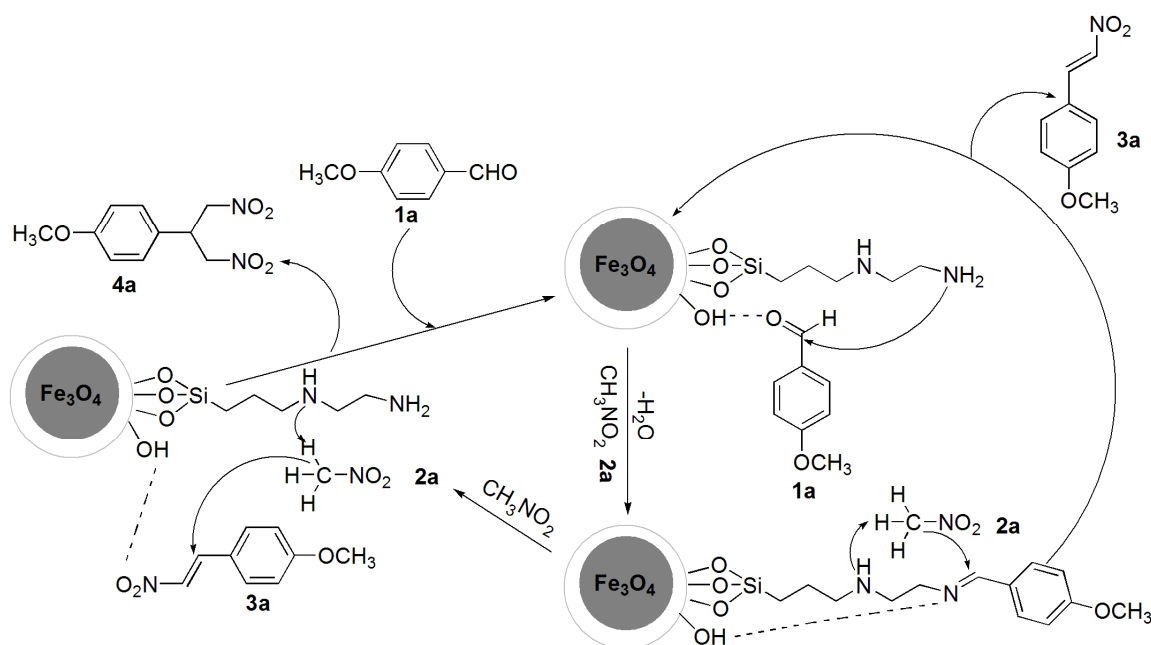
<sup>b</sup> Isolated yield based on anisaldehyde.

<sup>c</sup> Yield of 1,3-dinitroalkanes compounds.

In order to confirm the possible cooperative trifunctional catalysis mechanism, the following experiments were carried out as shown in Table 3. The content of primary amine nitrogen in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> (0.200 g) and NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (0.004 g) are equal. When ethylenediamine (0.004 g) was used in catalytic reaction, the yield was 63% (Table 3, entry 1). In a similar way, when using diethylamine (0.010 g) for catalytic reaction, the yield was only 47% (Table 3, entry 2). When ethylenediamine (0.004 g) and diethylamine (0.010 g) were used in catalytic reaction together, the yield was up to 70% (Table 3, entry 3). These indicated that primary amine and secondary amine collaboratively accelerated the reaction. In order to eliminate the effect of chlorine substituent and Si-OH groups, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Cl (0.200g) was used for the reaction between anisaldehyde and



nitromethane (Table 3, entry 4). Results showed that the separated chlorine substituent or Si-OH groups could hardly catalyze the reaction. When using  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  (0.200 g) to catalyze the reaction, the yield was high to 95% (Table 3, entry 5). These results suggested that the cooperative catalysis of primary and secondary amines was enhanced by Si-OH groups on the surface of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ . In addition, the yield of 1, 3-dinitroalkanes compounds **4a** could be obtained in 26% by prolonged reaction time to 8h. Combined with the experimental data and literatures<sup>17-19, 21, 22, 25-27</sup>, we speculated that the reaction between nitromethane and aromatic aldehyde under  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  was through a trifunctional cooperative catalysis mechanism in Scheme 3.



**Scheme 3** A possible cooperative trifunctional catalysis mechanism

The aromatic aldehyde **1a** is activated by both the silanol and primary amine on the surface of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  catalyst and reacts with an amino group to form an imine intermediate, the  $\alpha$ -proton of nitromethane **2a** is abstracted by secondary amine or

another amino group, accompanied by the nucleophilic attack of the deprotonated nitromethane on imine intermediate, which is also assisted by the silanol group resulting in the product nitroalkenes **3a**. Additionally, the Michael reaction between nitromethane **2a** which is activated by secondary amine or another amino group and nitroalkenes **3a** which might also be activated by the surface silanol group possibly occurs to obtain the 1,3-dinitroalkanes compound **4a**. Nucleophilic attack of the deprotonated nitromethane on aromatic aldehyde with electron-withdrawing groups on the aromatic rings might easily occur without the formation of imine intermediates, resulting in lower selectivity to nitroalkene formation.<sup>27</sup>

### 3.2.2 Separation of the catalyst and recycling tests

The recyclability of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  catalyst was also investigated for the reaction of anisaldehyde (0.3 mmol, **1a**) and nitromethane (5.0 mL, **2a**) at 80°C in air for 4h. After completion of the reaction, the solid catalyst was separated from the reaction mixture with the help of a magnet and washed with ethyl acetate and dichloromethane 3 times respectively. Without drying, the recovered catalyst was directly used in next run with new portions of reactants. The catalytic activity for the third consecutive cycles was 97%, 75%, 27% respectively. The yield decreased greatly from 97% to 27% after the third usage. We have also examined the catalytic activity of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  catalyst recovered at 80 °C. The same results were obtained as above. The total amount of nitrogen leaching after the third cycle was 4.5% as determined by elemental analysis (the amount of nitrogen is 1.78% before reaction and 1.70% after three cycles). Thermogravimetric analysis in figure 4 shows that  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  was relatively stable in air as a catalyst in experimental conditions. Combining the experiment results

with literature information, the decrease of catalytic activity might be the result of chemical poisoning of the surface of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  catalyst.<sup>36</sup> Although the exact deactivation mechanism of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  catalyst remains unclear, the formation of aminal seems to play a major role for remarkable catalyst deactivation.

#### 4 Conclusions

In conclusion, a magnetically separable trifunctional nanocatalyst  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  was designed and synthesized. The catalyst was found to be highly active for selective synthesis of nitroalkenes with nitromethane and aromatic aldehyde involving cooperative catalysis of primary amine, secondary amine and Si-OH groups. Under the optimized conditions, various representative substrates were extended to obtain the corresponding product in a moderate or excellent yield. In addition, a possible cooperative trifunctional catalysis mechanism was also proposed. The magnetic trifunctional nanocatalyst  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  has the prominent properties as follows: (a) simple and efficient separation (b) cooperatively accelerate a single reaction. The molecular design of more multifunctional surface and further applications to more organic reaction are currently being investigated in our laboratory.

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