Recyclable Fe₃O₄ Nanoparticles Catalysts for Aza-Michael Addition of Acryl Amides by Magnetic Field

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Abstract: A nanostructure-based catalytic system has the advantages of both homogeneous and heterogeneous catalysis. It is of great significance to develop the sustainable and green process of homogeneous catalytic reaction. We report a novel, efficient and recyclable magnetic Fe₃O₄ nanoparticles-catalyzed aza-Michael addition reaction of acryl amides, and the magnetic nanoparticles catalysts can be recovered by external magnetic field. Both primary amine and secondary amine can react with various acryl amides providing a good output to target products successfully at room temperature. Further experiments reveal that the magnetic Fe₃O₄ nanoparticles-based catalyst shows excellent yields, which can be recycled 10 times, and, at the same time, it maintains a high catalytically activity. In this catalytic system, the tedious separation procedures are replaced by external magnetic field, which gives us a different direction for choosing a catalyst in a nanostructure-based catalytic system.

Keywords: Fe₃O₄ nanoparticle; aza-Michael addition; recyclable catalyst; acryl amides; magnetic field; heterogeneous catalysis

1. Introduction

Environmental pollution caused by man-made waste and the decrease of natural resources is the main threat that has caught the attention of the whole world. The growing population needs more resources and naturally generates more waste. Land, air and fresh water, which are necessary for human life, all get affected by the release of chemical waste. For the sake of reduction in the harmful effects of the pollution and resource depletion, the best remedy is to develop the sustainable and atom-economic chemical process. This process can be improved upon by careful selection of starting materials and a catalytic system. Homogeneous catalysis is studied extensively as a powerful catalytic system, because of its special capabilities including high efficiency, flexible structures, high catalytic selectivity and activity, and so on. Nevertheless, the homogeneous catalyst is often difficult to isolate from reaction product, because both of the catalyst, reactants and products are same phase, which effects its extensive appliance [1]. Therefore, it is not only an environmentally-friendly but an atom-economic chemical process. The heterogeneous catalysis is distinguished from homogeneous catalysis by the different phases present during reaction. The main advantage of using a heterogeneous catalyst is the

relative ease of catalyst separation from the product. Therefore, the catalyst can be recycled and achieve the continuous chemical processes. The creation of a catalytic system, which has advantages of both homogeneous and heterogeneous catalysis, is of great significance. A nanostructure-based catalytic system provides an opportunity to meet the requirements, because the nanoparticles show not only large surface areas, but also tunable exposed surface, and high dispersity in the solvent [2].

Recently, many efforts have been made to use noble metal nanoparticles as catalysts in a homogeneous catalytic system, based on rationale design [3–17], e.g., cyclization reactions catalyzed by Pt nanoparticles [18], Heck coupling reactions and Ullmann coupling reactions of chlorobenzene catalyzed by Pd nanoparticles catalysts [19], and Heck and Suzuki reactions catalyzed by Pd nanoparticles [20], cycloisomerizations of enynes catalyzed by Au/CeO_2 nanocubes [21], and so on. However, the metal oxide has been more or less neglected. Compared with noble metal nanoparticles catalysts, the metal oxide is low-cost, low-toxicity and has tunable properties. Hence, a metal oxide nanoparticles-based catalytic system has great potential inorganic synthesis.

The Michael addition reaction is of such importance in inorganic synthesis [22]; thus, carbon-heteroatom and carbon-carbon bonds can be formed by this atom-economy and efficiency approach [23–27]. Especially, the aza-Michael addition reaction of acryl amides is a widely used in research and industry owing to its importance for several pharmaceutical products or important pharmaceutical intermediates, which can also be transformed into a large range of biologically active molecules under further treatment [28–30]. In traditional organic synthesis, the Michael addition reaction is catalyzed by strong bases, and the catalysts are quite difficult to recover and recycle, and moreover, the undesirable side reactions are unavoidable [31–34]. Therefore, this process is not sustainable and green chemistry. Herein, we report a novel, efficient and recyclable magnetic Fe_3O_4 nanoparticles-catalyzed aza-Michael addition reaction of acryl amides with amines, and the magnetic Fe_3O_4 nanoparticle catalysts can easily be recovered by external magnetic field.

2. Results and Discussion

Thermal decomposition of metal organic precursors is one of the best ways to prepare the high-quality monodisperse nanoparticles in high-boiling point solvent [35–40], such as, metal acetylacetonates [35,36], metal carbonyls, etc. The monodisperse Fe_3O_4 nanoparticles with good crystallinity and uniform size is obtained by thermal decomposition of the iron acetylacetonates dissolved in 1-octadecene at 300 °C using oleic acid and oleyl amine as surfactants under argon atmosphere. The size and shape of the obtained Fe_3O_4 nanoparticles were measured through using transmission electron microscopy (TEM). Figure 1 is representative images of obtained Fe_3O_4 nanoparticles. The perfectly spherical Fe_3O_4 nanoparticles are highly uniform, with diameter of 13 nm (Figure 1a). The high uniformity of these Fe_3O_4 nanoparticles allows the formation of nanoarrays arranged with long range order. After slow evaporation of a concentrated Fe_3O_4 nanoparticles solution in hexane, the super lattice of Fe_3O_4 nanoparticles are formed on the TEM grid (Figure 1b), The high-resolution TEM (HRTEM) image show that Fe_3O_4 nanoparticle is of single crystalline nature enclosed by the (111) plane and the surfaces are perfect without any sheathed amorphous phase (Figure 1c). The selected area electron diffraction (SAED) pattern (Figure 1d) further confirms that the spherical Fe_3O_4 nanoparticle is single crystalline nature. The SAED pattern exhibits that the *d* space is 0.24, 0.21, 0.17 and 0.13 nm, which correspond to the (222), (400), (422), and (533) planes of the standard cubic structure of Fe_3O_4 pattern.

The crystallinity and structure of the Fe_3O_4 nanoparticles are also confirmed by powder X-ray diffraction (XRD). The XRD pattern is illustrated in Figure 2. The diffraction peaks are indexed to (220), (311), (400), (511) and (440) reflections, corresponding to a cubic structure with lattice constants in the range of 0.5421–0.5432 nm (JCPDS card no. 11-0614, a = 0.83963 nm, space group *Fd-3m*). The relative intensity and peak position of all diffraction peaks are in good agreement with standard powder diffraction data, and no crystallized precursor is observed in the XRD pattern. The broadening of the reflections distinctly indicates the intrinsic nature of nanocrystals, which agrees well with the TEM results.
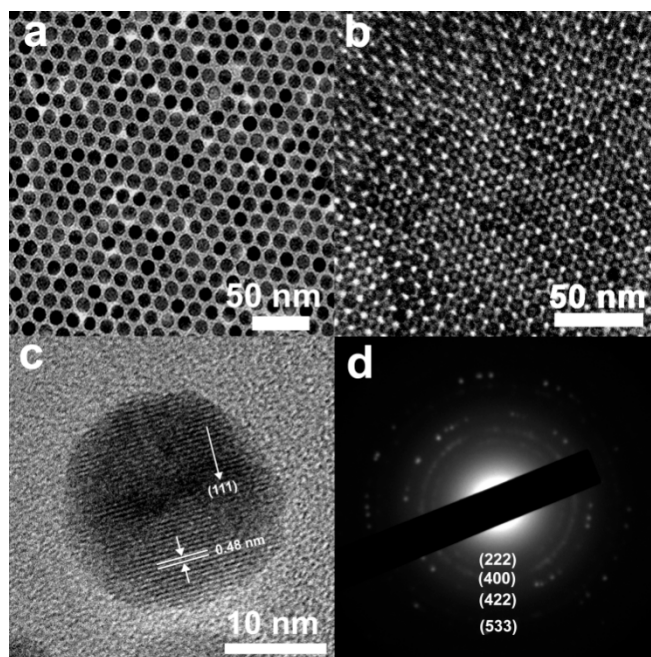
Figure 1. (**a**) Transmission electron microscopy (TEM) image of the prepared Fe_3O_4 nanoparticles; (**b**) The superlattice of Fe_3O_4 nanoparticles are formed on the TEM grid; (**c**) High-resolution TEM (HRTEM) image of the prepared Fe_3O_4 nanoparticles; (**d**) Selected area electron diffraction (SAED) pattern of the prepared Fe_3O_4 nanoparticles.
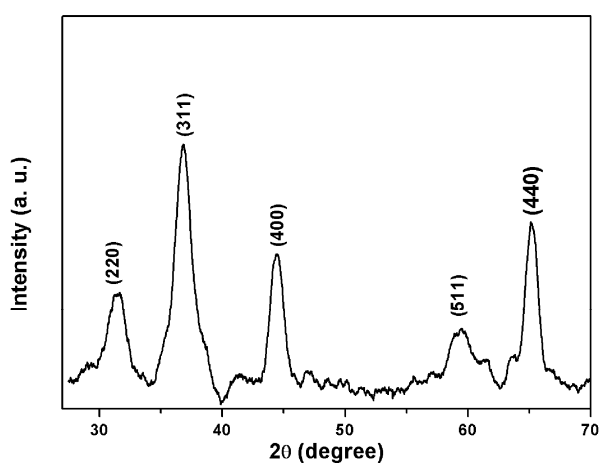

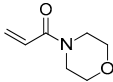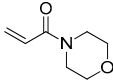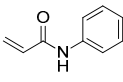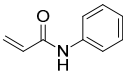**Figure 2.** Powder X-ray diffraction (XRD) of the prepared Fe_3O_4 nanoparticles.

The aza-Michael addition reaction of acryl amides is significant for preparing kinds of β-amino carbonyl compounds from readily manufactured raw materials in a sustainable and clean method [41–46]. Recently, the researches in aza-Michael addition by the imidazolium-based polymer [47], enzymes [48–51], and room-temperature ionic liquids (RTILs) have given a novelty way to achieve the important β-amino carbonyl derivatives [28]. These methods definitely have excellent potential as powerful tools which can build multiple molecules with different acryl amides, and in the meantime provide new catalytic cascade reaction sequences. Even if basic studies have effectively expanded the range of substrates for aza-Michael addition reaction, the relatively difficulty to separate the product and reuse the catalysts in the reaction have effected its application a lot. Moreover, the magnetic nanostructure-based catalyst is a prospective way to improve this situation effectively. In contrast, the smooth instances of magnetic nanostructure-based catalysts that display

creditable catalytic reactivity are as yet unusual in practice. We design a magnetic nanoparticles-based catalytic system, by using the magnetic Fe_3O_4 nanoparticles as catalysts, and the external magnetic field segregate catalyst readily with the reaction products by an external magnetic field.

We investigate the aza-Michael addition reaction of various substituents on N position of acryl amides catalyzed by the magnetic Fe_3O_4 nanoparticles. The reactions are carried out by using dichloromethane as the solvent normal pressure of atmosphere air at room temperature and the result is presented in Table 1. The magnetic Fe_3O_4 nanoparticles show excellent catalytic performance in the aza-Michael addition reaction, which can significantly enhance the yield of the desired product. The reactivity of Michael acceptors is affected by the substituent on the N position of acryl amide. The acrylamide and 1-morpholinoprop-2-en-1-one show a low reaction rate and yield (Table 1, entries 1, 3), and the *N*-phenylacrylamide exhibits higher the reaction rate and yield (Table 1, entries 5). The isolated yields are 38.1, 36.2 and 39.6, respectively. In contrast, under the magnetic Fe_3O_4 nanoparticles-catalyzed conditions, the acrylamide and 1-morpholinoprop-2-en-1-one are efficient Michael acceptors to give the corresponding products in 89% and 85.2% yields (Table 1, entries 2, 4). In addition, it is most significant that the isolated yield of *N*-phenylacrylamide reached up to 93.2% (Table 1, entry 6). It is worth mentioning that the magnetic Fe_3O_4 nanoparticles significantly improve the reaction rate and yield of acryl amide.

Table 1. Influence of the Fe_3O_4 nanoparticles on the aza-Michael addition of various substituent on N position of acryl amides with morpholine. [a]

Entry	Acryl Amide	Amine	Catalyst	Yield (%) [b]
1			-	38.1
2			Fe_3O_4 nanoparticles	89.0
3			-	36.2
4			Fe_3O_4 nanoparticles	85.2
5			-	39.6
6			Fe_3O_4 nanoparticles	93.2

[a] Reaction conditions: acryl amides (2 mmol), amines (2 mmol), and catalyst (10 mol %) in 1 mL of CH_2Cl_2 for 24 h at room temperature in a Schlenk tube; [b] Isolated yield.

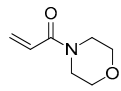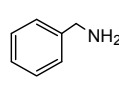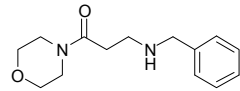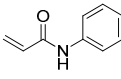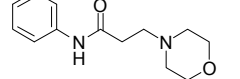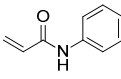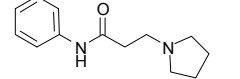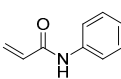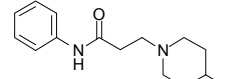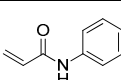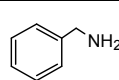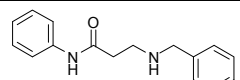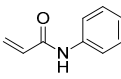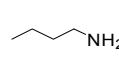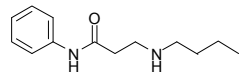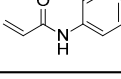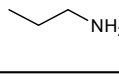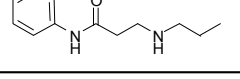Such a catalytic ability of the magnetic Fe_3O_4 nanoparticles-based catalyst is not novel to amines, other common amines substrates can be performed too. In addition, all of them performed high isolated yield (Table 2, entries 1–16). The secondary amines such as morpholine (Table 2, entries 1, 7 and 13), pyrrolidine (Table 2, entries 2, 8 and 14), 2-methylpiperidine (Table 2, entries 3 and 9), 4-methylpiperidine (Table 2, entries 4, 10 and 15) and 1-ethylpiperazine (Table 2, entries 5 and 11) are efficient Michael donors and the yield is more than 80%. Furthermore, the primary amine (phenylmethanamine) also exhibit high reaction rate and yield, and the isolated yields are 80.2, 90.1 and 80.1, respectively (Table 2, entries 6, 12 and 16). In addition, this aza-Michael

addition reaction can also be carried out on the acyclic amines. The n-butylamine and n-propylamine (Table 2, entries 17 and 18) have been tested and the isolated yields are 78.6% and 77.9%, respectively. The substituted amides and acyclic secondary amines cannot be catalyzed by the Fe_3O_4 nanoparticles in a reaction system.

Table 2. The magnetic Fe_3O_4 nanoparticles-catalyzed aza-Michael addition of acryl amides with various amines. [a]

Entry	Acryl Amides	Amine	Product	Yield (%) [b]
1				89.0
2				90.6
3				90.4
4				91.7
5				90.1
6				80.2
7				85.2
8				86.9
9				84.3
10				85.6
11				80.2

Table 2. *Cont.*

Entry	Acryl Amides	Amine	Product	Yield (%) [b]
12				90.1
13				93.2
14				81.2
15				84.6
16				80.1
17				78.6
18				77.9

[a] Reaction conditions: acryl amides (2 mmol), amines (2 mmol), and catalyst (10 mol %) in 1 mL of CH_2Cl_2 for 24 h at room temperature in a Schlenk tube; [b] Isolated yield.

According to all the experimental results, a feasible mechanism for Fe_3O_4 nanoparticles-catalyzed aza-Michael addition of acryl amide with amines is proposed in Scheme 1. Coordination of **1** with Fe_3O_4 nanoparticles leads to **I**; amine **2** added to the activated double bond to form **II**; Proton transfer of **II** gives product **3** and leaves Fe_3O_4 nanoparticles.
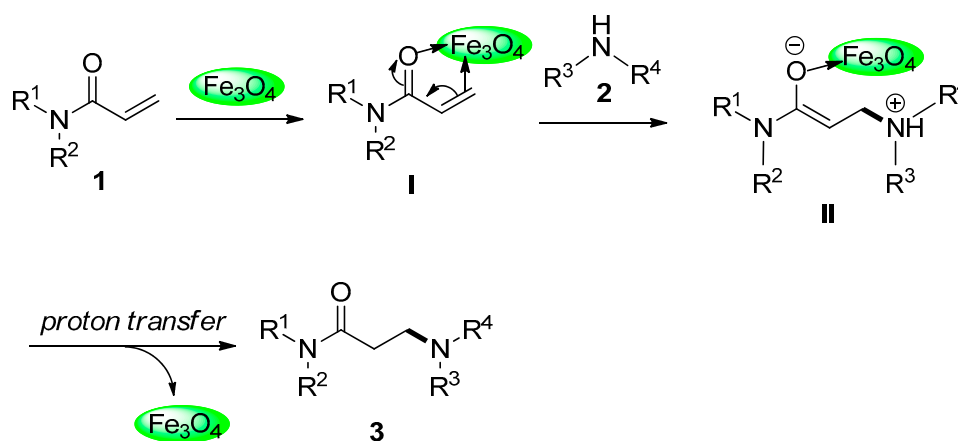
Scheme 1. A possible mechanism for Fe_3O_4 nanoparticles-catalyzed aza-Michael addition of acryl amides with amines.

It is generally agreed that the recovery of the catalyst system is the main factor to determine whether it has potential large-scale application in industry or not. To illustrate the recycling performance of the magnetic Fe_3O_4 nanoparticles-based catalyst, the model reaction of

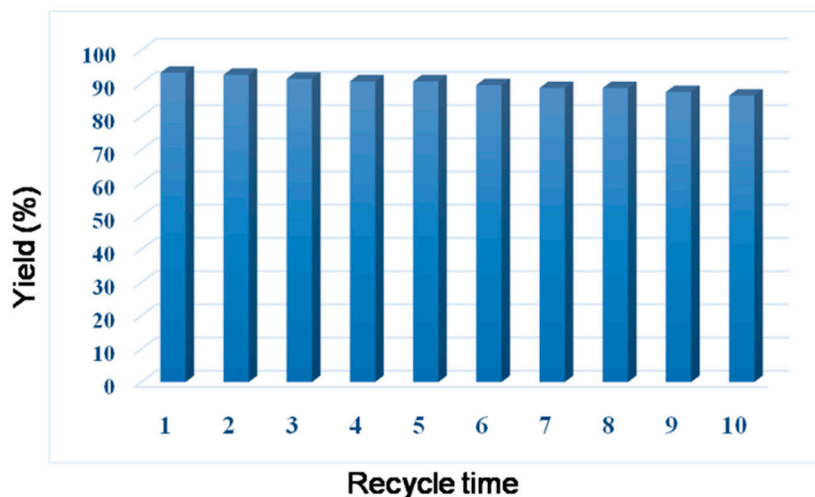N-phenylacrylamide with morpholine is chosen to investigate the reusability of the magnetic Fe_3O_4 nanoparticles-based catalyst. The magnetic Fe_3O_4 nanoparticles can be segregated readily with the reaction products by external magnetic field (Figure 3), which shows good recyclability. Moreover, the recycled catalyst shows the magnetic Fe_3O_4 nanoparticles are extremely stable with excellent catalytic activity of 86.3% after the tenth reuse (Figure 4). The isolated yields from the first to tenth catalytic reaction are 93.2, 92.6, 91.4, 90.6, 90.6, 89.5, 88.6, 88.6, 87.4 and 86.3, respectively. Because the outside of the Fe_3O_4 nanoparticles has been overlaped fractionally with organic compounds, the catalytic activity can decline mildly. In addition, the TEM image and powder XRD of the Fe_3O_4 nanoparticles after the catalytic reaction does not exhibit any appreciable aggregation or leaching (Figures S1 and S2). Based on the above experimental data, no catalytically active species have been leached from Fe_3O_4 nanoparticles in the reactive process, and the catalytically active species are Fe_3O_4 nanoparticles.
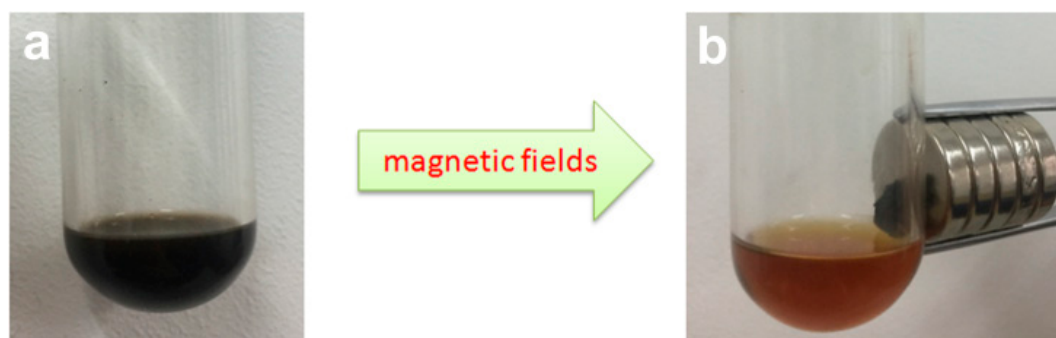
Figure 3. The magnetic Fe_3O_4 nanoparticles can be recovered from the reaction products by external magnetic field. (**a**) the reaction products and Fe_3O_4 nanoparticles before the external magnetic field; (**b**) the reaction products and Fe_3O_4 nanoparticles after the external magnetic field.

Figure 4. The reuses of magnetic Fe_3O_4 nanoparticles on the aza-Michael addition of *N*-phenylacrylamide with morpholine.

3. Experimental

3.1. Synthesis of Magnetic Fe_3O_4 nanoparticles

The magnetic Fe_3O_4 nanoparticles were prepared as previously reported involving two-steps: synthesis Fe_3O_4 seeds and growth of Fe_3O_4 nanoparticles [35]. $Fe(acac)_3$ (2 mmol), oleylamine (6 mmol), oleic acid (6 mmol), 1,2-hexadecanediol (10 mmol) and benzyl ether (20 mL) were added in a three-neck round bottom flask, then heated to 200 °C for 2 h. Then the mixture was heated to reflux at 300 °C

for 1 h under argon flow. The reaction was stopped by cooling to room temperature. The obtained Fe_3O_4 seeds were washed thrice with adding appropriate amount of ethanol and dispersed in hexane. $Fe(acac)_3$ (4 mmol), benzyl ether (20 mL), oleic acid (2 mmol), 1,2-hexadecanediol (20 mmol) and oleylamine (2 mmol) added in a three-neck round bottom flask, and then magnetically stirred under argon flow. 80 mg of Fe_3O_4 seeds were added and then the mixture was heated to 120 °C for 1 h and then heated to 200 °C for 2 h. After that, the mixture was further heated to 300 °C for 60 min under argon flow. The obtained Fe_3O_4 nanoparticles were washed thrice by adding an appropriate amount of ethanol and dispersed in hexane.

3.2. Characterization

The powder X-ray diffraction (XRD) patterns were recorded on a RigakuD/MAX-2000 diffractometer (rigaku corporation corporate, Tokyo, Japan) using Cu-Kα radiation (λ = 1.5406 Å). The transmission electron microscopy (TEM) observations were performed on a Philips Tecnai F20 FEG-TEM (FEI Company, Hillsboro, OR, USA) operated at 200 kV. The FTIR absorption spectrum was recorded on a Bruker spectrometer.

3.3. Representative Procedure for Catalytic Reactions

A mixture of acryl amides (2 mmol), amines (2 mmol) and the magnetic Fe_3O_4 nanoparticles (10 mol %) was stirred in 1 mL of CH_2Cl_2 for 24 h at 32 °C in a Schlenk tube. The reaction mixture was extracted with ethyl acetate when the reaction was completed (monitored by Thin Layer Chromatography (TLC)). The resulting crude product was purified with column chromatography by using petroleum ether/ethyl acetate or methanol/ethyl acetate as the eluent. The resulting products were characterized by ^{1}H NMR. The catalyst used in the reaction was segregated with external magnetic field and then used in subsequent reactions without further processing.

1. *3-morpholinopropanamide* (Table 2, entry 1). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 7.92 (s, 1H), 5.64 (s, 1H), 3.90–3.80 (m, 2H), 3.72 (s, 2H), 2.41–2.63 (m, 8H).
2. *3-(pyrrolidin-1-yl)propanamide* (Table 2, entry 2). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 8.00 (s, 1H), 5.38 (s, 1H), 2.86 (t, *J* = 6.2 Hz, 2H), 2.70 (s, 4H), 2.52 (t, *J* = 6.2 Hz, 2H), 1.91–1.80 (m, 4H).
3. *3-(2-methylpiperidin-1-yl)propanamide* (Table 2, entry 3). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 8.38 (s, 1H), 5.56 (s, 1H), 3.72 (q, *J* = 7.0 Hz, 2H), 3.40 (d, *J* = 11.9 Hz, 2H), 2.81 (t, *J* = 11.0 Hz, 2H), 1.89 (s, 1H), 1.67 (d, *J* = 12.7 Hz, 2H), 1.49 (d, *J* = 6.5 Hz, 2H), 1.3 (t, *J* = 7.0 Hz, 2H), 1.12 (d, *J* = 6.3 Hz, 3H).
4. *3-(4-methylpiperidin-1-yl)propanamide* (Table 2, entry 4). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 8.47 (s, 1H), 5.48 (s, 1H), 3.73 (q, *J* = 7.0 Hz, 2H), 2.94 (d, *J* = 11.4 Hz, 2H), 2.62–2.56 (m, 2H), 2.40 (t, *J* = 6.0 Hz, 2H), 1.98 (t, *J* = 12.3 Hz, 2H), 1.68 (d, *J* = 13.4 Hz, 1H), 1.25 (t, *J* = 8.3 Hz, 2H), 0.94 (d, *J* = 6.5 Hz, 3H).
5. *3-(4-ethylpiperazin-1-yl)propanamide* (Table 2, entry 5). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 8.09 (s, 1H), 5.47 (s, 1H), 2.68–2.60 (m, 3H), 2.47–2.37 (m, 11H), 1.10 (t, *J* = 7.2 Hz, 3H).
6. *3-(benzylamino)propanamide* (Table 2, entry 6). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 7.49(s, 1H), 7.23–7.25 (m, 4H), 6.26 (s, 1H), 3.71 (s, 4H), 1.33 (d, *J* = 6.9 Hz, 2H), 1.23 (t, *J* = 6.7 Hz, 2H).
7. *3-morpholino-1-morpholinopropan-1-one* (Table 2, entry 7). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 3.71 (t, *J* = 4.5 Hz, 4H), 3.68–3.60 (m, 2H), 3.60 (s, 4H), 3.45 (d, *J* = 4.7 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.52 (d, *J* = 19.6 Hz, 4H), 2.36 (s, 4H).
8. *1-morpholino-3-(pyrrolidin-1-yl)propan-1-one* (Table 2, entry 8). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 3.71–3.60 (m, 6H), 3.57 (d, *J* = 4.7 Hz, 2H), 2.93 (t, *J* = 7.3 Hz, 6H), 2.04 (s, 4H).
9. *3-(2-methylpiperidin-1-yl)-1-morpholinopropan-1-one* (Table 2, entry 9). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 3.70 (q, *J* = 7.0 Hz, 4H), 3.41 (d, *J* = 12.7 Hz, 4H), 2.79 (t, *J* = 11.1 Hz, 2H), 2.52 (d, *J* = 7.8 Hz, 2H), 2.41 (s, 2H), 1.85 (s, 1H), 1.68 (s, 1H), 1.46 (d, *J* = 9.8 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 2H), 1.06 (s, 3H).

10. *3-(4-methylpiperidin-1-yl)-1-morpholinopropan-1-one* (Table 2, entry 10). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 3.76–3.67 (m, 1H), 3.67–3.58 (m, 4H), 3.53–3.45 (m, 5H), 2.93 (d, *J* = 11.5 Hz, 2H), 2.79–2.71 (m, 2H), 2.63–2.55 (m, 2H), 2.06 (t, *J* = 11.0 Hz, 2H), 1.96 (s, 1H), 1.65 (d, *J* = 13.5 Hz, 2H), 0.93 (d, *J* = 6.5 Hz, 3H).

11. *3-(4-ethylpiperazin-1-yl)-1-morpholinopropan-1-one* (Table 2, entry 11). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 3.69–3.68 (m, 6H), 3.49 (d, *J* = 5.0 Hz, 2H), 2.53 (d, *J* = 8.0 Hz, 2H), 2.45–2.29 (m, 12H), 1.11 (t, *J* = 7.2 Hz, 3H).

12. *3-(benzylamino)-1-morpholinopropan-1-one* (Table 2, entry 12). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 7.49 (d, *J* = 6.2 Hz, 5H), 4.12 (s, 2H), 3.64 (d, *J* = 3.6 Hz, 4H), 3.54 (s, 4H), 2.97 (s, 2H), 2.03 (s, 2H), 1.24 (s, 1H).

13. *3-morpholin-4-yl-N-phenyl-propionamide* (Table 2, entry 13). ^{1}H NMR (400 MHz, CDCl$_3$) (ppm): δ 11.31 (s, 1H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 9.9 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 3.04 (d, *J* = 11.7 Hz, 2H), 2.72–2.64 (m, 4H), 2.55–2.47 (m, 2H), 2.07 (t, *J* = 10.8 Hz, 4H).

14. *N-phenyl-3-pyrrolidin-1-yl-propionamide* (Table 2, entry 14). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 9.97 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 3.73 (q, *J* = 7.0 Hz, 2H), 3.11 (t, *J* = 6.5 Hz, 2H), 2.08 (s, 4H), 1.25 (t, *J* = 7.0 Hz, 4H).

15. *3-(4-methyl-piperidin-1-yl)-N-phenyl-propionamide* (Table 2, entry 15). ^{1}H NMR (400 MHz, CDCl$_3$) (ppm): δ 10.76 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 3.82 (s, 2H), 2.87 (d, *J* = 23.3 Hz, 2H), 2.86 (d, *J* = 37.1 Hz, 2H), 2.71 (d, *J* = 29.6, 23.8 Hz, 2H), 1.74 (m, 1H), 1.25 (s, 4H), 0.86 (s, 3H).

16. *3-benzylamino-N-phenyl-propionamide* (Table 2, entry 16). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 10.44 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.41–7.25 (m, 7H), 7.07 (s, 1H), 3.88 (s, 2H), 2.97 (m, 2H), 2.59–2.51 (m, 2H), 1.94 (d, *J* = 6.7 Hz, 1H).

17. *3-butyl-N-phenyl-propionamide* (Table 2, entry 17). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ 10.51 (s, 1H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.24 (m, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 2.95 (m, 2H), 2.57 (t, *J* = 7.0 Hz, 4H), 1.37 (d, *J* = 8.6 Hz, 4H), 1.23 (s, 1H), 0.78 (s, 3H).

18. *3-propyl-N-phenyl-propionamide* (Table 2, entry 18). ^{1}H NMR (600 MHz, CDCl$_3$) (ppm): δ9.44 (s, 1H), 7.51 (s, 2H), 7.25 (s, 2H), 7.02 (s, 1H), 2.95 (s, 2H), 2.55 (d, *J* = 1.2 Hz, 4H), 1.57 (s, 1H), 1.42 (s, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

4. Conclusions

In conclusion, the magnetic Fe$_3$O$_4$ nanoparticles are used as catalyst in homogeneous catalytic system, and we have achieved the recovery of the catalyst by magnetic field in aza-Michael addition reaction, which is of great significance to develop the sustainable and green process of homogeneous catalytic reaction. In this catalytic system, the tedious separation procedures are replaced by an external magnetic field, which gives a different direction for picking a catalyst inhomogeneous catalysis. The magnetic Fe$_3$O$_4$ nanoparticles-based catalyst gives excellent yields at room temperature, and both primary amine and secondary amine can react with various acryl amides providing a good output to target products successfully. Further experiments reveal that the catalyst can be recycled 10 times, and also maintains a high catalytic activity. Meanwhile, this study in catalytic applications may be useful in the selection and design of a catalytic system with novel selectivity and activity in an even broader range of chemical reactions.

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