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# Highly efficient *N*-formylation of amines with ammonium formate catalyzed by nano-Fe<sub>3</sub>O<sub>4</sub> in PEG-400

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A simple and efficient protocol for the formylation of amines with ammonium formate with excellent yields catalyzed by  $Fe_3O_4$  nanoparticles in PEG-400 is described. Notably, this method shows excellent activity and chemoselectivity for the formylation of primary and secondary arylamines. Moreover, the nano- $Fe_3O_4$  catalyst and PEG-400 could be easily recovered and reused.

#### Introduction

Formylation of amines is an important transformation in organic synthesis, and has been widely used for amine protection in the synthesis of the complex organic molecules of natural products. Also, formamides are valuable intermediates for the synthesis of pharmaceutically active compounds such as substituted aryl imidazoles,1 1,2-dihydroquinolines,2 oxazolidinones3 etc.4,5 The formylation of amines is usually achieved by reacting amines with formic acid catalyzed by ZnO,6 [TMG]<sup>+</sup>,<sup>7</sup> ZnCl<sub>2</sub>,<sup>8</sup> sulfated titania,<sup>9</sup> Amberlite IR-120,<sup>10</sup> indium metal,<sup>11</sup> iodine,12 and sulfonic acid supported hydroxyapatite encapsulated y-Fe<sub>2</sub>O<sub>3</sub>.<sup>13</sup> Derivatives of formic acid like formate esters in the presence metal triflates,14 Bi(III) salts,15 heteropoly acids,16  $Al(HSO_4)_{31}$ ,<sup>17</sup> silphos[PCl<sub>3</sub>-(SiO<sub>2</sub>)<sub>n</sub>],<sup>18</sup> or orthoformates<sup>19,20</sup> have also been used for the conversion of amines into formamides. Notably, of these formylating agents, formic acid is corrosive and toxic, so it may affect acid-sensitive functional groups such as ether and ester bonds, and the number of side reactions may be increased, which is especially detrimental in the amineprotecting steps in the synthesis of complex natural products. There are several disadvantages of using formate esters and orthoformates, such as longer reaction times, lower yields and the relatively high cost of the reagents. In addition to the above mentioned methods, there have been reports in the literature<sup>21,22</sup> of formylation with formate salts as less expensive and efficient N-formylating agents for anilines and secondary amines in the absence of catalysts. Despite these methods being suitable for specific synthetic conditions, unfortunately, they still suffer from one or more disadvantages such as high

reaction temperatures, long reaction times, and the use of toxic solvents. Thus, there is still a need to explore an environmentally friendly method for this classic reaction.

In recent years, with the popularity of green chemistry, environmentally benign chemical processes or methods have been of great concern and extensive research has been carried out in this area. Polyethylene glycol, as an inexpensive, thermally stable, non-toxic, and recyclable polymer, has been widely used especially in the field of drug discovery. Moreover, polyethylene glycols with low molecular weights (<800) are employed as environmentally benign solvents in organic synthesis, it is hoped that they could become a substitute for volatile organic solvents. In addition, PEGs act as powerful phase transfer catalysts, like crown ethers, due to their special properties such as their cation complexation ability, which can lead to coordination with metal cations of different sizes and has been utilized in many useful organic transformations under mild reaction conditions, such as an N-arylation of amines,23 cross-coupling reaction,24-26 asymmetric dihydroxylation,27 aldol reaction,28 Baylis-Hillman reaction,29 multi-component condensation.30

Magnetic nanoparticles (MNPs), as a new class of catalyst, have been suggested to be a bridge between homogeneous and heterogeneous catalysis and are expected to exhibit special catalytic performance due to their ultrafine size and high surface area. Among the various magnetic nanoparticles, Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles have been used as a high performance catalyst and support, owing to them being inexpensive, environmentally benign, chemically stable and conveniently recovered after the reaction by simple magnetic separation. They have also been demonstrated to be an efficient catalyst for many useful chemical transformations, including thiolysis of epoxides,31 synthesis of diverse N-heterocycles,32 synthesis of α-aminonitriles,<sup>33</sup> synthesis of decahydroacridine derivatives,<sup>34</sup> synthesis of quinoxalines,<sup>35</sup> Sonogashira-Hagihara reactions,<sup>36</sup> dehydrogenation of ethylbenzene,37 Friedel-Crafts acylation reaction,38 trimethylsilyl protection of hydroxyl groups39 and three-component coupling of an aldehyde, alkyne and amine.40

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Considering the above points and our efforts towards the development of a new formylating synthetic method, here we report a green, mild and efficient method for the synthesis of formamides from amines with ammonium formate catalyzed by nano-Fe<sub>3</sub>O<sub>4</sub> in PEG-400. The protocol presented here provides an alternative and efficient strategy to achieve both chemoselectivity and catalyst recycling and would be a particularly good approach from the view point of green chemistry.

#### **Results and discussion**

The X-ray diffraction patterns of Fe<sub>3</sub>O<sub>4</sub> MNPs, are shown in Fig. 1. The position and relative intensities of all peaks ( $2\theta = 30.1^{\circ}, 35.4^{\circ}, 43.1^{\circ}, 53.4^{\circ}, 57^{\circ}$  and  $62.6^{\circ}$ ), which are assigned to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0), were consistent with the database in the JCPDS file (JCPDS19-0629),<sup>41</sup> indicating the crystalline cubic spinel of Fe<sub>3</sub>O<sub>4</sub> MNPs.

Fig. 2 shows IR spectra for  $Fe_3O_4$  MNPs, the strong absorption at 578 cm<sup>-1</sup> was characteristic of the Fe–O stretching vibration. The broad band at around 3500–3000 cm<sup>-1</sup> was attributed to adsorbed water. Also, the FT-IR adsorption showed no obvious differences in the characteristic adsorption peaks between fresh  $Fe_3O_4$  MNPs and  $Fe_3O_4$  MNPs after six uses.

Thermogravimetric analysis (TGA) and DTA curves of Fe<sub>3</sub>O<sub>4</sub> MNPs showed the mass loss of the organic substances as they decomposed with heating (Fig. 3). The initial weight loss from the Fe<sub>3</sub>O<sub>4</sub> MNPs up to 170 °C is due to the thermo desorption of solvents from the sample, while the weight loss between 170 and 420 °C may be associated to the thermal crystal phase transformation from Fe<sub>3</sub>O<sub>4</sub> to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. These results revealed that the catalyst was very stable under the reaction conditions.

TEM images of nano-Fe<sub>3</sub>O<sub>4</sub> are shown in Fig 4. It can be seen that the synthesized nanoparticles were uniform spheres with an average size of about 30 nm. Also, the catalysts were well dispersed in spite of the existence of some bigger structures that were likely due to the slight aggregation/coalescence of individual nanoparticles (Fig 4a). To our delight, the aggregation phenomenon was not clearly present after the catalyst had been used six times (Fig 4b). It is known that polyethylene glycols

311

400

<u>44</u>0

60

350

300

250

200

150

20

Relative Intensitiy

Fig. 1 X-Ray diffraction pattern of Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles.

40

2Theta(degree)

50



Fig. 2 FT-IR adsorption of  $Fe_3O_4$  magnetic nanoparticles. (a) Fresh, (b) after six uses.

with different molecular weights have recently been used as green stabilizers to protect metal nanoparticles preventing aggregation,<sup>42,43</sup> so we speculated that the Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles could be efficiently stabilized by PEG-400 during the reaction.

Initially, the reaction of aniline with ammonium formate was chosen as the model reaction (eqn (1)) to optimize the reaction conditions for the synthesis of benzamide. The results are summarised in Table 1.

$$\underbrace{ \bigvee_{\text{HCOONH}_4}}_{\text{HCOONH}_4} \xrightarrow{\text{nano-Fe}_3O_4(10\text{mol}\%)}_{\text{PEG}_{400}, 70^\circ\text{C}} \underbrace{ \bigvee_{\text{NHCHO}}}_{\text{NHCHO}}$$
(1)



Recently, Das<sup>44</sup> and co-workers reported that the formylation of aniline was carried out at room temperature in excellent yields by treatment with formic acid in PEG-400. Inspired by this good result, we surmised that PEG-400 might act as a phase transfer catalyst to promote the reaction and reasoned that use



Fig. 3 Thermo gravimetric analysis of  $Fe_3O_4$  magnetic nanoparticles. (a) TGA curve. (b) DTA curve.

30

220



Fig. 4 TEM of  $Fe_3O_4$  magnetic nanoparticles. (a) Fresh, (b) after six uses.

 Table 1
 The effect of catalytic conditions on the N-formylation of aniline

Run	Catalyst (mol%)	Solvent	Temperature (°C)	Yields <sup>c</sup> (%)
1 <sup><i>a</i></sup>		PEG-400	rt	_
$2^b$	Nano-Fe <sub>2</sub> O <sub>4</sub> (10)	PEG-400	70	97
3	CuO(10)	PEG-400	70	55
4	ZnO(10)	PEG-400	70	70
5	$Al_2O_3(10)$	PEG-400	70	78
6	Nano-Fe <sub>3</sub> O <sub>4</sub> (1)	PEG-400	70	69
7	Nano-Fe <sub>3</sub> O <sub>4</sub> (5)	PEG-400	70	86
8	Nano-Fe <sub>3</sub> O <sub>4</sub> (15)	PEG-400	70	97
9	Nano-Fe <sub>3</sub> O <sub>4</sub> (20)	PEG-400	70	96
10	Nano-Fe <sub>3</sub> O <sub>4</sub> (10)	PEG-400	40	35
11	Nano-Fe <sub>3</sub> O <sub>4</sub> (10)	PEG-400	50	62
12	Nano-Fe <sub>3</sub> O <sub>4</sub> (10)	PEG-400	60	83
13	Nano-Fe <sub>3</sub> O <sub>4</sub> (10)	PEG-400	80	95
14	Nano-Fe <sub>3</sub> O <sub>4</sub> (10)	PEG-400	90	80
15	Nano-Fe <sub>3</sub> O <sub>4</sub> (10)	CH <sub>3</sub> CN	70	89
16	Nano-Fe <sub>3</sub> O <sub>4</sub> (10)	DMF	70	85
17	Nano-Fe <sub>3</sub> O <sub>4</sub> (10)	Toluene	70	46
18	Nano-Fe <sub>3</sub> O <sub>4</sub> (10)	PEG-200	70	67
19	Nano-Fe <sub>3</sub> O <sub>4</sub> (10)	PEG-600	70	71

<sup>*a*</sup> Reaction conditions: aniline (10 mmol), ammonium formate (15 mmol), PEG-400 (15 mL), rt, 24 h. <sup>*b*</sup> Reaction conditions: aniline (10 mmol), ammonium formate (15 mmol), PEG-400 (15 mL), nano-Fe<sub>3</sub>O<sub>4</sub> (1.0 mmol), 70 °C, the reaction progress was monitored by TLC. <sup>*c*</sup> The isolated yield is stated.

of ammonium formate might lead to similar results. Unfortunately, when we mixed aniline (10 mmol) and ammonium formate (15 mmol) for 24 h at room temperature, no products were observed (Table 1, entry 1). Then, N-formylation was carried out in the presence of various metal oxides like CuO, ZnO, Al<sub>2</sub>O<sub>3</sub> and nano-Fe<sub>3</sub>O<sub>4</sub> under the same conditions. It was surprising to find that the nano-Fe<sub>3</sub>O<sub>4</sub> could rapidly induce Nformylation, which was complete in 30 min to give a quantitative yield of 99.2% (crude yield, the isolated yield was 97%) (Table 1, entries 2–5). The high efficiency here could be attributed to the large surface area and ultrafine size offered by the Fe<sub>3</sub>O<sub>4</sub> nanoparticles, which dispersed well in the PEG-400 during the reaction process to form a pseudo-homogeneous system and alleviate the disadvantages of the corresponding heterogeneous catalysts. Then, the influence of catalyst amount was investigated in the range of 1-20 mol% and the results in Table 1 (Table 1, entries 6-9) show that the catalyst amount of 10 mol% gave the highest product yield. When the catalyst amount was reduced to 1 mol%, aniline was converted to benzamide after a relatively long reaction time of 1.5 h. On the other hand, when the amount was above 10 mol%, there was no significant change in the conversion. Considering the economy of the reaction, an optimum catalyst amount of 10 mol% was chosen. In addition, the effect of reaction temperature was also investigated (Table 1, entries 10-14), and the highest yield of the product was obtained at 70 °C. A lower temperature (<50 °C) led to a sharp decrease in conversion because of the drop in mass transfer efficiency and insufficient mixing during the reaction. In contrast, a higher reaction temperature might lead to more side reactions due to the ease of oxidation of the amine group. As control experiments, we studied the impact of solvent using commercial solvents such as acetonitrile, DMF, toluene, PEG-200 and PEG-600 under the same conditions, the highest yield was obtained in PEG-400 (Table 1, entries 15-19). It was speculated that the polarity of solvents played an important role for the dissociation of ammonium formate, and polar solvents like CH<sub>3</sub>CN and DMF could increase the polarization of the formic group to facilitate the nucleophilic attack of the amine. However, PEG might facilitate a different catalytic pathway. It is known that liquid-phase polyethylene glycol can be considered to be an open chain of a crown ether, which has a helical structure, and it could fold into holes of different sizes. Not only could it complex with ions with different radii by changing the size of these holes, but some salts and most of the organic molecules are more soluble in it due to polar hydroxyl groups at both ends of the polyethylene glycol.<sup>45</sup> Besides, polyethylene glycols with different molecular weights have an obvious distinct complexation ability with cations of different sizes. Therefore, we thought that PEG-400 might act as a more powerful phase transfer catalyst, due to its improved complexation ability with ammonium cations compared with other reaction media, which could promote the maximum activity of a formate anion during the reaction (Scheme 1).

Based on the above good results, we continued to study the scope of this reaction protocol extending it to a series of various aromatic substituted primary and secondary arylamines. As



 $\ensuremath{\texttt{Scheme 1}}$  Phase transfer effect of PEG-400 by complexing with an ammonium cation.

#### Table 2 The scope of the N-formylation reaction of arylamines



Entry <sup>a</sup>	Substrate	Product <sup>b</sup>	Time (min)	Yields <sup>c</sup>	mp (°C)
1	NH <sub>2</sub>	NHCHO	30	97	47-48
2	CH3	NHCHO CH3	25	92	58-59
3	H <sub>3</sub> C	H <sub>3</sub> C NHCHO	25	90	55-57
4	NH <sub>2</sub> OH	NHCHO OH	30	94	129-131
5	HO NH2	НО	35	91	135-137
6	H <sub>3</sub> CO NH <sub>2</sub>	H <sub>3</sub> CO NHCHO	20	93	81-82
7	NH <sub>2</sub>	NHCHO CI	50	80	81-82
8	CI NH2	NHCHO CI	30	86	56-57
9	CI NH2	CI	60	83	100-102
10	Br NH <sub>2</sub>	Br	50	90	110-112
11	NH <sub>2</sub> NO <sub>2</sub>	NHCHO NO <sub>2</sub>	75	84	174-175
12	O <sub>2</sub> N NH <sub>2</sub>	O <sub>2</sub> N NHCHO	90	85	194-196
13	COOH	NHCHO COOH	60	87	167-168

R=-CH<sub>3</sub>,-CH<sub>3</sub>O,-OH,-CI,-Br,-NO<sub>2</sub>,-COOH



R=-CH<sub>3</sub>,-CH<sub>3</sub>O,-OH,-CI,-Br,-NO<sub>2</sub>,-COOH

Entry <sup>a</sup>	Substrate	Product <sup>b</sup>	Time (min)	Yields <sup>c</sup>	mp (°C)
14	NH2	N NHCHO	120	77	70-71
15	K CH3	CHO N CH <sub>3</sub>	60	84	123-124
16	N N	CHO N N	90	81	71-73

<sup>*a*</sup> *Reaction conditions*: substrate (10 mmol), ammonium formate (15 mmol), nano-Fe<sub>3</sub>O<sub>4</sub> (1.0 mmol), PEG-400 (15 mL), 70 °C, the reaction progress was monitored by TLC. <sup>*b*</sup> All products were purified by column chromatography on a silica gel using petrol ether–dichloromethane (5 : 2) as the eluent to afford the pure product and determined by melting point and HPLC analysis. <sup>*c*</sup> The isolated yield is stated.



Fig. 5 Recycling of  $Fe_3O_4$  MNPs for the *N*-formylation.

shown in Table 2, the reactions of all the substituted amines proceeded very efficiently and no side-reactions occurred. However, the reactions were largely dependent on the substituent on the aromatic ring in terms of reaction time and product yield. The reactions of substrates bearing an electron-donating group like methyl, methoxy, or hydroxyl (Table 2, entries 2–6) proceeded more effectively than the reactions of arylamines with an electron-withdrawing group such as chlorine, bromine, carboxyl or nitro (Table 1, entries 7–13). Moreover, the heterocyclic arylamines with



Scheme 2 The mechanism of nano- $Fe_3O_4$  catalyzed formylation.

heteroatom ortho to the amino group, which have a lone pair electrons, showed low reactivity and were converted to the corresponding formamides after a longer reaction time (Table 2, entry 14).

The recycling of the catalyst was examined for the *N*-formylation reaction of aniline. When the reaction was complete, ether was added to the mixture, the nano-Fe<sub>3</sub>O<sub>4</sub> catalyst could be recycled using a magnetic field and used six times without any appreciable loss in its catalytic activity (Fig. 5).

Hence, the reaction mechanism of nano-Fe<sub>3</sub>O<sub>4</sub> catalyzed *N*-formylation as a Lewis acid was shown in Scheme 2. We speculated that the reaction involved the complexation of the catalyst with the formic group, nucleophilic attack of the lone pair of electrons present in the amine to the carbonyl carbon of the formic group, then the removal of OH– occurs to afford the corresponding product.<sup>8,46</sup> In order to confirm this, we tested the pH of the reaction mixture and were delighted to find that the pH of the reaction mixture varied from 8.0 to 10.0 before and after the reaction, supporting our proposed reaction mechanism (Scheme 2).

## Conclusions

In conclusion, we have explored an efficient method for formylation of arylamines using nano- $Fe_3O_4$  as the catalyst in PEG-400. The mild reaction conditions and eco-friendly practicability made this protocol an attractive approach to prepare formamide derivatives. Furthermore, it is worth noting that this protocol is especially attractive because of the cheap and recyclable catalyst from the view point of green and sustainable chemistry.

## Experimental

#### General information

All starting materials were purchased from commercial sources and used without further treatment. Melting points were determined on a Perkin-Elmer differential scanning calorimeter. XRD were recorded on a Bruker Advance D8 X-ray diffractometer. IR spectra were recorded on a Nicolet IS-10 Fourier transform infrared spectrometer (KBr). Thermo gravimetric analyses were carried out on a Mettler Toledo-SDTA851e thermo gravimetric analyzer. TEM was carried out on a JEM-2100 transmission electron microscope. High performance liquid chromatography experiments were performed on a liquid chromatograph (Dionex Softron GmbH, America). The products were determined in some cases by comparison of their HPLC with those of authentic samples.

#### Preparation of Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles

The Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles were prepared with a coprecipitation method according to a previously reported procedure.<sup>47–53</sup> Firstly, FeCl<sub>3</sub>· 6H<sub>2</sub>O (5.4 g) and FeCl<sub>2</sub>· 4H<sub>2</sub>O (2.0 g) were dissolved in distilled water (50 mL) in a three-necked roundbottom flask (150 mL). The resulting solution was stirred with mechanical stirring under an N<sub>2</sub> atmosphere for 0.5 h. A solution of aqueous ammonia (10 mL, 25 wt%) was then added to the solution in a dropwise manner over a 30 min period. The reaction mixture was then stirred under room temperature for 3 h. The resulting Fe<sub>3</sub>O<sub>4</sub> magnetic particles were collected with a magnet and washed thoroughly with distilled water and ethanol three times, then dried under vacuum for 12 h to give Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles.

#### Typical procedure for N-formylation of aniline

Aniline (10 mmol) and ammonium formate (15 mmol) were added to a mixture of PEG-400 (15 mL) and  $Fe_3O_4$  nanoparticles (0.23 g) at 70 °C. The reaction mixture was stirred mechanically and monitored by TLC. After completion of the reaction (30 min), the mixture was extracted by ether three times. The organic solvent was evaporated giving crude formanilide and purified by column chromatograph on a silica gel using petrol ether–dichloromethane (5 : 2) as the eluent to afford the pure product in 97% yield; mp 47–48 °C. The product was found to be high purity by HPLC analysis.

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