

Magnetically recoverable CuFe_2O_4 nanoparticles as an efficient heterogeneous catalyst for green formylation of alcohols

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CHRONICLE

Article history:

Received August 26, 2018

Received in revised form

November 1, 2018

Accepted November 1, 2018

Available online

November 1, 2018

Keywords:

Alcohols

CuFe_2O_4

Formylation

Nanoparticles

Super paramagnetic

ABSTRACT

In this article, magnetically nanoparticles (MNPs) of CuFe_2O_4 were prepared and characterized using Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction and transmission electron microscopy techniques. Super paramagnetic CuFe_2O_4 was used as an efficient catalyst for green formylation of structurally diverse alcohols to the corresponding formyl esters using formic acid as a solvent (60-70 °C). All reactions were carried out successfully within 1-120 min to afford the products in 76-96 % yields. Reusability of CuFe_2O_4 MNPs was examined 5 times without significant loss of its catalytic activity.

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1. Introduction

Functional group protection has a crucial role in the synthesis of different kind of organic and pharmaceutical compounds.¹ Among the various protecting groups used for the hydroxyl function, formylation is one of the most common protecting methods because of easy and fast formation of formate and its deprotection under mild conditions.^{2,3} The development of heterogeneous reagents has become a main part of research in industry and in developing technologies because the reactions are carried out under mild conditions and the target molecules are easily separated from the reaction media.⁴⁻⁸ A literature review shows that formylation of hydroxyl group can take place by formylating agents in the presence of various reagents/catalysts such as $\text{K}_5\text{CoW}_{12}\text{O}_{40} \cdot 3\text{H}_2\text{O}$,⁹ $\text{In}(\text{OTf})_3$,¹⁰ silica triflate,¹¹ $\text{Bi}(\text{OTf})_3$,¹² $\text{Sc}(\text{OTf})_3$,¹³ $\text{Ce}(\text{OTf})_4$,¹⁴ $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$,¹⁵ bismuth(III) salts,¹⁶ $(\text{NH}_4)_8[\text{CeW}_{10}\text{O}_{36}] \cdot 20\text{H}_2\text{O}$,¹⁷ *p*-TsCl,¹⁸ TMSOTf,¹⁹ chloral,²⁰ DBSA,²¹ silica sulfuric acid,²² $\text{Mg}(\text{HSO}_4)_2$,²³ $\text{Zr}(\text{HSO}_4)_4$,²⁴ RHA-[pmim]HSO₄.²⁵ Although, various procedures have been reported for formylation of alcohols, however, most of these methods suffer from using vigorous reaction conditions, organic solvents, heavy metal contamination, expensive reagents/catalysts, long reaction times and low yields. Solvent-free conditions often lead to clean and eco-friendly procedure which do not have to remove and recycle solvents and reduces the harmful effects to the environment. Thus,

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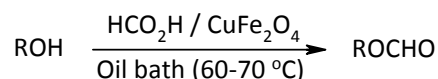
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doi: 10.5267/j.ccl.2018.010.002

development of simple methods which utilize mild and low-cost reagents under solvent-free conditions is still a subject of interest.

In recent years, the use of magnetic nanoparticles as recoverable heterogeneous catalysts has developed due to their various applications in organic transformations and catalysis.²⁶⁻³² Among these magnetic catalysts, copper ferrite nanoparticles have been used extensively in organic synthesis and different industrial chemical processes.³³⁻³⁵ CuFe_2O_4 has magnetic properties and it can be recovered easily from the reaction mixture using an external magnet.^{36,37} This nano-scale catalyst can be obtained by co-precipitation of copper(II) and iron(III) salts³⁸ and it also occurs naturally as a mineral. In line with the outlined strategies, herein, we wish to report an efficient and eco-friendly formylation of structurally diverse alcohols with formic acid in the presence of reusable CuFe_2O_4 under oil bath conditions (60-70 °C) (Scheme 1).



Scheme 1. Formylation of Alcohols with $\text{HCO}_2\text{H}/\text{CuFe}_2\text{O}_4$ System

2. Results and Discussion

Though the protection of alcohols by formyl group has been extensively studied in the presence of various catalysts or formylating agents, however, a literature review shows that the capability of magnetically nanoparticles of CuFe_2O_4 for the titled transformation has not been investigated yet. Prompting by this idea, we therefore decided to study formylation of benzyl alcohol as a model compound by ethyl formate or formic acid as an available and inexpensive formylating agents in the presence of CuFe_2O_4 MNPs. Optimization experiments were carried out under different reaction conditions. The illustrated results in Table 1 show that progress of the formylation reaction in formic acid in comparison to ethyl formate is so prominent. In addition, using the molar ratio of $\text{PhCH}_2\text{OH}/\text{CuFe}_2\text{O}_4$ (1:0.5) in HCO_2H (0.5 mL) at oil bath (60-70 °C) is the requirement for completing conversion of benzyl alcohol to benzyl formate within 1 min (entry 10). Subsequently benzyl formate was obtained in 90 % isolated yield. It is noteworthy that under drastic conditions (refluxing formic acid, bp: 100-101 °C), the rate of formylation reaction was accelerated to some extent (entry 9). However, according to the fact; higher temperature requires higher cost, therefore, the mild reaction conditions mentioned in entry 10 was selected as the optimum of this formylating protocol.

Table 1. Optimization experiments for formylation of benzyl alcohol to benzyl formate under different conditions^a

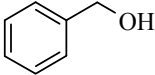
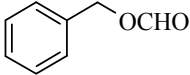
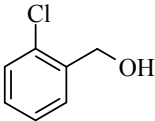
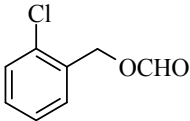
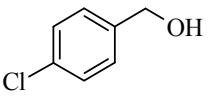
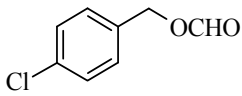
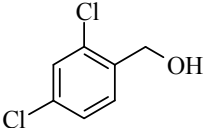
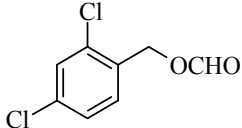
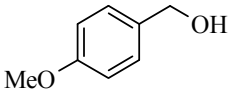
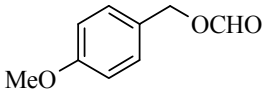
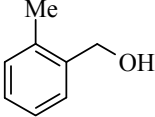
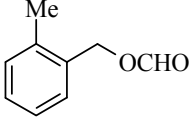
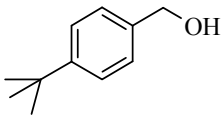
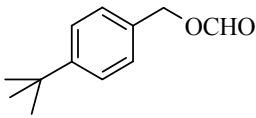
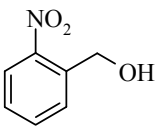
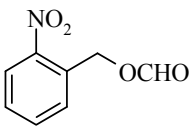
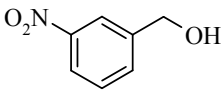
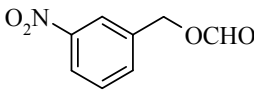
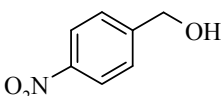
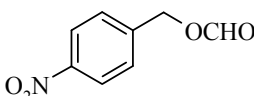
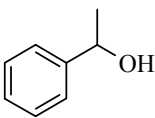
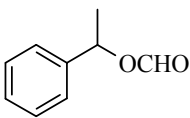
Entry	Ethyl formate (mL)	Formic acid (mL)	CuFe_2O_4 (mmol)	Condition ^b	Time (min)	Conversion (%)
1	0.5	-	-	Solvent-free/reflux	60	10
2	1.0	-	0.3	Solvent-free/reflux	60	20
3	1.0	-	0.5	Solvent-free/reflux	60	30
4	2.0	-	1.0	Solvent-free/reflux	60	40
5	-	0.5	-	Solvent-free/reflux	60	40
6	-	1.0	-	Solvent-free/reflux	60	50
7	-	0.5	0.3	Solvent-free/r.t.	30	60
8	-	0.5	0.4	Solvent-free/reflux	30	70
9	-	0.5	0.5	Solvent-free/reflux	30 sec	100
10	-	0.5	0.5	Solvent-free/Oil bath	1	100

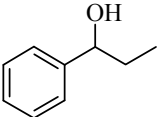
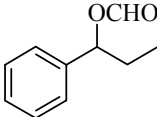
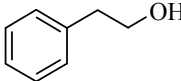
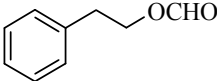
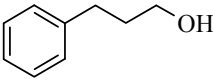
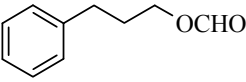
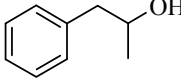
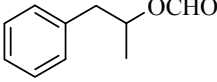
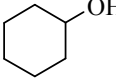
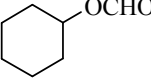
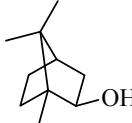
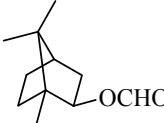
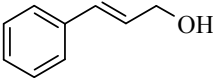
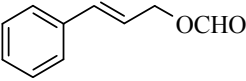
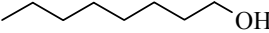
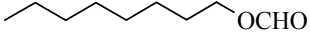
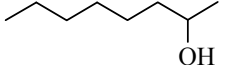
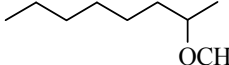
^a All reactions were carried out with 1 mmol of benzyl alcohol. ^b Temperature of oil bath was 60-70 °C.

Encouraged by the result, the capability of $\text{HCO}_2\text{H}/\text{CuFe}_2\text{O}_4$ system was more studied with the reaction of various benzylic primary and secondary alcohols possessing electron-releasing or withdrawing groups as well as aliphatic ones with formic acid at the optimized reaction conditions. Table 2 shows the general trend and versatility of this synthetic method. As seen, all reactions were

carried out successfully in the presence of CuFe_2O_4 MNPs (0.5 mmol) within 1-120 min to afford the corresponding formyl esters in high to excellent yields (76-96 %). The table also shows that the effect of substitutions on aromatic rings is noteworthy. Electron-releasing groups accelerated the rate of formylation reaction and in contrast withdrawing substitutions prolonged the reaction times through the deactivation of aromatic rings. Moreover, aliphatic primary and secondary alcohols perform the formylation reaction faster than benzylic ones. Entries 17 and 18 show that protocol of $\text{HCO}_2\text{H}/\text{CuFe}_2\text{O}_4$ is also efficient for formylation of hindered (borneol) and allylic alcohols (cinnamyl alcohol).

Table 2. Formylation of alcohols with $\text{HCO}_2\text{H}/\text{CuFe}_2\text{O}_4$ system^a

Entry	Substrate	Product	Time (min)	Yield (%) ^b	Ref.
1			1	90	9
2			15	80	11
3			10	85	11
4			20	80	11
5			2	92	9
6			10	90	24
7			1	96	24
8			120	76	9
9			120	77	9
10			90	78	9
11			4	80	24

12			3	83	24
13			3	80	9
14			2	84	9
15			13	88	24
16			7	90	9
17			4	92	24
18			10	85	11
19			8	85	9
20			6	85	9

^a All reactions were carried out with the molar ratio of alcohol/CuFe₂O₄ (1:0.5) in formic acid (0.5 mL) under oil bath conditions (60-70 °C). ^b Yields refer to isolated pure products.

Nano catalysts have the ability to reuse in the reactions because of their active surfaces and high stability. In this study, recycling and reusability of CuFe₂O₄ MNPs were examined in the formylation of benzyl alcohol with formic acid at the optimized reaction conditions. After completion of the reaction, the nanocatalyst was recovered with an external magnetic field, washed with EtOAc for removing contaminants and then reused for second run of the formylation reaction. Fig. 1 represents the reusability of copper ferrite for five times without significant loss of its catalytic activity.

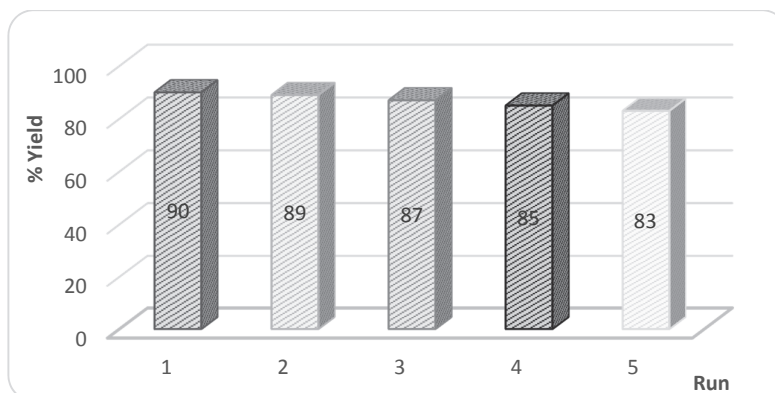


Fig. 1. Reusability of CuFe₂O₄ for Formylation of Benzyl Alcohol

CuFe₂O₄ nanoparticles were synthesized according to the reported procedure³⁵ and were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning

electron microscopy (SEM) and transmission electron microscopy (TEM). In FT-IR spectrum, the most intensive absorptions belong to the significant bands centered in 587 and 405 cm^{-1} at low energy. These characteristic features are assigned to vibrations of Cu-O bond in CuFe_2O_4 nanoparticles (Fig. 2). The absorption band at 587 cm^{-1} was attributed to stretching vibration of tetrahedral complexes and the absorption band at 405 cm^{-1} to that of octahedral complexes. The absorption band at 3420 cm^{-1} represents stretching vibration of surface OH groups.

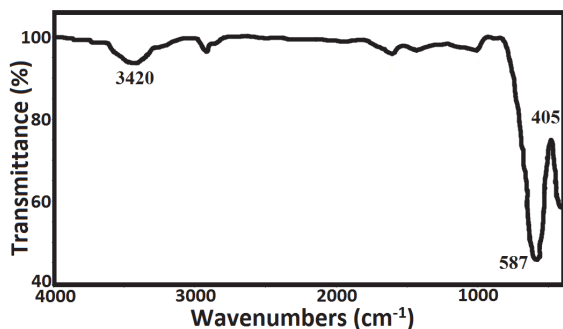


Fig. 2. FT-IR Spectrum of CuFe_2O_4 MNPs

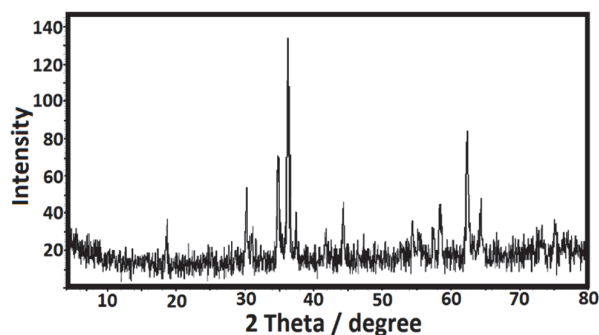


Fig. 3. X-ray Diffraction Pattern of CuFe_2O_4 MNPs

Calcination of CuFe_2O_4 at 900°C provided nanoparticles with an average size of 75 nm (calculated from Scherrer equation at $2\theta = 37^\circ$). XRD spectrum of the prepared CuFe_2O_4 exactly demonstrated tetragonality of the standard spinel structure of CuFe_2O_4 (JCPDS card No. 34-0425) with a good crystallinity (Fig. 3).

The morphology and size distribution of the prepared nano CuFe_2O_4 was then investigated by scanning electron microscopy (SEM). Fig. (4a) shows that the agglomeration in the prepared CuFe_2O_4 is high. The SEM analysis also exhibits that the size of nanoparticles varies from 75-116 nm. The TEM image of the sample is given in Fig. 4b.

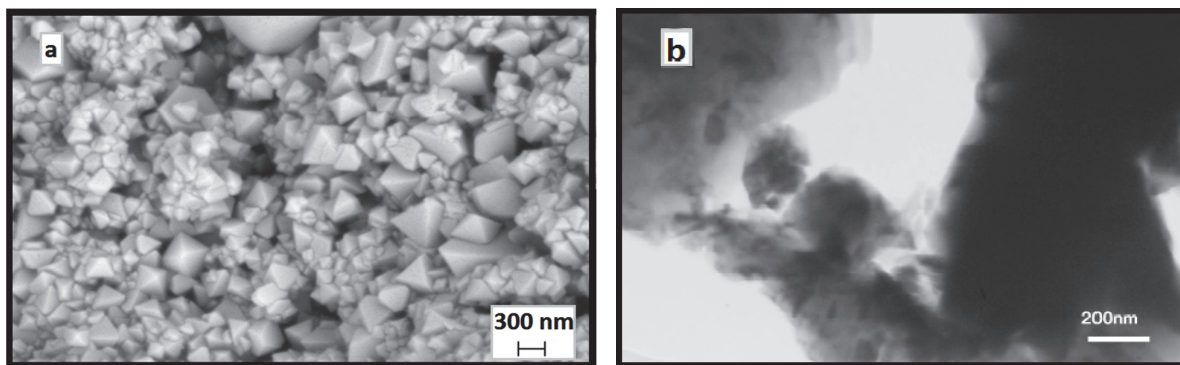


Fig. 4. SEM (a) and TEM Image (b) of CuFe_2O_4 MNPs

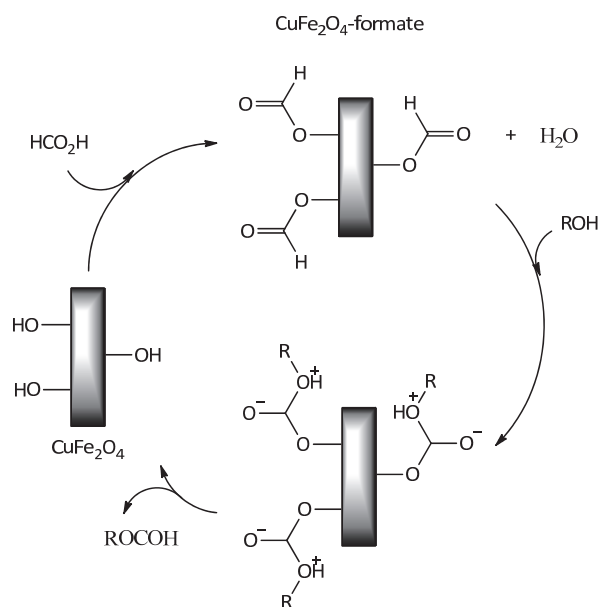
Suitability of this synthetic method was explored by a comparison of the formylation of benzyl alcohol catalysed with CuFe_2O_4 and other reported reagents (Table 3). Observation of the results shows that in view points of efficiency, availability and reusability of nanaocatalyst and mild reaction conditions the present protocol is more efficient or has a comparable efficiency.

Table 3. Comparison of the formylation of benzyl alcohol catalyzed by CuFe_2O_4 and other reported reagents^a

Entry	Reagents	Mol%	Conditions ^b	Time (min)	Yield (%)	Ref.
1	CuFe_2O_4	50	Solvent-free/Oil bath	1	90	-
2	$(\text{NH}_4)_8[\text{CeW}_{10}\text{O}_{36}] \cdot 20\text{H}_2\text{O}$	4	reflux	300	60	17
3	chloral	114	rt	270	62	20
4	$\text{K}_5\text{CoW}_{12}\text{O}_{40} \cdot 3\text{H}_2\text{O}$	1	reflux	60	90	9
5	DBSA	20	Solvent-free/rt	10	92	21
6	$\text{RHA} - [\text{pmim}]\text{HSO}_4$	10mg	Solvent-free	25	93	25
7	$\text{Zr}(\text{HSO}_4)_4$	20	rt	90	95	24

^a All reactions were carried out with 1 mmol of alcohol. ^b Temperature of oil bath was 60-70 °C.

Although the exact mechanism of this synthetic protocol is not clear, however, we think that a depicted mechanism (Scheme 2) maybe play a role in the formylation of alcohols with formic acid. The mechanism shows that through the existing of hydroxyl groups on the surface of CuFe_2O_4 followed by dehydration with formic acid, the CuFe_2O_4 -formate composite was prepared. Finally, nucleophilic attack of an alcohol with the prepared formate-composite produces the primarily nanocatalyst and formyl ester product.

**Scheme 2.** A Proposed Mechanism for Formylation of Alcohols with Formic Acid

3. Conclusions

In summary, we have shown that magnetically nanoparticles of CuFe_2O_4 as a recoverable heterogeneous catalyst can be used successfully for formylation of different kinds of alcohols with formic acid. All reactions were carried out successfully with the molar ratio of alcohol/ CuFe_2O_4 (1:0.5) in formic acid (0.5 mL) under oil bath conditions (60-70 °C). The product formyl esters were obtained in 76-96 % yields within 1-120 min. Low cost of the preparation of nanocatalyst, its remarkable reusability, mild reaction conditions, high to excellent yield of the products, short reaction times as well as the benefits of using solvent-free conditions are the advantages which make this protocol a synthetically useful addition to the present methodologies.

Acknowledgements

The authors gratefully acknowledged the financial support of this work by the research council of Urmia University.

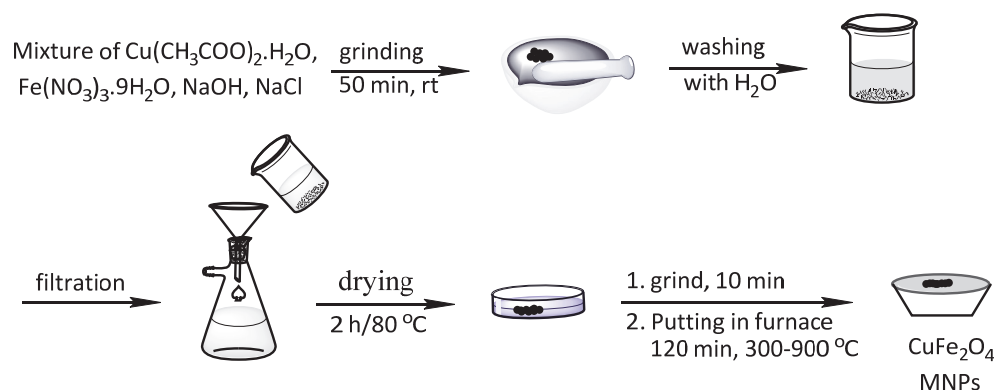
4. Experimental

4.1. Materials and Methods

All reagents and substrates were purchased from commercial sources and were used without further purification. FT-IR and $^1\text{H}/^{13}\text{C}$ NMR spectra were recorded on Thermo Nicolet Nexus 670 spectrophotometer and Bruker Avance 300 MHz spectrometer, respectively. The products were characterized by FT-IR and ^1H , ^{13}C NMR spectra followed by a comparison with authentic data. All yields refer to isolated pure products. TLC (silica gel 60 F₂₅₄ aluminium sheet) was used for the purity determination of the substrates, products and the reaction monitoring. XRD pattern of CuFe_2O_4 was recorded on a Bruker D8-Advanced diffractometer with graphite-monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) at room temperature. SEM images were determined on a LEO 1430 VP scanning electron microscopy. TEM images were recorded with a Philips CM30 at electron energy of 300 keV.

4.2. Preparation of CuFe_2O_4 nanoparticles

In a porcelain mortar, a mixture of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, NaOH , and NaCl (with molar ratio of 1:2:8:2 respectively) was grounded together (50 min). The reaction was occurred during the combination of materials and it was associated by losing heat. The colour of mixtures gradually was changed from blue to brown. Finally, it was converted to a black paste and was washed with distilled water for several times. After filtration, the powder was dried at 80°C for 2 h and then calcinated at 300°C , 500°C , 600°C , 700°C , 800°C and 900°C for 2 h (20 min for each temperature) to generate the final CuFe_2O_4 MNPs (Scheme 3).³⁹



Scheme 3. Synthesis of CuFe_2O_4 MNPs

4.3. A General procedure for solvent-free formylation of alcohols with $\text{HCO}_2\text{H}/\text{CuFe}_2\text{O}_4$ system

In a round-bottom flask (10 mL) equipped with a magnetic stirrer, a solution of alcohol (1 mmol) and formic acid (0.5 mL) was prepared. To the resulting solution, CuFe_2O_4 MNPs (0.5 mmol) was then added and the mixture was stirred magnetically in oil bath ($60\text{-}70^\circ\text{C}$) for the appropriate time mentioned in Table 2. After completion of the reaction, EtOAc (2 mL) was added and the reaction mixture was stirred for 10 min. The nanocatalyst was then removed from the reaction mixture using an external magnet. The mixture was dried over anhydrous sodium sulfate and passed through a short column of silica gel. Evaporation of the solvent under reduced pressure affords the pure formate product in 76-96% yield.

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