

# An eco-friendly *N*-formylation of amines using nano cerium oxide as a recyclable catalyst under solvent-free and ultrasound irradiation conditions at room temperature

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**Abstract:** A new method for the synthesis of formamides has been developed by the *N*-formylation of amines with formic acid in the presence of nano cerium oxide as an efficient and recyclable catalyst under ultrasound irradiation. The reaction system is remarkably simple and environmentally benign.

**Keywords:** *N*-Formylation, amine, nano cerium oxide, reusable catalyst, formic acid, ultrasound irradiation

## INTRODUCTION

Formamides are valuable intermediates in the synthesis of pharmaceutically important compounds [1,2]. In addition, the formamide moiety has been used to protect the nitrogen in amines [3] and in the synthesis of formamidines and isocyanides [4]. Also, formamides can act as Lewis base catalysts in reactions such as allylation, synthesis of acid chlorides from carboxylic acids and hydrosilylation of carbonyl compounds [5].

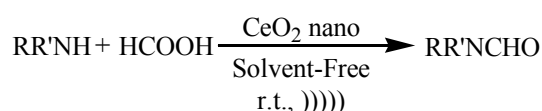
Several formylation reagents have been reported in the literature for the *N*-formylation of amines such as acetic formic anhydride [6], chloral [7], activated formic acid using *N,N*-dicyclohexylcarbodiimide [8] or *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride [9] activated formic esters [10] ammonium formate [11], 2,2,2-trifluoroethyl formate [12], Natrolite zeolite [13] and PEG-400 [14].

However, there are several obstacles which limit the applicability of these reagents [15]. In many cases, the reagents are toxic, sensitive to moisture, expensive or not available and cannot be stored. Among formylation agents in the *N*-formylation of amines, formic acid has received much attention because it is not explosive, flammable and expensive. Also, it can be easily stored and is neither moisture sensitive nor very volatile. Aqueous formic acid (85%) has previously been reported as a formylating agent under conventional heating. However, this method needs a Dean-Stark trap under reflux conditions in toluene and involves long reaction times [16]. Also, the formylation of anilines having electron-withdrawing groups was found to be difficult [16]. Also, most of the other *N*-formylation methods have disadvantages such as long reaction times, formation of side products, the use of organic solvents, thermal instability of catalysts and the use of homogeneous catalysts [14,15]. Thus, the development of an efficient and versatile method for the *N*-formylation of amines is an active ongoing research area.

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In recent years there has been a tremendous interest in various chemical transformations catalyzed by heterogeneous catalysis [17]. Among heterogeneous catalysts, metal nanoparticles have been used widely as efficient catalysts in organic reactions due to their high catalytic activity, ease of handling, reusability, and benign character [18]. The application of metal oxides, especially ceria, as effective catalysts for CO<sub>2</sub> fixation and transalkylation and organic synthesis has received considerable attention in the recent years due to their high catalytic activity [19]. Nagarkar and co-workers recently published Ullmann type coupling between 4-nitrochlorobenzene and a variety of phenols, amines and thiophenols in the presence of nano CeO<sub>2</sub> as an efficient, inexpensive, and environmentally benign heterogeneous catalyst [20].

In continuation of our recent studies on the application of heterogeneous catalysts and green chemistry [21], herein we report the *N*-formylation of amines using formic acid in the presence of a catalytic amount of nano cerium oxide [20] as a heterogeneous catalyst at room temperature under solventless conditions and ultrasound irradiation in high yields (Scheme 1).



**Scheme 1.** *N*-formylation of amines by using formic acid in the presence of nano cerium oxide.

## RESULTS AND DISCUSSION

The CeO<sub>2</sub> nanoparticles were prepared by ultrasonically modified CTAB assisted method [20]. The CeO<sub>2</sub> nano particles were characterized using powder XRD, TEM, SEM and EDAX [20]. TEM analysis shows particle size 4-5 nm. The calculated surface area was found to be 214 m<sup>2</sup>/g.

First of all, the amount of the catalyst was optimized by reacting 3-methylaniline (1.0 mmol) with formic acid (1.2 mmol) under solvent-free and ultrasound irradiation conditions at room temperature (Table 1). No reaction was observed in the absence of catalyst without ultrasonic irradiation (Table 1, entry 6). When the reaction was carried out at room temperature using CeO<sub>2</sub> nanoparticles and in the absence of ultrasonic irradiation, the product was obtained in lower yield and longer reaction time (Table 1, entries 1-3), while in the presence of ultrasonic irradiation, the yield increased and the reaction time is reduced (Table 1, entry 4). It is a well-established fact that ultrasound irradiation accelerates the reactions. In addition, the reaction was slow in the absence of catalyst (Table 3, entry 7), it indicated that combination method (ultrasound irradiation and CeO<sub>2</sub> nanoparticles) played a significant role on the product yield and reaction time. Based on these results, the best conversion was observed when the reaction was performed under solvent-free and ultrasound irradiation conditions in the presence of amine (1.0 mmol), formic acid (1.2 mmol) and CeO<sub>2</sub> nano (5 mol%) (Table 1, entry 4) No significant improvement on the yield was observed using higher amounts of the catalyst (Table 1, entry 5). We then used the optimal reaction conditions for

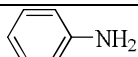
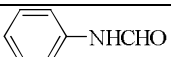
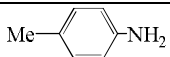
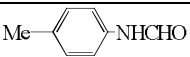
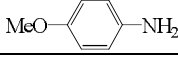
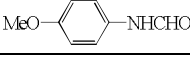
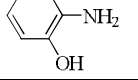
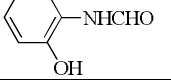

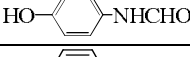
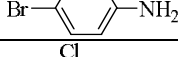
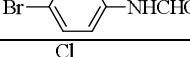
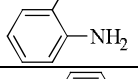
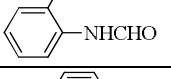
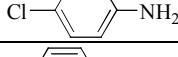
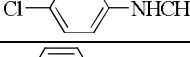
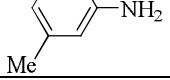
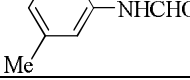
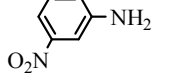
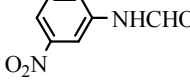
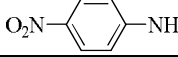
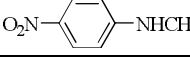
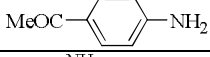
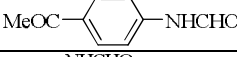

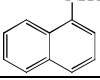
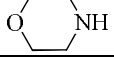
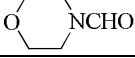
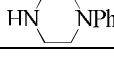
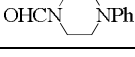
the *N*-formylation of different amines under solvent-free and ultrasound irradiation conditions and the results are shown in Table 2.

**Table 1.** The model reaction in the synthesis of *N*-(3-methylphenyl) formamide under conventional and ultrasound irradiation conditions at room temperature

Entry	Method	Catalyst (mol %)	Time (min)	Yield <sup>c</sup> (%)
1	Without US <sup>a</sup>	3.0	50	33
2	Without US <sup>a</sup>	5.0	50	38
3	Without US <sup>a</sup>	7.0	45	45
4	With US <sup>b</sup>	5.0	13	96
5	With US <sup>b</sup>	7.0	13	96
6	Without US <sup>a</sup>	0.0	100	0.0
7	With US <sup>b</sup>	0.0	35	75

<sup>a</sup> Reaction under conventional conditions. <sup>b</sup> The ultrasonic power 50 W, irradiation frequency 25 kHz. <sup>c</sup> Isolated yield.

**Table 2.** *N*-Formylation of amines with formic acid using CeO<sub>2</sub> nanoparticles at room temperature under solvent-free and ultrasound irradiation conditions<sup>a</sup>

Entry	Amine	Product	Time (min)	Yield <sup>b</sup> (%)
1			4	98, 95 <sup>c</sup>
2			2	95
3			2	96
4			6	92
5			11	93
6			35	94
7			35	93
8			15	95
9			13	96
10			85	92
11			120	88
12			90	89
13			12	93
14			20	91
15			50	93

16			15	94
17			35	91
18			120	90
19			5	89
20		No reaction	-	-
21		No reaction	-	-
22			40	87
23	HOCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	HOCH <sub>2</sub> CH <sub>2</sub> NHCHO	30	82

<sup>a</sup>Reaction conditions: amine (1.0 mmol), formic acid (1.2 mmol) and catalyst (5.0 mol %). <sup>b</sup>Yield refers to the pure isolated product. <sup>c</sup>Yield after the third cycle.

To study the effects of the nature of the substituents on the benzene ring of the amines, various formamides were synthesized from different amines containing both electron-releasing and electron-withdrawing groups in excellent yields under ultrasound irradiation. We also examined the scope of this reaction with a series of heterocyclic and aliphatic amines. The *N*-formylation of aliphatic and heterocyclic amines gave the corresponding formamides in high yields. In contrast with previously reported methods, this method is applicable for the *N*-formylation of 4-nitroaniline (Table 2, entry 11). Also, the *N*-formylation of secondary amines and steric hindered amines was carried out in high yield by this method (Table 2, entry 14, 15, 17, 18, 19 and 22). On the contrary, as seen in the Table 2, the present method provided high chemoselectivity in *N*-formylation of amines containing both the hydroxyl and the amino group (Entry 20 and 21). So, *O*-Formylation of phenols or alcohols did not take place under the applied reaction conditions.

To show the merits of our method in comparison with other reported methods, we compared some of results for *N*-formylation of benzylamine under various conditions. The results summarized in Table 3 indicated that, all the reactions catalyzed by nano cerium oxide proceeded with higher yields and lower reaction times compared with the reactions catalyzed by other previously reported methods.

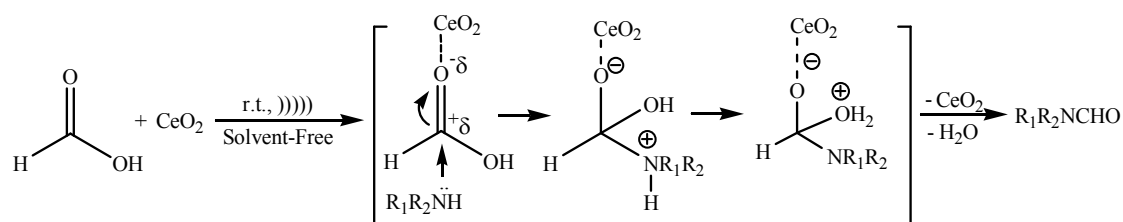
**Table 3.** Comparison of nano CeO<sub>2</sub> with reported catalysts in the *N*-formylation of benzylamine

Entry	Formylating method	Solvent	Temperature	Time	Yield (%)	Ref.
1	HCOOH, Sodium formate	-	r.t.	2.5 h	85	22
2	HCOOH, Anhydrous ZnCl <sub>2</sub>	-	70 °C	90 min	90	15
3	Methylformate	PhMe	r.t.	2 h	94	23
4	Ammonium formate	CH <sub>3</sub> CN	Reflux	6 h	88	11
5	HCOOH, PEG	-	r.t.	6 h	42	14
6	HCOOH, H <sub>2</sub> O <sub>2</sub> , Copper salt	MeOH	r.t.	75 min	80	24
7	HCOOH, Amberlite IR-120	-	MW, 320 W	95 min	92	25
8	HC(OEt) <sub>3</sub>	H <sub>2</sub> O	MW, 65 °C	32 h	49	26
9	HCOOH	-	80 °C	60 min	90	27
10	HCOOH, CeO <sub>2</sub> nano	-	))))), r.t.	15 min	94	This work

Nevertheless some advantages of our work are as below:

- Volatile and toxic organic solvent is not needed,
- Short reaction times,
- Mild reaction conditions,
- The high reaction temperature is not needed,
- The only by-product of this reaction is H<sub>2</sub>O. So, recrystallization and column chromatography are not needed,
- The reaction system is simple and chemoselective and the yields of the products are very high,
- The use of nano cerium oxide as a heterogeneous catalyst which can easily be recovered and reused.

The possible mechanism for the synthesis of formamides under ultrasound irradiation is shown in Scheme 2. The reaction of amine with formic acid occurs through the activation of the carbonyl group over surface of the catalyst followed by the nucleophilic attack of the amine NH. BET results show that surface area of nano cerium oxide is 214 m<sup>2</sup>/g [20]. nano cerium oxide may show complexation towards carbonyl group of formic acid and thus may enhance the electrophilic character. The breakdown of C-OH and N-H bonds in formic acid and amines facilitates the elimination of H<sub>2</sub>O as by product and the final formamides will be produced. A similar mechanism has been reported for the *N*-formylation of amines using the ZnCl<sub>2</sub> catalyst [15]



**Scheme 2.** Proposed mechanism for the *N*-formylation of amines with formic acid using nano cerium oxide.

The catalyst recycling is an important step as it reduces the cost of the process. We also investigated the recycling of the nano cerium oxide under solvent-free and ultrasound irradiation conditions. After completion of the reaction, ethyl acetate was added and the catalyst was filtered. We found that catalyst can be reused three times without the loss of activity (Table 2, entry 1).

The products were characterized by IR, NMR spectroscopy and from melting points and elemental analysis [13-16, 28]. Disappearance of one strong and sharp absorption band (-NH<sub>2</sub> stretching band) and appearance of a carbonyl stretching band in the IR spectra, were evidences for the formation of *N*-formyl derivatives. IR spectra showed two characteristic peaks, one between 3300 and 3400 cm<sup>-1</sup> (secondary NH) and the other between 1640 and 1680 cm<sup>-1</sup> (*N*-formyl, C=O). The relevant <sup>1</sup>H NMR spectrum shows two distinctive proton signals; one is related to NH of the *N*-formamides and another belongs to the aldehyde.

## CONCLUSION

In conclusion, we have developed a novel and highly efficient method for the synthesis of various formamides by treatment of amines with formic acid in the presence of nano cerium oxide as a reusable catalyst at room temperature under solvent-free conditions and ultrasound irradiation. The significant advantages of this methodology are high yields, cleaner reaction profiles, simple work-up procedure, excellent chemoselectivity, the use of inexpensive, non-toxic and environmentally benign catalyst and the possibility for reusing the catalyst. This methodology may find widespread use in organic synthesis for the preparation of formamides.

## EXPERIMENTAL

### General procedure for synthesis of nano ceria

CeO<sub>2</sub> nanoparticles were prepared by adding ammonia solution to an aqueous solution of cerium (III) nitrate in the presence of CTAB. In a typical procedure, added 1.0 g of Ce(NO<sub>3</sub>)<sub>3</sub> in a solution of CTAB dissolved in 100 cm<sup>3</sup> of water. Mole ratio of Ce/CTAB was kept at unity. pH of the solution was adjusted between 10-11 by adding 25% ammonia solution under vigorous stirring for 2-3 h. The resulting mixture was ultrasonicated for 10 min and then filtered off. The obtained precipitate was washed with water and subsequently with acetone and dried at 120 °C for 12 h. It was then calcined at 500 °C for 3 h [20].

### General procedure for the *N*-formylation of amines

A mixture of the appropriate amine (1.0 mmol), aq. formic acid (1.2 mmol) and nano cerium oxide (5.0 mol %) was irradiated by ultrasound for the appropriate time at room temperature. After completion of the reaction, ethyl acetate was added and the catalyst was removed by filtration. After removal of the solvent, the pure products were obtained and no recrystallization or column chromatography is needed. The melting point, IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR data of the unknown formamide is given as below:

#### 4-Phenylpiperazine-1-carbaldehyde (Table 2, entry 15)

M.p. 82-84 °C; FT-IR (KBr, cm<sup>-1</sup>): 2916, 2814, 1654, 1632, 1599, 1499, 1447, 1405, 1385, 1366, 1350, 1334, 1283, 1254, 1239, 1197, 1149, 1092, 1057, 1033, 1007, 916, 766, 693; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 10.35 (s, 1H), 8.55 (s, 1H), 6.92-7.33 (m, 5H, Ar-H), 3.72-3.16 (m, 8H); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 161.2, 151.4, 129.7, 121.4, 117.6, 50.9, 49.8, 46.0, 40.4.

## ACKNOWLEDGEMENT

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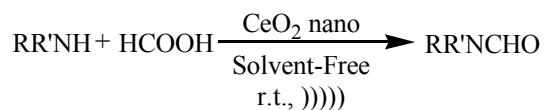
**An eco-friendly *N*-formylation of amines using nano cerium oxide as a recyclable catalyst under solvent-free and ultrasound irradiation conditions at room temperature**

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***N*-Formylation of amines**