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Nano silica supported ferric chloride as a green and efficient catalyst for one pot synthesis of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-ones

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ABSTRACT

An efficient green route for the preparation of naphthoxazinones, applying a three-component one-pot condensation reaction of 2-naphthol, aromatic aldehyde and urea in the presence of nano silica supported ferric chloride under solvent-free conditions has been developed. The present procedure offers several advantages such as short reaction time, simple workup, recovery and reusability of the catalyst.

***Keywords**: Multi-component, Nano silica, Naphthoxazinone, One-pot, Solvent free.*

1. Introduction

Solid supported reagents are unique acid catalysts that have become popular over the last two decades. The activity and selectivity of a reagent diffused on the surface of a support is amended as the effective surface area of the reagent is increased multifold and thus they more effective than the individual reagents [1]. Among various solid supports, nano silica is usually preferred since it displays many advantageous properties such as high surface area, excellent stability (thermal and chemical), good accessibility and organic groups can be robustly anchored to the surface; to provide catalytic centers [2,3].

Oxazinone, benzoxazinone and their derivatives are a significant class of heterocyclic compounds, because many of these derivatives display biological activities, such as HIV-1 reverse transcriptase inhibitors [4] and antibacterial properties [5]. In addition, naphthalene-condensed 1,3-oxazin-3-ones have also been used in the preparation of chiral amino phosphine ligands for asymmetric catalysis [6]. Thus far, only few reports for the synthesis of naphthalene-condensed oxazinone derivatives have been reported in the literature. Firstly, Holly and Cope synthesized aromatic oxazines through the Mannich reactions from phenols, formaldehyde and amines in 1944 [7]. Fulop *et al*. reported the condensation of amino alkylnaphthols as precursors with phosgene in the presence of triethylamine which gave naphthalene-condensed 1,3-oxazine-3-one derivatives in moderate yields [8]. Cimarelli and co-workers used carbonyl di-imidazole instead of phosgene for the synthesis of these compounds [9]. Recently, the preparation of naphtha-oxazine derivatives has been achieved in the presence of various catalyst such as *P*-TSA [10], [bmim]Br [11], TMSCl/NaI [12], $HClO_4$/ SiO_2 [13], phosphomolybdic acid [14], silica gel [15], ZnO NPs [16], Cu NPs [17], Thiamine hydrochloride [18] and TMSCl [19].

Herein, we present a procedure for the preparation of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-one derivatives under thermal and solvent-free conditions using nano silica supported ferric chloride.

2. Experimental

All reagents were purchased from Merck and Aldrich and used without further purification. The reaction was monitored by TLC using 0.2 mm Merck silica gel 60 F254 pre-coated plates, which were visualized with UV light. Melting points were measured on an Electrothermal 9200 apparatus. The IR spectra were recorded on FT-IR Magna 550 apparatus using KBr discs. The ^{1}H-NMR and ^{13}C-NMR spectra were determined on a Bruker Avance DRX-400 MHz instrument using TMS as the internal standard. The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer. Microscopic morphology of products was visualized by SEM (LEO 1455VP).

2.1. General procedure for the preparation of nano silica supported ferric chloride

In a 100 ml flask, nano silica gel (25 g) and $FeCl_3.6H_2O$ (2 g) (8% of the weight of nano-SiO_2) were vigorously

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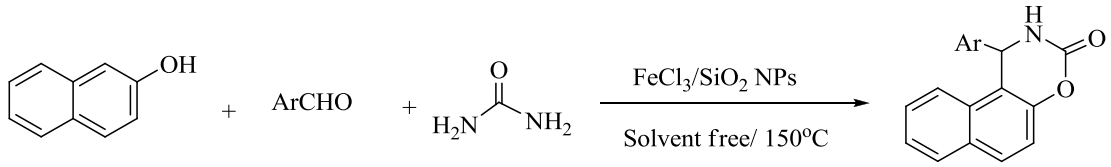

Scheme 1. Green synthesis of naphthoxazinone on $FeCl_3$/nano-silica gel under solvent free conditions.

stirred by magnetic stirrer under solvent-free conditions at room temperature for 24 h to achieve a homogeneous adsorption. A yellow powder was obtained. This powder was heated for 1 h at 100°C to give a brownish powder ("active" $FeCl_3$/nano-SiO_2 reagent).

2.2. General procedure for the preparation of 1,2-dihydro-1-arylnaphtho[1,2 e][1,3]oxazine-3-one derivatives

A mixture of β-naphthol (0.01 mol), aldehyde (0.01 mol), urea (0.012 mol), $FeCl_3$/nano-SiO_2 (0.4 mol % is equiv to 10^{-4} g) was finely grinded and heated with stirring at 150°C in an oil bath. The reaction was monitored by TLC. After cooling, the reaction mixture was dissolved in ethyl acetate and the mixture stirred for 5 min. The suspended solution was filtered and the heterogeneous catalyst was recovered. The ethyl acetate was evaporated and the crude product crystallized from MeOH to afford the pure product.

Selected spectral data

1,2-Dihydro-l-(3-methylphenyl)naphtho[1,2-e][1,3]oxazine-3-one. (4f): m.p. 206-208°C. IR (ν/cm^{-1}): 3264 (NH), 1746 (C=O), 1515, 815, 745. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm) δ: 2.21(3H, s, CH_3), 6.12(1H, s, CH), 7.04-7.12 (3H, m, Ar-H), 7.21 (1H, t, Ar-H), 7.35-7.48 (3H, m, Ar-H), 7.80 (1H, d, Ar-H), 7.93 (1H, d, Ar-H), 7.98 (1H, d, Ar-H), 8.80 (1H, s, NH). ^{13}C-NMR (100MHz, DMSO-d_6, ppm) δ: 21.47 (CH_3), 54.34 (CH), 114.47, 117.31, 123.51, 124.55, 125.53, 127.82, 129.08, 129.18, 129.31, 130.67, 130.87, 138.64, 143.28, 147.87, 149.82 (CO). Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.89; H, 5.19; N, 4.84. Found: C, 78.94; H, 5.14; N, 4.59.

1,2-Dihydro-l-(4-dimethylaminophenyl)naphtho[1,2-e] [1,3] oxazine-3-one. (4h): m.p. 218-219°C. IR (ν/cm^{-1}): 3224 (NH), 1734 (C=O), 1600, 850, 730. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm) δ: 2.80(6H, s, CH_3), 6.02 (1H, s, CH), 6.62 (2H, d, Ar-H), 7.08(2H, d, Ar-H), 7.35 (2H, d, Ar-H), 7.45(2H, t, Ar-H), 7.78 (1H, d, Ar-H), 7.95 (1H, t, Ar-H), 8.68(1H, s, NH). ^{13}C-NMR (100MHz, DMSO-d_6, ppm) δ: 53.88 (CH), 112.82, 115.13, 117.27, 123.10, 125.41, 126.44, 127.65, 128.09, 129.01, 130.32, 130.80, 130.86, 147.69, 149.97, 150.44 (CO). Anal. Calcd for $C_{20}H_{18}N_2O_2$: C, 75.47; H, 5.66; N, 8.80. Found: C, 75.40; H, 5.73; N, 8.89.

3. Results and discussion

In this literature, we report a new, simple, mild and effective procedure for the one-pot synthesis of naphthoxazinone derivatives using $FeCl_3$/nano-SiO_2 as a recyclable catalyst. This catalyst is safe, easy to handle and environmentally favorable. The reaction was carried out between aryl aldehydes, 2-naphthol and urea in the presence of mentioned catalyst (Scheme1).

As a results of our experiments we found that aromatic aldehydes containing both electron-withdrawing groups (including halide groups) or electron-donating groups (such as alkoxyl groups) reacted well to give the corresponding 1,2-dihydro-1-arylnaphtho [1,2-*e*] [1,3]oxazine-3-ones in good yields. The results are summarized in Table 1.

In order to investigate the high catalytic activity of $FeCl_3$.nano-SiO_2 in compared to $FeCl_3$, nano-SiO_2 and $FeCl_3$.SiO_2, we have performed a model study using benzaldehyde, 2-naphthol and urea by use of certain value

Table 1. Preparation of naphthoxazine-3-one derivatives.

Products	Ar	Time (min)	Yield[a] %	m.p. (°C.)		Ref
				Found	Report	
4a	C_6H_5	10	85	217-218	217-219	17
4b	4-$MeOC_6H_4$	20	82	189-190	189-190	16
4c	4-MeC_6H_4	20	78	163-164	163-165	16
4d	4-BrC_6H_4	7	90	216-117	217-218	17
4e	4-ClC_6H_4	7	95	204-205	204-206	17
4f	3-MeC_6H_4	12	79	206-208	206-208	17
4g	4-^{i}prC_6H_4	15	92	171-172	171-173	12
4h	4-$N(CH_3)_2C_6H_4$	20	80	218-219	-	-
4i	2-thiophen	7	80	209-211	209-210	13

[a]Yields refer to the pure isolated products.

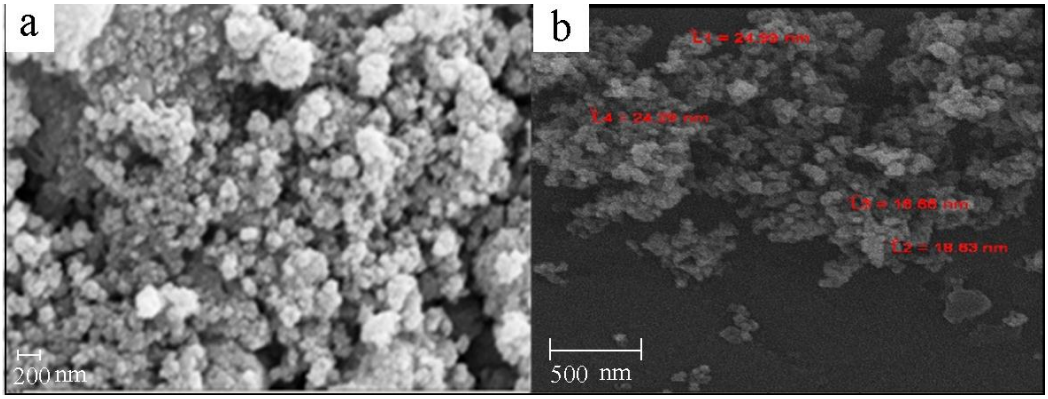

Fig. 1. SEM image of the (a) $FeCl_3$.nano-SiO_2 and (b) nano-SiO_2.

Table 2. Reaction of benzaldehyde, 2-naphthol, and urea in diverse catalytic conditions at 150°C

Entry	Catalyst[a]	Time	Yiled,[b] %
1	None	2h	0
2	$FeCl_3$	2h	25
3	Nano-SiO_2	2h	15
4	$FeCl_3$.SiO_2	1h	75
5	$FeCl_3$.nano-SiO_2	10min	85

[a]The reaction was carried out under solvent-free conditions.
[b]Isolated yield.

of catalysts at 150 °C under solvent-free conditions (Table 2).

Table 2 clearly illustrates that among four mentioned catalysts, nano silica supported ferric chloride is an effective catalyst in terms of reaction times and yields of product, because of the supported nano-SiO_2 increase contact surface of materials. The SEM image of $FeCl_3$/nano-SiO_2 is shown in Fig. 1a. As can be seen from the figure, the sample shows a nanocrystalline structure. As indicated in Fig. 1a the white particles are $FeCl_3$ which supported on nano SiO_2 gray particles. This expression was approved by the nano silica SEM image which is in Fig 1b.

To show the merit of the present work in comparison with the previously reported, we compared results of FeCl3/nano-SiO2 with other catalysts in the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-one. As shown in Table 3, $FeCl_3$/nano-SiO_2 can act as effective catalyst with respect to reaction times, yields and the obtained products.

To determine the optimum quantity of nano silica supported ferric chloride in reaction of benzaldehayde, 2-naphthol and urea under thermal and solvent free conditions, we used different amounts including 0.2, 0.4, 1, 2.5 and 4 mol% of nano silica supported ferric chloride. The best amount of corresponding catalyst was obtained 0.4 mol% in 10 min.

To evaluate the stability of the catalytic activity and the potential for recycling, we completed several catalytic

Table 3. Copmarison of the results of using $FeCl_3$/nano-SiO_2 with other catalysts[a].

Entry	Catalyst	Conditions	Time/Yield (%)
1	ZnO NPs[16]	Solvent-free; 150 °C; catalyst (0.3 equiv)	60 min/90
2	Cu NPs[17]	PEG-400; room temperature; catalyst (0.001 g)	60 min/89
3	Thiamine hydrochloride[18]	150 °C; catalyst (0.5 mmol)	30 min/85
4	TMSCl[19]	DMF; 140 °C; catalyst (10 mg)	12h/83
5	TMSCl/NaI[12]	CH_3CN/DMF; 140 °C; catalyst (1.5 equiv)	2.6h/86
6	$HClO_4$/ SiO_{213}	Solvent-free; 150 °C; catalyst (2 mol%)	1h/88
7	PTSA[10]	Solvent-free; 160 °C; catalyst (0.3 mmol)	1.5h/63
8	$FeCl_3$/nano-SiO_2[15]	Solvent-free; 160 °C;	1.8h/78
9	phosphomolybdic acid[14]	DMF; 100°C; catalyst (0.001 mmol)	3h/89
10	$FeCl_3$/nano-SiO_2[b]	Solvent-free; 150 °C; catalyst (0.4 mol%)	7min/95

[a]Based on 4-Chlorobenzaldyde (0.01 mol), 2-naphthol (0.01 mol) and urea (0.012 mol).
[b]This work.

Table 4. The catalyst reusability for the synthesis of naphthoxazinones.

Entry	Cycle	Time (min)	Yield (%)[a]
1	fresh	10	85
2	1	10	85
3	2	12	85
4	3	12	84
5	4	18	84
6	5	18	84

[a]Isolated yield.

Table 5. Effect of solvents on the preparation of 1,2-dihydro-l-phenylnaphtho[1,2-*e*][1,3]-oxazine-3-oneat reflux conditions.

Entry	Solvent	Time (h)	Yield (%)[a]
1	EtOH	2	0
2	DMF	2	10
3	$CHCl_3$	2	0
4	H_2O	2	0
5	Solvent free	10 min	85

[a]Isolated yield.

cycles. In each cycle, $FeCl_3$/nano-SiO_2 was washed with ethanol and dried under vacuum to remove the residual solvent. The catalyst could be reused for five times with a minimal loss of activity (Table 4).

In order to survey the effect of the solvents on the preparation of naphthoxazinone derivatives, the reaction of benzaldehayde, 2-naphthol and urea was carried out in various solvents (Table 5). It is observed that the excellent results were obtained in solvent-free conditions at 150 °C using $FeCl_3$/nano-SiO_2 as catalyst.

4. Conclusion

In conclusion, we have demonstrated that nano silica supported ferric chloride is a new, efficient and green catalyst for the synthesis of naphthoxazine-3-one derivatives. The one-pot three-component condensation of aryl aldehydes, 2-naphthol and urea in the presence of $FeCl_3$.nano-SiO_2 afforded naphthoxazinones under thermal solvent-free conditions. The distinguished features of this method are shorter reaction times, simple work-up, environmentally benign, excellent yield, cost effective recovery and reusability of catalyst for a number of times without appreciable loss of activity in comparison with other reported methods.

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