

Article

Nano-sized silica supported FeCl₃ as an efficient heterogeneous catalyst for the synthesis of 1,2,4-triazine derivatives



Davood Habibi*, Somayyeh Vakili

Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, 6517838683, Hamedan, Iran

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1. Introduction

Solid supported FeCl₃ has been widely used as a reusable and efficient heterogeneous catalyst in organic syntheses. For example, polyaniline nano-fiber supported FeCl₃ was used as the catalyst for the acylation of alcohols and amines [1]. Rice husk supported FeCl₃ nanoparticles was used for the chemoselective 1,1-diacetate protection and deprotection of aldehydes [2]. Polymer supported FeCl₃ was used as the catalyst for the high yield synthesis of 1,5-benzodiazepine derivatives under solvent free conditions and microwave irradiation [3]. Silica supported FeCl₃ was used in various organic reactions [4–6]. Recently, we used FeCl₃-SiO₂ as a reusable heterogeneous catalyst for the synthesis of 5-substituted 1*H*-tetrazoles via [2+3] cycloaddition of nitriles and sodium azide [7].

Currently, nano-particles have attracted considerable research interest as an efficient support for homogeneous catalysts in synthetic chemistry due to their high specific surface

ABSTRACT

The one-pot synthesis of a series of 1,2,4-triazines from the reactions of semicarbazide or thiosemicarbazide with various $\alpha_{,\beta}$ -dicarbonyl compounds under reflux conditions in a EtOH-H₂O (9:1) mixture as solvent and catalyzed by nano-sized silica supported FeCl₃ (FeCl₃@SiO₂) was investigated. The FeCl₃ content of the catalyst was measured by atomic absorption to get the adsorption capacity. The reactions gave high yields of the product and the catalyst was easily separated and reused for successive reaction runs without significant loss of activity.

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areas [8]. The advantages of these nano-particles include high activity, strong oxidizing ability, moderate to high Lewis acidity, non-toxicity, reusability, and long term stability [9,10]. The size of the nano particle as adsorbent determines its adsorption capacity [11].

Recently, the use of silica supported reagents has received considerable importance in organic syntheses because of their ease of handling, enhanced reaction rates, better selectivity, simple workup, low cost, ease of preparation, and recoverability of catalysts. In the past few years, silica supported acids like silica sulfuric acid [12], $BF_3 \cdot SiO_2$ [13], silica gel/NaHSO₄ [14] or HClO₄-SiO₂ [15], have received significant attention as efficient catalysts in various organic transformations due to their high acidity, easy handling, and low cost.

Most heterocycles participate in the metabolic pathway of live organisms and perform several biochemical functions and are widely used in medicine industry. Nearly 60% of the pharmaceuticals used in therapeutic systems are *N*-functionalized

^{*} Corresponding author. Tel: +98-81-38380922; Fax: +98-81-38380709; E-mail: davood.habibi@gmail.com

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heterocycles. One of the important type of the *N*-functionalized heterocycles are 1,2,4-triazines. It has been reported that the 1,2,4-triazine derivatives possess a broad spectrum of biological activities. For example, they have shown antifungal [16], anti-cancer [17], anti-bacterial [18], analgesic [19], and anti-ti-tumor activities [20,21].

The reactions of α,β -dicarbonyl compounds with various α,γ -nucleophiles like semicarbazide or thiosemicarbazide are important procedures for the synthesis of triazines [22–25]. Many of these methods have drawbacks such as low yields or prolonged time period and application of hazardous and expensive catalysts or solvents. Therefore, the development of greener, clean, and environmentally friendly approaches is desirable.

Unfortunately, the adsorption capacity of the adsorbent was not calculated, and the precise amount of FeCl₃ on the catalyst was not known in most reactions. Also, the leaching probability of FeCl₃ from the surface of the catalyst was not investigated in most reports. So there are demands for preparing the right supported catalyst with the most efficient content of FeCl₃ for synthesizing organic intermediates and fine chemicals.

Concerning the versatility and high efficiency of solid supported FeCl₃, and the importance of the substituted 1,2,4-triazines, here we report the one-pot synthesis of a series of 1,2,4-triazines from the reactions of semicarbazide or thiosemicarbazide with various α,β -dicarbonyl compounds under reflux in a EtOH-H₂O (9:1) mixture as solvent with a FeCl₃@SiO₂ catalyst (Scheme 1).

2. Experimental

2.1. Material and instruments

Semicarbazide HCl, thiosemicarbazide, SiO₂ of various particle sizes and α,β -dicarbonyl compounds, were purchased from Merck Chemical Company and used without further purification. IR spectra were recorded on a Bruker 500 spectrophotometer with KBr pellets. ¹H and ¹³C NMR spectra were obtained on a Bruker 300 MHz Avance spectrometer with DMSO-*d*₆ as solvent. Ultrasonication was performed in a TRANSSONI 660/H ultrasound cleaner with a frequency of 35 KHz and an output power of 70 W.

2.2. Preparation of the nano-sized SiO₂:FeCl₃ catalyst (FeCl₃@SiO₂)

In a typical procedure, nano-sized SiO_2 (0.25 g) was added to a solution (1250 ppm) of FeCl₃ (31.25 mg) in dried EtOAc (25



Scheme 1. Synthesis of 1,2,4-triazine derivatives with NSSSFe.

mL) and the mixture was stirred for 24 h at 20 °C. The resulting mixture was centrifuged and filtered and the solid material was stirred in fresh EtOAc (25 mL) for a further 1 h. The concentration of the remaining Fe³⁺ in the separated solution was determined by atomic absorption. The FeCl₃ content of the prepared catalyst was 66.9 mg of FeCl₃ per g of FeCl₃@SiO₂. As indicated in the TEM image of FeCl₃@SiO₂ (Fig. 1), no detectable change in the size was observed after the adsorption of FeCl₃ on the nano-sized silica.

2.3. General procedure for the one-pot synthesis of 1,2,4-triazin derivatives

A mixture of α,β -dicarbonyl substrates (1 mmol), semicarbazide or thiosemicarbazide (1 mmol) and FeCl₃@SiO₂ (25 mg) in EtOH-H₂O (9:1, 5 mL) mixture as a solvent was refluxed. After completion of the reaction, which was monitored with TLC, the resulting mixture was filtered and the solid was washed with EtOAc and H₂O. The structures of the resulting products were established on the basis of their ¹H NMR, ¹³C NMR, and CHN analysis.

6,7-Dihydro-5-methyl-5*H*-cyclopenta[*e*][1,2,4]triazine-3-ol (Entry 1). Pale yellow solid; mp = 250–252 °C; IR (KBr, cm⁻¹): ν 3500, 3000, 1689; ¹H NMR (DMSO,90 MHz): δ 6.4 (m, 5H), 1.09 (d, 3H), 11.03 (s, 1H) and 9.5 (s, 1H); ¹³C NMR (DMSO, 22.5 MHz): δ 11, 22.5, 27, 32.7, 137.5, 148 and 154; Anal. Calcd for C₇H₉N₃O (%): C 55.62, H 6.00, N 27.80, O 10.58; Found (%): C 54.43; H 5.2, N 31.51, O 8.86.

5,6-Diphenyl-1,2,4-triazine-3-ol (Entry 2). Pale white solid; mp = 231–233 °C; IR (KBr, cm⁻¹): ν 3500, 3300, 1687; ¹H NMR (DMSO, 90 MHz): δ 7.0 (m, 11H) and 13.51 (s, 1H); ¹³C NMR (DMSO, 22.5 MHz): δ 127.99, 128.16, 128.77, 128.93, 129.28, 130.78, 134.48, 135.73, 142.30, 153.35 and 167.28; Anal. Calcd for C₁₅H₁₁N₃O (%): C 72.28, H 4.45, N 16.86, O 6.42; Found (%): C 71.12, H 4.61, N 17.51, O 6.76.

5*H*-[1,2,4]triazino[5,6-*b*]indol-3-ol (Entry 3). Pale yellow solid; mp = 281–283 °C; IR (KBr, cm⁻¹): ν 3470, 3300, 1700; ¹H NMR (DMSO, 90 MHz): δ 7.12 (m, 5H), 11.02 (s, 1H) and 11.72 (s, 1H); ¹³C NMR (DMSO, 22.5 MHz): δ 110.77, 120.15, 122.16,



Fig. 1. The TEM image of FeCl₃@SiO₂.

130.32, 130.92, 1414.42, 154.95 and 162.66; Anal. Calcd for $C_9H_6N_4O$ (%): C 58.06, H 3.25, N 30.09, O 8.59; Found (%): C 59.04, H 2.82, N 30.38, O 7.76.

Snaphto[1,2-*e*](1,2,4)-triazin-9-ol (Entry 4). Pale white solid; mp = 281–283 °C; IR (KBr, cm⁻¹): ν 3470, 3300, 1700; ¹H NMR (DMSO, 90 MHz): δ 6.8–8.3 (m, 6H), 10 (s, 1H) and 11.73 (s, 1H); ¹³C NMR (DMSO, 22.5 MHz): δ 123.17, 126.9, 127.99, 128.16, 128.52, 130.4, 133.54, 135.43, 136.87, 142.79, 155.40 and 156.15; Anal. Calcd for C₁₃H₇N₃O (%): C 70.58, H 3.19, N 19.00, O 7.23; Found (%): C 69.73, H 3.82, N 18.89, O 7.74.

Phenanthro[9,10-*e*][1,2,4]triazin-3-ol (Entry 5). Pale light yellow solid; mp = 229–231 °C; IR (KBr, cm⁻¹): ν 3464, 3200, 1688; ¹H NMR (DMSO, 90 MHz): δ 7.7–8.7 (m, 9H) and 14 (s, 1H); Anal. Calcd for C₁₅H₉N₃O (%): C 72.87, H 3.67, N 16.99, O 6.47; Found (%): C 72.54, H 3.19, N 17.12, O 7.15.

(1,2,4)-Triazin-3-ol (Entry 6). Pale white solid; mp = 216–218 °C; IR (KBr, cm⁻¹): ν 3464, 3200, 1688; ¹H NMR (DMSO, 90 MHz): δ 6.0 (s, 2H), 7.4 (s, 1H) and 10.33 (s, 1H); ¹³C NMR (DMSO, 22.5 MHz): δ 145.17, 150.9 and 161.99; Anal. Calcd for C₃H₃N₃O (%): C 37.12, H 3.11, N 43.29, O 16.48; Found (%): C 37.45, H 3.82, N 42.71, O 16.02.

5,6-Diethyl(1,2,4)-triazin-3-ol (Entry 7). Pale light yellow solid; mp = 219–220 °C; IR (KBr, cm⁻¹): ν 3472, 3276, 1685; ¹H NMR (DMSO, 90 MHz): δ 2.24–2.6 (m, 6H), 7.4 (m, 4H), 9.00 (s, 1H) and 10.22 (s, 1H); ¹³C NMR (DMSO, 22.5 MHz): δ 10.39, 10.7, 23.65, 129.65, 145.52 and 148.92; Anal. Calcd for C₇H₁₁N₃O (%): C 54.89, H 7.24, N 27.43, O 10.44; Found (%): C 54.00, H 8.53, N 26.45, O 11.02.

2*H*-[1,2,4]triazino[5,6-*b*]indole-3(5*H*)-thione (Entry 8). Pale light yellow solid; mp = 254–257 °C; IR (KBr, cm⁻¹): ν 3395; ¹H NMR (DMSO, 90 MHz): δ 8 (m, 4H), 11.5 (s, 1H) and 12.7 (s, 1H); ¹³C NMR (DMSO, 22.5 MHz): δ 107.89, 116.8, 117.82, 119.24, 126.12, 139.28, 159.58 and 175.74; Anal. Calcd for C₉H₆N₄S (%): C 53.45, H 2.99, N 27.70, S 15.86; Found (%): C 53.10, H 3.2, N 27.53, S 16.17.

Phenanthro[9,10-*e*][1,2,4]triazine-3(2*H*)-thione (Entry 9). Pale light yellow solid; mp = 218–222 °C; IR (KBr, cm⁻¹): ν 3391; ¹H NMR (DMSO, 90 MHz): δ 7.5–8.3 (m, 8H) and 13.8 (s, 1H); ¹³C NMR (DMSO, 22.5 MHz): δ 110.93, 119.87, 120.84, 122.25, 131.14, 131.97, 142, 26, 162.55 and 178.71; Anal. Calcd for C₁₅H₉N₃S (%): C 68.42, H 3.45, N 15.96, S 12.18; Found (%): C 68.12, H 3.68, N 16.23, S 11.97.

5,6-Diphenyl-1,2,4-triazine-3(2*H*)-thione (Entry 10). Pale white solid; mp = 212–214 °C; IR (KBr, cm⁻¹): v 3421; ¹H NMR (DMSO, 90 MHz): δ 7.3 (m, 10H) and 15.2 (s, 1H); ¹³C NMR (DMSO, 22.5 MHz): δ 126.0, 128.75, 155.97, 157.63, 169.13 and 180.71; Anal. Calcd for C₁₅H₁₁N₃S (%): C 67.9, H 4.18, N 15.84, S 12.08; Found (%): C 68.25, H 4.87, N 15.31, S 11.57.

3. Results and discussion

3.1. Effect of the catalyst particle size

To investigate the effect of the catalyst particle size on the rate and yield, the reaction between benzil (1 mmol) and semicarbazide HCl (1 mmol) in a EtOH-H₂O (9:1) mixture as solvent was studied as the model reaction under reflux using various



Fig. 2. Effect of catalyst particle size on the rate and yield of the model reaction. Reaction conditions: benzil (1 mmol), semicarbazide HCl (1 mmol), solid catalyst (25 mg), EtOH-H₂O (9:1, 5 mL), reflux.

sizes of SiO₂. The results are presented in Fig. 2.

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As shown in Fig. 2, in comparison with the catalyst-free condition, the reaction rate and yield were both improved when the reaction was carried out in the presence of the catalyst. In addition, by supporting FeCl₃ on SiO₂ and decreasing the particle size of SiO₂, the reactions were completed in shorter times. These results can be explained on the basis of the differences in the FeCl₃ content on SiO₂ with various particles sizes. To prove this, the amount of adsorbed FeCl₃ per unit mass of the adsorbent SiO₂ (mg/g), *q*_e, was calculated using Eq. (1) where *C*₀ and *C*_e are the initial and final concentrations (mg/L = ppm) of FeCl₃ respectively, *V* is the solution volume (L) and *m* is the mass of SiO₂ as adsorbent (g).

$$e = (C_0 - C_e)V/m \tag{1}$$

By using the atomic absorption technique for determining C_{e} , the amount of FeCl₃ adsorption on the various particle sizes of SiO₂ was determined. The FeCl₃ content per g of solid catalyst decreased as the particle size was increased (Fig. 3).

3.2. Effect of solvent on FeCl3 adsorption on nano-sized SiO2



Fig. 3. FeCl₃ content in FeCl₃@SiO₂ of different particle sizes.



Fig. 4. FeCl₃ adsorption on the nano-sized SiO₂ catalyst with different solvents.

To study the effect of the solvent on the adsorption process, nano-sized SiO₂ (0.25 g) was added to the solutions (1250 ppm) of FeCl₃ (31.25 mg) in various solvents (25 mL) and stirred for 24 h. The resulting mixture was then worked-up and the catalyst separated by the procedure described above. The FeCl₃ content of the catalyst was determined by Fe³⁺ atomic absorption from C_e in Eq. (1). The amount of FeCl₃ adsorbed on the nano-sized SiO₂ with different solvents indicated that EtoAc provided the highest FeCl₃ content (Fig. 4).

3.3. Effect of FeCl₃ concentration on the FeCl₃ content of the FeCl₃@SiO₂ catalyst

In order to obtain a high efficiency of the FeCl₃ concentration in providing the most adsorption on nano-sized SiO₂, we examined the FeCl₃ contents on the prepared catalysts using various concentrations of the FeCl₃ solution. Different concentrations of FeCl₃ in EtOAc (25 mL) were placed in six separate flasks containing nano-sized SiO₂ (0.25 g) and stirred at room temperature for 24 h. The content of each flask was centrifuged and filtered to separate the solid catalyst which was dried in an oven at 100 °C. Finally, the concentration of Fe³⁺ was determined by atomic absorption using C_e in Eq. (1). The results are summarized in Table 1.

It is evident that no significant change of the FeCl₃ content of the FeCl₃@SiO₂ catalyst occurred with increase of the concentration of FeCl₃ beyond 1250 ppm (Table 1, Fig. 5).

3.4. Optimizing the reaction conditions

Table 1

Effect of \mbox{FeCl}_3 concentration on the \mbox{FeCl}_3 content of the $\mbox{FeCl}_3@\mbox{SiO}_2$ catalyst.

Entry	C_0 (ppm)	C _e (ppm)	$q_{ m e}$
1	250	26.376	22.3624
2	500	30.338	46.9662
3	750	223.272	56.6728
4	1000	351.694	64.8306
5	1250	580.782	66.9218
6	1500	819.469	68.0531
7	1750	1054.761	69.5239
8	2000	1299.763	70.0237



Fig. 5. FeCl $_3$ content on the FeCl $_3$ @SiO $_2$ catalyst versus concentration of FeCl $_3$.

To optimize the reaction conditions, the effects of the $FeCl_3@SiO_2$ catalyst and other reaction parameters on the model reaction were studied (Table 2).

The results shown in Table 2 indicated that the best result in terms of the reaction rate and yield was obtained when the reaction was conducted under reflux in a EtOH-H₂O (9:1) mixture as solvent with FeCl₃@SiO₂ with a FeCl₃ content of 66 mg per g catalyst (Entry 5). A decrease in the yield was observed when the reaction was performed under ultrasound irradiation using a similar catalyst composition (Entries 13 and 14). When the reaction was carried out in the presence of unloaded nano-SiO₂, the rate and yield were both reduced significantly (Entry 2). Moreover, in the absence of the catalyst, the yield was very low (Entry 1).

In order to establish the scope of this methodology, we conducted the reaction of semicarbazide or thiosemicarbazide with a series of α,β -dicarbonyl compounds with different substituents under the optimum conditions (Table 2, Entry 5). All the reactions proceeded smoothly to afford the corresponding products in quantitative yields as summarized in Table 3.

Table 2

Reaction parameters and catalytic activity of the $FeCl_3@SiO_2\ catalyst$ with the model reaction.

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Entry	(FeCl ₃ content/ nano-SiO ₂ , mg/g)	Condition	Solvent	Time (h)	Isolated yield (%)
1	No catalyst	Reflux	EtOH	6	Trace
2	Neat nano-SiO ₂	Reflux	EtOH	6	15
3	22	Reflux	EtOH	6	58
4	66	Reflux	EtOH	6	68
5	66	Reflux	EtOH-H ₂ O (9:1)	6	90
6	66	Reflux	DMSO	6	70
7	66	Reflux	DMF	6	60
8	66	Reflux	EtOH-H ₂ O (1:1)	6	59
9	66	Reflux	CHCl ₃	6	Trace
10	66	Reflux	EtOAc	6	Trace
11	66	Reflux	H ₂ O	6	36
12	66	40 °C	EtOH-H2O (9:1)	6	23
13	66	Sonication (50 °C)	EtOH-H ₂ O (9:1)	6	31
14	66	Sonication (60 °C)	EtOH-H ₂ O (9:1)	6	38

Reaction conditions: benzil (1 mmol), semicarbazide HCl (1 mmol), solid catalyst (25 mg), solvent (5 mL).

Table 3
Synthesis of 1,2,4-triazine derivatives catalyzed by FeCl ₃ @SiO ₂ .

Entry	(Thio) semicarbazide	Dicarbonyl	Product	m.p. (°C)	Yield (%)	Time (h)
1	H ₂ N NH ₂ H		OH N N N	250-252	97, 96 ª, 94 ^b , 92 ^c	5
2	H ₂ N NH ₂	Ph Ph		231-233	80	4
3	H ₂ N NH ₂ H			281-283	86	4
4	H_2N H_2N H_2N H_2 H_2N H_2 H_2N H_2 H_2N H_2 H_2N H_2 H_2N	$\langle \cdot \rangle$	HO N N	281-283	73	5
5	H ₂ N H ₂ NH ₂		HO N N	229-231	78	6
6	H ₂ N NH ₂	0~~0		216-218	60	6
7	H ₂ N NH ₂			219-220	80	6
8	H_2N H_2N H_2 H_2N H_2 H		H N S	254-257	72	4
9	H ₂ N NH ₂ H			218-222	86	6
10	H ₂ N H ₂ NH ₂	O Ph Ph	HS N N Ph Ph	212-214	92	5

3.5. Recycling of the catalyst

In order to study the stability and reusability of the catalyst, the reaction mixture was centrifuged after the completion of the reaction. The separated solid was washed with ethyl acetate (2×5 mL) and dried under vacuum (20 °C). The recovered catalyst was reused for three consecutive runs without any significant loss of activity (Table 3, Entry 1).

4. Conclusions

 $FeCl_3@SiO_2$ is a suitable solid catalyst for the synthesis of 1,2,4-triazine derivatives in EtOH/H₂O mixture as solvent under reflux. In comparison with other reported methods, this

procedure gave the products in shorter reaction times and quantitative yields.

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