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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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ABSTRACT

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 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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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

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], BF₃·SiO₂ [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

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-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 FeCl_3 on the catalyst was not known in most reactions. Also, the leaching probability of FeCl_3 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 FeCl_3 for synthesizing organic intermediates and fine chemicals.

Concerning the versatility and high efficiency of solid supported FeCl_3 , 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 $\text{FeCl}_3@SiO_2$ catalyst (Scheme 1).

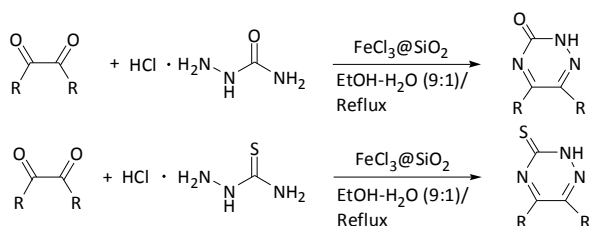
2. Experimental

2.1. Material and instruments

Semicarbazide HCl, thiosemicarbazide, SiO_2 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 $SiO_2:FeCl_3$ catalyst ($FeCl_3@SiO_2$)

In a typical procedure, nano-sized SiO_2 (0.25 g) was added to a solution (1250 ppm) of $FeCl_3$ (31.25 mg) in dried EtOAc (25



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

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 Fe^{3+} in the separated solution was determined by atomic absorption. The $FeCl_3$ content of the prepared catalyst was 66.9 mg of $FeCl_3$ per g of $FeCl_3@SiO_2$. As indicated in the TEM image of $FeCl_3@SiO_2$ (Fig. 1), no detectable change in the size was observed after the adsorption of $FeCl_3$ on the nano-sized silica.

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

A mixture of α,β -dicarbonyl substrates (1 mmol), semicarbazide or thiosemicarbazide (1 mmol) and $FeCl_3@SiO_2$ (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-5H-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.

5H-[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,

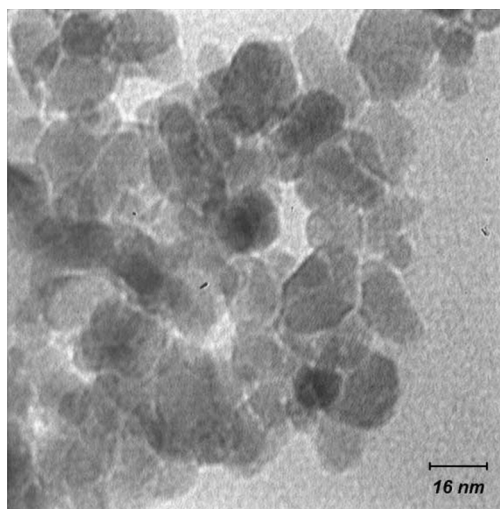


Fig. 1. The TEM image of $FeCl_3@SiO_2$.

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