g-C_3N_4/Ni nanocomposite: an efficient and eco-friendly recyclable catalyst for the synthesis of quinoxalines

Afsaneh Rashidizadeh, Hossein Ghafuri*

Catalysts and Organic Synthesis Research Laboratory, Department of Chemistry, Iran University of Science and Technology, Tehran16846-13114, Iran

**E-mail: ghafuri@iust.ac.ir*

Abstract

Nowadays, with increasing environmental concerns, the development of sustainable and friendly heterogeneous catalysts has attracted more and more attention in both the scientific and industrial communities. Hence, the use of nanocatalysts with well-defined structures, environmentally benign, high catalytic activity, and high chemical stability are desirable instead of corrosive and hazardous chemicals. In recent years, polymeric mesoporous graphitic carbon nitride (g-C_3N_4) has turned out to be a fascinating choice for catalyst or catalyst support due to the special physical and chemical properties, thermal stability, non-toxicity, unique electronic properties, and large surface area. The incorporation of nitrogen atoms in the carbon architecture of the g-C_3N_4 gives rise to the active chemical sites exposed on the surface. On the other hand, depositing metal nanoparticles onto g-C_3N_4 is an effective strategy to enhance the catalytic activity of g-

C_3N_4. In the present study, g-C_3N_4/Ni as a recyclable, highly efficient heterogeneous catalyst with a good porous structure have been prepared and its catalytic activity was investigated for the synthesis of quinoxaline derivatives.

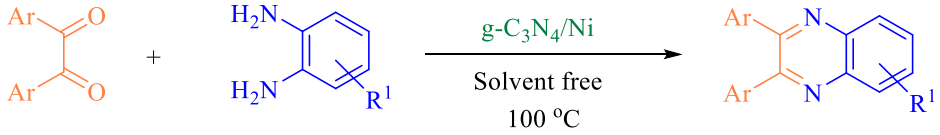
Keywords: Graphitic carbon nitride (g-C_3N_4), Ni nanoparticles, Quinoxaline derivatives.

1. Introduction

Quinoxaline derivatives represent an important class of nitrogen-containing heterocyclic compounds as they have shown a broad spectrum of biological activities and they have been used as antiviral, antibacterial, anticancer, antitumor, and antitubercular [1, 2]. They have also been found applications as useful intermediates in organic synthesis, dyes, electroluminescent materials, cavitands, and organic semiconductors [3-6]. Based on these properties a number of synthetic strategies have been developed for the preparation of quinoxalines, which include condensation of aryl 1,2-diamine with a 1,2-dicarbonyl compound in refluxing ethanol or acetic acid for 2–12 h giving 34–85% yields [7].

Over the past decades, the development of supported-heterogeneous catalysts has attracted significant scientific and technological interest due to their tunable physical and chemical properties [8]. Among the carbon based materials, graphitic carbon nitride (g-C_3N_4) as a two dimensional conjugated polymer with high thermal and chemical stability can be easily prepared by one-step polymerization of nitrogen-rich organic molecules like cyanamide, urea, thiourea, melamine and dicyandiamide [9]. Furthermore, g-C_3N_4 has recently found wide range of applications in material science, catalysis, electronic and optical fields due to its special structure and unique properties [10-12]. The incorporation of nitrogen atoms in carbon architecture also provides anchor sites for the immobilization of active species and metal nanoparticles when g-

C_3N_4 is utilized as a heterogeneous catalyst support, which in turn lead to the improvement of catalytic performance. For this purpose, herein we first reported g-C_3N_4/Ni nanocomposite as an eco-friendly heterogeneous catalyst for the synthesis of quinoxaline derivatives (Scheme 1).



Scheme 1. Synthesis of quinoxaline derivatives catalyzed by g-C_3N_4/Ni

2. Experimental

2.1. General

All solvents, chemicals and reagents were purchased from Merk, Fluka and Aldrich chemical companies. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. FT-IR spectra were obtained over the region 400-4000 cm^{-1} with a Shimadzu IR-470 spectrometer using KBr pellets. ^{1}H-NMR spectra were recorded on a Bruker DRX-500 Advance spectrometer at 500 MHz. All the organic products were known and the structures of the isolated products were confirmed by comparison with previously reported data.

2.2. *Preparation of bulk g-C_3N_4*

Bulk g-C_3N_4 powder was prepared with the reported method. The melamine was heated at 550 ^oC in a furnace for 4h in static air at a ramp of 2.5 ^oC min^{-1} and the obtained yellow solid was grinded into powder in a mortar.

2.3. Preparation of g-C_3N_4/Ni nanocomposite

g-C_3N_4/Ni catalysts with a Ni loading of 10 wt % were prepared via a facile wet chemical reduction. Briefly, 0.50 g-C_3N_4 bulk was introduced into 300 mL distilled H_2O at 25 °C under constant stirring, and an appropriate amount of $NiCl_2.6H_2O$ solution (6 g L^{-1}) was added into the solution. After stirring at 25 °C for 1 h, 0.1 M NaOH was slowly added into the mixed solution to adjust the pH at the constant value of 9.5. During the subsequent stirring for another 2 h, given amounts of $NaBH_4$ solution (freshly prepared, n$NaBH_4$: nNi =15:1) was rapidly injected into the g-C_3N_4-$NiCl_2$ solution, while continuously stirring the resultant mixture for 3 h again at 25°C. Then, the suspension was filtered and extensively washed with distilled water till chloride species remained in the reaction solution is free. Eventually, the powers were dried in oven at 50 °C for overnight to get g-C_3N_4/Ni samples.

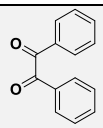
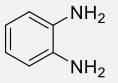
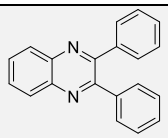
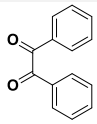
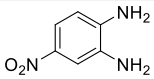
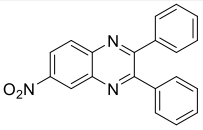
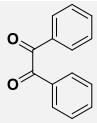
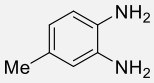
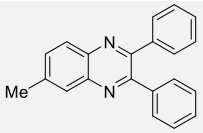
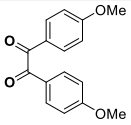
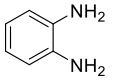
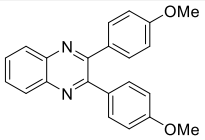
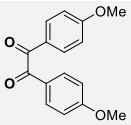
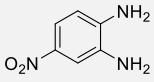
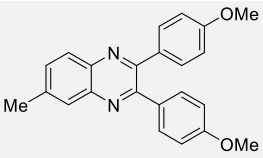
2.4. General synthesis of quinoxaline derivatives

A mixture of 1,2-diamine (1.0 mmol), 1,2-diketone (1.0 mmol) in the presence of g-C_3N_4/Ni (20.0 mg) was stirred at 100 ^oC for the appropriate reaction time. EtOH was added after completion of the reaction, and the catalyst was recovered by filtration and washed with ethanol and reused five times in other fresh reactions without a significant loss of activity. Then products afforded by evaporation of the solvent and recrystallization from ethanol.

3. Results and discussion

To show the catalytic activity of g-C_3N_4/Ni a series of quinoxalines were synthesized by the condensation of various 1,2-diaryldiketones and o-phenylenediamine derivatives under solvent-free condition (Table 1). It seems noteworthy to mention that the reaction in the absence of catalyst could not lead to any product formation. Therefore, it was found that 10.0 mg of the catalyst (g-C_3N_4/Ni) is sufficient to give the desired products in excellent yields.

Table 1. Synthesis of quinoxaline derivatives catalyzed by g-C_3N_4/Ni under solvent-free condition.

Entry	Dicarbonyl	Diamine	Product	Time (min)	Yield (%)	Mp (Ref.)
1				15	96	128-129 [13]
2				25	95	185-188 [14]
3				15	93	110-113 [15]
4				30	90	147-149 [15]
5				45	92	124-126 [16]

4. Conclusions

To conclude, a high-effective, low cost, and ecofriendly heterogeneous catalyst was synthesized by a facile approach. The prepared g-C_3N_4/Ni can act as a novel recyclable catalyst for the synthesis of quinoxaline derivatives through a green and facile method. The key advantages of this protocol are high yields, short reaction times, safe and easy workup, and environmentally benign reaction conditions.

Acknowledgements

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