

Proceedings

# g-C<sub>3</sub>N<sub>4</sub>/Ni Nanocomposite: An Efficient and Eco-Friendly Recyclable Catalyst for the Synthesis of Quinoxalines <sup>†</sup>

Afsaneh Rashidizadeh and Hossein Ghafuri \*

Catalysts and Organic Synthesis Research Laboratory, Department of Chemistry, Iran University of Science and Technology, Tehran 16846-13114, Iran; rashidizadeh@chem.iust.ac.ir

\* Correspondence: ghafuri@iust.ac.ir

<sup>†</sup> Presented at the 22nd International Electronic Conference on Synthetic Organic Chemistry, 15 November–15 December 2018; Available Online: <https://sciforum.net/conference/ecsoc-22>.

Published: 24 April 2019

**Abstract:** Presently, 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, that are environmentally benign, with 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<sub>3</sub>N<sub>4</sub>) has turned out to be a fascinating choice for catalyst or catalyst support due to its 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<sub>3</sub>N<sub>4</sub> gives rise to the active chemical sites exposed on the surface. On the other hand, depositing metal nanoparticles onto g-C<sub>3</sub>N<sub>4</sub> is an effective strategy to enhance the catalytic activity of g-C<sub>3</sub>N<sub>4</sub>. In the present study, g-C<sub>3</sub>N<sub>4</sub>/Ni as a recyclable and highly efficient heterogeneous catalyst, with a good porous structure, has been prepared and its catalytic activity was investigated for the synthesis of quinoxaline derivatives.

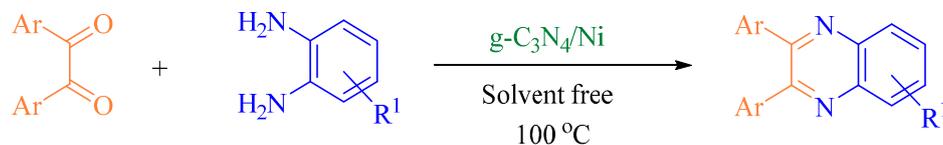
**Keywords:** graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>); Ni nanoparticles; quinoxaline derivatives

## 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 antiviral, antibacterial, anticancer, antitumor, and antitubercular uses [1,2]. They have also been found in 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<sub>3</sub>N<sub>4</sub>) as a two-dimensional conjugated polymer with a high thermal and chemical stability can easily be prepared by one-step polymerization of nitrogen-rich organic molecules like cyanamide, urea, thiourea, melamine, and dicyandiamide [9]. Furthermore, g-C<sub>3</sub>N<sub>4</sub> has recently found a 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 the carbon architecture also provides anchor sites for the

immobilization of active species and metal nanoparticles when g-C<sub>3</sub>N<sub>4</sub> is utilized as a heterogeneous catalyst support, which in turn leads to the improvement of catalytic performance. For this purpose, herein we first report the g-C<sub>3</sub>N<sub>4</sub>/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<sub>3</sub>N<sub>4</sub>/Ni.

## 2. Experimental

### 2.1. General

All solvents, chemicals, and reagents were purchased from Merck, 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 of 400–4000 cm<sup>-1</sup> with a Shimadzu IR-470 spectrometer using KBr pellets. <sup>1</sup>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<sub>3</sub>N<sub>4</sub>

Bulk g-C<sub>3</sub>N<sub>4</sub> powder was prepared with the reported method. The melamine was heated at 550 °C in a furnace for 4 h in static air at a ramp of 2.5 °C min<sup>-1</sup> and the obtained yellow solid was grinded into powder in a mortar.

### 2.3. Preparation of g-C<sub>3</sub>N<sub>4</sub>/Ni Nanocomposite

g-C<sub>3</sub>N<sub>4</sub>/Ni catalysts with a Ni loading of 10 wt% were prepared via a facile wet chemical reduction. Briefly, 0.50 g g-C<sub>3</sub>N<sub>4</sub> bulk was introduced into 300 mL distilled H<sub>2</sub>O at 25 °C under constant stirring and an appropriate amount of NiCl<sub>2</sub>·6H<sub>2</sub>O solution (6 g L<sup>-1</sup>) 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<sub>4</sub> solution (freshly prepared, nNaBH<sub>4</sub>:nNi = 15:1) was rapidly injected into the g-C<sub>3</sub>N<sub>4</sub>-NiCl<sub>2</sub> 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 until the chloride species that remained in the reaction solution were free. Eventually, the powders were dried in oven at 50 °C overnight to get g-C<sub>3</sub>N<sub>4</sub>/Ni samples.

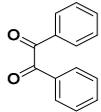
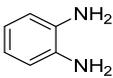
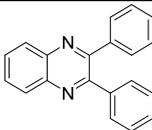
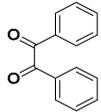
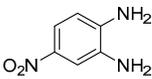
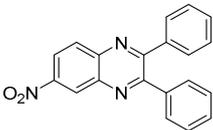
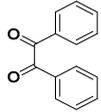
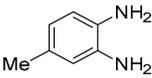
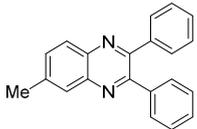
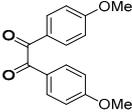
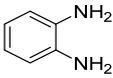
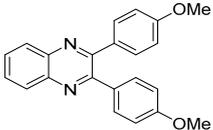
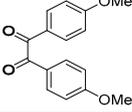
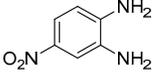
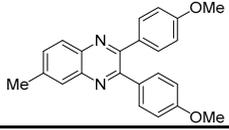
### 2.4. General Synthesis of Quinoxaline Derivatives

A mixture of 1,2-diamine (1.0 mmol) and 1,2-diketone (1.0 mmol) in the presence of g-C<sub>3</sub>N<sub>4</sub>/Ni (20.0 mg) was stirred at 100 °C 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 were afforded by the evaporation of the solvent and recrystallization from ethanol.

## 3. Results and Discussion

To show the catalytic activity of g-C<sub>3</sub>N<sub>4</sub>/Ni a series of quinoxalines were synthesized by the condensation of various 1,2-diaryldiketones and o-phenylenediamine derivatives under a solvent-free condition (Table 1). It seems noteworthy to mention that the reaction in the absence of a catalyst could not lead to any product formation. Therefore, it was found that 10.0 mg of the catalyst (g-C<sub>3</sub>N<sub>4</sub>/Ni) is sufficient to give the desired products with excellent yields.

**Table 1.** Synthesis of quinoxaline derivatives catalyzed by g-C<sub>3</sub>N<sub>4</sub>/Ni under a 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<sub>3</sub>N<sub>4</sub>/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.

**Acknowledgments:** The authors gratefully acknowledge the partial support from the Research Council of the Iran University of Science and Technology.

#### References

1. Refaat, H.; Badran, M.; Botros, S.; El-Gendy, A.; Abdou, N.; El-Assi, H.; Salem, A. g-C<sub>3</sub>N<sub>4</sub>/Ni nanocomposite: An efficient and eco-friendly recyclable catalyst for the synthesis of quinoxalines. *Bull. Pharm. Sci.* **2001**, doi:10.3390/ecsoc-22-05651.
2. Hazeldine, S.T.; Polin, L.; Kushner, J.; White, K.; Bouregeois, N.M.; Crantz, B.; Palomino, E.; Corbett, T.H.; Horwitz, J.P. II. Synthesis and biological evaluation of some bioisosteres and congeners of the antitumor agent, 2-(4-[(7-chloro-2-quinoxalinyloxy]phenoxy)propionic acid (XK469). *J. Med. Chem.* **2002**, *45*, 3130–3137.
3. Sakata, G.; Makino, K.; Kurasawa, Y. Reaction of Quinoxalin-2-ones with Difluorocarbene. *J. Fluorine. Chem.* **1992**, *59*, 417–422.
4. Dailey, S.; Feast, W.J.; Peace, R.J.; Sage, I.C.; Till, S.; Wood, E.L. Synthesis and device characterisation of side-chain polymer electron transport materials for organic semiconductor applications. *J. Mater. Chem.* **2001**, *11*, 2238–2243.
5. Sonawane, N.; Rangnekar, D.J. An efficient synthesis of quinoxalines catalyzed by monoammonium salt of 12-tungstophosphoric acid. *Heterocycl. Chem.* **2002**, *39*, 303–308.
6. Sessler, J.L.; Maeda, H.; Mizuno, T.; Lynch, V.M.; Furuta, H. Anion Recognition in Supramolecular Chemistry. *JACS* **2002**, *124*, 13474–13479.
7. Brown, D.J.; Taylor, E.C.; Ellman, J.A. *Quinoxalines, Supplement 2*; John Wiley & Sons: Hoboken, NJ, USA, 2004.
8. Gupta, P.; Paul, S. Solid Acids: Green Alternatives for Acid Catalysis. *Catal. Today* **2014**, *236*, 153–170.

9. Ong, W.-J.; Tan, L.-L.; Ng, Y.H.; Yong, S.-T.; Chai, S.-P. Graphitic Carbon Nitride (g-C<sub>3</sub>N<sub>4</sub>)-Based Photocatalysts for Artificial Photosynthesis and Environmental Remediation: Are We a Step Closer To Achieving Sustainability? *Chem. Rev.* **2016**, *116*, 7159–7329.
10. Zhang, L.; Xiao, J.; Wang, H.; Shao, M. Carbon-Based Electrocatalysts for Hydrogen and Oxygen Evolution Reactions. *ACS Catal.* **2017**, *7*, 7855–7865.
11. Habibi-Yangjeh, A.; Akhundi, A.J. Novel ternary g-C<sub>3</sub>N<sub>4</sub>/Fe<sub>3</sub>O<sub>4</sub>/Ag<sub>2</sub>CrO<sub>4</sub> nanocomposites: magnetically separable and visible-light-driven photocatalysts for degradation of water pollutants. *Mol. Catal. A Chem.* **2016**, *415*, 122–130.
12. Sun, J.; Fu, Y.; He, G.; Sun, X.; Wang, X. Green Suzuki–Miyaura coupling reaction catalyzed by palladium nanoparticles supported on graphitic carbon nitride. *Appl. Catal. B* **2015**, *165*, 661–667.
13. Hasaninejad, A.; Zare, A.; Mohammadzadeh, M.R.; Shekouhya, M. Oxalic acid as an efficient, cheap, and reusable catalyst for the preparation of quinoxalines via condensation of 1, 2-diamines with  $\alpha$ -diketones at room temperature. *Arkivoc* **2008**, *13*, 28–35.
14. Jafarpour, M.; Rezaeifard, A.; Ghahramaninezhad, M.; Tabibi, T. Reusable  $\alpha$ -MoO<sub>3</sub> nanobelts catalyzes the green and heterogeneous condensation of 1, 2-diamines with carbonyl compounds. *New J. Chem.* **2013**, *37*, 2087–2095.
15. Harsha, K.B.; Rangappa, K.S. One-step approach for the synthesis of functionalized quinoxalines mediated by T3P®–DMSO or T3P® via a tandem oxidation–condensation or condensation reaction. *RSC Adv.* **2016**, *6*, 57154–57162.
16. Daragahi, S.A.H.; Mohebat, R.; Mosslemin, M.H. Green and Eco-Friendly Synthesis of Quinoxalines by Brønsted Acidic Ionic Liquid Supported on Nano-SiO<sub>2</sub> under Solvent-Free Conditions. *Org. Prep. Proced. Int.* **2018**, *50*, 301–313.



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).