
# Sulfonated graphitic carbon nitride (Sg-$C_3N_4$): Highly efficient heterogeneous organo-catalyst for the condensation reactions

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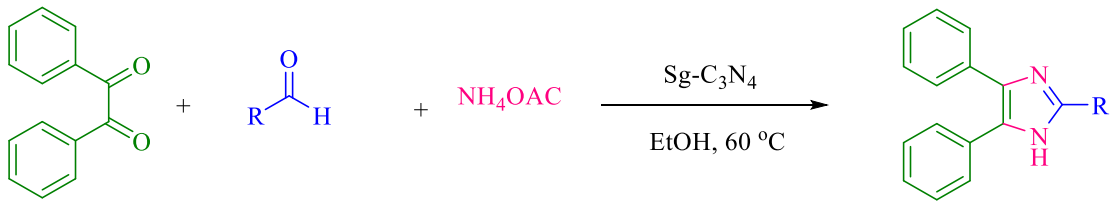
**Abstract**

Nowadays, constructing solid acid catalysts with well-defined structures, environmentally benign, high catalytic activity, easy separation, and high chemical stability is the most important area of industrial and environmental concerns. Over the past few decades, porous conjugated polymers have been employed as stable catalysts support for various organic transformations. Among these materials, graphitic carbon nitride (g-$C_3N_4$) has been widely studied in the field of photocatalysis and heterogeneous catalysis, due to its high surface area and great physical and chemical stability. Herein, we report the synthesis of sulfonated graphitic carbon nitride (Sg-$C_3N_4$) as an efficient solid acid catalyst for the preparation of various biologically nitrogen-containing heterocyclic compounds under mild reaction conditions.

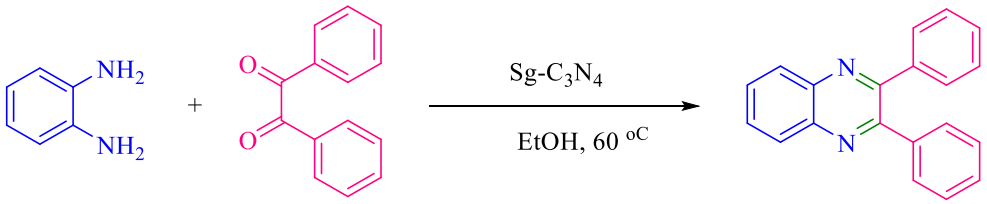
**Keywords**: Solid acid catalyst; Sulfonated graphitic carbon nitride (Sg-$C_3N_4$); Green synthesis; Condensation reaction.

## 1. Introduction

In condensation reactions several compounds usually by releasing ethanol or water joining together and form a carbon-heteroatom bond. Heterocyclic compounds can form by condensation reactions. These compounds using in so many fields such as agriculture, pharmaceutical and biological fields. Common heteroatoms in these compounds are oxygen, nitrogen, and sulfur. They can use as an antioxidant, sanitizer and developer [1]. Imidazole and quinoxaline derivatives are heterocyclic compounds that have medicinal, biological and antitumoral properties, use in agriculture and pharmaceutical industries [2]. Researchers have been investigated antifungal, anti-bacterial, anti–inflammatory, antitubercular activity, and anti-cancer activity of imidazole and quinoxaline derivatives [3]. Imidazole and quinoxaline derivatives form by three or four component condensation reaction by a catalyst. Catalysts in condensation reactions can be acidic or basic. Heterogeneous catalysts such as mesoporous silica [4] are used in this reaction, but they suffer from low yields, long reaction time, and toxic reagents [5]. Herein, we applied graphitic carbon nitride nanosheets (g-$C_3N_4$) as a catalyst support, due to its promising chemical and physical properties such as electronic structure, large surface area, and high thermal stability. Herein, we reported the synthesis of imidazole and quinoxaline derivatives by sulfonated graphitic carbon nitride (Sg-$C_3N_4$) in excellent reaction times.




**Scheme 1.** Synthesis of imidazole derivatives catalyzed by Sg-$C_3N_4$.




**Scheme 2.** Synthesis of quinoxaline derivatives catalyzed by Sg-$C_3N_4$.

## 2. Experimental

### *2.1. General*

All chemicals and solvents were purchased from Merck and Flucka companies and used without any purification. FT-IR spectra were recorded on a Shimadzu 100 FT-IR spectrometer in KBr.

### 2.2. *Preparation of g-$C_3N_4$ nanosheets*

The g-$C_3N_4$ bulk was prepared by heating melamine at 550 °C with a ramp rate of 2.5 °C/min and maintained at this temperature for another 4 h. To synthesize the g-$C_3N_4$ nanosheets, the bulk g-$C_3N_4$ was treated with concentrated HCl. 1.0 g bulk g-$C_3N_4$ powder was added to 100 mL of concentrated HCl, which was preheated to 80 °C. The dispersion was continuously stirred for 12 h at 80 °C. After that, the mixture was washed and purified with extensive deionized water to remove the superfluous HCl. The purified g-$C_3N_4$ was dispersed into 400 mL of deionized water with sonication method for 2 h. The dispersed g-$C_3N_4$ was centrifuged at 5000 rpm for several times to remove unexfoliated aggregates or nanoparticles in the dispersion. The protonated g $C_3N_4$ nanosheets were left in the supernatant.

### *2.3. Preparation of Sg-$C_3N_4$*

g-$C_3N_4$ nanosheets (0.5 g) was dispersed in dry $CH_2Cl_2$ (5.0 mL) and then was added to a suction flask that was equipped with a constant pressure dropping funnel and a gas inlet tube for

conducting HCl gas over an adsorbing solution. After that, $ClSO_3H$ (1.0 mL) was added dropwise over 30 min at room temperature. Then, the mixture was stirred for 2 h and the solvent was evaporated under reduced pressure to obtain Sg-$C_3N_4$, followed by washing with water for several times.

*2.4. General method for the synthesis of imidazole derivatives*

In this reaction 1.0 mmol aldehyde, 1.0 mmol benzil, 5.0 mmol ammonium acetate, 20.0 mg Sg-$C_3N_4$ and 2.0 mL ethanol as solvent were mixed, put in oil bath in 60 $^oC$ in appropriate time. Next, the catalyst were separated by filtration, the solvent was evaporated under vacuum. The obtained crude product was purified by recrystallization from ethanol.

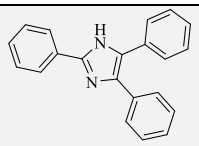
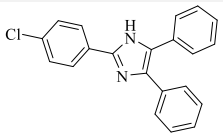
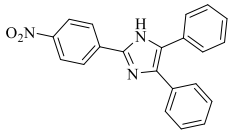
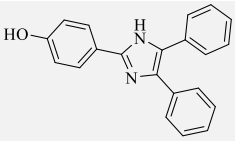
*2.5. General method for synthesis of quinoxaline derivatives*

In this reaction 1.0 mmol 1,2-diketone, 1.0 mmol 1,2-diamine, 20.0 mg Sg-$C_3N_4$ and 2.0 mL ethanol as solvent were mixed, put in oil bath in 60 $^oC$ in appropriate time. Next, the catalyst were separated by filtration, the solvent was evaporated under vacuum. The obtained crude product was purified by recrystallization from ethanol.

## 3. Results and discussion

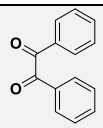
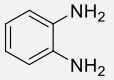
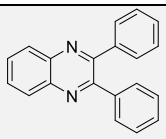
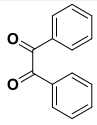
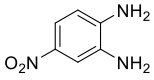
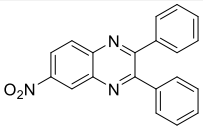
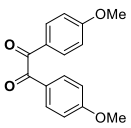
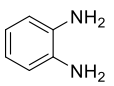
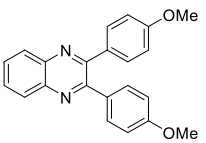
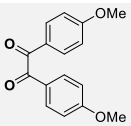
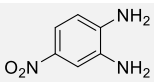
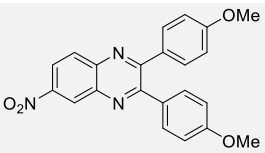
To indicate the merits of Sg-$C_3N_4$ in organic synthesis, we applied the Sg-$C_3N_4$ as a catalyst for the preparation of imidazoles and quinoxalines through condensation reactions (Table 1, 2). It seems noteworthy to mention that these condensation reactions in the absence of catalyst could not lead to any product formation. Therefore, it was found that 20.0 mg of the catalyst (Sg-$C_3N_4$) is sufficient to give the desired products in excellent yields.

**Table 1.** Synthesis of imidazole derivatives catalyzed by Sg-$C_3N_4$.[a]

| Entry | Product | Time (min) | Yield (%)[b] | Mp ºC (Ref.) |
|---|---|---|---|---|
| **1** |  | 10 | 94 | 276-280 [6] |
| **2** |  | 15 | 96 | 284-285 [7] |
| **3** |  | 15 | 95 | 241-242 [8] |
| **4** |  | 10 | 90 | 243-244 [9] |

[a] Reaction conditions: 1.0 mmol aldehyde, 1.0 mmol benzil, 5.0 mmol ammonium acetate, and 20.0 mg catalyst in 2.0 mL EtOH at 60 ºC. [b] Isolated yields.

**Table 2.** Synthesis of quinoxaline derivatives catalyzed by Sg-$C_3N_4$.[a]

| Entry | Dicarbonyl | Diamine | Product | Time (min) | Yield (%)[b] | Mp ºC (Ref.) |
|---|---|---|---|---|---|---|
| **1** |  |  |  | 5 | 95 | 130-131 [10] |
| **2** |  |  |  | 15 | 91 | 185-187 [11] |
| **3** |  |  |  | 5 | 93 | 146-148 [12] |
| **4** |  |  |  | 15 | 90 | 190-193 [13] |

[a] Reaction conditions: 1.0 mmol 1,2-diamine, 1.0 mmol 1,2-diketone and 20.0 mg catalyst in 2.0 mL EtOH at 60 °C.
[b] Isolated yields.

## 4. Conclusions

In summary, we have introduced an efficient heterogeneous catalyst (Sg-$C_3N_4$) through a facile and simple procedure starting from commercially available raw materials. It was found that the Sg-$C_3N_4$ can be utilized as an efficient heterogeneous catalyst for the condensation reactions for the synthesis of imidazole and quinoxaline derivatives in short reaction times and excellent yields under mild reaction conditions. This procedure can be classified as a new protocol for the preparation of synthetically, biologically and pharmaceutically relevant derivatives.

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