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Proceedings Sulfonated Graphitic Carbon Nitride (Sg-C₃N₄): A Highly Efficient Heterogeneous Organo-Catalyst for Condensation Reactions ⁺

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Abstract: Currently, constructing solid acid catalysts with well-defined structures, environmentally benign, with high catalytic activity, easy separation, and high chemical stability is the most important area of industrial and environmental concern. Over the past few decades, porous conjugated polymers have been employed as stable catalyst supports for various organic transformations. Among these materials, graphitic carbon nitride (g-C₃N₄) 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-C₃N₄) 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-C₃N₄); green synthesis; condensation reaction

1. Introduction

In condensation reactions several compounds usually by releasing ethanol or water join together and form a carbon-heteroatom bond. Heterocyclic compounds can thus be formed by condensation reactions. These compounds are used in many fields such as agriculture, pharmaceutical, and biological fields. Common heteroatoms in these compounds are oxygen, nitrogen, and sulfur. They can be used as an antioxidant, sanitizer, and developer [1]. Imidazole and quinoxaline derivatives are heterocyclic compounds that have medicinal, biological, and antitumoral properties, as well as use in agriculture and pharmaceutical industries [2]. Researchers have been investigating antifungal, anti-bacterial, anti-inflammatory, antitubercular activity, and anti-cancer activity of imidazole and quinoxaline derivatives [3]. Imidazole and quinoxaline derivatives form by a three or four component condensation reaction with 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-C₃N₄) as a catalyst support, due to its promising chemical and physical properties such as electronic structure, large surface area, and high thermal stability. We report also the synthesis of imidazole (Scheme 1) and quinoxaline derivatives (Scheme 2) by sulfonated graphitic carbon nitride (Sg-C₃N₄) in excellent reaction times.



Scheme 1. Synthesis of imidazole derivatives catalyzed by Sg-C₃N₄.



Scheme 2. Synthesis of quinoxaline derivatives catalyzed by Sg-C₃N₄.

2. Experimental

2.1. General

All chemicals and solvents were purchased from Merck and Fluka 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-C₃N₄ Nanosheets

The g-C₃N₄ 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-C₃N₄ nanosheets, the bulk g-C₃N₄ was treated with concentrated HCl. An amount of 1.0 g bulk g-C₃N₄ 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 amounts of deionized water to remove the superfluous HCl. The purified g-C₃N₄ was dispersed into 400 mL of deionized water with the sonication method for 2 h. The dispersed g-C₃N₄ was centrifuged at 5000 rpm several times to remove unexfoliated aggregates or nanoparticles in the dispersion. The protonated g C₃N₄ nanosheets were left in the supernatant.

2.3. Preparation of Sg-C₃N₄

 $g-C_3N_4$ nanosheets (0.5 g) were dispersed in dry CH₂Cl₂ (5.0 mL) and then added to a suction flask equipped with a constant pressure dropping funnel and a gas inlet tube for conducting HCl gas over an adsorbing solution. After that, ClSO₃H (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-C₃N₄, followed by washing with water 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 an oil bath at 60 °C in for the appropriate time. Next, the catalyst was separated by filtration and 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-C₃N₄ and 2.0 mL ethanol as solvent were mixed, put in an oil bath at 60 $^{\circ}$ C for the appropriate time. Next, the catalyst

was separated by filtration and the solvent was evaporated under vacuum. The obtained crude product was purified by recrystallization from ethanol.

3. Results and Discussion

To determine the merits of Sg-C₃N₄ in organic synthesis, we applied Sg-C₃N₄ as a catalyst for the preparation of imidazoles and quinoxalines through condensation reactions (Tables 1 and 2). It seems noteworthy to mention that these condensation reactions in the absence of catalyst did not lead to any product formation. Therefore, it was found that 20.0 mg of the catalyst (Sg-C₃N₄) was sufficient to give the desired products in excellent yields.

Entry	Product	Time (min)	Yield (%) ^b	Mp °C (Ref.)
1		10	94	276–280 [6]
2		15	96	284–285 [7]
3	O ₂ N-()-HN-() N-()-N-()-()-()-()-()-()-()-()-()-()-()-()-()-	15	95	241–242 [8]
4	HO-C-HN-C	10	90	243–244 [9]

Table 1. Synthesis of imidazole derivatives catalyzed by Sg-C₃N₄ ^a.

^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 $^{\circ}$ C. ^b Isolated yields.

Entry	Dicarbonyl	Diamine	Product	Time (min)	Yield (%) ^b	Mp °C (Ref.)
1		NH ₂ NH ₂		5	95	130–131 [10]
2		O ₂ N NH ₂ NH ₂	O ₂ N N	15	91	185–187 [11]
3	o O O O O Me	NH ₂ NH ₂	OMe N OMe	5	93	146–148 [12]
4	O O O O O O O Me	O ₂ N NH ₂ NH ₂	O ₂ N N OMe	15	90	190–193 [13]

Table 2. Synthesis of quinoxaline derivatives catalyzed by Sg-C₃N₄ ^a.

 $^{^{\}rm a}$ 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. $^{\rm b}$ Isolated yields.

4. Conclusions

To summarize, we introduced an efficient heterogeneous catalyst (Sg-C₃N₄) through a facile and simple procedure starting from commercially available raw materials. It was found that Sg-C₃N₄ can be utilized as an efficient heterogeneous catalyst for the condensation reactions for the synthesis of imidazole and quinoxaline derivatives with short reaction times and excellent yields under mild reaction conditions. This procedure can be classified as a new method for the preparation of synthetically, biologically, and pharmaceutically relevant derivatives.

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