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SULFONATED POROUS CARBON (SPC)-CATALYZED SYNTHESIS OF BENZOTHIAZOLE DERIVATIVES IN WATER

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GRAPHICAL ABSTRACT



Abstract A simple and efficient procedure has been developed for the synthesis of benzothiazole derivatives in water by the condensation of 2-aminothiophenol with aldehydes in the presence of Sulfonated porous carbon (SPC). This method provides a simple and efficient protocol in terms of mild reaction conditions, clean reaction profiles, small quantity of catalyst, and simple workup procedure.

Keywords Benzothiazole; sulfonated porous carbon; water; microwaves irradiation

INTRODUCTION

Benzothiazole and its derivatives are found in numerous pharmaceutical agents with a diverse range of biological properties.^{1–8} Their significance is also due to their applications in the treatment of autoimmune, inflammatory, epilepsy, analgesia, viral, cancer, tuberculosis diseases, and the prevention of organ transplant rejection.^{1–3}

Many methods have been reported in the literature for the synthesis of benzothiazoles. Traditional methods include (i) condensation of 2-aminothiophenols with aldehydes,⁴ carboxylic acids,⁵ acid chlorides,⁶ esters,⁷ or nitriles⁸ and (ii) oxidative cyclization

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of thiobenzanilides using various oxidants.^{9–14} Recently, a one-step preparation of benzothiazole derivatives by the aqueous reaction of the corresponding thioamidinium salts and 2-aminothiophenol has been reported.¹⁵ However, many of these existing methods are accompanied by one or more disadvantages such as the use of volatile organic solvents, costly air sensitive reagents,^{4a} prolonged reaction time,¹⁶ multistep reaction sequences, high reaction temperature, requirement of extreme pH, tedious work-up procedures,^{4e} and generation of solid wastes.^{17,18} Therefore, more attention has been directed to overcome the above limitations by providing an efficient and convenient protocol for the synthesis of 2-substituted benzothiazoles.

Due to environmental and economic considerations in recent years, heterogeneous catalysts have been gained some advantages with respect to the homogeneous systems, such as ease of recovery, recycling, and enhanced stability. Porous carbon materials and products based on them are diffuse in many actual scientific applications. They are used as supports for different catalytic processes, fuel cells, and capacitors. Porous carbon materials with high surface areas and well-developed porosities have attracted substantial attention because they can fulfill most of the desirable properties required for a suitable catalyst support. The stability in aggressive media at elevated temperature, feasibility of control parameters of the porous structure surface area in a broad range, and the physicochemical properties are the major advantages of carbon materials.^{19–27}

The application of microwaves (MW) irradiation as an energy-efficient heat source for accelerating chemical reactions has been reported in the literatures. Reactions that previously required hours to run to completion can now be finished within minutes.^{28,29}

Moreover, carrying out organic reactions in water has become highly desirable in recent years to meet environmental considerations. The use of water as a sole medium of organic reactions would greatly contribute to the development of environmentally friendly processes.

Herein, an efficient and convenient procedure for the synthesis of benzothiazole derivatives in water using Sulfonated Porous Carbon (SPC) as a heterogeneous catalyst under reflux conditions and microwave irradiation (Scheme 1) is reported.



RESULTS AND DISCUSSION

The reaction of 2-aminothiophenol with benzaldehyde was selected as the model substrate and studied its synthesis in water using SPC as catalyst, to optimize the reaction conditions. The results of these optimization experiments are presented in Table 1. The effect of catalyst loading was studied by carrying out the experiments with different amounts of SPC, without any catalyst under identical conditions and these results are presented in the Table 1 (Entries 1–5). In the absence of an acid catalyst, the yield of 2-phenylbenzothiazole was only 16% in duration 10 h after beginning of reaction at refluxing temperature. Increasing the catalyst loading from 0.03 to 0.07 g was found to decrease reaction time

Entry	Catalyst	Added amount (g)	Reflux ^a Yield (%)	Microwave ^b Yield ^c (%) ^c
1	_	_	3	5
2	SPC	0.03	61	31
3	SPC	0.05	67	46
4	SPC	0.07	90	92
5	SPC	0.1	92	93

Table 1 The condensation of 2-aminothiophenol with benzaldehyde under different reaction conditions

^aAt 90 min, ^bat 6 min, and ^cisolated yield.

substantially and further increase of catalyst loading to 0.1 g decreased the reaction time marginally. When the model reaction was carried out under microwave irradiation, it gave comparatively higher yields of products in shorter reaction time (Table 1, Entries 1–5).

The protocol developed for the synthesis of 2-arylbenzothiazoles and 2arylformylbenzothiazoles consists of the stirred mixture of substrate and catalytic amount of SPC (0.07 g) in water (3 mL) at refluxing temperature and microwave irradiation.

The catalytic performance of the SPC was investigated for the synthesis of 2phenylbenzothiazole in water. The reaction product (2-phenylbenzothiazole) measured as a function of time at refluxing temperature over the SPC, amorphous sugar catalyst (ASC),³⁰ and protonated Nafion.

The surface areas, acid densities, added amount, and initial rate of 2phenylbenzothiazole formation (catalytic activity) for all samples are summarized in Table 2.

Compared with the heterogeneous catalysts, SPC, ACS, and NR50, the sulfonated porous carbon with initial rate of 81.6 μ mol/min indicate a higher catalytic activity in 2-phenylbenzothiazole formation reaction. The yield of reaction was 90%, 41.7%, and 24.4% for SPC, ACS, and NR50 catalyst, respectively, using the same equivalent H⁺ at time 90 min (Table 2). The higher catalytic activity of sulfonated porous carbon is due to high specific surface area, high acid site density, and high density of mesoporous (which provide good access to the SO₃H groups on the surface of the carbon material).

The generality of this approach has been demonstrated by a facile and effortless synthesis of a wide variety of 2-substituted benzothiazole as shown in Table 3. All the substrates studied were smoothly converted to the corresponding benzothiazole without using additional oxidants.

Catalyst	Total surface area (m ² /g)	Acid density $(\text{mmol H}^+/\text{g})^a$	Added amount (g)	mmol H ⁺	Initial formation rate ^b $(\mu \text{mol min}^{-1})^c$	Yield ^d
SPC	1200	4.55	0.07	0.3	81.6	90
ASC	5	3.5	0.09	0.3	46.7	41.7
Nafion	< 0.1	0.9	0.35	0.3	24.0	24.4

Table 2 Catalytic activity of the tested catalysts under reflux reaction conditions

^{*a*}Determined by titration with NaOH, ^{*b*}under reflux condition, ^{*c*}the initial rate of a reaction is the instantaneous rate at the certain time (30 min) of the reaction, and ^{*d*}isolated yield.

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	R	Product	Reaction condition				
			Reflux		Microwave		
Entry			Time (min)	Yield ^a (%)	Time (min)	Yield ^a (%)	Ref.
1		3a	90	90	6	92	31a
2	Ň	3b	70	86	5	89	31b
3	но	3c	230	85	14	85	31a
4	MeO	3d	150	87	9	89	31c
5	Me	3e	70	87	5	85	4b
6	Ph	3f	70	83	5	85	31d
7	F	3g	70	85	5	86	31a
8	CI	3h	100	90	6	91	31e
9	Br	3i	70	85	5	85	31a
10	O ₂ N O ₂ N	3ј	70	87	5	87	31a
11	СС	3k	110	88	7	90	31b

Table 3 The reaction of 2-aminothiophenol with aldehydes in the presence of SPC under reflux conditions

(Continued on next page)

 Table 3 The reaction of 2-aminothiophenol with aldehydes in the presence of SPC under reflux conditions (Continued)



^aIsolated yield.

As shown in Table 3, a series of 2-substituted benzothiazole was synthesized with the catalyst SPC at refluxing temperature and microwave irradiation. This procedure is applicable to variety of aromatic and heteroaromatic aldehydes, which produced the corresponding 2-aryl benzothiazoles smoothly and in good yields (Table 3, Entries 1–13).

The substitution groups on the aromatic aldehydes ring (electron-releasing or electron-withdrawing groups) have no obvious effect on the yields and reaction time under the above optimal conditions. However, aromatic aldehydes with strongly electron-releasing groups on aromatic ring such as 4-methoxybenzaldehyde gave the product with good yield in a longer reaction time (Table 3, Entry 3).

We have also examined the condensation reaction of arylformylaldehyde with 2-aminothiophenol in the presence of SPC in water for the synthesis of 2-arylformylbenzothiazoles. The reactions were completed within 230–250 min with good yields (Table 3, Entries 14, 15). When the same reaction was conducted under microwave irradiation, it gave good yields of product in a shorter reaction time.

Table 4 compares the efficiency of the SPC with the efficiency of other catalysts in the synthesis of 2-phenylbenzothiazole obtained by other groups. The data in Table 4 show that some protocols took much longer time (Entries 11, 13, and 15), some used extra oxidants (Entries 1–4), no recovery catalyst (Entries 5–7,10), or low yields of products (Entries 11–15).

Entry	Catalyst	Condition (medium)	Time (min)	$\operatorname{Yield}^{b}(\%)$	Ref.
1	CAN ^c (0.1 mmol)/H ₂ O ₂ (30%, 4 mmol)	50 °C	13	97	4b
2	Fe(NO ₃) ₃ (0.1 mmol)/H ₂ O ₂ (30%, 4 mmol)	50 °C	14	97	32a
3	Co(NO ₃) ₂ (0.5 mmol) 6H ₂ O/H ₂ O ₂ (30%, 1 mmol)	80 °C (DMF)	15	93	4g
4	$K_2S_2O_8$ (1 mmol)-CuSO ₄ (0.01 mmol)	60 °C (H ₂ O-SDS)	40	90	4h
5	CTAB $(0.05 \text{ mmol})^d$	Reflux (H ₂ O)	90	98	4h
6	β -Cyclodextrin (1 mmol)	50 °C (H ₂ O)	75	92	32b
7	NH ₄ Cl (0.7 mmol)	Room temperature (CH ₃ OH)	30	84	32c
8	Sulfamic acid (100 mg)	Reflux (H ₂ O)	300	58	32d
9	Sulfamic acid (100 mg)	Under MW (solvent free)	10	70	32d
10	PTSA ^e (0.1 mmol)	70 °C (H ₂ O)	90	97	32c
11	Amberlite-IR 120 (100 mg)	Reflux (H ₂ O)	300	51	32d
12	Amberlite-IR 120 (100 mg)	Under MW (solvent free)	10	64	32d
13	Acidic Al ₂ O ₃ (100 mg)	Reflux (H ₂ O)	300	45	32d
14	Acidic Al ₂ O ₃ (100 mg)	Under MW (solvent free)	10	57	32d
15	SSA^{f} (100 mg)	Reflux (H ₂ O)	300	76	32d
16	SSA (100 mg)	Under MW (solvent free)	10	91	32d
17	ASC (30 mg)	Reflux (H ₂ O)	90	41.7	This Work
18	ASC (30 mg)	Under MW (H ₂ O)	6	51.5	This Work
19	Nafion (116 mg)	Reflux (H ₂ O)	90	24.4	This Work
20	Nafion (116 mg)	Under MW (H ₂ O)	6	31.7	This Work
21	SPC (23 mg)	Reflux (H ₂ O)	90	90	This Work
22	SPC (23 mg)	Under MW (H ₂ O)	6	92	This Work

Table 4 Comparison of results using SPC catalyst with results obtained with other catalysts in the synthesis of2-phenylbenzothiazole^a

^{*a*}Reaction conditions: the reactions were performed with benzaldehyde (1 mmol) and 2-aminothiophenol, ^{*b*}isolated yield, ^{*c*}ceric ammonium nitrate, ^{*d*}cetyltrimethyl ammonium bromide, ^{*e*} *p*-toluenesulfonic acid, and ^{*f*}silica sulfuric acid.

To check the reusability and recyclability of the catalyst (SPC), we have carried out the synthesis of 2-phenylbenzothiazole under similar reaction conditions. The catalyst was separated by filtration after completion of the reaction. It has also been dried and used for subsequent experiments after adding fresh substrate and water under similar reaction conditions. For three catalytic cycles, the yields and reaction times remained the same. The reaction time was found to increase gradually with the comparable yields of the 2-phenylbenzothiazole in subsequent recycle experiments.

In conclusion, we have developed an aqueous and general efficient method for the synthesis of 2-substituted benzothiazoles by the condensation of aryl, arylformyl aldehydes with 2-aminothiophenol in the presence of catalytic amount SPC in water. Compared to previous reported methods, the present protocol features simple work-up, environmentally benign, good yields, no requirement of extra oxidants, and use of the cheap catalyst.

EXPERIMENTAL

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. Melting points were measured on an Electrothermal 9100 apparatus. Thin layer chromatography (TLC) was used to monitor all reactions and all yields refer to isolated products. ¹H NMR spectra were recorded on a Bruker-Avance AQS 300 MHz using tetramethylsilane (TMS) as an internal standard. The specific surface area and mean pore diameter (dp) were calculated from adsorption isotherms of nitrogen at 77 K using the standard Brunauer–Emmett–Teller (BET) equation and were obtained on a NOVA 2200, Quantachrome Corporation, Version. Microwave reactions were conducted in a modified microwave oven fitted with a condenser (Samsung MF 45, Korea).

Preparation of SPC

Pine wood powder was used as starting material in the preparation of porous carbon material. In a typical procedure, wood powder (10 g) was impregnated with ZnCl₂ by immersion in aqueous solution of HCl (1.0 M, 50 mL) containing ZnCl₂ (20 g) under mechanical agitation at 25 °C for 15 h. After that the supernatant liquid was separated by filtration and the remaining solid was oven dried at 80 °C for 24 h. Then, the ZnCl₂impregnated wood powder was placed in a boat like small size ceramic container and heated gradually from room temperature to 500 °C. The heating gradient was not faster than 10 °C min⁻¹. The heating time at maximum heat (500 °C) treatment temperature was 1 h. Thereafter, the sample was washed by heating in the aqueous HCl solution (5%, 100 mL) at 100 °C for 1 h. Then, the resulting solid was filtered and rinsed with warm distilled water (50 $^{\circ}$ C) to confirm that the wash solution is free of zinc ions. The resultant activated porous carbon material was finally dried at 80 °C in an oven for approximately 24 h. Then, the activated porous carbon material (5 g) was heated for 15 h in oleum (18-24 wt% SO₃, 100 mL) at 150 °C under N₂ in order to introduce SO₃H. After heating and then cooling to room temperature, distilled water (400 mL) was added to the mixture. The black precipitate was filtered and repeatedly washed with boiling distilled water until impurities such as sulfate ions were no longer detected in the wash water. The sample was finally dried overnight in an oven at 80 °C to afford the sulfonated acid catalyst.^{26,27,32}

General Procedure for the Preparation of 2-Substituted Benzothiazoles

A mixture of aldehyde (3 mmol), 2-aminothiophenol (3 mmol), SPC (0.07g), and water (3 mL) was stirred at specified times under reflux condition or microwave irradiation (at 180 W) (Table 3). The reaction was monitored by TLC. After completion of the reaction, the product was extracted with ethyl acetate (3 \times 10 mL). The organic layer dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel (300–400 mesh) using an ethyl acetate/petroleum ether mixture as the eluent to afford a pure product. When necessary, the crude products were purified through recrystallization from 95% ethanol.

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