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Phosphoric acid/titanium oxide-zirconium oxide as an effective reusable nanocatalyst for microwave-promoted synthesis of 2-arylbenzothiazole derivatives

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This study aims to demonstrate an approach for the synthesis of 2-arylbenzothiazole derivatives. Benzaldehyde and 2-aminothiophenol were reacted in a one-step process using ethylene glycol as the optimal solvent, promoting a sustainable methodology. Titanium and zirconium salts served as catalysts to facilitate the reaction, while phosphoric acid was used to activate the metal oxide mixture. The catalyst was recyclable and could be reused after repeated washing. The structure of the H_3PO_4/TiO_2–ZrO_2 (1 : 1)-surf catalyst was characterized using several techniques, including FT-IR, XRD, FE-SEM, and EDX analyses. The structures of the synthesized organic compounds were confirmed by melting point determination, FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy, and mass spectrometry analyses.

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1. Introduction

Thiazoles constitute a subclass of heterocyclic organic compounds within the azole family, possessing a five-membered aromatic ring incorporating a pyridine-like nitrogen atom at position 3 and a thiophene-like sulfur atom at position 1 (Fig. 1).[1]

The thiazole system is a structural component of many biologically active compounds, including natural compounds such as vitamins (thiamine), epothilone (an anticancer drug), penicillin, and carboxylase enzymes.[2] Benzothiazoles, comprising a thiazole ring fused to a benzene ring, contain a heterocyclic framework with nucleophilic and electrophilic sites, which can be functionalized and act as protecting groups for carbonyl functionalities (Fig. 1). Molecules containing the benzothiazole nuclei have been reported to have antiallergic,[4] antidiabetic,[5] and anti-inflammatory activities. Derivatives of 2-arylbenzothiazoles have antitumor activity, and 6-nitrobenzothiazole and 6-aminobenzothiazole have antibacterial properties.[6] These compounds are vitally important as antioxidants and resin stabilizers in the polymer industry (Fig. 2), and Swedish researchers have also upgraded some benzothiazole-based monomethine cyanine dyes with fluorescent properties.[7]

A catalyst[8–10] is a substance that, when introduced into a reaction system, enhances the reaction rate by decreasing the activation energy required for the transition state while remaining chemically unchanged throughout the process.[11–13] Acid catalysts are extensively employed across various industries, including the petrochemical, chemical, and refining sectors, to accelerate reaction rates and improve process efficiency.[14,15] Liquid acids such as HF and H_2SO_4 are widely used in industry, but the toxic nature of these catalysts, as well as high catalyst consumption, problems with recovery and separation, and large amounts of catalyst waste, have led to a general trend towards the use of solid acid catalysts.[16,17] Nowadays, replacing liquid acids with solid acids for the production and extraction of chemicals has received considerable attention owing to the ease of catalyst separation

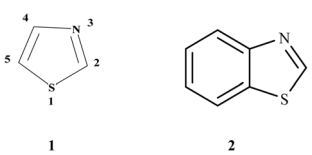

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Fig. 1 Structures of the thiazole ring (1) and benzothiazole (2).

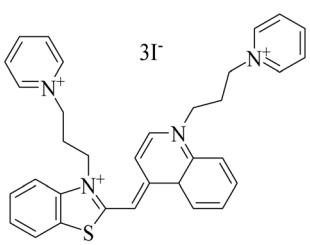

Fig. 2 Structure of the antioxidant and resin stabilizer combination used in the polymer industry.

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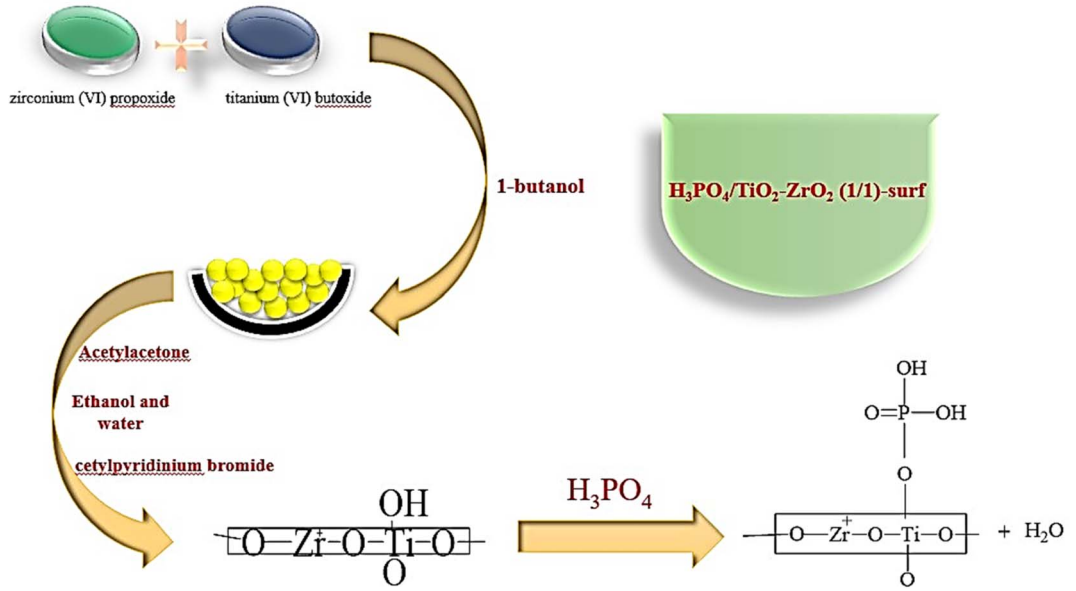


Fig. 3 Preparation of the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst.

from the reaction medium, improved catalyst recovery, increased product selectivity, and reduced corrosion problems.[18–20] Mixed metal oxides containing more than one type of metal atom are a significant class of catalysts.[21] The use of mixed metal oxides instead of a single metal oxide is preferable because mixed metal oxides have a larger surface area, enhanced surface acidity, and better thermal stability and mechanical strength than a single metal oxide.[22,23] The use of ZrO_2 as a support has advantages over other commercial supports such as alumina and silica oxides.[24] Some of these advantages include strong interaction with the active phase, high thermal stability and inertness (compared with other commercial supports).[25] This metal oxide is unique among metal oxides in exhibiting all four key chemical properties: acidic and basic behavior, as well as both oxidative and reductive capabilities. Upon modification with sulfate ions, the support transforms into a superacid.[26] However, the primary limitation of this catalyst is its rapid deactivation, which is likely attributed to coke formation. In this case, more active and stable catalysts are obtained by combining this metal oxide with transition metals, especially noble metals.[27,28]

This protocol outlines the fabrication of a novel catalyst employing catalytic amounts of $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf under microwave-assisted conditions. This catalyst facilitates efficient one-pot chemical reactions for the synthesis of structurally diverse 2-arylbenzothiazoles *via* the condensation of 2-aminothiophenol with various aldehydes. Although the 2-arylbenzothiazole framework is well-known, developing a recyclable heterogeneous catalytic system for its synthesis under microwave-assisted conditions remains an important challenge.[3]

2. Experiments

2.1. Materials and apparatus

All reagents employed in this study were of high purity and obtained from Merck, Aldrich and Fluka Chemical Companies. A Thermo Scientific 9200-point instrument was employed to determine the melting points of the synthetic organic compounds. A microwave device, model GE4020W, manufactured by Samsung, was used to perform the reactions. A Thermo Nicolet IMPACT-400 FT-IR spectrophotometer was employed to record Fourier transform infrared (FT-IR) spectra. Measurements were performed using potassium bromide (KBr)[29] pellets over the spectral range of 400–4000 cm^{-1}. We utilized 1-hydrogen nuclear magnetic resonance (^1H NMR) and 13-carbon nuclear magnetic

Table 1 Prepared $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst with different molar percentages of H_3PO_4

Entry	Amount of catalyst (mole% of H_3PO_4)	Amount of H_3PO_4 (mL)	Amount of mixture of metal oxide (g)
1	5	0.034	0.95
2	10	0.07	0.9
3	15	0.1	0.85
4	20	0.14	0.8
5	25	0.17	0.75
6	30	0.2	0.7
7	35	0.24	0.65

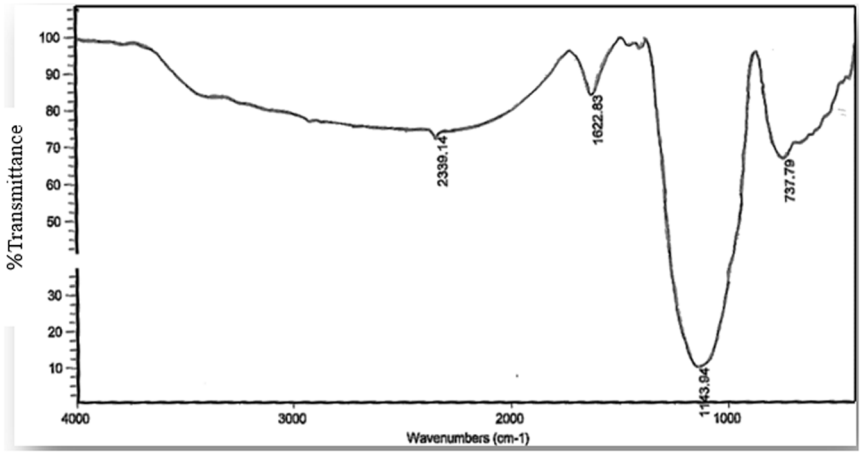


Fig. 4 Fourier transform infrared (FT-IR) spectrum of the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst.

resonance (^{13}C NMR) spectroscopy to analyze the hydrogen and carbon atoms in the compounds using a Bruker DRX-400 spectrometer. Deuterated chloroform ($CDCl_3$) served as the solvent in the spectral analysis. Mass spectra were recorded on an Agilent Technology (HP) MS Model: 5973 Network Mass Selective Detector in electron impact (EI) ionization mode with an ionization voltage of 70 eV.[30] A Philips X'Pert PW 3040 powder X-ray diffractometer was employed to record XRD patterns using CuKα radiation. The powder X-ray diffraction (XRD)[31] analysis was carried out using the X'Pert HighScore Plus instrument. Field-emission scanning electron microscopy (FE-SEM)[32] was employed to examine the surface morphology of the modified catalyst, while energy-dispersive spectroscopy (EDS)[33] was used to characterize its elemental composition.

2.2. General procedure for preparation of $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf

2.2.1. Preparation of the $TiO_2–ZrO_2$ (1/1)-surf metal oxide mixture with a molar ratio of titanium/zirconium = 1 modified by surfactant. To prepare the metallic $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf mixture in a Ti/Zr = 1 molar ratio, 4.68 g of zirconium propoxide (70 wt% dissolved in 2-propanol) and 5 mL of 1-butanol were initially transferred into a 250 mL Erlenmeyer flask. This solution was stirred for 5 minutes to ensure complete homogenization. Subsequently, 3.43 g of titanium *n*-butoxide (99%) was added to the prepared solution, resulting in a clear yellow solution after approximately 20 minutes. In the next step, 1.01 g of acetyl acetone was added to the above solution and magnetically stirred for 15 minutes. Then, separately, 1 mmol of the cetylpyridinium bromide surfactant was dissolved in 2 mL of ethanol and 4 mL of deionized water and added to the main reaction mixture. Afterwards, 2 mL of deionized water was slowly added to the solution under continuous stirring, which instantly led to the formation of a transparent yellow gel. The resulting gel was left in a fixed location for 48 hours to complete gelation and hydrolysis of the alkoxide. Then, it was placed in an oven at 110 °C for 12 hours to remove the solvent and water. At last, to eliminate the unreacted natural materials on the surface of the metal oxide blend (calcination), the obtained

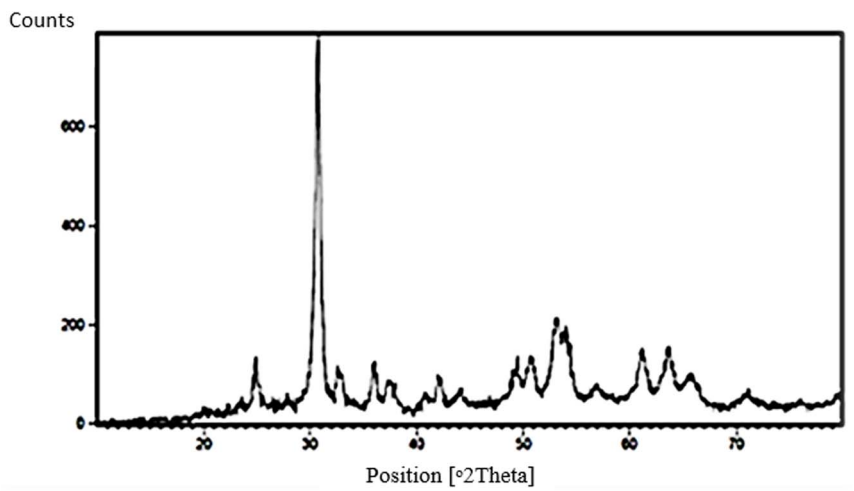


Fig. 5 XRD pattern of the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst.

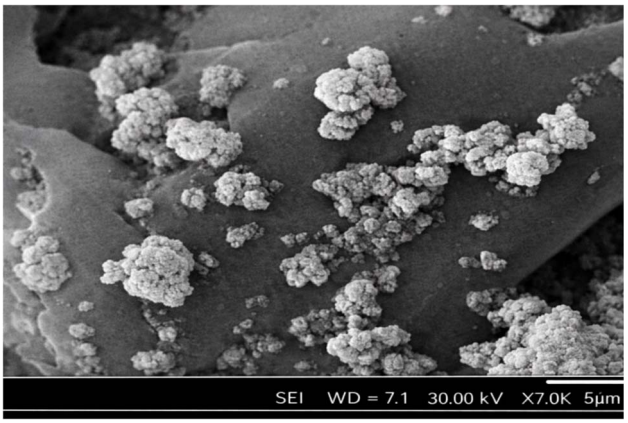


Fig. 6 FE-SEM image of the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst.

precipitate was placed an oven at 500 °C for 6 hours. The above-prepared substrate was named $TiO_2–ZrO_2$ (1/1)-surf.

2.2.2. Method for preparing the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst containing 30 wt% of phosphoric acid. To prepare the catalyst with 30 wt% phosphoric acid, first 0.2 mL (0.3 g) of phosphoric acid (85%) was dissolved in 25 mL of deionized water in a 100 mL beaker and 0.7 g of the $TiO_2–ZrO_2$ (1/1)-surf metal oxide mixture was added to it. The prepared solution was mixed for about one hour with magnetic stirring at room temperature and then the temperature of the stirring solution was gradually increased until all the water was removed. Then, the resulting white precipitate was dried at 110 °C for 12 hours and calcined in an oven at 500 °C for 6 hours. Finally, the obtained white powder of 30 wt% $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf was stored in a suitable container for use in reactions. The addition of cetylpyridinium bromide as a surfactant improved the dispersion and prevented the agglomeration of the TiO_2 and ZrO_2 nanoparticles, leading to a higher surface area. The incorporation of H_3PO_4 was confirmed the FT-IR and EDX analyses.

2.2.3. Preparation of the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst with different weight percentages of phosphoric acid. Different weight percentages of phosphoric acid were removed from the catalyst by dissolving calculated amounts of phosphoric acid (85%) in 25 mL of deionized water in a 100 mL beaker containing the corresponding amount of the $TiO_2–ZrO_2$ (1/1)-surf metal oxide mixture. The prepared solution was mixed for about one hour by magnetic stirring at ambient temperature and then the temperature of the stirrer was gradually increased until all the water was removed. Then, the resulting white precipitate was placed in a dryer to dry at 110 °C for 12 hours and then calcined in an oven at 500 °C for 6 hours and used in reactions.

2.3. General procedure for the synthesis of 2-arylbenzothiazoles with the catalyst of 30 wt% phosphoric acid under microwave conditions

In a 50 mL beaker, 2 mmol of 2-aminothiophenol and 2 mmol of aromatic aldehyde (4-nitrobenzaldehyde as a model reaction) were added, each completely dissolved in 5 mL of ethylene glycol, and 0.04 g of the prepared catalyst containing 30 wt% of phosphoric acid was added to the mixture, and the response vessel was irradiated in a microwave oven at a power of 300 W. The progress of the reaction was monitored *via* TLC (thin-layer chromatography). Upon completion of the reaction, the reaction mixture was diluted with ethyl acetate, filtered, and the catalyst was washed several times with ethyl acetate and acetone. Then, the catalyst was placed in an oven at 90 °C for one hour and then placed in a furnace at 550 °C for 4 hours. Finally, the washed catalyst was preserved for use in subsequent reactions. The final products were recrystallized and purified using ethanol after solvent evaporation. The obtained products were identified by physical and spectroscopic data and compared with the literature.[34,35]

2.4. Selected spectroscopic and physical data

*2.4.1. 2-(2-Hydroxyphenyl)-benzothiazole (**3b**).* Yellow solid; $m.p_{rep.}$ = 127 °C–128 °C; $m.p_{lit.}$ = 126 °C–128 °C;[34] IR (KBr)/ν (cm^{-1}): 3285, 3090, 2900, 1619, 1590, 1490, 1423, 874, 7517; ^1H NMR (400 MHz, $CDCl_3$)/δ (ppm): 6.95–699 (t, 1H, J = 8.0 Hz, Ar–H) 7.12 (d, 1H, J = 8.0 Hz, Ar–H), 7.38–7.44 (m, 2H, Ar–H) 7.50–7.54 (t, 1H, J = 8.4 Hz, Ar–H) 7.71 (d, 1H, J = 8.0 Hz, Ar–H)

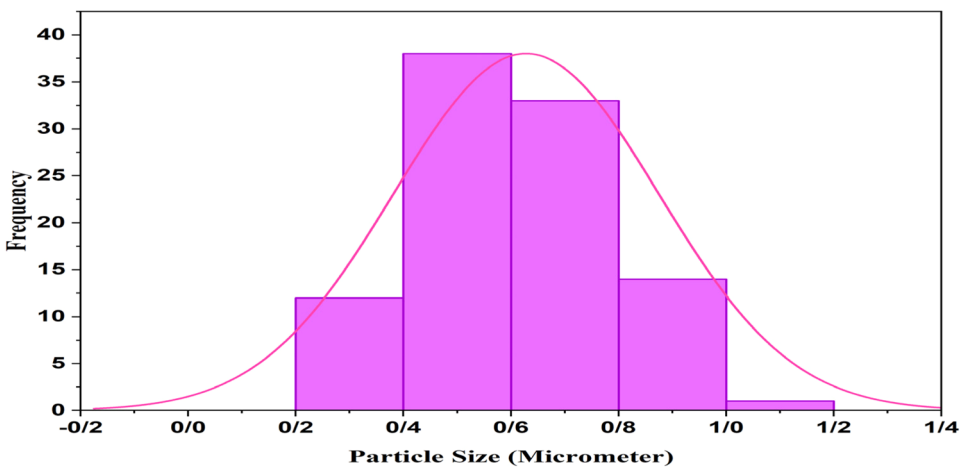


Fig. 7 Particle size distribution histogram with the Gaussian curve for the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst.

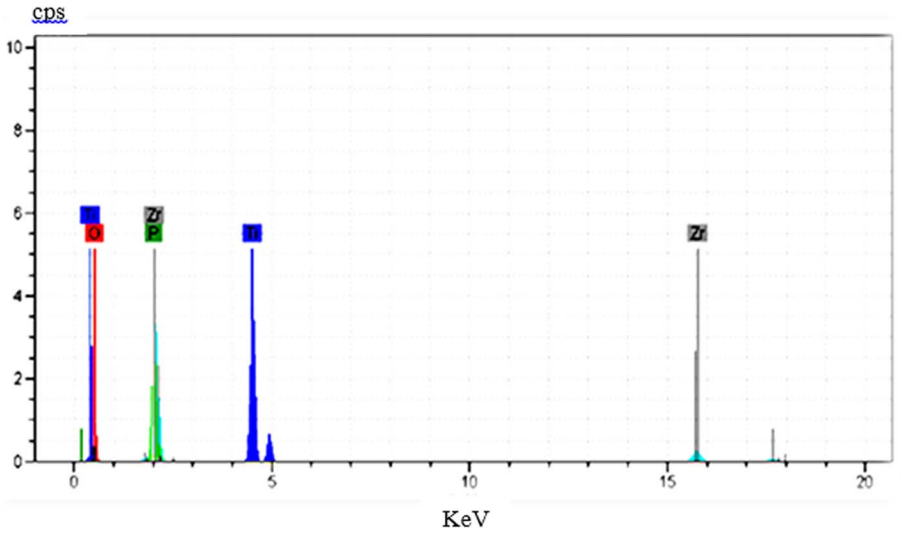


Fig. 8 EDX elemental mapping of the H_3PO_4/TiO_2–ZrO_2 (1/1)-surf catalyst.

Table 2 Optimization of the catalyst amount for the synthesis of **3i**[a]

Yield (%)	Amount of catalyst (g)	Amount of H_3PO_4 (mole% of H_3PO_4)	Entry
45	0.03	5	1
51	0.03	10	2
63	0.03	15	3
72	0.03	20	4
75	0.04	20	5
82	0.03	25	6
90	0.04	25	7
90	0.03	30	8
96	0.04	30	9
95	0.05	30	10
92	0.04	35	11
85	0.05	35	12

[a] Reaction conditions: 2-aminothiophenol (2 mmol), 4-nitrobenzaldehyde (2 mmol) and H_3PO_4/TiO_2–ZrO_2 (1/1)-surf catalyst (0.04 g by 30 wt% of H_3PO_4) in ethylene glycol as the solvent at 300 W.

Table 3 Optimization of the solvent for the synthesis of **3i**[a]

Yield (%)	Time (minute)	Solvent	Entry
80	7	Chloroform	1
85	6	Dichloromethane	2
20	10	Water	3
70	8	Acetonitrile	4
83	6	Methanol	5
92	5	Ethylene glycol	6
45	6	DMF	7

[a] Reaction conditions: 2-aminothiophenol (2 mmol) and 4-nitrobenzaldehyde (2 mmol) in the presence of H_3PO_4/TiO_2–ZrO_2 (1/1)-surf catalyst (0.04 g by 30 wt% of H_3PO_4) in the selected solvent at 300 W.

7.92 (d, 1H, J = 8.4 Hz, Ar–H) 8.01 (d, 1H, J = 8.0 Hz, Ar–H) 12.54 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$)/δ (ppm): 116.80, 117.88, 119.54, 121.52, 122.19, 125.56, 126.70, 128.43, 132.60, 132.77, 151.84, 157.96, 169.39; MS (EI, *m*/*z*): 217 (M+, 1.8), 200 (37), 183 (5.7), 167 (16.5), 136 (100), 124 (81), 107 (78), 97 (13), 77 (50), 65 (30), 51 (18), 41(3).

*2.4.2. 2-(4-Methoxyphenyl)-benzothiazole (**3c**).* White solid; $m.p_{rep.}$ = 120 °C–122 °C; $m.p_{lit.}$ = 120 °C–122 °C;[34] IR (KBr)/v (cm^{-1}): 3021, 3048, 2837, 1609, 1590, 1483, 1249, 830; ^{1}H NMR (400 MHz, $CDCl_3$)/δ (ppm): 3.90 (s, 3H, OCH_3) 7.04 (d, 2H, J = 10.0 Hz, Ar–H) 7.34 (t, 2H, J = 8.0 Hz, Ar–H) 7.57 (t, 1H, J = 8.0 Hz, Ar–H) 7.74 (d, 1H, J = 8.0 Hz, Ar–H) 8.21 (d, 2H, J = 10.0 Hz, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$)/δ (ppm): 55.47, 114.38, 121.53, 122.83, 124.81, 126.23, 126.42, 129.13, 134.86, 154.21, 161.94, 167.89; MS (EI, *m*/*z*): 243 (12.5), 242 (38), 241 (M+, 100), 226 (15.8), 198 (23), 171 (3.5), 154 (5.4), 139 (0.8), 127 (1.6), 108 (2.8), 82 (2.8), 69 (6.9).

3. Results and discussion

3.1. Preparation and characterization of the H_3PO_4/TiO_2–ZrO_2 (1/1)-surf catalyst

The use of ZrO_2 as a support in the preparation of catalysts has advantages over other commercial bases such as alumina and silica oxides. These advantages include its strong interaction with the active phase, high thermal stability and inert nature

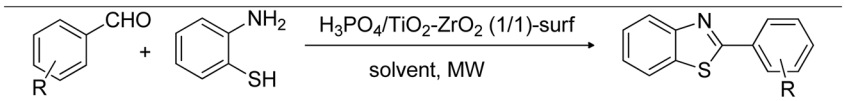
Table 4 Optimization of the microwave power for the synthesis of **3i**[a]

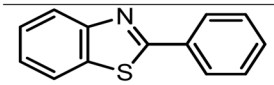
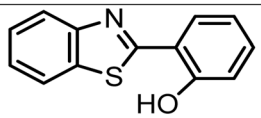
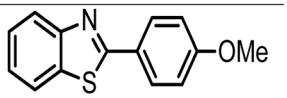
Yield (%)	Power (watt)	Time (minute)	Entry
50	100	15	1
65	100	18	2
65	180	10	3
75	180	12	4
85	300	4	5
92	300	6	6
92	450	6	7

[a] Reaction conditions: 2-aminothiophenol (2 mmol), 4-nitrobenzaldehyde (2 mmol) and H_3PO_4/TiO_2–ZrO_2 (1/1)-surf catalyst (0.04 g by 30 wt% of H_3PO_4) in ethylene glycol as the solvent at the selected microwave power.

compared to other commercial bases. This metal oxide also has four chemical properties: acidic and basic behavior and oxidation and reduction capability. Another advantage of this metal oxide is that when it is combined with transition metals, especially noble metals, in the preparation of catalysts, it yields highly active and stable catalysts, and increases their thermal stability. In this study, first, a mixture of metal oxides, TiO_2–ZrO_2, was prepared with a molar ratio of 1 : 1, and in the next step, phosphoric acid was used to activate the prepared metal oxide mixture, and acid catalysts with different molar percentages of phosphoric acid were prepared and used under different conditions in the preparation of 2-arylbenzothiarols. The reason for using phosphoric acid is that it is milder than common mineral acids, such as sulfuric acid, and therefore causes fewer side reactions. To prepare this metal oxide mixture, zirconium(VI) propoxide was used as the zirconium source, together with deionized water, 1-butanol as the solvent, cetylpyridinium bromide as a surfactant, and phosphoric acid and titanium(VI) butoxide as the titanium source. After preparing the aforementioned metal oxide mixture, calcination was performed to remove excess organic compounds present in it. To do this, the metal oxide mixture TiO_2–ZrO_2 (1/1)-surf was placed in a furnace at a temperature of 550 °C. In addition to removing the organic compounds, the calcination process also removes water inside the compounds, which strengthens the structure of the metal oxide mixture and increases its stability. The substrate prepared by this method was named TiO_2–ZrO_2 (1/1)-surf. After the preparation of the surfactant-modified TiO_2–ZrO_2 (1/1)-surf metal oxide mixture, phosphoric acid was used as a suitable mineral acid to activate it and prepare the solid acidic catalyst, and the acidic catalyst was prepared using different molar percentages of phosphoric acid (Fig. 3).

Table 5 Synthesis of the 2-arylbenzothiazoles catalyzed by H_3PO_4/TiO_2–ZrO_2 (1/1)-surf[a]



3a-l, Yield[b] (%), Time (min), melting point $_{rep}$ (°C), melting point $_{lit}$ (°C), reference		
		
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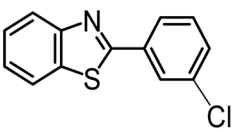	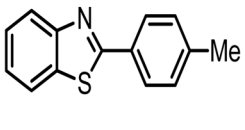	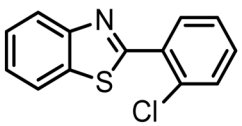
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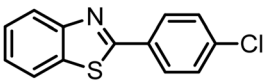
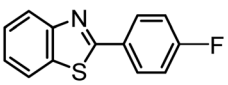
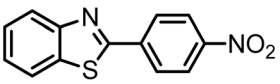
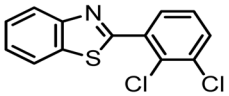
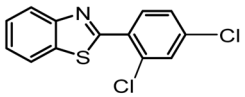
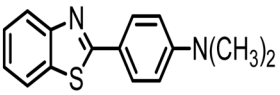
		
3g: 90, 4, 114-116, 116-118, [35]	3h: 87, 6.5, 99-101, 101-103, [34]	3i: 92, 3.5, 227-229, 226-228, [35]
		
3j: 92, 4, 118-120, 119-121, [34]	3k: 91, 4.5, 142-144, 140-143, [35]	3l: 85, 5, 160-162, 160-162, [34]

[a] Reaction conditions: 2-aminothiophenol (2 mmol), benzaldehyde (2 mmol) and H_3PO_4/TiO_2–ZrO_2 (1/1)-surf catalyst (0.04 g by 30 wt% of H_3PO_4) in ethylene glycol as the solvent at 300 W. [b] Isolated yield.

Table 6 Comparison of the catalytic activity of the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst with other reported catalysts for the synthesis of 2-arylbenzothiazoles

Entry	Product	Catalyst loading	Conditions	Time (min)	Yield (%)[a]	Ref.
1	**3d**	H_2SO_4/SiO_2 (5 mg)	Ethanol and r.t	8	85	This work
2				40	64	34
3	**3g**	Silica sulfuric acid (100 mg)	MW and 45 W	4	90	This work
4				10	90	35
5	**3b**	CdS nanospheres (CdSNS) (5 mg)	Visible light, methanol, and r.t	3.5	92	This work
6				20	98	37

[a] Isolated yield.

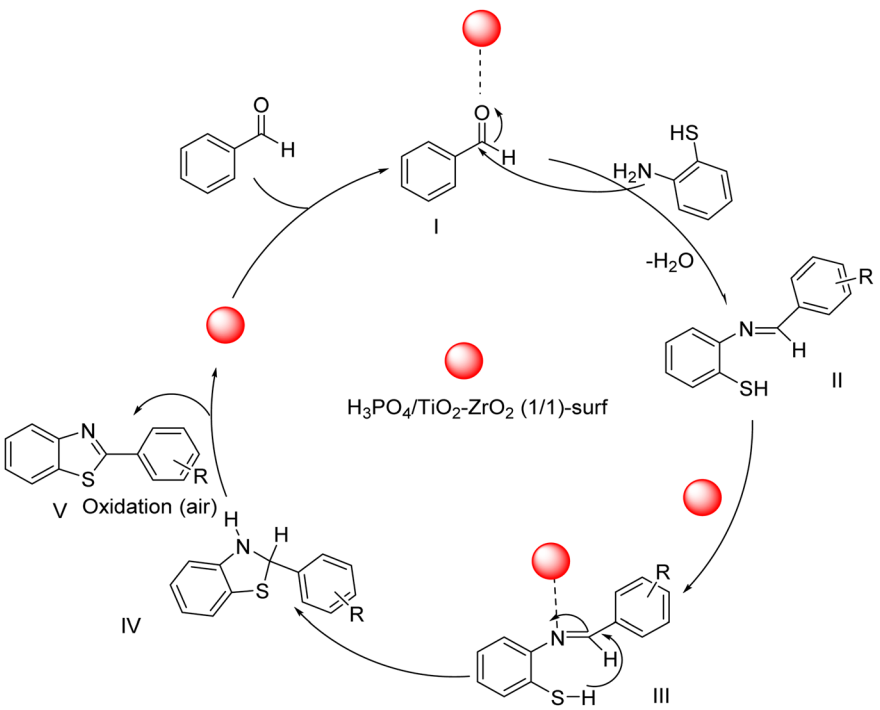
As can be seen in Table 1, the desired catalyst was prepared with different percentages of phosphoric acid, and the catalyst with the optimal amount is listed in entry 4.

The FT-IR spectrum of the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst is shown in Fig. 4. As can be seen in this Figure, the FT-IR spectrum of the prepared catalyst has several characteristic peaks, where the stretching vibration of the phosphorus–oxygen bond (P–O–P) is observed at 737 cm^{-1} and the stretching vibration of the phosphorus bond attached to the hydroxyl groups (P–OH) is observed at 1143 cm^{-1}.[36] Also, the bending vibrations related to the (O–H) bonds are observed at 1622 cm^{-1} and the vibration shown in the region between 2100 cm^{-1} and 3200 cm^{-1} is related to the stretching vibration of the oxygen–hydrogen bonds (O–H).

The Fig. 5 displays the diffraction pattern of the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst. In general, the X-ray diffraction pattern for the surfactant-modified metal oxide mixture $TiO_2–ZrO_2$ (1/1)-surf does not show a specific peak, but after phosphoric acid was immobilized on it, peaks appear in its XRD pattern.

Fig. 6 shows the morphology of the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst. The prepared $TiO_2–ZrO_2$ (1/1)-surf metal oxide mixture has a bladed and flat structure. The size of each particle is in the range of 30–50 nm and no crystalline part is seen in the structure of the metal oxide mixture. The uniformity in the shape and size of the prepared sample particles makes them a suitable substrate for catalytic use. In this figure, the morphology of the optimized catalyst after immobilization of phosphoric acid on the surfactant-modified metal oxide mixture is visible, where the spots observed on the substrate indicate the presence of phosphoric acid.

Moreover, the particle size distribution (PSD) of the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst was determined to be 0.6281 micrometer with a standard deviation of 0.2470 micrometer (Fig. 7).



Scheme 1 Proposed reaction mechanism for the synthesis of the 2-arylbenzothiazole derivatives.

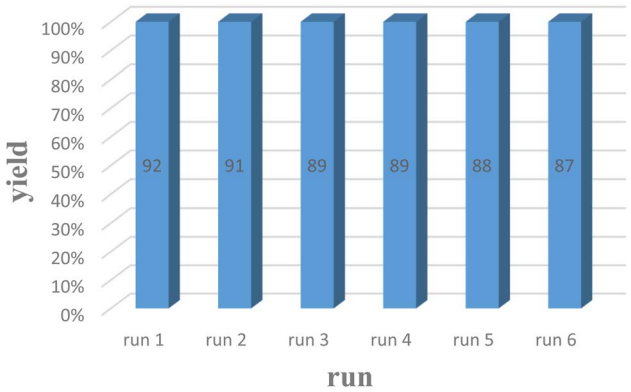


Fig. 9 Reusability results for the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst under the model reaction.

Energy-dispersive X-ray (EDX) spectroscopy analysis was performed to determine the percentages of the elements constituting the catalyst, as shown in Fig. 8. In this figure, the peaks corresponding to the titanium, zirconium, phosphorus and oxygen elements are visible and their ratios indicate the structure of the catalyst, which are relatively similar to the theoretical values.

3.2. Investigation of catalytic activity

The primary objective of this study was to design and prepare $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf as a catalyst for use in the synthesis of 2-arylbenzothiazoles. The effects of solvent type, catalyst amount and microwave power (watt) on product preparation were investigated to optimize the process. Table 2 shows the optimal amount of catalyst.

In this part of our study, the reaction for the synthesis of 2-arylbenzothiazoles from 4-nitrobenzaldehyde and 2-aminothiophenol was carried out in different solvents under microwave irradiation. Since solvent choice greatly influences the performance of reactions under microwave irradiation, selecting a suitable solvent is crucial, as it significantly affects the reaction efficiency and duration. Table 3 presents the results of investigating the effect of several polar protic and polar aprotic solvents on synthesis of 2-arylbenzothiazoles.

In the reaction for the synthesis of 2-arylbenzothiazoles using the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst under microwave irradiation, after optimizing the solvent, the required power and time were investigated. In this case, the reactants were exposed to microwave irradiation at varying powers and durations, and at the end of each reaction, the yield was determined. Table 4 shows the yield of this reaction at different microwave powers.

After optimizing the reaction conditions, the generality of this method for other aromatic aldehydes in the reaction with 2-aminothiophenol was examined by preparing various 2-arylbenzothiazole compounds in the presence of the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst. The results of these studies are presented in Table 5.

According to the table above, it can be concluded that, in the reaction mechanism where nucleophilic attack on the aldehyde occurs, electron-withdrawing groups increase the reaction rate, resulting in the highest yield and the shortest reaction time.

Table 6 illustrates a comparison of some results with those of recent related works. It was concluded that the use of the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst is the best case for the multicomponent reaction for the production of 2-arylbenzothiazoles under microwave irradiation, as it gives excellent results in terms of yield, reaction time, and amount of catalyst used.

3.3. Proposed reaction mechanism

Scheme 1 depicts the crucial role of the catalyst in this reaction. The condensation reaction between various aromatic aldehydes and 2-aminothiophenol in the presence of an acid catalyst is one of the most common methods for the preparation of 2-arylbenzothiazoles. Firstly, the catalyst has the ability to activate

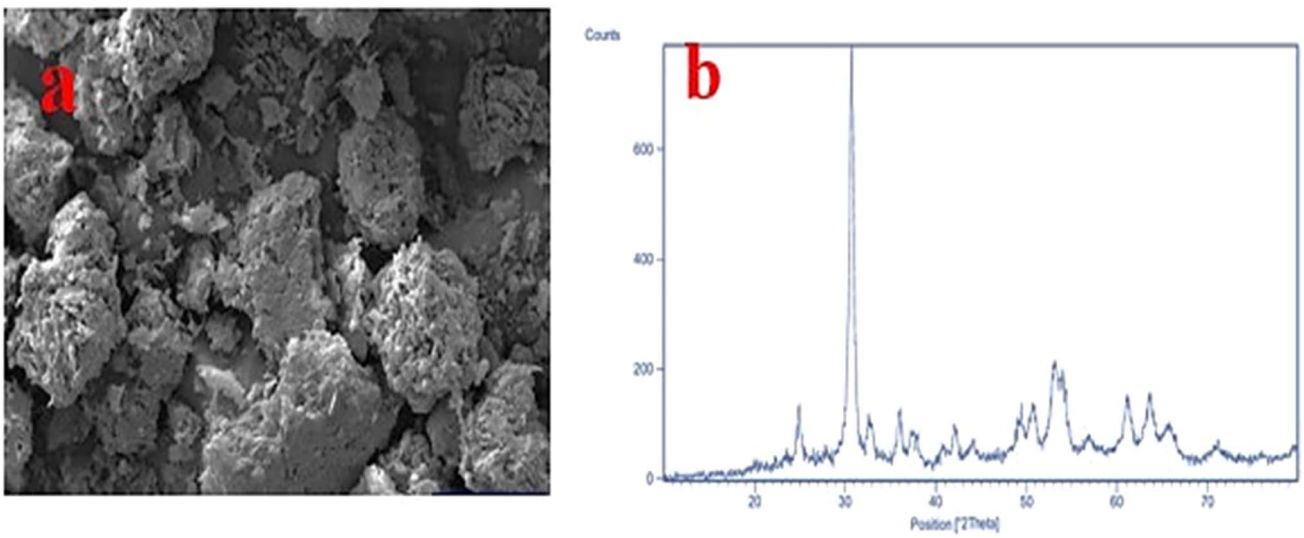


Fig. 10 FE-SEM image (a) and XRD pattern (b) after reusing the $H_3PO_4/TiO_2–ZrO_2$ (1/1)-surf catalyst.

Table 7 Stability of the catalyst under various conditions[a]

Yield (%)	Time (min)	pH	Condition
89	10	2	Acidic
86	10	10	Basic
92	10	7	Neutral

[a] H_3PO_4/TiO_2–ZrO_2 (1/1)-surf catalyst (0.04 g by 30 wt% of H_3PO_4) in ethylene glycol as the solvent at 300 W

the oxygen atom of the carbonyl group of the aldehyde due to the presence of phosphoric acid and TiO_2–ZrO_2 on its surface, which enables it to act as both a Brønsted acid and a Lewis acid, respectively. Therefore, the catalyst facilitates the formation of intermediate I. Then, the nitrogen atom of 2-aminothiophenol acts as a nucleophile and attacks the carbonyl carbon, resulting in the elimination of a water molecule, and the formation of intermediate II. Next, intermediate III is formed, which undergoes a sequence of proton transfer and substitution steps. During this process, the catalyst functions not only as a proton source but also as a mediator that stabilizes charged intermediates and lowers the activation energy of the transformation. In the later stages, the oxidant promotes the oxidative conversion of the sulfur-containing intermediate IV, ultimately leading to the formation of the desired heteroaromatic product V. The regeneration of the proton donor ensures continuity of the catalyst cycle. Consequently, the synergistic effect of the catalyst enhances the reaction efficiency and shortens the reaction time.

3.4. Reusability

The recovery of the H_3PO_4/TiO_2–ZrO_2 (1/1)-surf catalyst for the production of 2-arylbenzothiazole derivatives under microwave conditions was investigated by optimizing the microwave power, solvent and catalyst amount. After the reaction was complete, the catalyst was separated by dispersing it in ethyl acetate, followed by filtration and washing several times with ethyl acetate and acetone. The recovered catalyst was dried in an oven at 90 °C for one hour, and then heated at 550 °C for 4 hours to remove the residual solvent and excess organic materials. After these steps, the catalyst was used in similar reactions. The results of the reactions using the recovered catalyst under microwave conditions, tested six times with 4-nitrobenzaldehyde and 2-aminothiophenol, are shown in Fig. 9.

Fig. 10a and b show the FE-SEM image and XRD pattern of the recovered catalyst after six uses, respectively. The morphology of the catalyst remained essentially unchanged after six times of recovery and reuse, demonstrating its stability and durability, as shown in the FE-SEM image. Furthermore, the XRD pattern of the catalyst (Fig. 10b) obtained after six times of reuse is in close agreement with the initial experiment, indicating that its atomic structure remains unchanged after repeated recovery and reuse.

To investigate the stability of the catalyst under acidic, basic and neutral conditions, the prepared catalyst was investigated under model reaction conditions. The reaction mixture containing the catalyst in ethylene glycol solvent was irradiated with microwaves for 10 minutes under each condition (acidic, basic and neutral). Then, the catalyst was separated from the reaction medium, washed and dried. Then, it was reused in the model reaction, and the results are shown in Table 7. The results indicate that the catalyst exhibits good stability under acidic, basic and neutral conditions.

In addition, the hot filtration method was used to investigate the possibility of component leakage from the H_3PO_4/TiO_2–ZrO_2 (1/1)-surf catalyst. The catalyst was separated from the reaction mixture after 1.45 min using solvent diffusion. The progress of the reaction in the filtrate was monitored by TLC, after which the mixture was promptly heated. No further reaction progress was observed after filtration, confirming that the H_3PO_4/TiO_2–ZrO_2 (1/1)-surf catalyst did not leach any material during the process, as indicated by the hot filtration test results.

4. Conclusion

In summary, this study presents the H_3PO_4/TiO_2–ZrO_2 (1/1)-surf catalyst as a highly effective solid acid catalyst for synthesizing 2-arylbenzaldehyde compounds using ethylene glycol as a solvent under microwave irradiation. The advantages of this catalyst include durability, ease of separation, reusability and[1–37] affordability. These characteristics were confirmed through different scientific techniques including FT-IR, XRD, FE-SEM, and EDS analyses. The one-pot multicomponent reaction employing this catalyst offers several benefits, such as a shorter reaction time, higher efficiency compared with other catalysts used in 2-arylbenzothiazole synthesis, the use of microwave irradiation, high product yields, and easy cleanup.

Conflicts of interest

This paper's authors declare that they do not have any competing financial interests or personal relationships to influence their work.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d5na01041a.

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