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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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Abstract

This study aims to demonstrate an environmentally friendly approach for the synthesis of 2-arylbenzothiazole derivatives. The benzaldehyde and 2-aminothiphenol were reacted in a one-step process using ethylene glycol as the optimal solvent, promoting a more 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 spectroscopy, ^{1}H NMR, ^{13}C NMR, and mass spectrometry.

Keywords: Acid catalyst, Multicomponent reaction, Reusability, 2-Arybezethiazoles, Microwave irradiation

1. Introduction

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

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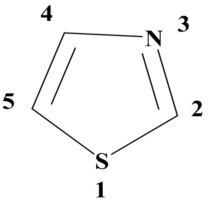

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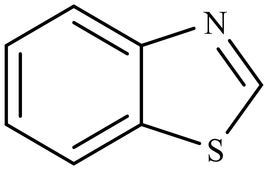

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Figure 1. Thiazole ring (**1**) and Benzothiazole (**2**)

The thiazole system has been found in the structural part of many useful compounds that have numerous biological properties, such as forming one of the structural components of natural compounds including vitamins (thiamine), epothilone (an anticancer drug), penicillin, and carboxylase [2]. Benzothiazoles, comprising a thiazole ring fused to a benzenepart, contain a heterocyclic framework with nucleophilic and electrophilic sites to functionalization, and can act as a covering groups for carbonyl functionalities (Figure 1). Molecules containing benzothiazole nuclei have been reported to have antiallergic [4], antidiabetic [5], and anti-inflammatory properties. Derivatives of 2-arylbenzothiazoles have antitumor properties, and 6-nitrobenzothiazole and 6-aminobenzothiazole have antibacterial properties [6]. These compounds are vitally important as antioxidants and resin stabilizers in the polymer industry (Figure 2), and Swedish researchers have also upgraded some benzothiazole-based monomethine cyanine dyes with fluorescent properties [7].

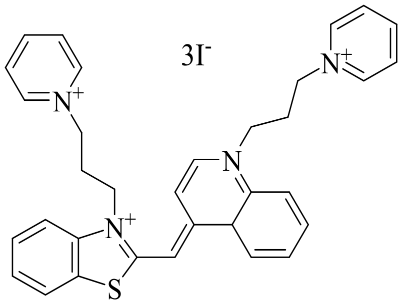

Figure 2. Antioxidant and resin stabilizer combination in the polymer industry

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A catalyst [8–10] is a substance that, when introduced into 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 for reasons such as ease of catalyst separation 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 reason for using mixed metal oxides instead of a single metal oxide is that mixed metal oxides have a larger surface area, their surface acidity is also increased, and they also show 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 to 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, likely attributes to coke formation. More active and stable catalysts are obtained by combining this metal oxide with transition metals, especially noble metals, in the ZrO_2 system [27,28].

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This protocol outlines the fabrication of a novel catalyst through employing catalytic amounts of H_3PO_4/TiO_2-ZrO_2 (1/1)-surf under microwave condition is reacted. This catalyst helps an efficient one-pot chemical reaction for 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 their synthesis under microwave condition remains an important challenge.

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. Thermo scientific 9200-point machine was procured to find out at what temperature the synthetic organic compounds start to melt. A microwave device, model GE4020W, manufactured by Samsung, was used to perform the reactions. We used a machine called thermo Nicolet IMPACT-400 FT-IR spectrophotometer to determine the 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 the 1-hydrogen nuclear magnetic resonance (^1H NMR) and 13-carbon nuclear magnetic resonance (^{13}C NMR) spectra to measure the hydrogen and carbon in a chemical by a Bruker DRX-400 spectrometer. Deuterated chloroform ($CDCl_3$) served as both the solvent in the spectral analysis. Mass spectra were recorded on an Agilent Technology (HP) MS Model: 5973 Network Mass Selective Detector, instrument by Electron Impact (EI) Ionization mode with an ionization voltage of 70 eV [30]. The Philips XPert PW 3040 powder X-ray diffractometer machine produced patterns using CuKa radiation. Powder X-ray diffraction (XRD) [31] involves studying these patterns in a special way. The analysis was carried out with Xpert High score plus. Field emission scanning

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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 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 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. The 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 previous solution was magnetically stirred for 15 minutes. Then, separately, 1 mmol of the surfactant cetylpyridinium bromide 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 dispose of the unreacted natural materials on the surface of the metal oxide blend (calcination), the coming about precipitate was put in 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 a magnetic stirring at room temperature and then the temperature of the stirring 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. 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 the reactions. The addition of celtylpyridinum bromide as a surfactant improved the dispersion and prevented agglomeration of 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 H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst with different weight percentages of phosphoric acid

Different weight percentages of phosphoric acid from the catalyst were dissolved by removing the calculated amounts of phosphoric acid (85%) in 25 mL of deionized water in a 100 mL beaker and a corresponding amount 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 by magnetic stirrer 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 the reactions.

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

In a 50 mL beaker, 2 mmol of 2-aminothiophenol and 2 mmol of aromatic aldehyde (4-nitrobenzaldehyde as a model reaction), each completely dissolved in 5 mL of ethylene glycol, were transferred, and 0.04 g of the arranged catalyst containing 30% wt. of phosphoric acid was added to the mixture, and the response vessel was irradiated in a microwave oven with a power of 300 W. The progress of the reaction was monitored by using 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].

Selected spectroscopic and physical data

2-(2-Hydroxyphenyl)-benzothiazole (3b). Yellow solid; m.p $_{\text{rep.}}$= 127-128 ^{o}C; m.p $_{\text{lit.}}$= 126-128 ^{o}C [34]; IR (KBr)/ ν (cm^{-1})= 3285, 3090, 2900, 1619, 1590, 1490, 1423, 874, 7517; ^{1}H 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) 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-Methoxyphenyl)-benzothiazole (3c). White solid; m.p $_{\text{rep.}}$= 120-122 ^{o}C; m.p $_{\text{lit.}}$= 120-122 ^{o}C [34]; IR (KBr)/ ν (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).

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3. Results and Discussion

3.1. Preparation and characterization of 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: strong interaction with the active phase, high thermal stability and the inert nature of this metal oxide compared to other commercial bases. This metal oxide also has four chemical properties: acidic and basic behavior, oxidation and reduction capability. Another benefit 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 this action also increases 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 an acid catalyst with different molar percentages of phosphoric acid was 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 a zirconium source, deionized water, 1-butanol as a solvent, cetylpyridinium bromide as a surfactant, phosphoric acid and titanium (VI) butoxide as a titanium source. After preparing the aforementioned metal oxide mixture, calcination was used 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 remove 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 the metal oxide mixture and prepare the solid acidic catalyst,

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and the acidic catalyst was prepared with different molar percentages of phosphoric acid (Figure 3).

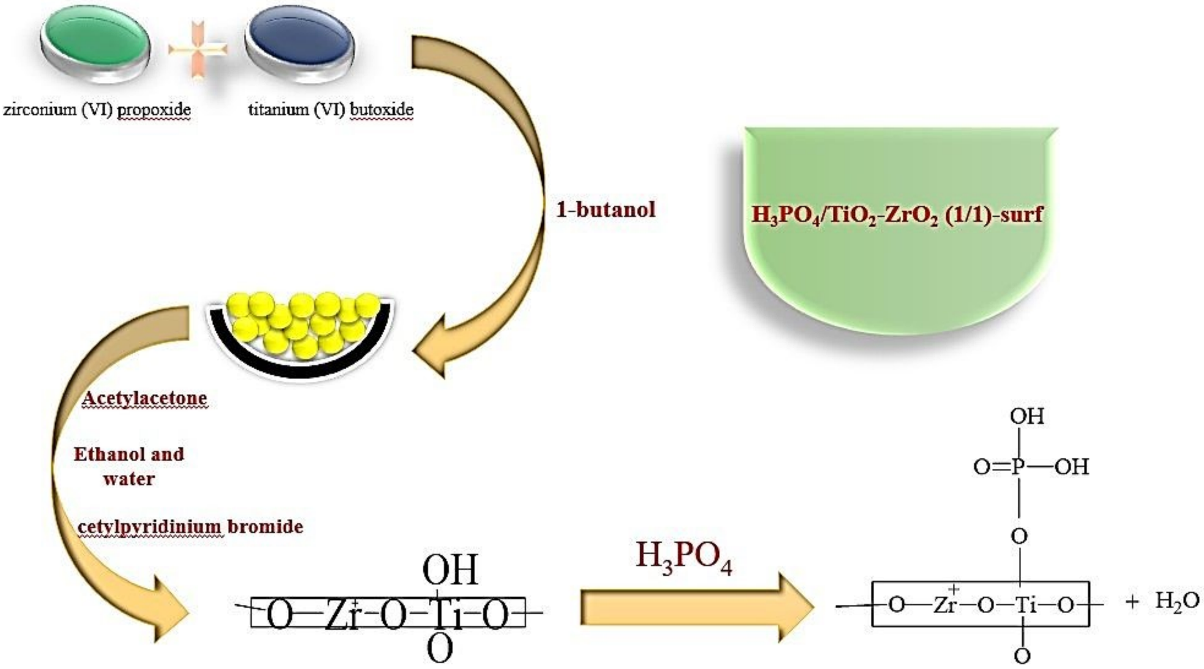

Figure 3. Preparation of the H_3PO_4/TiO_2-ZrO_2 (1/1)-surf

In Table 1, the desired catalyst has been prepared with different percentages of phosphoric acid, and as is clear, the catalyst with the best amount is listed in entry 4.

Table 1. The 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 the 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

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7	35	0.24	0.65

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

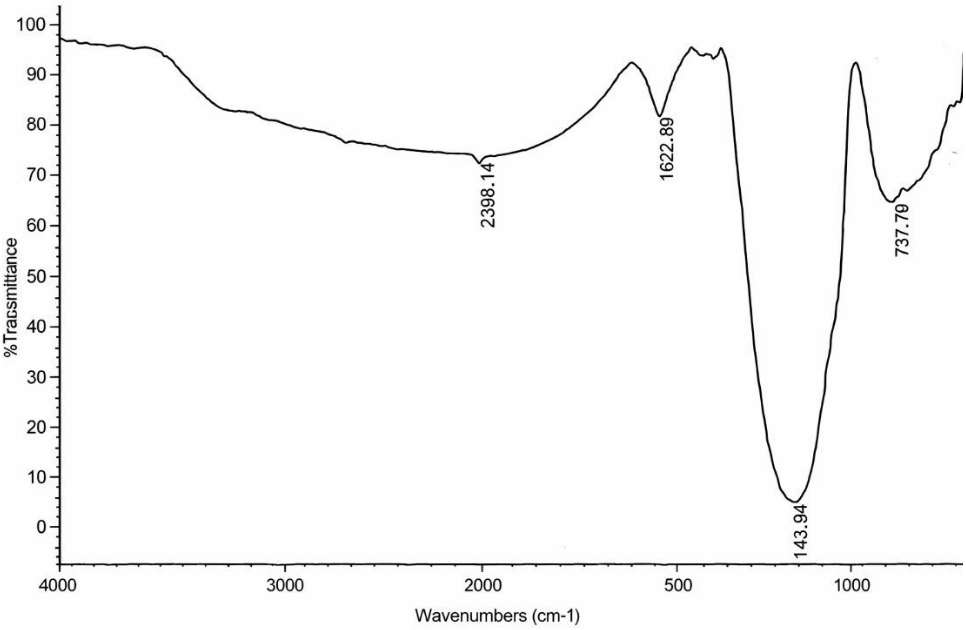

Figure 4. Infrared spectra (FT-IR) of H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst

The Figure 5 displays the diffraction pattern of 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 is immobilized on it, its XRD pattern is shown in Figure 5.

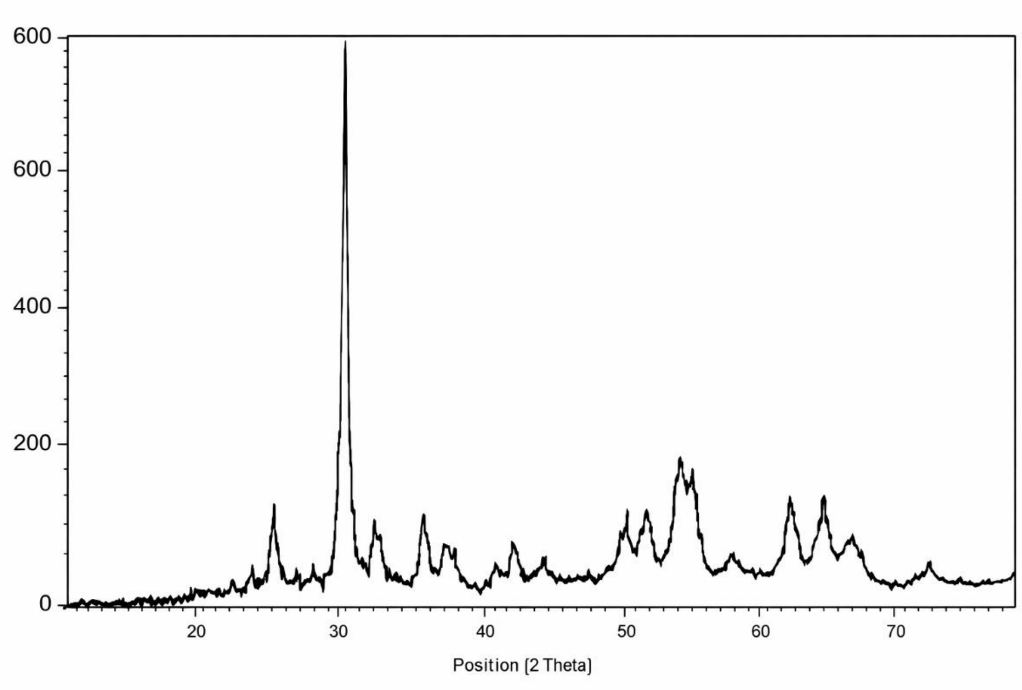

Figure 5. XRD pattern of H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst

The Figure 6 shows the morphology of 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 and the uniformity in the shape and size of the prepared sample particles makes it a suitable substrate for catalytic use. In this Figure, the morphology of the optimized catalyst after placing phosphoric acid on the metal oxide mixture modified with surfactant is visible and also the observation of spots on the metal oxide mixture substrate has well determined the placement of phosphoric acid on the catalyst.

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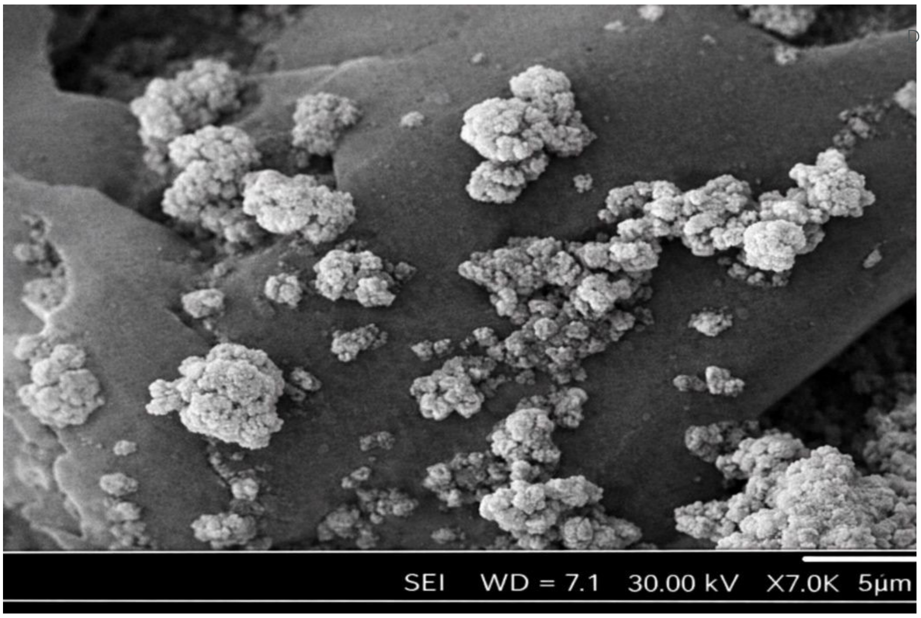

Figure 6. FE-SEM images of the $H_3PO_4/TiO_2\text{-}ZrO_2$ (1/1)-surf catalyst

Moreover, the particle size distribution (PSD) of $H_3PO_4/TiO_2\text{-}ZrO_2$ (1/1)-surf catalyst was achieved 0.6281 micrometer with a standard deviation of 0.2470 micrometer (Figure 7).

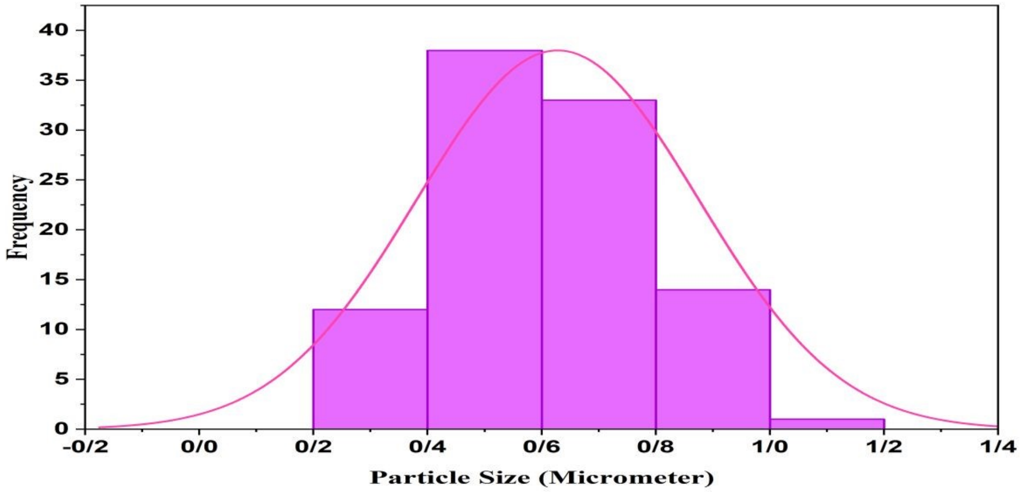

Figure 7. Particle size distribution histogram with a Gaussian curve of $H_3PO_4/TiO_2\text{-}ZrO_2$ (1/1)-surf catalyst

X-ray analysis (EDX) was used to determine the percentages of the elements constituting the catalyst in Figure 8. In this Figure, the peaks corresponding to the elements titanium,

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zirconium, phosphorus and oxygen are visible and their ratios indicate the structure of the catalyst, which are relatively similar to the theoretical values.

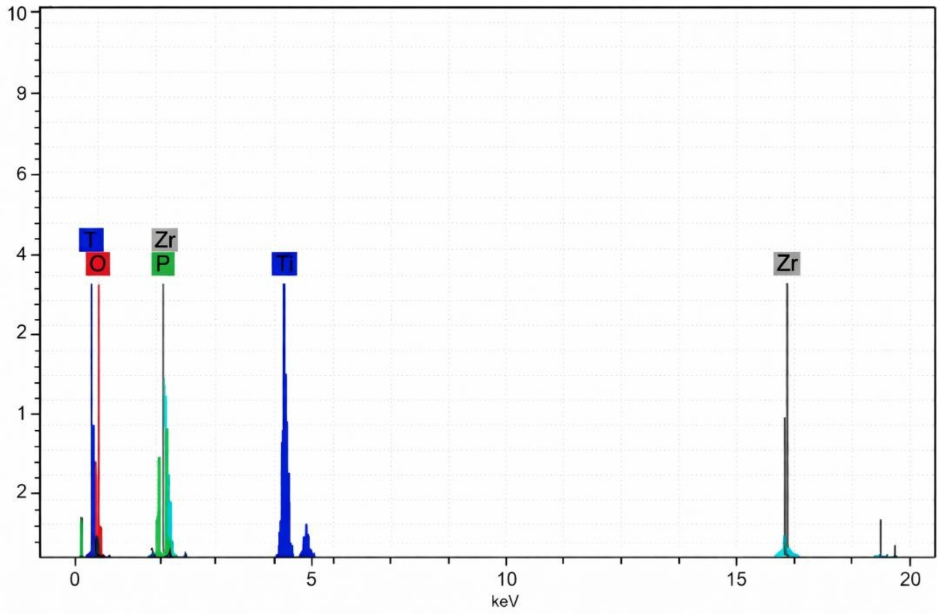

Figure 8. EDX of H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst

3.2. Investigation of Catalytic Activity

The primary objective of this research is to design and prepare H_3PO_4/TiO_2-ZrO_2 (1/1)-surf to be used as catalyst in the synthesis of 2-arylbenzothiazoles. To optimize the solvent types, the catalyst amounts and different microwave power values (watts) for product preparation, these factors were investigated. In Table 2 is shown optimal the amounts of this catalyst.

Table 2: the optimization of catalyst amount for the synthesis of 3i^a

Entry	Amount of H_3PO_4 (mol % of H_3PO_4)	Amount of catalyst (g)	Yield (%)
1	5	0.03	45
2	10	0.03	51
3	15	0.03	63

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4	20	0.03	72
5	20	0.04	75
6	25	0.03	82
7	25	0.04	90
8	30	0.03	90
9	30	0.04	96
10	30	0.05	95
11	35	0.04	92
12	35	0.05	85

[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 solvent at 300 w

In this part of the research, the reaction of preparing 2-aryl benzothiazols using 4-nitrobenzaldehyde and 2-aminothiophenol was carried out in different solvents under microwave irradiation. Since one of the important factors that must be considered for better performance of reactions under microwave irradiation is the selection of a suitable solvent for the reaction, because in reactions carried out under microwave irradiation, the type of solvent selected is of particular importance in the rate of reaction efficiency and determining the reaction time. Table 3 gives the results of investigating the effect of several types of polar protic and polar non-protic solvents on the reaction of preparing 2-aryl benzothiazols.

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

Entry	Solvent	Time (minute)	Yield (%)
1	Chloroform	7	80

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2	Dichloromethane	6	85
3	water	10	20
4	Acetonitrile	8	70
5	methanol	6	83
6	Ethylene glycol	5	92
7	DMF	6	45

[a] Reaction conditions: 2-aminothiophenol (2 mmol), 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 selected solvent at 300 w

In the reaction of preparing 2-arylbenzothiazols using the catalyst H_3PO_4/TiO_2-ZrO_2 (1/1)-surf under microwave irradiation, after optimizing the solvent, the required power and time were investigated. In this way, the reactants were exposed to microwave irradiation at different irradiations and different times, and at the end of each reaction, the yield of these reactions was determined. Table 4 shows the yield of this reaction at different microwave irradiations.

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

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

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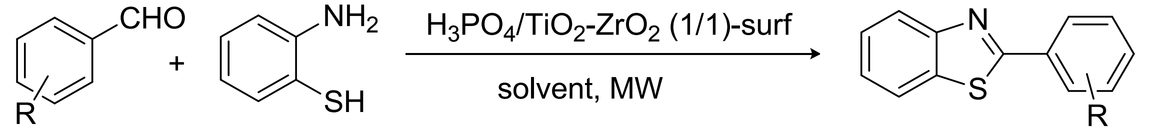
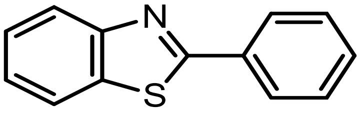
[a] Reaction conditions: 2-aminothiophenol (2 mmol), 4-nitrobenzaldehyde (2 mmol) and H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst (0.04 g by 30% wt. of H_3PO_4) in ethylene glycol as solvent at selected microwave power

After optimizing the various reaction conditions and to prove the generality of this method for other aromatic aldehydes in the reaction with 2-aminothiophenol, using the optimized reaction conditions, the preparation of various compounds of 2-arylbenzothiazoles in the presence of the H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst was investigated, and the results of these studies are given in Table 5.

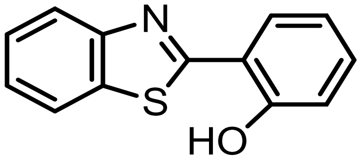
Table 5. Synthesis of 2-arylbenzothiazoles catalyzed by H_3PO_4/TiO_2-ZrO_2 (1/1)-surf [a]



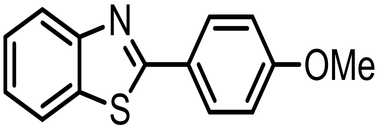
3a-l, Yield [b] (%), Time (min), melting point$_{rep}$ (°C), melting point$_{lit}$ (°C), reference



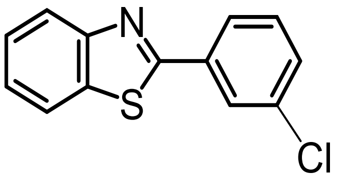
3a: 84, 6.5, 110-112, 11-112, [34]



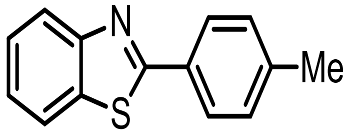
3b: 92, 3.5, 12, 127-128, 126-128, [34]



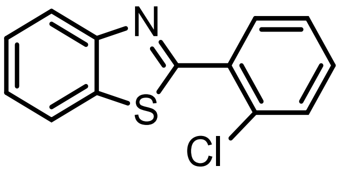
3c: 90, 4, 120-122, 120-122, [34]



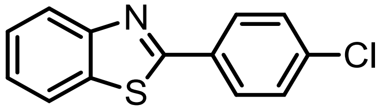
3d: 85, 8, 125-127, 126-128, [34]



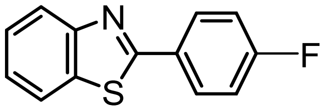
3e: 88, 5, 82-84, 83-85, [34]



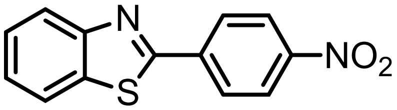
3f: 87, 5, 72-74, 72-74, [35]



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]

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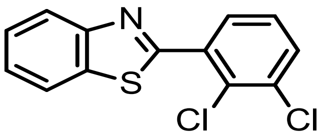
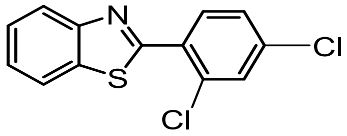
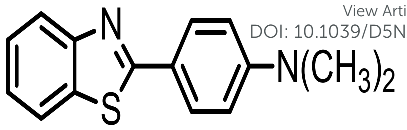


3j: 92, 4, 118-120, 119-121, [34]



3k: 91, 4.5, 142-144, 140-143, [35]



3l: 85, 5, 160-162, 160-162, [34]

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[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 solvent at 300 w

[b] Isolated yield

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

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

Table 6. The 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	Condition	Time (min)	Yield (%)[a]	Ref.
1	**3d**	H_2SO_4/SiO_2 (5 mg)	Ethanol, r.t	8	85	This work
2				40	64	34
3	**3g**	Silica sulfuric acid (100 mg)	MW, 45w	4	90	This work
4				10	90	35

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5	**3b**	CdS nanosphere (CdSNS) (5 mg)	Visible light, methanol, r.t	3.5	92	This work
6				20	98	[37]

^{a} Isolated yield

3.3. Proposed reaction mechanism

Scheme 1 depicts a 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. First, the catalyst has the ability to activate the oxygen of carbonyl group of aldehyde due to the presence of phosphoric acid and TiO2-ZrO2 on its surface, which makes this catalyst act as both a Bronsted acid and a Lewis acid, respectively. Therefore, the catalyst helps to produce the intermediate I. Then, the 2-aminothiophenol nitrogen as a nucleophile attacks the carbonyl carbon by resulting in the elimination of a water molecule, intermediate (II) is formed. Next, an intermediate (III) is formed, which undergoes a sequence of proton transfer and substitution steps. During this process, the catalyst acts not just 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 the continuity of the catalyst cycle. Consequently, the synergistic effect present in the catalyst has increased the reaction efficiency and also reduced the reaction time.

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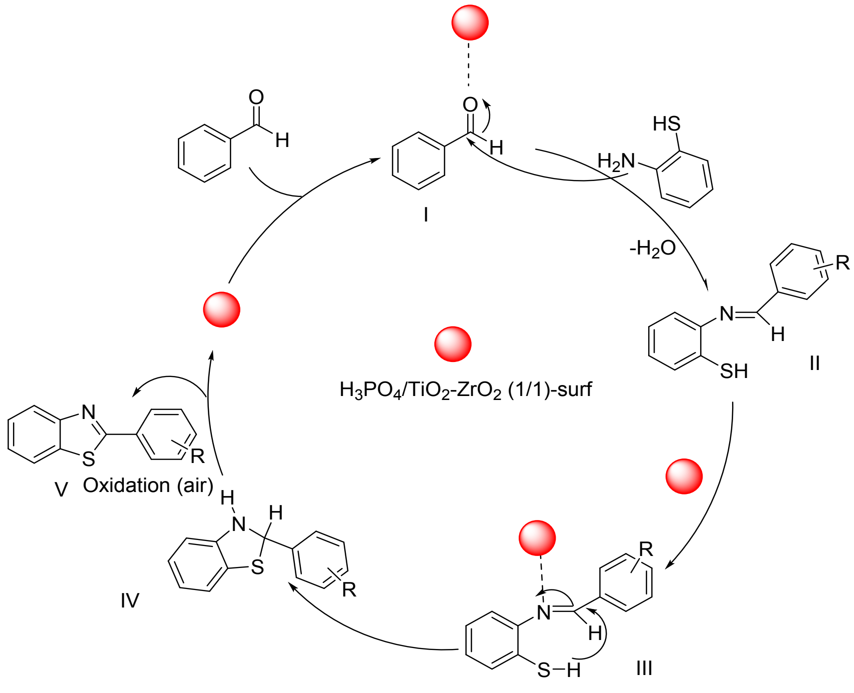

Scheme 1: Proposed reaction mechanism for the synthesis of 2-arylbenzothiazole derivatives

3.4. Reusability

The recovery of 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 appropriate microwave radiation power, solvent and the optimal amount of catalyst. When the reaction was over, the catalyst was separated by spreading in ethyl acetate, filtered and the catalyst was washed several times with ethyl acetate and acetone. Then it was placed in an oven at 90 °C for one hour and then placed in an oven at 550 °C for 4 hours to remove the solvent and excess organic materials in the catalyst and after these steps it was used in similar reactions. Then, in subsequent reactions, the compounds for this group were used. The reaction results, in the vicinity of the recovered catalyst under microwave conditions, for six times of testing with 4-nitrobenzaldehyde and 2-aminothiophenol are shown in Figure 9.

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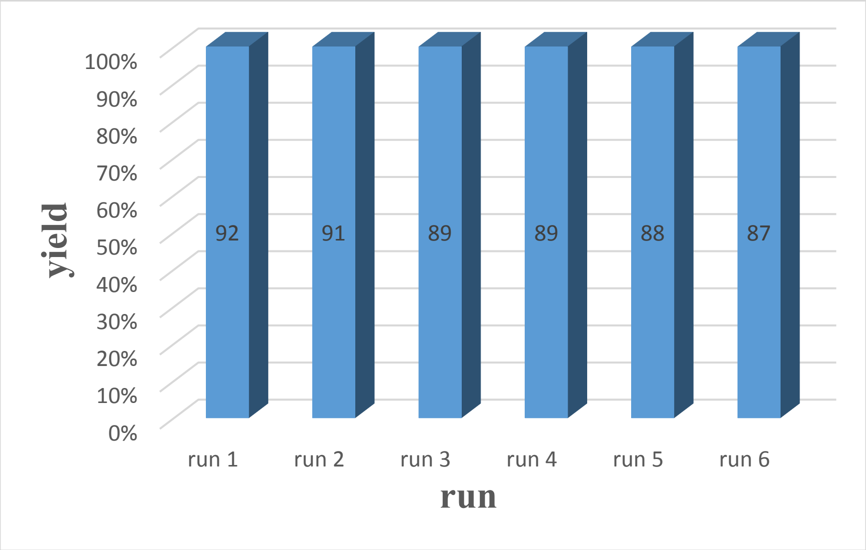

Figure 9. The reusability results of H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst under the model reaction

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

To investigate the stability of the catalyst in acidic, basic and neutral conditions, the prepared catalyst was investigated under model reaction conditions. The reaction in the presence of catalyst in ethylene glycol solvent was irradiated with microwaves for 10 minutes in each of acidic, basic and neutral conditions. Then, the catalyst was separated from the reaction medium and after washing and drying. Then, it was reused in the model reaction, the results of which are shown in Table 7. The results of this Table show that the catalyst prepared under acidic, basic and neutral conditions has good stability.

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Table 7. The stability of the catalyst in various conditions

Condition	pH	Time (min)	Yield (%)
acidic	2	10	89
basic	10	10	86
neutral	7	10	92

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 solvent at 300 w

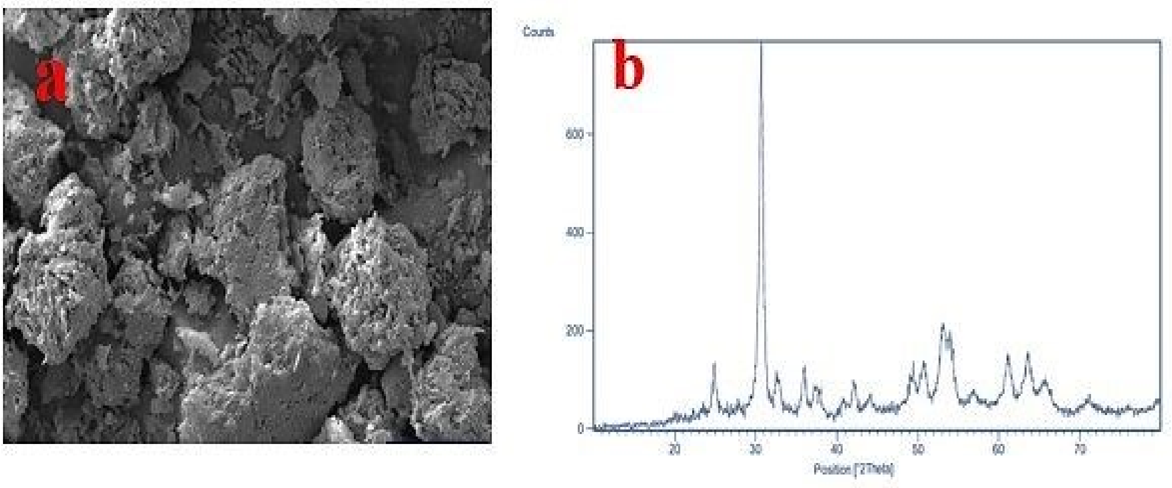

Figure 10. FE-SEM (a) and XRD pattern (b) after reusability of the H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst.

In addition, a hot filtration method was used to investigate the possibility of leakage of components 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 filtered mixture was monitored by TLC, after which the mixture was promptly heated. After filtration, no reaction progress was observed, confirming that the H_3PO_4/TiO_2-ZrO_2 (1/1)-surf

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catalyst did not leak any material during the process, as indicated by the hot filtration test results.

4. Conclusion

In summary, this research presents the H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst as a highly effective solid acid catalyst for synthesizing 2-arylbezaldehyde compounds using an environmentally friendly solvent under microwave irradiation. The catalyst's benefit properties include durability, ease to separate, reusability, affordability, and environmental friendliness. These characteristics were proven through different scientific techniques such as; FT-IR, XRD, FE-SEM, and EDS. The utility of a one-pot multicomponent reaction with the mentioned catalyst offers several advantageous points: it is a short process, greater efficiency than other catalysts used in 2-arylbezothiazole synthesis, supports the power of microwave irradiation, produces high product yields, and facilitates easy cleanup.

Data availability

The data supporting this article have been included as part of the Supplementary Information.

Declaration of Competing Interest

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

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Data availability

The data supporting this article have been included as part of the Supplementary Information.