



SBA-15-SO₃H catalysed room temperature synthesis of 2-aryl benzimidazoles and benzothiazoles

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Abstract

Herein, we report the synthesis of sulfonic acid functionalized SBA-15 by post-synthetic functionalization of mesoporous SBA-15. The successful incorporation of sulfonic acid moiety into the SBA-15 framework could be confirmed by physico-chemical characterization. The nature of acidic sites was confirmed using temperature-programmed desorption of ammonia. A simple synthetic route for the synthesis of 2-aryl benzimidazoles and benzothiazoles using SBA-15-SO₃H as a green heterogeneous catalyst at room temperature was investigated. 100% conversion and an isolated yield of 70–85% could be obtained. The green synthetic approach offers reaction under ambient conditions, a simple work-up procedure, good to excellent yield and easy product isolation along with good recyclability.

Keywords Heterogeneous catalysis · Sulfonic acid functionalized SBA-15 · Benzimidazoles · Benzothiazoles

Introduction

Green chemistry (also known as sustainable chemistry) is an emerging area of current research targeting the greening of chemical synthesis in the chemical industry. It advocates the invention of environmentally benign chemical processes involving the consumption of renewable resources and eliminating/reducing the generation of waste at the source emphasizing atom/circular economy [1–4]. Heterogeneous catalysis can go a long way in realizing the goals of sustainable chemistry by providing alternate synthetic strategies involving reusable and recyclable solid catalysts for fine chemical synthesis [5]. Solid acids form eco-friendly substitutes for

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commonly used hazardous and corrosive homogeneous liquid acid catalysts such as HCl, HNO₃, H₂SO₄, HF etc. [6]. Replacing conventional production with sustainable routes alleviates environmental and economic concerns.

N-containing heterocyclics especially benzimidazoles and benzothiazoles have gained significant interest on account of their broad spectrum of biological activities and potential applications [7–20]. The myriad pharmaceutical applications have contributed to the considerable research focus on the development of new synthetic routes for these compounds. The most common method of synthesis involves the condensation of an arylene diamine or 2-aminothiophenol with a carboxylic acid [21, 22] or its derivatives [23, 24] under vigorous reaction conditions or under microwave irradiation. Another method is the condensation of an aldehyde with arylene diamine or 2-aminothiophenol [25–27] and is the extensively followed synthetic approach due to the easy availability of aryl aldehydes. A detailed literature survey of the synthetic approaches for benzimidazoles and benzothiazoles reveals diverse catalytic systems and methodologies employed for their synthesis [7, 22–45].

The discovery of ordered mesoporous materials (pore size 2–50 nm) has been a breakthrough in the field of material chemistry. The versatility of porous silica-based organic–inorganic hybrids catalysts is attributed to the structural robustness of the inorganic framework and functional characteristics of organic moieties [46]. These multi-functional silica-based hybrid catalysts possess diverse types of active sites (acid, base, redox) enabling them to facilitate a whole spectrum of organic transformations [47–51]. SBA-15 is a class of mesoporous silica material having a uniform hexagonal array of mesoporous with narrow pore size distribution. The large surface area in combination with the tunability of pore size and easy functionalization of the silanol groups with acidic, basic and redox moieties renders them widely used materials in heterogeneous catalysis. The introduction of SO₃H moieties is reported to lend strong Brønsted acidity assisting the catalytic activity [52, 53]. Sulfonic acid functionalized SBA-15 has been explored extensively for a wide range of catalytic conversions [54–64].

2-Aryl benzimidazole synthesis over mesoporous silica-based materials has been reported in the literature [35, 36, 65–73]. Solvent selective formation of di and monosubstituted benzimidazoles over mesoporous silica supported ytterbium catalyst was demonstrated by Samanta et al. [65]. Mesoporous silica supported samarium and CuO was reported as recyclable heterogeneous catalyst for the synthesis 2-substituted benzothiazole [72]. Cobalt-anchored SBA-15 [66] and Al-MCM-41 [70] have been tried for benzimidazole synthesis. The coupling reaction of 2-iodoaniline, potassium sulfide and benzaldehyde over bimetallic Cu-Al supported on SBA-15 could produce benzothiazoles in excellent yields [67]. An organometallic type catalyst prepared through surface modification of silica nanoparticles with 3-chloropropyltriethoxysilane (CPTES) and thiocarbonylhydrazide (TCH) followed by metal–ligand coordination with Ni (II) for benzimidazole synthesis was reported by Kalhor et al. [64]. Functionalized MCM-41 [67, 71, 74], hexagonal mesoporous silica [69] as catalysts for benzimidazole and thiazole synthesis has also been reported. Further, sulfonic acid functionalized materials have also been explored for benzimidazole synthesis [75–79]. Only isolated reports are available regarding synthesis of 2-aryl benzimidazoles over sulfonic acid functionalized SBA-15. However, to the

best of our knowledge, synthesis of benzothiazoles over SBA-15-SO₃H has not been reported yet. Herein, we present the catalytic activity of sulfonic acid functionalized mesoporous SBA-15 for the synthesis of 2-arylbenzimidazoles and benzothiazoles. A high yield of isolated products could be obtained under optimized reaction conditions in ethanol with considerable scope for catalyst recyclability.

Experimental

Materials and methods

Pluronic 123, Tetraethyl orthosilicate (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) were purchased from Sigma-Aldrich. Sulfuric acid (H₂SO₄, 95%), Hydrochloric acid (HCl, 35%) were purchased from Merck. All other chemicals, benzaldehyde, 2-aminothiophenol, o-phenylenediamine, toluene, hydrogen peroxide (30 wt%) were supplied by Spectrochem. All reagents and solvents were of analytical grade and used as such without any further purification.

Synthesis of SBA-15

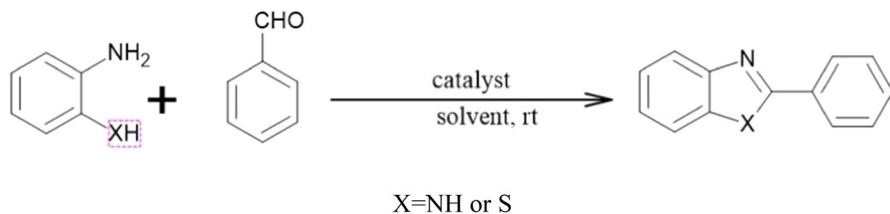
SBA-15 was prepared based on a slight modification of the procedure reported by Zhao et al. [80]. As reported in our previous work [81], 4.4 g of triblock copolymer P123 was dispersed in 30 mL distilled water and stirred for 1.5 h. To the dispersed solution, 120 g 2 M HCl was added and the stirring was continued for 2 h. This was followed by dropwise addition of 9 g of TEOS under continued stirring for 1 h. The resulting solution was aged for 24 h followed by hydrothermal treatment at 100 °C for 48 h. The precipitate was then filtered, washed with distilled water, dried overnight at 70 °C in a hot air oven and calcined at 450 °C for 8 h.

Functionalization of SBA-15

The functionalization of SBA-15 was done by the post-grafting method. To 0.5 g SBA-15, 5 mL MPTMS and 10 mL toluene were added and refluxed for 6 h at 60 °C. The precipitate was filtered, thoroughly washed with methanol and distilled water and dried overnight at 70 °C to get thiol functionalized SBA-15. The oxidation of thiol functionality was achieved by treatment with 5 mL H₂O₂ and a drop of H₂SO₄. The solid obtained was filtered, washed, and dried to get SBA-15-SO₃H.

Catalyst characterization

The synthesized catalysts were subjected to structural and morphological characterization. Small angle XRD was recorded on a Bruker AXS D8 Advance powder diffractometer using Cu K_α radiation (wavelength 1.54 Å) source. Fourier transform infrared spectroscopy (FTIR) spectra were obtained from JASCO model 4100 FTIR spectrometer. Thermal stability of the catalytic systems was tested in a Perkin Elmer



Scheme 1 General scheme for the synthesis of 2-aryl benzimidazoles/Benzothiazoles. X = NH or S

Diamond TG/DTA analyzer at a heating rate of 10 °C/min under nitrogen atmosphere. Morphological characterization was obtained from SEM and TEM analyses. The TEM images were recorded using a JEOL JEM 2100 microscope with a resolution of 0.24 nm operated under the voltage of 200 kV. SEM–EDX analysis was done in JEOL JSM-6390LV with magnification 5× to 300,000×. The surface area and pore volume characteristics were determined by N₂ adsorption/desorption isotherms in a Micromeritics Gemini VI version 3.03 analyser after degassing at 200 °C for 4 h. XPS analysis was conducted on PHI 5000 Versa Probe II, ULVAC-PHI Inc., USA equipped with micro-focused (200 μm, 15 kV) monochromatic Al K_α X-ray source (hν = 1486.6 eV). Both survey spectra and narrow scans (high-resolution spectra) were recorded. Survey scans were recorded with an X-ray source power of 50W and pass energy of 187.85 eV. High-resolution spectra of the major elements were recorded at 46.95 eV pass energy. XPS data were processed using PHI's Multipack software.

General procedure for the synthesis of 2-phenyl benzimidazole/thiazoles

For a typical run, a mixture of *o*-phenylenediamine (OPD)/2-aminothiophenol (1 mmol) (for benzimidazole/benzothiazole) and benzaldehyde (1 mmol) in 10 mL solvent was taken in a 50 mL flask and stirred at room temperature in presence of catalyst (50 mg) for a definite time interval (Scheme 1). The progress of the reaction was monitored by TLC and the filtrate was subjected to GC–MS analysis in an Agilent 7890A system. The product isolation was achieved by pouring the reaction mixture into chilled water containing ice. The precipitate formed was then filtered, washed, dried and recrystallized from ethanol.

Results and discussion

Characterization of the catalyst

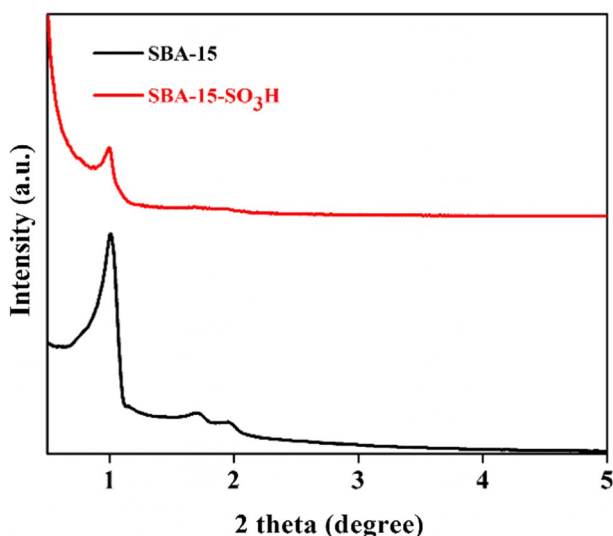
The results of the BET surface area analysis (Table 1) imply the successful incorporation of sulfonic acid moieties into the framework. SBA-15 exhibited a surface area of 697 m²/g which upon functionalization reduced to 568 m²/g. A slight reduction in pore volume and pore diameter was also observed in SBA-15-SO₃H indicating the partial filling of the mesopores. This is in line with the previous literature

Table 1 Physical characterisation of SBA-15 and SBA-15-SO₃H

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Interplanar distance $d_{(100)}$ (nm)	Unit cell parameter (a_0) (nm)	Wall thickness (nm)
SBA-15	697	0.28	2.13	8.75	10.10	7.97
SBA-15-SO ₃ H	568	0.23	2.04	8.95	10.28	8.24

reports [58, 82, 83]. The decrease may also be attributed to the occlusion of pores by propyl sulfonic acid groups inhibiting N₂ diffusion. [58]. The enhancement in wall thickness may be attributed to the incorporation of sulfonic acid moieties onto the surface. The N₂ adsorption–desorption isotherms (Fig. S1) can be correlated to Type IV with H1 hysteresis loop at relative pressures 0.6 to 0.8 which are characteristics of mesoporous materials. The retention of the hysteresis loop in SBA-15-SO₃H indicates the preservation of the mesoporous framework after functionalization.

The small angle XRD patterns of the pure SBA-15 (Fig. 1) exhibited three well-resolved peaks at 2θ values 0.99°, 1.55° and 1.9° corresponding to the reflections from (100), (110) and (200) planes. These peaks are the characteristics of mesoporous materials with *p6mm* hexagonal space group [81]. The XRD pattern remained essentially unchanged in SBA-15-SO₃H emphasising the stability of the hexagonally closed-packed mesoporous framework. A reduction in the peak intensity after functionalization is evocative of a small disruption in the long-range order caused by post-grafting treatment and oxidation [55, 56, 59]. Such a lowering of intensity has been reported during the incorporation of other species also [65]. The reduction in intensity may also be a consequence of the lowering

**Fig. 1** XRD patterns for SBA-15 and SBA-15-SO₃H

of crystallinity during post grafting [57]. It has to be specially mentioned that no considerable alterations were observed in the lattice parameters (Table 1) once again confirming the retention of the mesoporous framework.

The FTIR spectra of SBA-15, thiol functionalized SBA-15 and sulfonic acid functionalized SBA-15 (Fig. 2) exhibited a broad peak around 3450 cm^{-1} assigned to the O–H stretching vibration of the surface silanol groups and adsorbed moisture. The characteristic vibrations of mesoporous silica could be identified: band at 960 cm^{-1} (Si–O bending vibration), 800 cm^{-1} (symmetric stretching vibrations of Si–O–Si) and wide band between 1000 and 1300 cm^{-1} (asymmetric stretching vibrations of Si–O–Si) [81]. The attachment of the mercaptopropyl group on the silica surface was identified by the bands at 2940 cm^{-1} and 2850 cm^{-1} which are due to the asymmetric and symmetric stretching peaks of methylene group. A weak peak around 2600 cm^{-1} is due to the S–H stretching vibrations [84].

The thermal stability of the as-prepared samples was investigated by TG-DTG analysis (Fig. S2). The weight loss below $130\text{ }^{\circ}\text{C}$ in both cases may be assigned to the removal of physisorbed water. The absence of a significant weight loss in 150 – $270\text{ }^{\circ}\text{C}$ region confirms the complete removal of the surfactant during calcination process. In the case of sulfonic acid functionalized SBA-15, the weight loss observed beyond $400\text{ }^{\circ}\text{C}$ may be ascribed to the decomposition of the sulfonic acid moiety [54, 55].

The textural and morphological characteristics of the samples were obtained from SEM–EDX (Fig. S3) and TEM analysis (Fig. S4). TEM images reveal the hexagonally aligned mesopores and parallel pore channels which are retained after sulfonic acid functionalization [58, 60, 75]. This is in alignment with the preservation of mesoscopic structure as evidenced by BET and XRD data. EDX

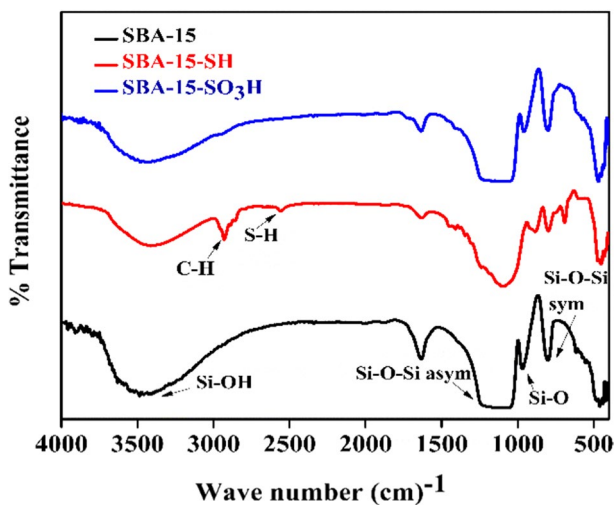


Fig. 2 FT-IR spectra of SBA-15, thiol functionalised SBA-15 (SBA-15-SH) and sulfonic acid functionalized SBA-15 (SBA-15-SO₃H)

analysis reveals a sulfur content of 1.1 wt% in the functionalized sample confirming the inclusion of SO_3H moiety into SBA-15 framework.

Effective functionalization of SBA-15 could be further confirmed by XPS analysis (Fig. 3 and S5). The C1s spectra indicate the presence of the propyl group while that of S 2p establishes the inclusion of sulfonic acid moiety. The O1s peak at 532.3 eV may be assigned to Si–O–Si linkage. The binding energy for Si 2p was found to be at 103.7 eV consistent with previous reports [75]. The single peak at a binding energy of 169 eV observed for S 2p confirms the +6 oxidation state of S which in turn indicates the complete oxidation of the thiol group [56].

Catalytic activity

Synthesis of 2-aryl benzimidazole

The selection of a proper solvent is a crucial step in organic synthesis. A preliminary scanning of the solvent effect was done at room temperature for a time interval of 24 h (Fig. S6). Less polar and aprotic solvents like dichloroethane, tetrahydrofuran and toluene were found to be unsuitable for the reaction whereas polar solvents like ethanol, acetonitrile gave the highest yield of product. Ethanol being a green solvent

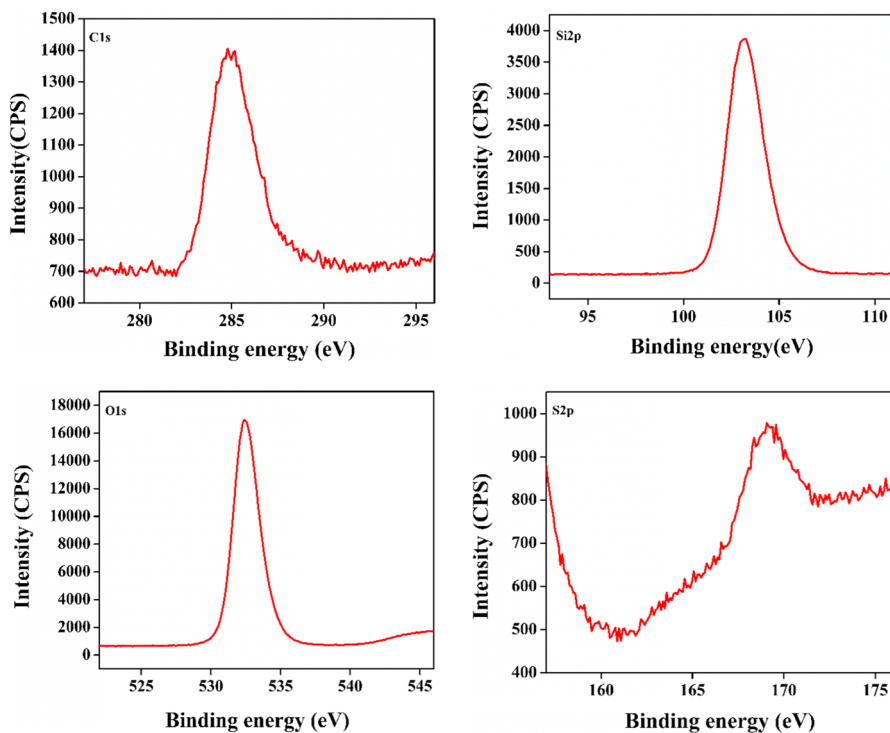


Fig. 3 Core level XPS spectra of SBA-15-SO₃H

was selected for further studies. In order to assess the catalytic performance, parallel runs were conducted over unfunctionalized SBA and also para-toluene sulfonic acid (PTSA). Without catalyst, the product yield was negligible while pristine SBA-15 gave a yield of around 40%. The activity of SBA-15 could be assigned to the silanol groups contributing towards acidity. For PTSA and SBA-15-SO₃H, the yields obtained were 78% and 85%. The higher activity of SBA-SO₃H relative to the PTSA may be attributed to the enhanced surface area and exposed active sites provided by the SBA-15 support. Such an enhancement in activity upon heterogenization is reported in the literature [85–87]. To have a more quantitative perspective of the enhancement in activity in terms of the sulfonic acid functionalities, an estimation of sulfonic acid groups was carried out (Table S1). Higher activity of SBA-15-SO₃H despite its lesser amount of sulfonic acid moieties may be a consequence of easy access of the reactants to the active sites as compared to PTSA.

The scope and efficiency of the protocol were tested using substituted aldehydes containing both electron releasing and withdrawing groups and a series of 2-aryl benzimidazole derivatives were synthesized. The product formation was confirmed by GCMS analysis (representative chromatograms are provided in Fig. S7) and the isolated product yields are reported in Table 2. In all cases, corresponding 2-aryl benzimidazoles were obtained in 70 to 80% yield indicating that substituent functionality did not have a pronounced impact. The recyclability of the catalyst was also tested and reuse up to five successive runs was observed without significant loss in activity (Fig. 4).

Synthesis of 2-aryl benzothiazole

As in the previous case, the reaction between 2-aminothiophenol and benzaldehyde was carried out with 1:1 molar ratio over 0.05 g catalyst using a series of solvents for a duration of 3 h (Fig. S8). As in the case of benzimidazoles, nonpolar solvents gave poor yields. Acetonitrile was found to be the best solvent giving a yield of 90% while ethanol gave a yield of around 84%. So further reactions were carried out in acetonitrile. The progress of the reaction with time was monitored using acetonitrile as solvent. The product yield increased with time up to 3 h and thereafter no significant change could be observed (Fig. S9).

The scope of the methodology was screened by using a series of substituted aldehydes and the result is tabulated (Table 3). The product formation was confirmed by GCMS analysis and representative chromatograms are included in (Fig. S7). Irrespective of the nature of the substituent a yield in the range 78 to 85% was obtained indicating the generality of the synthetic route. The catalyst could be reused without a significant loss in activity up to five successive runs (Fig. 5).

Before probing into the mechanistic aspects driving the reaction, the acidity of the neat and functionalized catalysts was evaluated temperature programmed desorption of ammonia. The samples were saturated with ammonia gas at room temperature and then subjected to a progressive temperature rise. The categorization of acid sites into weak, moderate and strong depends on the temperature range at which ammonia is desorbed [88, 89]. Weakly adsorbed ammonia

Table 2 Synthesis of 2-aryl benzimidazoles

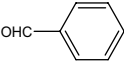
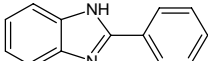
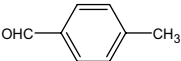
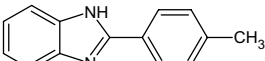
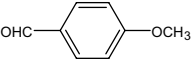
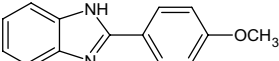
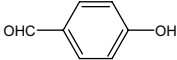
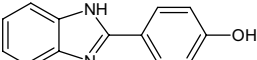
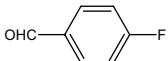
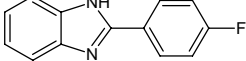
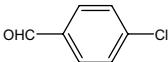
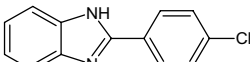
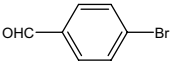
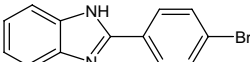
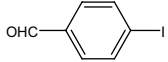
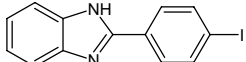
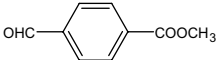
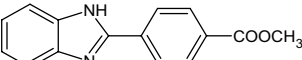
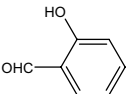
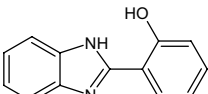
Entry	Aldehyde	Benzimidazole	Yield (%) (isolated)
1			85
2			80
3			79
4			77
5			82
6			81
7			78
8			74
9			82
10			70

Table 2 (continued)

Time: 24 h, room temperature, *o*-phenylene diamine and aldehyde -1 mmol, catalyst: 0.05 g, solvent: ethanol

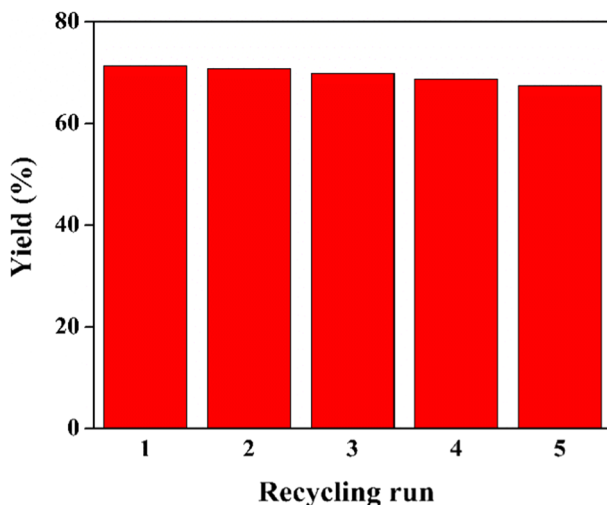


Fig. 4 Recyclability study of the catalysts for the synthesis of 2-aryl benzimidazole. Time: 24 h, room temperature, benzaldehyde and *o*-phenylene diamine: 1 mmol, catalyst: 0.05 g, solvent: ethanol

is easily desorbed at relatively low temperatures (below 150 °C). Desorption in the interval 150–300 °C may be assigned to moderate acid sites while high temperature desorption indicates strong acidity. The signal obtained in the present case (Fig. 6) reveals the presence of weak acid sites in SBA-15 which contributes towards its mild activity. Incorporation of sulfonic acid groups imparts strong acidic character boosting its activity.

Based on the literature reports [90], a plausible mechanism for SBA-15-SO₃H catalyzed formation of 2-aryl benzimidazole or benzothiazole may be sketched (Scheme 2). Sulfonic acid group can facilitate the protonation of the carbonyl oxygen of the aromatic aldehyde. The consequent enhancement in the electrophilicity of the carbonyl carbon improves the ability of aromatic aldehyde to form a Schiff base intermediate by reacting with amino group of *o*-phenylenediamine or 2-aminothiophenol. The second NH₂ group of *o*-phenylenediamine or the SH group of 2-amino thiophenol then donates a lone pair of electron to the intermediate resulting in the formation of a five-membered ring via intramolecular ring closing. The deprotonation of positively charged N or S by the negatively charged catalyst species regenerates the catalyst. On air oxidation, the intermediate thus formed yields the corresponding 2-aryl benzimidazole or benzothiazole. A comparative evaluation of the activity of our catalytic system with available literature reports for the synthesis of 2-aryl benzimidazoles and thiazoles is provided (Table S2).

Table 3 Synthesis of 2-aryl benzothiazoles using substituted aldehydes

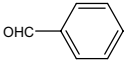
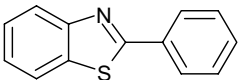
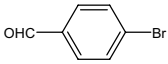
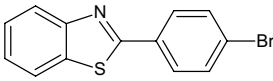
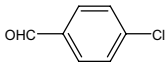
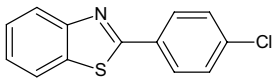
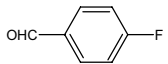
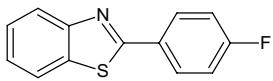
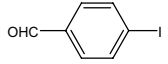
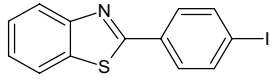
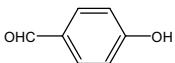
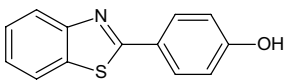
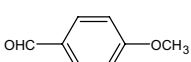
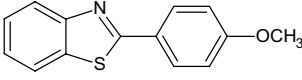
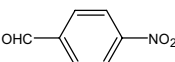
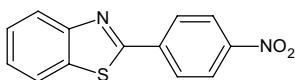
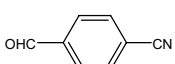
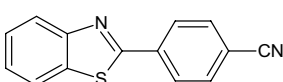
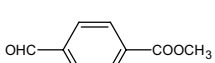
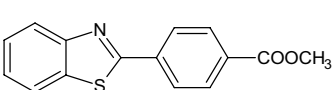
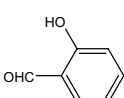
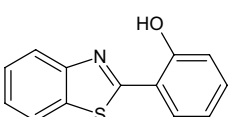
Entry	Aldehyde	Benzothiazole	Yield (%)
1			89
2			80
3			86
4			84
5			79
6			86
7			87
8			83
9			82
10			79
11			84

Table 3 (continued)

Time: 3 h, room temperature, 2-aminothiophenol and aldehyde: 1 mmol, catalyst: 0.05 g solvent: acetonitrile

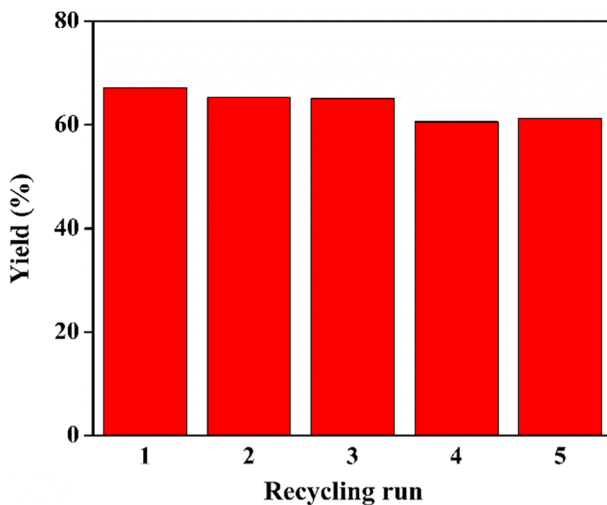


Fig. 5 Reusability study of the catalysts for the synthesis of 2-Aryl benzothiazole. Time: 3 h, Room temperature, 2-aminothiophenol and benzaldehyde: 1 mmol, catalyst: 0.05, g solvent: acetonitrile

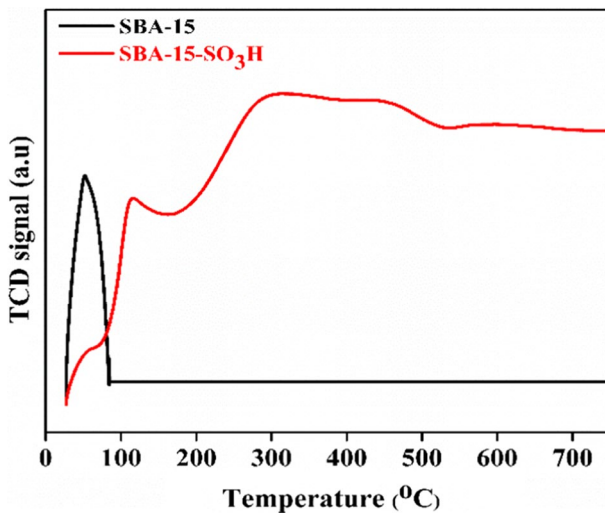
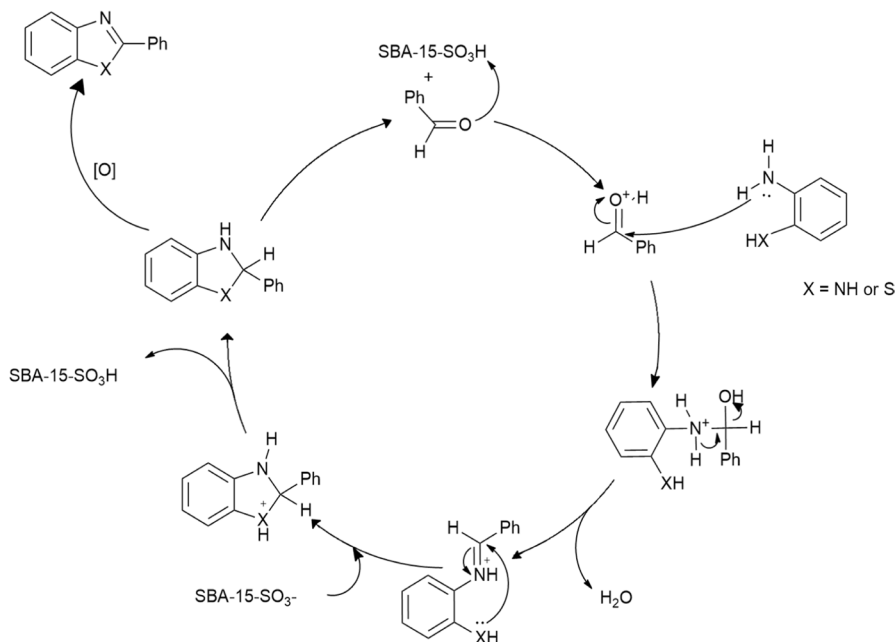


Fig. 6 Temperature Programmed Desorption of ammonia profiles for SBA-15 and SBA-15-SO₃H



Scheme 2 Plausible reaction mechanism for the synthesis of 2-Aryl benzimidazoles and benzothiazoles

Conclusion

To summarize, we present here a simple synthetic route for the 2-aryl benzimidazoles and benzothiazoles catalyzed by sulfonic acid functionalized SBA-15 under ambient conditions. The catalyst was found to be highly stable and could be reused up to five successive runs without a significant loss in activity. The product isolation was quite simple avoiding any tedious work up strategy.

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Declarations

Competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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